Report of the second RCM on

*Radiation Curing of Composites for Enhancing the Features and Utility in Health Care and Industry*

Cairo, Egypt, 26-30 November 2012

*Working Material*
EDITORIAL NOTE

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Composite materials combine properties of the individual components in a synergetic manner to produce a variety of materials in an efficient and cost-effective manner. Thus, composite materials today are being used in various applications from sports equipment, automotive and aerospace industries to food packaging and artificial organs. Materials reinforced with nanoscale components are adding new dimensions to composite materials and enable further major improvements in functional and structural properties. The incorporation of only a few percent of nano-sized particles can make dramatic property changes that may result in sensing, actualization or self-healing properties of the resulting composite. Several major issues need to be addressed to utilize the full potential of such nanofillers, and among them: (i) incompatibility or weak interfacial bonding between the matrix and the nanoscale component, and (ii) agglomeration of nanosized component during processing resulting in inhomogeneous distribution. According to the results of ongoing investigation and products preparation in several Member States institutions, radiation technology offers a way of overcoming these challenges by grafting of appropriate monomers/polymers onto the nanofiller surface thereby fixing their morphology and at the same time making them compatible with the host polymer. Additionally, radiation techniques offer the possibility for simultaneous synthesis of the nanoparticle component and crosslinking of the matrix of the composite that is not possible to achieve by other techniques. With the availability of lower cost self-shielded low energy electron beam accelerators, this process is increasingly becoming available for developing member states.

In order to use the advantages of radiation techniques and address the needs of Member States for producing advanced composite materials, this CRP aims to support MS to develop methodologies and protocols for new abrasion resistant coating formulations, radiation curable nano-composites from natural polymers, new biodegradable packaging materials suitable for radiation sterilization, and new methods to modify surface characteristic of nanosized materials to enhance polymer fillers interaction. This CRP provides a forum for knowledge and technology transfer among the participating institutions, as well as promotes early involvement of developing countries in knowledge-intensive R&D programs.

The first RCM of the CRP was convened in Vienna on 18-22 July 2011. The report from this meeting is available as Working Material at http://www-naweb.iaea.org/napc/iachem/working_materials/RC1207-1-report.pdf.

The second RCM was convened on 26-30 November 2012 in Cairo, Egypt, where the participants presented their achievements centred on the specific objectives of this CRP, and agreed on the work plan for the next 18 months. This meeting report contains these information, in a concise way in the Summary part, and with full details in the individual reports of the participants. The participant from Canada could not attend this meeting, but made available her report for inclusion here.

The IAEA wishes to thank all participants of the Meeting for their valuable contributions. The IAEA officer responsible for this Research Coordination Meeting was Agnes Safrany of the Division of Physical and Chemical Sciences.
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EXECUTIVE SUMMARY

1.1. Introduction

1.1.1. Composite and nanocomposite materials

Composite materials combine properties of the individual components in a synergetic manner to produce a variety of materials in an efficient and cost-effective manner. Thus, composite materials today are being used in various applications from sports equipment, automotive and aerospace industries to artificial organs. Their utilization is expected to further increase in the next decades since multi-functional composites are the key for advanced structures and devices.

The incorporation of micro-size inorganic particulate materials is an established method of enhancing specific properties of polymeric materials for many industrial products. However, high concentrations (typically 20-30% by volume) of these additives are required to achieve the targeted properties. In some cases this high filler loadings adversely affects the processability of the composite, energy demands for processing are increased and the weight of the end material is much higher as compared to the neat polymer. Nano-size materials, like carbon nano-tubes (CNTs), possess much superior mechanical and thermal properties and incorporation of such materials in the polymer composites is expected to increase the mechanical and thermal characteristics of the polymers at extremely low filler concentrations. Additionally, nanofillers may impart other, either bulk or surface, desired properties, such as shrinkage control, lighting strikes protection, radiation resistance or shielding, erosion or corrosion protection, controlled wetting and adhesion.

Similarly, blend of polymers such as natural rubber and ethylene-vinyl acetate (NR/EVA,) natural rubber –polypropylene (NR/PP) and polypropylene (PP) with the incorporation of nanoclay as specialty materials are being investigated for application in automotive parts and packaging. Radiation curable nanocomposites containing nano silica can give additional benefits, and their potential to be utilized as coating materials for flooring, wall panel, and furniture products with high scratch and abrasion resistance properties has already been shown. Other improvements like self-cleaning properties can be reached by changing the nature of particles.

One of the important areas where nanocomposites are expected to play an important part is their use as catalysts in industrial applications due to their very high surface area.

There are significant opportunities for future developments of nanocomposites in health care as advanced delivery devices that include site-specific or self-regulated drug delivery, targeted radiotherapy, targeted imaging systems and integrated diagnostic and therapeutic micro-/nanodevices.

1.1.2. Challenges

Several major issues need to be addressed to utilize the full potential of such nanocomposites, and among them:
due to the incompatible surface properties, the interfacial bonding between the polymer segments and nanofiller is weak and needs to be improved by chemically modification of the nanofiller,

due to their high surface area, that is several orders of magnitude higher than the conventional fillers, they tend to agglomerate in the polymer matrices during processing and the full potential of their expected properties is not achieved,

due to their high surface area, the nanoparticles may exhibit unwanted catalytic activity,

there are numerous health and toxicity concerns associated with nanofillers, and

there are unmet clinical needs for safer and better-tolerated drugs and “active” nanoparticles as tags in the diagnosis and treatments of various diseases integrated into scaffolds for tissue engineering, embedded or attached to fibres and fabrics to obtain smart patches, smart bandages or bed linens, etc.

1.1.3. The role of radiation in addressing the challenges

Radiation technology offers an excellent way of overcoming some of these challenges as the characteristics of these nanosized fillers can be suitably modified by grafting of appropriate monomers/polymers onto their surface thereby altering their morphology and at the same time making them compatible with the host polymers. Unlike conventional methods, radiation grafting can be carried out at room temperature and without any initiators avoiding the incorporation of toxic chemical byproducts. Nanoparticles can more easily be homogeneously dispersed in liquid media (monomers, solvent plus monomers, sol/gels, etc.) followed by a quick polymerization step by radiation at ambient temperature thereby retaining the initially obtained homogeneous distribution resulting in a better dispersion of the nano-filler materials. The desired characteristics of the product thus can be achieved at lower filler content resulting in the formation of a light-weight material with superior mechanical properties in an energy efficient manner. Additionally, by keeping the nanoparticles in solution may eliminate some toxicity concerns too.

1.1.4. Scope of this CRP

In order to use the advantages of radiation techniques and address the needs of Member States for producing advanced composite materials for various applications, this CRP started in 2010. The CRP aims to support MS to develop methodologies and protocols for new abrasion resistant coating formulations, radiation curable nano-composites from natural polymers, new biodegradable packaging materials suitable for radiation sterilization, and new methods to modify surface characteristic of nano-sized materials to enhance polymer fillers interaction. This CRP also provides a forum for knowledge and technology transfer among the participating institutions, as well as to promote early involvement of developing countries in knowledge-intensive R&D programs to enhance their level of competence and confidence and promote the local spin-off initiatives.

1.2. CRP overall objective

To enhance member States capability in the use of radiation technology for production of nano-composites with enhanced safety, stability and functionality for advanced applications.
1.2.1. **Specific research objectives**

Support the production and technology transfer of advanced polymer nano-composites by using the demonstrated advantages of radiation technology for:

- Protocols for preparation of new scratch and abrasion resistant coating formulations with enhanced surface finishing
- Preparation methods for radiation curable nano-composites from natural polymers
- Preparation of protocols and specifications for new biodegradable packaging materials suitable for radiation sterilization
- New methods to modify surface characteristic of nano-sized materials to enhance polymer fillers interaction

1.2.2. **Expected research output**

- Protocols for scratch and abrasion resistant coating formulations with enhanced surface finishing
- Preparation methods for new radiation curable nano-composites from natural polymers
- Specification and protocols for biodegradable packaging materials suitable for radiation sterilization
- New methods to modify surface characteristic of nano-sized materials to enhance polymer fillers interaction

The participating institutions are expected to contribute to one or more specific research objectives. The results will be presented in international conferences and published in scientific journals.

1.2.3. **Achievements**

The first RCM was held 18-22 July 2011 in Vienna, Austria, where the 14 participants presented and discussed the status in the field, agreed on the work plan for the first 18 months and indicated collaboration possibilities. The report from this meeting is available as Working Material at [http://www-naweb.iaea.org/napc/iachem/working_materials/RC-1207-1-report.pdf](http://www-naweb.iaea.org/napc/iachem/working_materials/RC-1207-1-report.pdf).

The second RCM was convened between 26-30 November 2012 in Cairo, Egypt, and was attended by 14 participants, who presented their achievements centered around the specific objectives of this CRP:

1.2.3.1. **Protocols for preparation of new scratch and abrasion resistant coating formulations with enhanced surface finishing**

The curing of scratch and abrasion resistant coatings, having relatively high nanopowder content, with good gloss properties, has been achieved by UV light and electron beam (EB). Control of gloss properties was achieved by using either unmodified silica nanoparticles or organophilic silica. In addition to UV & EB irradiation, vacuum UV (VUV) lamps (172 nm excimer) were used for photoinitiator-free curing of acrylate-based nanocomposites. (GERMANY, MALAYSIA, INDIA)
1.2.3.2. Preparation methods for radiation curable nano-composites from natural polymers (or monomers)

Protocols for extraction, purification and modification of xyloglucan (XG), a naturally abundant, non-food feedstock polysaccharide, were established. $^{60}\text{Co}\gamma$-irradiation in air and at room temperature was applied to control the molecular weight (MW) and MW distribution as well as the temperature-responsive behavior of a partially degalactosylated xyloglucan variant.

Chemical modification of xyloglucan with nitrocinnamic acid was performed in order to graft nitrocinnamate pendant groups through an esterification reaction, thereby inducing reversible photocrosslinking to the XG nanoparticles and/or films. (ITALY)

Radiation curable composites incorporating cellulose nanocrystals have been developed successfully. (CANADA).

Protocols for the preparation of Ramie nanowhiskers have been selected, evaluated and implemented for the several gram productions of aqueous supensions as well as of freeze-dried nanocrystals. A robust methodology has been developed for preparing films and bulk materials using radiation curable polyurethane acrylate emulsions. Procedures for characterizing composite materials, cured by exposure to UV (conventional, LED) or EB radiation, have been developed and validated. (FRANCE)

Nanocomposite with silver nanoparticles, incorporated in polymer matrix based on chitosan and PVA, were synthesized by gamma irradiation. Sizes of silver nanoparticles were in the range of 10-20 nm. Size of nanoparticles and optical properties of nanocomposites were controlled varying the ratio of chitosan to PVA. (SERBIA)

Radiation curable epoxidised palm oil acrylate (EPOLA) was found nontoxic. The test was conducted following the OECD guideline for testing of Chemicals, Acute, Oral Toxicity 423.1987. (MALAYSIA)

1.2.3.3. Preparation of protocols and specifications for new biodegradable packaging materials.

Protocols for preparation of biodegradable films with good mechanical and barrier properties from polycaprolactone (PLC) and graphene oxide nanosheets were developed. (EGYPT)

High-density polyethylene was blended with starch and reinforced with different amounts of modified nanoclay. Irradiation at sterilization doses was found to enhance the mechanical properties. Morphological studies showed good compatibilization between the polymer and the filler. (PAKISTAN)

Starch-grafted-PLA was synthesized in lab-scale experiment to be used as a compatibilizer for blending of PLA and cassava starch. The scale-up synthesis of the compatibilizer is in progress. Radiation-induced crosslinking of PLA was done in the presence of a crosslinking agent to determine the optimum condition. Thermoplastic starch (TPS) was prepared from cassava starch and glycerol. (THAILAND)
1.2.3.4. **New methods to modify** surface characteristics of nano-sized materials to enhance polymer fillers interaction

In–situ polymerization of inside the MMT by 26% polymer loading results with the formation of a new organomodified clay which has been used in the preparation of EVA/MMT nanocomposites. Full exfoliation has been achieved at low MMT loading improving the mechanical properties by 50% over pure EVA. (TURKEY)

Carbon nanofiber (CNF) surfaces were modified by radiation-induced grafting of acrylic acid (AA). The functionalized surfaces contain up to 20% of oxygen. (BRASIL)

Carbon nanotube reinforced polycaprolactone based films were irradiated to produce films with better water vapour permeability, oxygen and CO₂ permeability. Surface and interfaces morphologies of the composites were studied by scanning electron microscopy (CANADA).

Modification and characterization of natural and biodegradable based polymers (methylcellulose, chitosan, polycaprolactone) with trimethylolpropane trimethacrylate (TMPTMA), silane or 2-hydroxyethyl methacrylate (HEMA) in presence of Nanocrystaline cellulose were done using irradiation to improve the mechanical and barrier properties (CANADA).

Inhibition phenomena due to functional groups present at the surface of the carbon fibres were evidenced as the most probable cause of the weak transverse properties of radiation curable high performance composites. Surface treatment and specific sizing involving sulfur compounds were shown to improve significantly the transverse properties of unidirectional composite materials. (FRANCE)

1.2.3.5. **Additional achievements**

Numerous important additional achievements were reported, categorized as follows:

**Magnetic nanocomposites and ionomers**

The synthesis of magnetic nanocomposite films by electron beam irradiation of copolymer of 2-ethylhexyl acrylate (2-EHA) and acrylic acid (AA), and FeCl₃ and Fe₃O₄ has been achieved. The magnetization results show a combination of ferromagnetic behavior (hysteresis) at relatively small magnetic fields with superparamagnetic behavior at large fields.

It was also demonstrated that the magnetization increases with magnetite concentration up to about 10% Fe (in the form of Fe₃O₄). (USA)

Microfluidization and irradiation treatment were used to obtain better dispersion of nano fibers in suspension containing antimicrobial compounds for immobilization in biopolymers in presence of nanocrystalline nanocellulose. (CANADA).

A protocol was developed to measure the control release of active compounds from the films during time using FTIR analysis (CANADA).
A methodology to encapsulate antimicrobial compounds and probiotic in a polymer containing nanopolymers (beads and films) was done and gamma irradiation in presence of the active beads and films was used to assure food safety.

**Metal and metal oxide nanoclusters/nanoparticles**

Silver nanoparticles were synthesized by gamma irradiation in presence of chitosan and PVA as stabilizing agents. Ag NPs were spherical in shape, with well-defined size up to 20 nm. (SERBIA)

Double and triple polymer/metal ions complexes based on PAA and copper coordinated by polymers carrying primary and secondary amine groups have been used as matrices for the synthesis of Cu metal nanoclusters with controlled size and size distributions in the range of 2–220 nm. Oxidation stability of copper nanoclusters has been improved in respective polymer thin films. (TURKEY)

Colloidal silver nanoparticles were synthesized by -irradiation using PVA and PVP as stabilisers and test production of 50L/box was carried out in an industrial irradiator.

Antimicrobial porous ceramics loaded with Ag NPs (200-300 mg/kg) were prepared by using an aminosilan coupling agent. Preliminary results of Ag NPs release and antimicrobial effects by flow test showed that porous ceramic AgNPs material is effective for water purification. (VIETNAM)

Composites microgels of PVA/AAc-TiO2, showing better reproducibility for dye photocatalytic degradation, were successfully prepared. (EGYPT)

Radiation synthesis of silver and silver halides nano- and microparticles of defined distribution, stabilized in molecular sieves, track membranes and polymeric membranes, was achieved. (POLAND)

**Matrix for nanocomposites**

Crosslinking of PVA in the presence of chitosan was performed in order to obtain PVA/CS polymer networks as a matrix for further incorporation of silver nanoparticles. (SERBIA)

**Elastomer-based nanocomposites**

Light-weight and high-modulus EPDM/PCR/MWNT nanocomposites were prepared by radiation processing. The crosslinking density and elastic modulus were increased linearly with the nanofiller content, improving the oil resistance of the EPDM/PCR blends. (INDIA).

**1.3. Summary of participants reports**

**1.3.1. Brazil**

**Summary**

Radiation processing has potential application in modifying carbon nanofibers in order to produce useful defects in the graphite structure and create reactive sites. In this study is
proposed a methodology for radiation grafting processing to modify carbon nanofiber surfaces by grafting acrylic acid on carbon nanofiber surface. The samples were submitted to indirect and direct radiation process. Several parameters were changed such as acrylic acid concentration, radiation dose and percentage of inhibitor to achieve functionalization with higher percentage of oxygen functional groups on carbon nanofiber surface and better dispersion. The samples were characterized by Raman and X-ray Photoelectron Spectroscopies. The dispersion stability upon storage was visually investigated and direct process of radiation grafting showed better results. Carbon nanofiber directed irradiated with electron beam and gamma in a solution of acrylic acid with 6% of Inhibitor (FeSO₄₇H₂O) had and increase of 20% of oxygen content onto carbon nanofiber surface. The Auger D-parameter for the the samples direct irradiated grafted ranged between 17.0-17.7 compared to 21.1-18.9 of the unirradiated ones. This indicated that these samples had less sp² and more sp³ bonding characteristics than unirradiated samples. This can be an indication of C=C bond breaking leading to the formation of new sp³ carbon atoms on carbon nanofiber surface with oxygen functional groups grafted. The samples grafted presented a good and stable dispersion. As an immediate next step we intend to manufacture nanostructured composites with this modified carbon nanofiber to assess the impact of these modifications on macroscopic properties and evaluate the adhesion between these modified nanofibers and polymeric matrix.

1.3.2. Canada

Summary

Biopolymeric (methylcellulose, chitosan and alginate) films were prepared by solution casting and their thermo-mechanical properties were evaluated. Nano crystalline cellulose (NCC) was incorporated into the optimized biopolymeric films. It was found that NCC acted as an excellent reinforcing agent which improved the mechanical properties of the films significantly. The NCC containing biopolymeric films were exposed to gamma radiation (2-25 kGy) and it revealed that biopolymeric films gained strength below 5 kGy dose. Monomer grafting onto the biopolymers were carried out to improve the filler (NCC)-matrix (biopolymers) compatibility. Two monomers (Trimethylol propane tri-methacrylate and 2-Hydroxyethyl methacrylate) were grafted using gamma radiation at 5-25 kGy doses. It was found that monomers were successfully grafted with biopolymers and NCC. Grafted films showed excellent mechanical properties. NCC and carbon nanotubes (CNT) were also incorporated in polycaprolactone-based films prepared by compression molding. It was found that NCC (5% by wt) and CNT (0.2% by wt) improved the mechanical properties of the PCL films significantly. The nano materials containing PCL films were gamma irradiated and found better mechanical and barrier properties. Surface morphology of the nano films was studied by scanning electron microscopy.

Work Plan

— The future research will focus on the development of active compounds using encapsulation technologies to immobilize natural antimicrobial agents into films based on chitosan, methylcellulose, supramolecules polymeric films and grafted films using monomeric compounds. The use of microfluidization of formulations based on nanocomposite will be also done for film developments. Structure-function
relationships should be investigated in order to determine the optimal parameters that influence the efficiency of the treatment such as radiation dose, nature of polymer, cross-linking/grafting degree, concentration of active compounds, etc. Bioactive films submitted to gamma radiation will be evaluated for their physicochemical improvement and their capacity to increase the shelf-life of meat (ex: ham) and vegetable products. The antimicrobial efficacy of the films in combination with low dose γ-irradiation will be also investigated in ready-to-eat (RTE) food model against foodborne pathogens like *Listeria monocytogenes*.

Also, beads will be making with irradiated alginate at the optimal doses of irradiation and the cross-linked polymers will be used to immobilize active compounds (natural antimicrobial compounds and also probiotic bacteria). The antimicrobial efficiency of the beads to protect and to assure a control release of the natural antimicrobial compounds will be evaluated in situ in meat system. The efficiency of the beads to protect the viability of probiotic bacteria will be evaluated during storage time at room and at 4 °C. Finally, combined effect of γ-irradiation and microencapsulated antimicrobials microbeads on cooked ham against *L. monocytogenes* during storage at 4°C will be evaluated.

Antimicrobial nanocomposite films will be prepared by the incorporation of natural antimicrobial agents such as, organic acids, bacteriocins, spice and fruit extracts, etc.

Scientific papers should result from these applied research works. Also, in order to satisfy the expected research outputs of IAEA packaging concept project, important data should be delivered as related to functional properties of developed bioactive films and their effect on overall food quality, using gamma radiation technology.

**1.3.3. Egypt**

**Summary**

Trails were made to improve mechanical and barrier properties of PCL for food packaging purposes. The radiation crosslinking of linear PCL would add an extra possibility to the ways of modifying mechanical and physical properties of PCL. Also, mechanical and barrier properties of PCL may also improved by adding reinforcing compounds (fillers like graphene oxide). Study on the improvements of PCL by electron beam irradiation in the presence of polyfunctional monomers was carried out. The effect of gel content on the physical and biodegradability properties of PCL was investigated. Mixing graphene oxide nano-sheets with PCL to produce Poly(caprolactone)/graphene oxide nanocomposite films was studied. The addition of low amount of GO or polyfunctional monomer significantly improved both strength and barrier properties of PCL-based films. The oxygen transmission rate (OT) and water vapor permeability (WVP) decreased significantly with the rise of GO in PCL films. Biodegradability of the PCL was not affected by adding GO. 25kGy gamma irradiation dose slightly improved the strength and barrier properties of PCL/O nanocomposite films. PCL-GO films could be used as a high load bearing films in food packaging. On the other side, microgel from PVA/AA was successfully prepared using electron beam irradiation. To improve the PVA microgel functionality and gel fraction, chains of polyacrylic acid (PAA) were incorporated into PVA microgel by radiation grafting technique. The increase in the acrylic acid (AA) content as well as PVA Mwt is accompanied by a mutual increase in the gel fraction and a decrease in the swelling %. Immobilization of different TiO2 concentrations on the surface of the prepared PVA-AA microgel was carried out. The structural changes in
the prepared PVA-AA microgel immobilized with TiO2/ were investigated using FTIR, EDX and XRD. Photo-degradation efficiency of TiO2/ PVA-AA microgel against metnil yellow dyes was studied. The efficient photo-catalytic ability of PVA/AA–TiO2 composite microgel is reflected in the determined photo bleaching rate of the dye. TiO2/ PVA-AA microgel activity increases with the increase of the amount of TiO2 and results in an increase in the rate of the photo-degradation reaction. Easily recovery and better reproducibility made TiO2/PVA/AA of great important in practice use as a photocatalytic degradation composite materials for the safe treatment of textile wastewater.

Work Plan

— Chemical modification and functionalized of graphene sheets by incorporating functional reagents having antioxidant and antimicrobial properties will be carried out to be use as a fillers for enhance the properties of some traditional packaging materials.

— Antioxidant and antimicrobial properties of the prepared composite packaging materials will be investigated.

— Effect of ionizing radiation on the properties and oxidation stability of the prepared nano-composites films will be studied.

— Preparation of smart polymeric packaging materials to be applied as intelligent packaging materials will be studied using. (e.g. polyaniline, polythiophene, polypyrrole,) as well as reactive monomers.

— These smart packaging materials could be prepared or modified using ionizing radiation or radiation.

— Practical study on a possible uses of such prepared materials as sensors or indicator for detecting food spoilage will be considered.

1.3.4. France

Summary

Cross-linking polymerization initiated by high energy radiation is a very attractive technology for the fabrication of high performance composite materials. The method offers many advantages compared to conventional energy- and time-consuming thermal curing processes. Free radical and cationic polyaddition chemistries have been investigated in some details by various research groups along the last years. A high degree of control over curing kinetics and material properties can be exerted by adjusting the composition of matrix precursors as well as by acting on process parameters.

However, the comparison with state-of-the-art thermally cured composites revealed the lower transverse mechanical properties of radiation-cured composites and the higher brittleness of the radiation-cured matrix. We have investigated several points related to these issues, and particularly the reduction of the matrix shrinkage on curing, the wettability of carbon fibers, the design of fiber-matrix interface and the use of thermoplastic toughening agents. A drastic enhancement of the $K_{IC}$ value exceeding 2 MPa.m$^{1/2}$ was also obtained for acrylate-based matrices toughened with high $T_g$ thermoplastics.

Improving fiber-matrix adhesion and upgrading polymer network toughness are thus two major challenges in this area. Particular attention was paid on the functional groups present at
the surface of carbon fibers. A study of the reactivity under electron beam of various acrylate monomers demonstrates that the inhibiting behaviour of these functions can be overcome by introducing in the reactive formulations various sensitizing agents that enhance the sensitivity towards high energy radiation. Significant improvements were achieved on transverse strain at break by applying original surface treatments on the fibers so as to induce covalent coupling with the matrix.

The second research axis of our project deals with the study of radiation curable nano-composites including cellulose nano-crystals (CNC) for enhancing the mechanical and the transport properties of the materials. We have selected and adapted protocols for the synthesis of cellulose nano-whiskers by acid hydrolysis of ramie fibers. The lab-scale procedure yields CNCs under the form of aqueous suspensions or of freeze-dried material. Bulk materials and films were prepared by blending the CNCs with polyurethane acrylate emulsions and by subsequent evaporation of water in appropriate molds. The reactivity under UV or EB radiation was studied by varying the curing conditions. Preliminary testing of mechanical properties reveals the enhancement of stiffness of the composite compared to the binder cured in the absence of filler. Further investigation on the composition-dependence of the key mechanical and transport properties is currently underway. Other types of fibers and matrices will be assessed during the coming months.

1.3.5. Germany

Summary

Photopolymerization of multifunctional acrylates is one of the most efficient methods for the production of highly crosslinked polymer coatings. In addition, the embedding of inorganic nanoparticles has drawn increasing attention in recent years due to the improvements in various coating properties including abrasion and scratch resistance. Compared to electron beam assisted curing, UV curing normally requires the addition of photoinitiators which absorb the incident light and generate sufficient radicals to start polymerization reactions. However, unconverted photoinitiator residues as well as low molecular fragments of the photoinitiator may cause disadvantages of the coating such as odour, toxicity, and yellowing which is especially harmful for clear coats.

The project proposed under this CRP has the objective of the self-initiation of any acrylate resin, i.e. photoinitiator-free UV curing. This is in fact possible but the absorption spectrum of the acrylate formulation has to match the emission spectrum of the UV source used. Unfortunately, acrylates (having absorption bands at wavelengths $\lambda < 220$ nm) do not or only weakly absorb in the spectral region of the commonly applied mercury arc lamps. It was reported that acrylates can undergo photopolymerization without photoinitiators by irradiation with short-wavelength vacuum(V) UV. To elucidate the effect of VUV irradiation on radiation curing of acrylate/nanoparticle formulations, a real-time (ATR) FTIR spectrometer attached to a UV lamp set-up consisting of a monochromatic 172 nm excimer lamp and/or a polychromatic medium pressure mercury arc lamp will be applied. The conversion of the acrylic C=C bonds will be monitored in the presence/absence of photoinitiators and air/nitrogen. The effect of 172 nm irradiation on radical formation and self initiation of the photopolymerization as well as on the properties of the nanocomposite coatings will be studied and compared with EB curing.
Work Plan

— Preparation of various acrylate/nanoparticle (e.g. Al₂O₃, SiO₂, TiO₂, ZnO) formulations
— VUV/UV radiation curing of neat acrylate and acrylate/nanoparticle formulations with or without photoinitiators
— Characterization of nanocomposite materials (cured with or without photoinitiators) by DMA, Taber-Abraser and Universal Hardness
— Real-time ATR FTIR curing studies with of neat acrylate and acrylate/nanoparticle formulations by VUV/UV lamps with or without photoinitiators

1.3.6. India

Summary

Varying compositions of Polychloroprene rubber (PCR) Ethylene-propylene diene monomer (EPDM) 50:50 blend containing Multiple Walled Carbon Nanotube (MWNT) as nanoparticulate filler (0.5-10%) were prepared and their efficacy for radiation crosslinking was analyzed by gel-content, Charlesby-Pinner parameter and crosslinking density measurements. Gel content measurement indicated insensitivity of the PCR/EPDM to radiation on incorporation of MWNT into the matrix. The elastic modulus increased while elongation at break decreased with radiation dose. The reinforcing mechanism of nanocomposites was studied by various micromechanics models which predicted higher modulus than the experimentally observed results, indicating agglomeration in the nano-composites. The thermal stability and Tₘ of the PCR and EPDM were not significantly affected by MWNT introduction into the blend matrix.

Work Plan

— Investigations on the synergistic interactions between nanofillers and radiation crosslinking.
— Experiments on the radiation assisted surface modification of nanoparticles to improve dispersion and interfacial compatibility.
— Synthesis of novel conducting nanocomposites for the development of toxic volatile vapours (VOCs) sensor.
— Radiation cured high performance inorganic-organic nanocomposite coatings containing layered silicates and metal NPs.
— Development of high performance composites for PTC/ NTC application using selective percolation in thermoplastic alloys.
— Development of compatibiliser in polymer blends and nanocomposites by using radiation induced grafting.
— Surface modification of nano filler by radiation processing to improve interaction with polymers.
1.3.7. Italy

Summary

Polysaccharide micro/nanoparticles, incorporating stabilizers (natural antioxidants), pro-degrading agents (such as enzymes or metal oxide nanoparticles) or other active ingredients, can be considered ideal chaperones to introduce various and heterogeneous substances into polysaccharide films in virtue of their structural affinity. The possibility of obtaining biodegradable and colloidal stable nanoparticles from xyloglucan has been here investigated.

Xyloglucans are a major class of structural polysaccharides found in the primary cell walls of higher plants. They are particularly interesting raw materials for their excellent film forming properties, thermal stability and hydroxyl rich, highly branched molecular structure, which controls hydrophobicity and solubility characteristics and, thereby, temperature or solvent responsiveness. If the branching degree and molecular weight are properly modified, stable xyloglucan nanoparticles dispersions can be obtained.

During the first part of this CRP protocols for xyloglucan purification and dispersion in water in the form of stable colloids have been developed. $^{60}$Co γ irradiation has been applied to modify the molecular weight distribution of a partially degalactosylated xyloglucan variant. Aqueous dispersions of the irradiated materials have been characterized by both dynamic light scattering measurements at different temperatures and gel filtration chromatography. The aggregation kinetics at 37°C of nonirradiated and irradiated variants have been studied by dynamic light scattering measurements in order to confirm their temperature-responsive behavior, when dispersed in water at low concentration. Chemical modification of xyloglucan with nitrocinnamic acid has been performed in order to graft nitrocinnamate pendant groups through an esterification reaction, thereby inducing reversible photocrosslinking. The success of the reaction has been confirmed through UV-vis and FTIR spectroscopies, whereas a more quantitative estimation of the derivatisation degree is undergoing.

Work Plan

— Static and dynamic light scattering studies at the variance of the angle to elucidate the organization of the polymer chains constituting the nanoparticles.
— Investigation of UV responsive properties of XG-CN both in form of micro/nanoparticles and thin films.
— Study of incorporation and triggered release of active ingredients from the micro/nanoparticles and micro/nanoparticles loaded polysaccharide films.

1.3.8. Malaysia

Summary

Composite materials combine properties of the individual components in a synergetic manner to produce a variety of materials in an efficient and cost effective manner. Thus, composite materials are being used in various applications from automotive to furniture industries. Materials reinforced with nanoscale components are adding new dimensions to composite materials and enable further major improvements in functional and structural properties. The
incorporation of only a few percent of nano-sized particles can make dramatic property changes that may result in enhancing physical and mechanical properties of the resulting composite. Several major issues need to be addressed to utilize the full potential of such nanofillers i.e. incompatibility or weak interfacial bonding between the matrix and the nanoscale component, and agglomeration of nanosized component during processing resulting in inhomogeneous distribution. UV/EB technology offers a way of overcoming these challenges by grafting of monomers/polymers including natural polymer onto the nanofiller surface thereby fixing their morphology and at the same time making them compatible with the host polymer.

Polymerization active silico-organic nanoparticles could be prepared by heterogeneous condensation (in situ reaction) and formed crosslinking in the polymeric substrates. With a relatively high nanopowder content of the nanodispersions, these coating materials could still be cured by UV light and electron beam (EB) to produce excellent polymeric composites. These coating materials show better resistances toward scratch and abrasion properties compared to pure acrylates.

Malaysian Nuclear Agency has developed ultraviolet (UV) curable overprint varnishes (OPVs) from epoxidized palm oil resins. We can substitute several percent of synthetic resins with epoxidized palm oil resins from natural polymers. These materials offer excellent gloss and scuff resistance. Overprint varnishes (OPVs) are coatings applied to an already printed sheet or web. UV curable coatings are solvent-free and ideal for hard-to-dry substrates. UV curable OPVs, as the name suggests, are cured when exposed to UV light. The materials produced by curing with UV technology will have several features such as (1) Increase in productivity – Shorter curing time; (2) Saving energy - The energy consumption of the process is lower; and (3) Environmental friendly technology – Biodegradable, non-toxic and reduce/eliminate the volatile organic compound (VOC) emissions.

Nuclear Malaysia has collaborated with several small and medium industries (SME) to commercialize this project i.e. the UV curable overprint varnishes (OPV). We have a pilot plant for this project with capacity between 50kg to 100kg.

**Work Plan**

- To prepare and synthesize radiation curable materials based on silica nanoparticles by heterogeneous hydrolytic condensation technique using natural polymers.
- To analyze the resins and hybrid materials.
- To formulate the basic radiation curable coating materials using natural polymers and to apply coating and curing process.
- To characterize and test the samples/materials by different techniques.
- To evaluate the final products

**1.3.9. Pakistan**

**Summary**

The combined effect of molecular weight of chitosan and zinc oxide on antimicrobial properties was carried out in this study. Chitosan having molecular weight in the range of 220
kDa to 73 kDa was extracted from crab shell using various conditions. The molecular weight of obtained chitosan was further lowered by gamma radiation in various environments. Chitosan in dry, wet and solution form was exposed to gamma rays in the dose range of 15 to 150 kGy. The effect of gamma radiation on the molecular weight of chitosan was characterized using viscometry, infrared spectroscopy and X-ray diffraction. The results showed that the physical state of chitosan and radiation dose greatly affect the molecular weight. At given dose, lowest molecular weight chitosan was obtained from chitosan in solution form. The antibacterial response of the radiation degraded chitosan was studied against gram-positive and gram-negative bacteria. In order to enhance the antibacterial property, chitosan was mixed with ZnO.

The influence of chitosan molecular weight and Zn(II) content on the structural and antimicrobial properties of the complexes was also envisaged. The FTIR and XRD analysis of the complexes revealed the formation of different molecule structure with different zinc content. The in-vitro antimicrobial studies of the chitosan and chitosan/Zn (II) complexes were evaluated against Pseudomonas aeruginosa, staphylococcus CNS, Escherichia coli, Staphylococcus aureus 28 and Staphylococcus aureus ATTC using wells assay diffusion method. The complexes showed wide spectrum of effective antimicrobial activities, which were further improved by using low molecular weight chitosan. The complexes had an excellent antifungal activity and no growth of Aspergallious fumigatus and Fusarium solani were observed after two weeks.

1.3.10. Poland

Summary

The work reported was concentrated on the radiation supporting synthesis and curing of nanocomposites suitable for practical applications. In the last decades ultrafine metal particles have attracted considerable interest as a distinct state of matter with unique physical and chemical properties. It was demonstrated that one of the method to avoid problems with size distribution of some metal particles is to produce them inside well-defined frameworks of crosslinked gels, molecular sieves or polymeric templates.

The investigated systems were constructed from two components: a matrix either made of polymeric material or inorganic molecular sieves and metal particles stabilize in the previously prepared framework. The investigated structures were received using radiation techniques. The following tasks were realized:

- Studies of interaction between inorganic and polymeric components in a hybrid system. pH-responsive bi- and tri-component hydrogels were constructed via radiation treatment. The crosslinking density considerably influenced swelling behavior as for lower doses the process was more efficient than for higher one. The obtained materials were swelled with Ag⁺ aqueous solutions. Upon radiation induced reduction the metal particles were stabilized in the hydrogel matrix or in the PVA films and the effect depended on radiation dose, dose rate and chemical nature of the hydrogels. Hydrogel structures composed of hydrophilic polymers linked through chemical intermolecular bonds were tested in the presence of Ag⁺ and Cu²⁺ as indicators. pH-responsive characteristic was determined on a basis of swelling capacity that decreases mainly due
to the screening effect of cations. Additionally the effect is a consequence of metal ion complexation with the polymer network which enhances its apparent cross-link density.

— Paramagnetic silver clusters in sodalite:
In dehydrated sodalite loaded with different guest anions silver agglomeration occurs directly after irradiation at liquid nitrogen temperature, when silver atoms and cations are not mobile. It requires preliminary arrangement of silver cations during thermal dehydration process. We postulate that $\text{Ag}_8^{7+}$ octamer is formed by trapping radiolytically produced electron by a set of eight silver cations located in the same cage. Silver agglomeration process in sodalites is controlled first of all by water molecules located inside sodalite cages. The higher degree of dehydration the larger amount of empty cages inside which migration of the reduced silver species is easier. The type of guest anion plays rather secondary role. On the other hand, the nuclearity of silver clusters stabilized in sodalites depends also on the size of sodalite crystallites.

— Template deposited microstructures of silver haloids
Template synthesis of silver halide microstructures ($\text{AgCl}$, $\text{AgBr}$) using track-etched membranes with pore diameters from 0.2 $\mu$m up to 2.3 $\mu$m have been performed. It was confirmed that silver halides microrods in membrane pores and micrograins on membrane surfaces were deposited. Migration of silver cations through track membrane is more intensive than chloride ions.
Color of the silver haloids microstructures practically does not change in scattering visible light what is in contrast with darkening of silver halides prepared in bulk. The microstructures darkened after exposure to UV (366 nm) and EB (10 MeV) what was confirmed by a photometric method. The effect results from changes in micrograins morphology identified by SEM. It seems that silver halide microstructures can be used as indicators of UV or ionizing radiation.

Work Plan

— Application of ionizing radiation for preparation of biodegradable packaging materials based on polysaccharide nanocomposites. The studies will be concentrated on the preparation of the edible and biodegradable films and coatings based on polysaccharides, proteins and lipids.

— Stabilization of nanoparticles in the polymeric matrices. Investigations will be focused on e.g. curing of thermoset composites by radiation treatment.

1.3.11. Serbia

Summary

The major challenges in designing of polymer nanocomposites are the ability to control the size and the morphology of dispersed nanoparticles, as well as to achieve their homogeneous distribution through the polymer matrix. The gamma irradiation induced reduction of metal ions in polymers i.e. radiolytic in situ formation of metal nanoparticles in the presence of polymers is particularly suitable for preparation of nanocomposites based on metal nanoparticles incorporated in polymer matrix.

The research activities in Serbia are related to radiolytic synthesis of nanocomposites with Ag-nanoparticles (Ag NPs) incorporated in polymer matrix composed of chitosan (CS) and/or
poly(vinyl alcohol) (PVA). The obtained results indicate the good stability of Ag NPs as well as uncrosslinked Ag-CS/PVA nanocomposites over a long period of time. It was found that the composition of CS/PVA matrix affects the size of the obtained Ag NPs, as well as the parameters such as density, molar concentration and the effective surface area, calculated from the experimentally obtained UV-Vis absorption spectra and spectra obtained by simulation according to the Mie theory. Spherical morphology of Ag NPs was confirmed by SEM analysis, with the average diameter of particle around 13 nm. Microstructural analysis of Ag-CS/PVA nanocomposite was performed by XRD measurement, and obtained results indicate that Ag NPs have face centered cubic structure, with the crystalline domains around 12 nm. The results of FTIR spectroscopy showed that the stabilization of Ag NPs occurs through their interaction with −OH and −NH₂ groups of the polymers, and that the interaction increases with increasing of PVA content in the blends.

Moreover, it was confirmed that gamma irradiation method is suitable for formation of crosslinked PVA/CS polymer networks, which can serve as a matrix for further radiolytic in situ incorporation of Ag NPs, in order to obtain crosslinked nanocomposites. Swelling investigations of obtained PVA/CS hydrogels show that the increasing of CS content influenced the swelling properties of hydrogels as well as network parameters. The investigation of diffusion properties of PVA/CS hydrogels indicate that systems shows non-Fickian diffusion, when the rates of diffusion and polymer chain relaxation are comparable.

**Work Plan**

— Radiolytic synthesis of Ag and/or Au nanoparticles in hydrogels based on CS and PVA, previously obtained by gamma irradiation.

— Investigations of possibility of one-step synthesis of nanocomposite systems in order to achieved simultaneously crosslinking of polymers and in situ synthesis of noble metal nanoparticles.

— Characterization of nanocomposite systems by swelling measurements in order to investigate swelling kinetics, diffusion properties and network parameters. Formation of metal nanoparticles in polymer networks and interaction between nanofiller and polymer matrix will be followed by UV-vis and FTIR spectroscopy, respectively. Investigation of shape, structure, size and size distribution of metal nanoparticles as well as properties of nanocomposites will be performed by TEM, SEM; AFM, XRD and mechanical measurements. In addition, the antibacterial properties of the synthesized nanocomposite systems will be tested.

**1.3.12. Thailand**

**Summary**

This research project aims to apply the use of radiation processing to prepare biodegradable composites from poly(lactic acid) or polylactide (PLA) and cassava starch. The major problem of blending PLA with starch is a very poor compatibility between hydrophilic starch and hydrophobic PLA. Our on-going research has succeeded to improve the compatibility between hydrophobic natural rubber and hydrophilic silica by radiation-induced admicellar polymerization of isoprene on the silica surface. The results showed that the modified silica is more compatible to natural rubber, resulting in improved properties of the rubber compounds.
The results strongly confirm the effectiveness of surface modification of silica through admicellar polymerization. Hence, this research intends to improve the compatibility between PLA and starch by similar concept, using radiation-induced grafting polymerization.

**Current Status**

— Cassava starch-grafted-PLA (CS-g-PLA) was synthesized from the surface modification of starch by reacting with L-lactic acid. The surface modified starch was mixed with L-lactide to induce the ring-opening graft polymerization of L-lactide onto the modified starch to yield CS-g-PLA. The CS-g-PLA was confirmed by FTIR.

— Radiation-induced crosslinking of PLA was done, in the presence of a crosslinking agent (TAIC), using gamma radiation. The mixing of PLA and the crosslinking agent was done using a twin-screw extruder. Optimum concentration of the crosslinking agent and optimum dose were determined.

— Thermoplastic starch (TPS) was prepared from cassava starch and glycerol. The prepared TPS will be used as a control (the blend between PLA and starch, without a plasticizer). The TPS was mixed with PLA (with and without TAIC) using the twin-screw extruder.

**Work Plan**

— The synthesis of CS-g-PLA will be optimized. CS-g-PLA will be synthesized in a large amount to be use as a plasticizer for PLA and cassava starch.

— The properties of the polymer blends (with and without the plasticizer, with and without nanoclay) will be compared.
  - PLA
  - PLA + TPS
  - PLA + TPS + CS-g-PLA

1.3.13. Turkey

**Summary**

In polymer/clay nanocomposites when small amount of clay mineral is randomly and homogeneously dispersed on molecular level in a polymer matrix, the mechanical, thermal and barrier properties of these materials become superior to the precursor polymers. Polymers have been successfully reinforced using glass fiber, talc, calcium carbonate and other inorganic fillers. The content of the filler is usually between 20-40% of composite. In these systems polymers and fillers are not homogeneously mixed on a microscopic scale, and the interaction between the polymer matrix and the filler is limited due to small interface. If the filler however is of molecular size then mechanical properties could be further improved. If platelets of nm dimensions wer used instead of fibers, the contact surface would become much larger.

Since clay minerals especially montmorillonite (MMT) are composed of several layers of silicates they have very high potential for the preparation of polymer nanocomposites. The problem of incompatibility between nonpolar, hydrophobic polymers like polyolefines and polar and hydrophilic clays can be overcome by using organomodified clays. Such
organomodified clays are commercially available. This is an approach based on the chemical modification of clays by introducing quaternized ammonium salts in between the silicate layers thus exposing these layers for further interaction with the polymer matrix. Compatibility between the untreated MMT and polyolefin can be improved on the other hand by using chemically modified polymers, generally maleic anhydride grafted polymers as compatibilization agents.

In this Research Project we made use of ionizing radiation to modify either the base polymer or MMT to make them compatible in the preparation of nanocomposites. We prepared polypropylene/MMT nanocomposites by using radiation degraded and oxidized PP as compatibilization agent. Ethylene/vinyl acetate copolymer (EVA) / MMT nanocomposites were prepared by modifying the MMT by radiation-induced, in-situ polymerization of a charged monomer within the spacings between the silicate layers. Optimum doses were determined to achieve the highest compatibilization which was followed by mechanical tests. The characterization of both nanocomposites were made by spectroscopic and thermal analyses as well as by positron annihilation life-time measurements to determine the changes taking place in free volume holes in the nanocomposites. Full exfoliation in radiation modified MMT has been achieved at 3-5% loading improving the mechanical properties by 50% over the pure EVA copolymer.

Double and triple polymer/metal ion complexes based on PAA and Copper coordinated by polymers carrying primary and secondary amin groups have been used as matrices for the synthesis of copper nanometalclusters with controlled size and size distributions in the range of 2-20nm. Oxidation stability of copper nanoclusters has been improved in polymer thin films.

1.3.14. USA

Summary

Ionomers based on magnetically active ions and nanocomposites based on magnetic oxide nanoparticles were incorporated into acrylate co-polymers using ionizing radiation in the form of Co-60 gamma rays or electron beam irradiation. The applied radiation doses and dose rates affect the 2-ethylhexylacrylate/acrylic acid co-polymerization and, consequently, the size and distribution of the ionomers or nanoparticles throughout the structure formed upon reacting the co-polymer with a salt of the magnetic ion or with a dispersion of oxide nanoparticles. As a result, the irradiation conditions are ultimately responsible for controlling the magnetic properties of the product. This makes it possible to obtain different types of magnetic behavior for different applications by adjusting the irradiation conditions to generate a desired degree of polymerization and a desired distribution of the acrylic acid functionalities. Preparation of the co-polymer through the use of ionizing radiation makes it possible to avoid the use of chemical initiators, which later occupy sites within the structure of the co-polymer and are thus likely to interfere with the formation of the magnetic ionomers and nanocomposites. Radiation-induced synthesis of co-polymers can also be performed without having to use, and later to remove, volatile solvents. Thus, radiation technology offers a highly advantageous pathway for the synthesis of magnetic ionomers and nanocomposites, which are currently attracting much attention because of their potential use in imaging, drug delivery, magnetic storage, and other advanced applications.
Work Plan

— Future work for this project includes the continuation of characterization of the magnetic nanocomposites and ionomers and measurements of magnetic properties over a broad range of concentrations of the magnetic species.
— Correlations between the spectroscopic observations of magnetic particle size and the supermagnetic and ferromagnetic behavior will also be developed.
— Detailed characterization of the nanostructure will be performed in order to obtain a clear picture of the distribution of Fe in the co-polymer.

1.3.15. Vietnam

Summary

Synthesis of silver nanoparticles colloids by γ-irradiation using PVA and PVP as stabilizer was carried out. The conversion dose (Ag⁺ → Ag⁰) for Ag⁺ concentration of 5, 10 and 20 mM was measured by UV-vis spectroscopy. Test production of colloidal silver nanoparticles solution (50L/box) has been conducted for 5 mM Ag⁺/1% PVP/5% C₂H₅OH on a gamma industrial irradiator. The average diameter of silver nanoparticles is of 10-15 nm measured by TEM. Characteristics of porous ceramic samples particularly specific surface area (m²/g), average pore size (Å) and pore volume (cm³/g) were determined. Porous ceramic samples were functionalized by treatment with aminosilan and then impregnated in colloidal silver nanoparticles solution for fixing through coordination bonds between –NH₂ groups and silver atoms. The silver content attached in ceramic was of about 200-300 mg/kg. Preliminary results of silver release from porous ceramic into filtrated water together with the results of antimicrobial effect for E. coli by flow test show that the porous ceramic/silver nanoparticles material is promising for application for drinking water purification.

1.4. Conclusions

The participants of the CRP have reached the following conclusions:

New scratch and abrasion resistant coating formulations:

— Formulation containing inorganic additives and control of radiation initiated polymerization were identified as the key strategies for developing coatings with enhanced surface finishing.
  • Preparation and synthesis of radiation curable materials based on new ingredients such as epoxidized palm oil acrylate (EPOLA) and functionalized silica and alumina particles by heterogeneous hydrolytic condensation technique have been shown to be very promising in terms of enhanced properties.
  • Optimization of the curing conditions by using conventional radiation sources such as UV lamps, LEDs and EB would offer a better control over desired properties with respect to various target applications. Irradiation with VUV photons emitted from 172 nm excimer lamps results in the activation of C=C and C=O bonds offers an additional means for achieving micro-scaled surface structuration as well as photoinitiator-free UV curing of acrylate-based composites. Therefore, VUV
irradiation may become an alternative to electron beam curing in food packaging applications.

**Preparation methods for radiation curable nano-composites from natural polymers (or monomers):**

— Radiation processing has been proved to be a useful tool for tailoring the molecular properties of xyloglucan (XG) to develop polysaccharide nanoparticles as photo-responsive carriers of various ingredients into bio-plastic films. Compatibility of XG nanoparticles with the matrix will rely on the structural similarity between the dispersant and the polymer matrix, the biodegradability of the nanocomposite film being preserved.

— Gamma irradiation can be used to synthesize colloidal stable AgNPs in ambient, laboratory conditions for several months. Similarly, stable AgNPs were incorporated into CS/PVA matrices to obtain nanocomposites with controllable optical properties.

— Cellulose nanocrystals can be efficiently added to polyurethane acrylate emulsions and to aqueous pre-polymer solutions to obtain radiation curable coatings and bulk materials.

**Preparation of protocols and specifications for new biodegradable packaging materials**

— Low amount of graphene oxide (GO) nanomaterials under the form of sheet significantly improved mechanical and barrier properties of PCL films. Radiation stability and biodegradability of such composites was not affected by the presence of the GO. These compositions could be used for mechanically resistant high load bearing films in food packaging.

— Introduction of modified clay into blends of PE and plasticized starch led to significant reinforcement in packaging materials intended to be used in radiation sterilizable products.

— PLA-grafted-starch was demonstrated as an efficient compatibilizer for blending PLA with cassava starch. Optimum conditions were determined for radiation-induced crosslinking of PLA using a crosslinking agent, to achieve better controlled thermal properties.

— Biodegradable polymer grafting by gamma radiation with TMPTMA, silane, hema, combined with nanoparticles filling, were reached by characterizing the structure and the rheological (mechanical and barrier) properties of resulting grafted/reinforced films.

— PCL-based films reinforced by CNT using gamma radiation led to significant reinforced packaging materials.

— Microfluidisation and irradiation treatment for better dispersion of nanofibers in suspension has permitted the development of a methodology to encapsulate antimicrobial compounds,

— A protocol to measuring the control release of active compounds was also developed and permitted a rapid measure to evaluate the control release of active compounds.

— A methodology to encapsulate antimicrobial compounds and probiotic bacteria in polymers and combination with irradiation was also developed to assure food safety.
New methods to modify surface characteristics of nano-sized materials to enhance polymer fillers interaction:

— Organo modification of clay using charged monomers impregnated in the clay by irradiation was demonstrated as a successful technique to induce compatibility into clay. Nanocomposites prepared by using radiation-modified MMT and EVA showed 50% improvements in elastic modulus and tensile strength as compared to EVA.

— Functionalization of carbon nanofibers by radiation grafting of acrylic acid is confirmed as a suitable technique to modify the surface properties.

— The inhibiting effects on free radical reactions of functional groups at the surface of carbon fiber were effectively overcome by sulfur-based surface treatment and/or sizing.

Magnetic nanocomposites and ionomers

— The particle sizes of the magnetite (Fe₃O₄) control the ratio between ferromagnetization and supermagnetization.

— Acrylic acid content and MW of radiation polymerized poly(2-ethylhexyl acrylate-co-acrylic acid) copolymers are the key parameters controlling the chelation properties for magnetic nanoparticle formation.

— The magnetization results show a combination of ferromagnetic behavior (hysteresis) at relatively small magnetic fields with superparamagnetic behavior at large fields.

Metal and metal oxide nanoclusters/nanoparticles

— Production of silver nanoparticles colloid with controlled size (10-20 nm) can be carried out in large scale (Ag 500 mg/L @ 10 m³/day) by using industrial gamma irradiator.

— Reusable TiO₂ nanoparticles embedded in PVA/PAAc microgels prepared using EB were successfully used for photo-catalytic degradation of Mentail Yellow dye.

Matrix for nanocomposites

— Porous ceramic loading with AgNPs proved to be highly antimicrobial material which can be used for water purification.

— It was demonstrated that silver nanoclusters and silver halides having micro and submicro structures might be deposited in sodalite structures and in track membrane pores, respectively. Such a template supported synthesis assure control over the particle size and distribution.

— Semi-interpenetrating networks of PVA and CS were synthesized with proper crosslinking density by gamma irradiation for allowing subsequent in situ generation of silver nanoparticles.

Elastomer-based nanocomposites

— Light-weight and high-modulus EPDM/PCR/MWCNT nanocomposites were prepared by radiation processing. The oil resistance of EPDM/PCR blends was improved by radiation crosslinking, while simultaneously preserving elastic properties.
1.5. Recommendations

1.5.1. General recommendations

Participants are highly recommended and advised to:

- Elucidate mechanisms and kinetics of radiation induced processes
- Study the structure function relationships of irradiation induced on polymer
- Achieve advanced characterization of nanocomposites at different dimension scales by using all techniques made available by the participants of this CRP
- Take into account ageing and stability issues of the nanomaterials and nanocomposites (evolution of properties, mechanism and kinetics of degradation)
- Be aware of concerns related to the fate of nano-sized materials and more generally from the by-products.

1.5.2. Specific recommendations

- The use of epoxidized palm oil acrylate (EPOLA) has been recommended to be extended for a replacement of oil-based coating applications.
- The extension of the use of new metal and metal oxide nanoparticles such as Ag, TiO$_2$ and ZnO has been encouraged for radiation-curable formulations yielding scratch resistant coatings with hydrophilic and antibacterial properties.
- VUV irradiation has been recommended to be used for achieving micro-scaled surface structurization as well as photoinitiator-free UV curing of acrylate-based nanocomposites.
- It is recommended to study more systematically the composition effects and the influence of processing parameters on the structural features and mechanical properties of the nanocomposites.
- For elastomer applications, it is needed to develop compatible nanofillers for polymer nanocomposites, particularly by radiation processing of nanofillers with functional monomers.

1.5.3. Recommendation for the 3rd RCM

The participants have recommended the last meeting to be held in Palermo, Italy, in the second quarter of 2014.
PUBLICATIONS RESULTING FROM THE COORDINATED RESEARCH PROJECT


KRSTIĆ, J., SPASOJEVIĆ, J., RADOSAVLJEVIĆ, A., ŠILJEGOVIĆ, M., KAČAREVIĆ-POPOVIĆ, Z., “Optical and structural properties of radiolytically in situ synthesized silver nanoparticles stabilized by chitosan/poly(vinyl alcohol) blends”, manuscript was submitted for publication in the Radiation Physics and Chemistry, current status is “Under Review”.


NIK GHAZALI NIK SALLEH, MOHD SOFIAN ALIAS, HANS–JÜRGEN GLÄSEL AND REINER MEHNERT (2012). UV/EB Curing of Nanocomposites for Enhancing their Functionality and Utility


YASIN, T., NISAR, M., SHAFIQ, M., NHO, Y., AHMAD, R., “Influence of Sepiolite and Electron Beam Irradiation on the Structural and Physicochemical Properties of Polyethylene/Starch Nanocomposites”, Polymer Composites, accepted for publication
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<td>USA</td>
<td>Planned: Italy</td>
<td>AAc-grafted-PVP nanoparticles for imaging</td>
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<td>Mr. Mohamad AL-SHEIKHLY</td>
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<td>Planned: Germany</td>
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<tr>
<td></td>
<td>Mr. Nguyen Quoc Hien</td>
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<td></td>
</tr>
</tbody>
</table>
REPORTS BY PARTICIPANTS OF THE COORDINATED RESEARCH PROJECT
DEVELOPMENT OF RADIATION PROCESSING TO FUNCTIONALIZE CARBON NANOFIBER TO USE IN NANOCOMPOSITES FOR INDUSTRIAL APPLICATION

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Radiation process has potential application in modifying the structure of carbon fibers and carbon nanofibers in order to produce useful defects in the graphite structure and create reactive sites. In this study is proposed a methodology for radiation grafting processing to modify carbon nanofiber surfaces by grafting acrylic acid on carbon nanofiber surface. The samples were submitted to indirect and direct radiation process. Several parameters were changed such as acrylic acid concentration, radiation dose and percentage of inhibitor to achieve better oxygen content and dispersion. The samples were characterized by Raman and X-ray Photoelectron Spectroscopies. The dispersion stability upon storage was visually investigated. The samples that were added to a solution of acrylic acid with 6% of inhibitor and were direct irradiated at 100 kGy dose presented higher oxygen content and better dispersion.

1. Introduction

The complex morphology of carbon nanofibers (CNFs) requires careful control of the surface to promote properties required for end use because CNFs are not highly compatible with most polymers. Therefore, it is necessary to modify, or “functionalize”, the surfaces through chemical or physical techniques to produce optimized polymer composites. The most commonly used approach is oxidation. Oxidizing the nanocarbon surface creates active sites (polar sites) which may prepare the nanocarbon surface for further chemical reaction or “grafting” with additional organic groups. Carboxylic acid groups are often considered the most desirable oxygen functional groups because of the variety of chemical reactions that can be conducted with these groups. For example, carboxylic acid groups have the ability to initiate cationic polymerization of vinyl monomers, and they can facilitate the chemical grafting of amine or epoxy groups to carbon nanotube surfaces [1]. Polymers with amino side groups can be grafted onto the oxidized nanotubes through amide formation, leading to high solubility in most organic solvents and water. Alkyl chains with amine groups can be covalently attached onto the oxidized nanotubes using a carboxylate-ammonium salt that also improves the solubility of the nanotubes. For application of carbon nanofiber as a catalyst support, carboxylic acid plays an important role because it confers an acidic character to the carbon surface and they can be used as catalyst anchoring sites during ion exchange preparation [2]. In polymer composites reinforced with carbon nanofillers, covalent bonding functional groups are intended to improve the efficiency of load transfer from the nanocarbon particle to the polymer matrix. However, the presence of these bonding alters the otherwise perfect structure of the basal plane and therefore lowers the strength of the nanoparticle. Optimum functionalization is therefore a balance of these two factors. Interface plays a major role in materials in general because it will determine the mechanical and physical properties of the resulting composite materials. The large differences between the elastic properties of
the matrix and the fiber are transmitted to the fiber through the interface [3]. There are several methods to functionalize carbon fiber and these modifications promote changes in composite properties [4-19]. It is believed that functionalization increases reactivity on the fiber surface allowing them to better disperse into the matrix resulting in more uniform properties [20]. Existing surface treatment methods include wet chemical, electrochemical, gas or plasma phase and polymer coating processes [21]. Many of these functionalization processes depend on having an oxidized nanocarbon surface as a starting point because oxidation is used as purification method as well as to create polar sites to allow a specific functional group to graft to the carbon nanofiber surface. Hydroxyl, carbonyl, ester, quinine, and carboxyl groups are typically found on a CNF surface after an oxidizing process. In general, oxidation processes are time consuming, energy inefficient, and may generate toxic residues. Acid oxidation is the most common process used to oxidize CNFs.

Good results have been achieved, but it requires careful control because the unintentional or excessive damage to the structure. In addition, it delivers a high amount of chemical waste to the environment. For example, to oxidize 4.5 mg carbon nanofiber oxidation with nitric acid (70% v/v) generated around 6 liters of chemical contaminated water used to wash the oxidized nanofiber. Evora et al. explored the use of a high energy electron beam as the only available technique for selective area surface modification of CNFs through controlled parameters such as radiation dose, sample temperature, and environment [22-23].

2. Samples description

The descriptions of the samples are present in Tables 1 and 2. The samples presented in Table 1 shows the samples submitted to indirect radiation grafting process and it is better described in the item 3.1. PR-25-PS-XT carbon nanofibers were irradiated up to 1000 kGy and added to solutions containing different monomers. In Table 2 is presented samples submitted to direct radiation grafting process that is described in item 3.2. PR-25-PS-XT carbon nanofibers were added to solutions containing acrylic acid and irradiated with gamma and electron beam radiation.

2.1. Indirect radiation grafting process

The samples that were submitted to indirect radiation grafting process are shown in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Dose (kGy)</th>
<th>Monomers (%)</th>
<th>Condition of grafting solution after grafting reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR-25-PS-XT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>water/methanol</td>
<td>0</td>
<td>8</td>
<td>Not dispersed</td>
</tr>
<tr>
<td>water/methanol</td>
<td>1000</td>
<td>8</td>
<td>Good dispersion</td>
</tr>
<tr>
<td>MMA/water/methanol</td>
<td>1000</td>
<td>8</td>
<td>Good dispersion</td>
</tr>
<tr>
<td>Styrene/water/methanol</td>
<td>1000</td>
<td>8</td>
<td>Very bad dispersion</td>
</tr>
<tr>
<td>PEG/water/methanol</td>
<td>1000</td>
<td>8</td>
<td>Very good dispersion</td>
</tr>
<tr>
<td>Ac.Ac/water/methanol</td>
<td>1000</td>
<td>8</td>
<td>Good dispersion</td>
</tr>
</tbody>
</table>
It was expected, based on previous work, that 1000 kGy irradiated PR-25-PS-XT had an increase of oxygen functional groups on the surface and therefore a better dispersion in polar solvents. Similar results were obtained in current investigation. The samples irradiated and treated with monomers showed better dispersion and stability in a 50/50 vol% water/methanol solution than non-irradiated nanofiber, except the sample treated with styrene. The samples treated with PEG had the dispersion stable for 10 days (see Figure 1).

2.2. Direct radiation grafting process

The samples that were submitted to direct radiation grafting process are shown in Table 2.

**TABLE 2. SAMPLES PREPARED WITH ACRYLIC ACID SUBMITTED TO DIRECT RADIATION GRAFTING PROCESS**

<table>
<thead>
<tr>
<th>Samples Name</th>
<th>Samples Name</th>
<th>Dose (kGy)</th>
<th>AA (%)</th>
<th>FeSO₄·7H₂O (%)</th>
<th>Condition of grafting solution after grafting reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAI</td>
<td>pristine as received</td>
<td>0</td>
<td>None</td>
<td>None</td>
<td>Bad dispersion</td>
</tr>
</tbody>
</table>

Fig. 1. Dispersion of PR-25-PS irradiated up to doses 1000 kGy and mixed with monomers (MMA, Styrene, PEG, Acrylic acid).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Radiation</th>
<th>Inhibitor</th>
<th>Gel</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA2</td>
<td>pristine/acetona</td>
<td>0</td>
<td>20%</td>
<td>1%</td>
<td>Bad dispersion</td>
</tr>
<tr>
<td>GA3</td>
<td>pristine/acetona</td>
<td>1000 kGy</td>
<td>0</td>
<td>0</td>
<td>Not performed</td>
</tr>
<tr>
<td>GA4</td>
<td>pristine/acetona</td>
<td>1000 kGy</td>
<td>175 kGy</td>
<td>gamma</td>
<td>0</td>
</tr>
<tr>
<td>GA5</td>
<td>pristine/acetona</td>
<td>100 kGy</td>
<td>gamma</td>
<td>20%</td>
<td>3%</td>
</tr>
<tr>
<td>GA6</td>
<td>pristine/acetona</td>
<td>100 kGy</td>
<td>gamma</td>
<td>20%</td>
<td>1%</td>
</tr>
<tr>
<td>GA7</td>
<td>pristine/acetona</td>
<td>150 kGy</td>
<td>gamma</td>
<td>20%</td>
<td>1%</td>
</tr>
<tr>
<td>GA8</td>
<td>pristine/acetona</td>
<td>175 kGy</td>
<td>gamma</td>
<td>20%</td>
<td>1%</td>
</tr>
<tr>
<td>GA 8.1</td>
<td>pristine/acetona</td>
<td>175 kGy</td>
<td>gamma</td>
<td>8%</td>
<td>1%</td>
</tr>
<tr>
<td>GA 8.2</td>
<td>pristine/acetona</td>
<td>175 kGy</td>
<td>gamma</td>
<td>15%</td>
<td>1%</td>
</tr>
<tr>
<td>GA 8.3</td>
<td>pristine/acetona</td>
<td>175 kGy</td>
<td>gamma</td>
<td>30%</td>
<td>1%</td>
</tr>
<tr>
<td>GA9</td>
<td>pristine</td>
<td>10 kGy</td>
<td>gamma*</td>
<td>33%</td>
<td>1%</td>
</tr>
<tr>
<td>GA10</td>
<td>pristine</td>
<td>0</td>
<td>gamma</td>
<td>33%</td>
<td>Blank</td>
</tr>
<tr>
<td>GA11</td>
<td>pristine/acetona</td>
<td>50 kGy</td>
<td>ebeam</td>
<td>Good dispersion and no issue to filter</td>
<td></td>
</tr>
<tr>
<td>GA 11.1</td>
<td>pristine/acetona</td>
<td>100 kGy</td>
<td>ebeam</td>
<td>8%</td>
<td>6%</td>
</tr>
<tr>
<td>GA 11.2</td>
<td>pristine/acetona</td>
<td>150 kGy</td>
<td>ebeam</td>
<td>Gel</td>
<td></td>
</tr>
<tr>
<td>GA 11.3</td>
<td>pristine/acetona</td>
<td>0</td>
<td>ebeam</td>
<td>Gel</td>
<td></td>
</tr>
<tr>
<td>GA 12</td>
<td>pristine</td>
<td>175 kGy</td>
<td>gamma</td>
<td>30%</td>
<td>1%</td>
</tr>
<tr>
<td>GA 13</td>
<td>pristine/acetona</td>
<td>100 kGy</td>
<td>gamma</td>
<td>10%</td>
<td>6%</td>
</tr>
<tr>
<td>GA 14</td>
<td>pristine/acetona</td>
<td>100 kGy</td>
<td>gamma</td>
<td>10%</td>
<td>10%</td>
</tr>
</tbody>
</table>

* Source of Institute of Advanced Studies

Figure 2 shows the sample is GA5, GA 13 and GA14. All samples were irradiated at 100 kGy with different percentage of inhibitor (FeSO₄·7H₂O). The GA5 sample has lower addition of FeSO₄·7H₂O than in GA 13 and GA 14 samples allowing the homopolymerization to occur. GA 13 presented an excellent dispersion after radiation grafting process. GA 14 had a good dispersion however not very stable. Addition of inhibitor to the acrylic acid solution is needed to minimize homopolymerization. At the same time, hindering of the grafting reaction cannot be excluded, the minor consequence being lowering of grafting yield. Clochard et al. used Mohr’s salt as an inhibitor and concluded that with increasing inhibitor concentration, the grafting yield of PVDF films falls from 130% to 70%. As the inhibitor is able to diffuse in the film, it speeds up the termination reaction of the grafting polymerization thus leading to lower grafting yields [12].
Fig. 2. Illustration of some samples presented in Table 2. a) PR-25-PS-XT cleaned with acetone mixed with acrylic acid + 3% FeSO₄·7H₂O and irradiated at 100 kGy dose, b) PR-25-PS-XT cleaned with acetone mixed with acrylic acid + 6% FeSO₄·7H₂O and irradiated at 100 kGy dose (estable and excelente dispersion) PR-25-PS-XT cleaned with acetone mixed with acrylic acid + 10% FeSO₄·7H₂O and irradiated at 100 kGy dose.

2.2.1. Samples description summary for direct radiation grafting process

2.2.1.1. Gamma radiation

(1) In GA2 (Blank), GA6, GA7 and GA8- Carbon nanofiber were add to same percentage of acrylic acid and percentage of FeSO₄·7H₂O.

(2) GA5 and GA6- Carbon nanofiber were add to same percentage of acrylic acid but different percentage of FeSO₄·7H₂O and irradiated at same dose (100 kGy).

(3) GA 3 and GA 4- This experiment was not performed. The objective of this experiment is to take advantage of polar sites available on the carbon nanofiber that was irradiated in previous experiments whose results have already been presented when the project was proposed.

(4) GA 8, GA 8.1, GA 8.2 and GA 8.3- carbon nanofiber were added to different percentage of acrylic acid, same percentage of FeSO₄·7H₂O and irradiated at same dose (175 kGy).

(5) GA 9 and GA 10- Sample irradiated at Institute of Advanced Studies.

(6) GA13 and GA14- Carbon nanofiber were add to same percentage of acrylic acid, irradiated at same dose (100 kGy), but different percentage of FeSO₄·7H₂O.
2.2.1.2. Electron Beam radiation

(1) GA11, GA11.1 and GA11.2- Carbon nanofiber were added to the same percentage of acrylic acid and the percentage of FeSO$_4$·7H$_2$O, but irradiated at different doses.

(2) GA11.3 (Blank) - Carbon nanofiber were added to the same percentage of acrylic acid and the percentage of FeSO$_4$·7H$_2$O, but irradiated at different doses.

3. Development of grafting process using electron beam

3.1. Indirect radiation grafting process

Pyrograf III™ Vapor Grown Carbon Nanofibers (VGCF) was purchased from Applied Science Inc. (Cedarville, Ohio). We selected the PR-25-PS-XT grade, which has an average diameter of 80 nm and has been heated treated in inert atmosphere up to 1100°C to remove polyaromatic hydrocarbon and metal catalyst impurities from the surface. This grade has a good balance of mechanical and electrical properties. Materials were irradiated with a pulsed linear accelerator operated by the University of Dayton Research Institute (Dayton, Ohio). This equipment was operated with the following parameters: beam energy 3 MeV, pulse rate 150 pulses/sec, pulse width 5 msec, pulse current 120 mA/pulse (equates to 0.09 mA time-averaged beam current), and air gap of 35 cm, resulting in a dose rate of approximately 16.7 kGy/min. The details of the electron beam accelerator system are described in detail by Klosterman [24].

Dried as-received PR-25-PS-XT was irradiated in the form of a loose powder with bulk density of approximately 0.032 g/cm$^3$. PR-25-PS-XT loose powder was irradiated in air up to 1000 kGy. Part of these irradiated samples was soaked into MMA, styrene, PEG, acrylic acid and epoxy solution with water/methanol (50% vol) to pursue preirradiation grafting process. The preirradiated grafted samples were then repeatedly washed with deionized water until neutral pH was reached to remove the residual monomers and by products. X-ray Photoelectron Spectroscopy (XPS) provides an average for the content of functional groups of the first 10-15 molecules layer. The XPS results are presented in Table 3 and O-C and O=C increased on sample irradiated and immersed into acrylic acid solution.

TABLE 3. XPS RESULTS OF PR-25-PS POWDER IRRADIATED 1000 KGY MIXED WITH DIFFERENT MONOMERS DISSOLVED IN WATER/METHANOL (50% VOL)

<table>
<thead>
<tr>
<th>Carbon nanofiber</th>
<th>Surface oxygen (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-C</td>
</tr>
<tr>
<td>Non-irradiated/water/methanol</td>
<td>2.0</td>
</tr>
<tr>
<td>1000/water/methanol</td>
<td>3.9</td>
</tr>
<tr>
<td>1000/MMA/water/methanol</td>
<td>4.0</td>
</tr>
<tr>
<td>1000/Styrene/water/methanol</td>
<td>4.0</td>
</tr>
<tr>
<td>1000/PEG/water/methanol</td>
<td>3.9</td>
</tr>
<tr>
<td>1000/Ac.Ac/water/methanol</td>
<td>4.9</td>
</tr>
<tr>
<td>1000/epoxy/acetone</td>
<td>15.1</td>
</tr>
</tbody>
</table>
In early experiment, the data showed that carbon nanofiber mixed with water/methanol (50% vol) did not bring any damage to nanofiber surface.

Sample irradiated and immersed into epoxy solution shows a strong O-C oxygen peak, consistent with epoxy groups. Although it has been observed so far is that always irradiated samples have more O than non irradiated ones, but there were no significant differences among the samples. The samples treated with epoxy should have a low level of nitrogen in addition to carbon and oxygen. The C1s spectra obtained for the samples treated with epoxy (see Figure 3) indicated the presence of C-O bonding (286.5 eV).

![C1s- 1000 kGy/epoxy](image)

*Fig. 3. XPS spectra of C1s of PR-25-PS irradiated at 1000 kGy, soaked into epoxy solution with water/methanol (50% V) and washed with deionized water to remove the residual monomers and by-products.*

The samples were characterized by Raman spectroscopy and the results are shown in Fig. 4. The peaks near 1575 and 1325 cm\(^{-1}\) correspond to the G band due to stretching vibrations of the sp\(^2\)-hybridized carbon and the disordered D band attributed to defective carbon atoms, respectively. The samples treated with acrylic acid had the D frequency shifted to left 5.5 cm\(^{-1}\) and G frequency did not change.
Fig. 4. Raman spectroscopy results of PR-25-PS irradiated at 1000 kGy, soaked into monomers solution with water/methanol (50% vol) and washed with deionized water to remove the residual monomers and by products.

The intensity ratio of D band to G band in the Raman spectra has been widely used to evaluate the defects in carbon nanomaterials. In Table 4 is presented the ID/IG ratios of all the samples. The increase of ID/IG ratios may indicate generation of defects on carbon nanofiber surface due to the covalent bonding formation with functional groups grafted on carbon nanofiber surface. The results presented in Figure 4 and Table 4 showed that there are no meaningful changes in the carbon nanofiber structure.

<table>
<thead>
<tr>
<th>Carbon nanofiber</th>
<th>ID/IG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non irradiated/water/methanol</td>
<td>3.61±0.14</td>
</tr>
<tr>
<td>1000/water/methanol</td>
<td>3.61±0.10</td>
</tr>
<tr>
<td>1000/MMA/water/methanol</td>
<td>3.75±0.05</td>
</tr>
<tr>
<td>1000/Styrene/water/methanol</td>
<td>3.67±0.06</td>
</tr>
<tr>
<td>1000/PEG/water/methanol</td>
<td>3.32±0.40</td>
</tr>
<tr>
<td>1000/Ac.Ac/water/methanol</td>
<td>3.67±0.06</td>
</tr>
</tbody>
</table>
A blank of a sample exposed to epoxy was prepared to certify the percentage of oxygen content and make sure that these oxygen groups attached on carbon nanofiber surface and the samples irradiated and non irradiated was washed with acetone to verify if there was covalent bonding formation. The radiation process did not influence the increasing of oxygen content on carbon nanofiber surface and the oxygen attached on the surface was dissolved in acetone washing process as show in Table 5. The C 1s spectra for all three of these samples showed a relatively intense C-O carbon peak, characteristic of epoxide bonding, and a weak satellite peak (at ~291 eV binding energy) that is characteristic of aromatic groups. The samples rinsing with acetone has removed most of the epoxy resin. For each of these two samples, the oxygen level is lower, and there is no distinct shoulder due to C-O bonding in the C 1s spectrum. In spite of the fact that the results did not show any meaningful results, the samples present a good dispersion except the one treated with styrene.

### Table 5. XPS Results of Indirect Radiation Grafting Samples

<table>
<thead>
<tr>
<th>Carbon Nanofiber</th>
<th>Surface oxygen (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O-C</td>
</tr>
<tr>
<td>1000/epoxy</td>
<td>15.1</td>
</tr>
<tr>
<td>Washed with water</td>
<td></td>
</tr>
<tr>
<td>1000/epoxy</td>
<td>5.8</td>
</tr>
<tr>
<td>Washed with acetone</td>
<td></td>
</tr>
<tr>
<td>epoxy/acetone</td>
<td>14.5</td>
</tr>
<tr>
<td>Washed with water</td>
<td></td>
</tr>
<tr>
<td>epoxy/acetone</td>
<td>5.0</td>
</tr>
</tbody>
</table>

### 3.2. Direct radiation grafting process

#### 3.2.1. Electron beam radiation

##### 3.2.1.1. Procedure

As-received PR-25-PS-XT samples were washed with acetone, dried in a vacuum oven at 60°C for 24 hour. Carbon nanofibers were weighed, and then immersed in solutions of acrilic acyd with 6% of inhibitor metal salt (FeSO₄·7H₂O). The acrylic acid was purchased from MERK and it is stabilized with 200 ppm of hydroquinone. The samples were poured into petri dish and irradiated with a direct accelerator operated by the Instituto de Pesquisas Energéticas e Nucleares (IPEN- São Paulo/Brazil). The samples were irradiated with an industrial electron accelerator Dynamitron, from Radiation Dynamics Inc., model DC 1500/25-JOB 188 that was operated with the following parameters: beam energy 1.5 MeV, pulse current 5.62 mA, 5 kGy/pass with dose rate of 22.42 kGy/sec. The samples were irradiated with 50, 100 and 150 kGy (see Figure 5).
3.2.2. Gamma radiation

3.2.2.1. Procedure

The graft copolymerization was carried out using the direct radiation technique. The reaction was conducted in an inert atmosphere in the presence of N₂ gas. Dried pristine PR-25-PS samples were dispersed in solution of acrylic acid in presence of inhibitor metal salt (FeSO₄·7H₂O) in glass ampoule. The mixtures were purged with dry nitrogen for 7 min to remove dissolved oxygen and then sealed. The ampoules were then irradiated using a Cobalt-60 irradiator, Gammarcell model 220, series 142, manufactured by Atomic Energy of Canada Limited. The activity is now of 64.946 TBq (1755.1 Ci) - 06/2012. This equipment consists of 35 pencil cobalt-60, C-185 and 7810 types (which are sealed sources) and are within a shield, even when in operation (see Figure 6 and 7). The Gammarcell design provide uniform gamma field and the samples were irradiated at a dose rate of 1.48 kGy/h.

Fig. 6. Sources irradiator Gammarcell 220 - with 26 Co-60 pencil type C-185 and 9 Co-60 pencil type 7810.
3.2.3. Results

The aim of this part of the project was to search for better parameters to set up metrology of direct radiation induced grafting process to modified carbon nanofiber surface. Twenty samples were irradiated with cobalt-60 and 3 samples were irradiated with electron beam. Different parameters were applied to the samples and the condition of the grafting solution after grafting reaction is presented in Table 1 and 2. Undesirable homopolymerization took part in most of the samples because either the dose was high or the percentage of inhibitor was low. It can be concluded, in advance, that the dose limit for modification of carbon nanofiber surface by direct radiation induced grafting process (electron beam and gamma) is 100 kGy and the percentage of inhibitor should be between 3-6%.

Therefore, seven not gelled samples were investigated by several characterization techniques, such as: Thermogravimetry (TGA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), X ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). This report presents XPS results.

The surface oxygen content of the nanofibers was characterized with X-ray Photoelectron Spectroscopy (XPS) analysis. All analysis were conducted in a K- Alpha XPS equipment from ThermoFisher Scientific with a 400 µm X-ray spot size and with the low energy electron/argon ion charge neutralization system turned on. XPS survey spectra (0-1350 eV) were collected for all samples to provide qualitative and quantitative surface analysis information. The technique is sensitive only to surface atoms and the results are reported in terms of atom % oxygen (O), % nitrogen (N) and % Ferro (Fe).

The C1s spectra obtained for the seven samples (see Figure 8 and 9) indicated the presence of various amount of C-O, C=O and O=C-O surface functional groups on the seven samples however samples GA11, GA 11.1, GA13, GA14 (irradiated) had the highest intensity peaks for O=C-O bonding (~ 289.7 eV).
Fig. 8. High Resolution C 1s XPS spectra for unirradiated samples.

Fig. 9. High Resolution C 1s XPS spectra for irradiated samples.

The surface composition (atomic %) is presented in Table 5 and 6. The results given by XPS analysis showed a significant increase of oxygen content for the samples irradiated. The
sample with 6% of $\text{FeSO}_4\cdot7\text{H}_2\text{O}$ and irradiated at dose of 100 kGy had higher percentage oxygen therefore offering excellent and very stable dispersion.

TABLE 6. XPS RESULTS OF UNIRRADIATED PR-25-PS, A BLANK AND PR-25-PS GRAFTED WITH ACRYLIC ACID USING AN INDUSTRIAL ELECTRON ACCELERATOR DYNAMITRON, FROM RADIATION DYNAMICS INC., MODEL DC 1500/25-JOB 188 AT DOSES OF 50, 100 AND 150 KGY

<table>
<thead>
<tr>
<th>Carbon nanofiber</th>
<th>Surface oxygen (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>GA1</td>
<td>2.5</td>
</tr>
<tr>
<td>GA11.3</td>
<td>4.9</td>
</tr>
<tr>
<td>GA 11</td>
<td>14.6</td>
</tr>
<tr>
<td>GA 11.1</td>
<td>18.4</td>
</tr>
</tbody>
</table>

TABLE 7. XPS RESULTS OF UNIRRADIATED PR-25-PS, A BLANK AND PR-25-PS GRAFTED WITH ACRYLIC ACID USING $\gamma$-RAYS AT DOSES OF 100 KGY.

<table>
<thead>
<tr>
<th>Carbon nanofiber</th>
<th>Surface oxygen (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>GA1</td>
<td>2.5</td>
</tr>
<tr>
<td>GA2</td>
<td>7.0</td>
</tr>
<tr>
<td>GA 13</td>
<td>20.3</td>
</tr>
<tr>
<td>GA 14</td>
<td>16.8</td>
</tr>
</tbody>
</table>

It has been shown in the published literature that, after differentiation, $\text{c KLL Alger spectra}$ can give important information regarding the relative amount of $\text{sp}^2$ and $\text{sp}^3$ bonding in carbon materials by the so called Auger "D-parameter" [25]. The D-parameter value gives an indirect measure of the % $\text{sp}^2$ character of the material (see figure 10).

The measured Auger D-parameter for samples GA1, GA 2 and GA 11.3 (see Figure 11) is higher and similar to the literature reference for graphite and indicates a significant amount of $\text{sp}^2$ bonding on the surface. These three samples also had the lowest oxygen concentrations among the samples.

The Auger D-parameter for the other four samples (see Figure 12) ranged between 17.0-17.7 indicated that these samples had less $\text{sp}^2$ and more $\text{sp}^3$ bonding characteristics compared to samples GA1, GA2 and GA 11.3. This can be an indication of $\text{C=C}$ bond breaking leading to the formation of new $\text{sp}^3$ carbon atoms on CNT surface with oxygen functional groups.
Fig. 10. Illustration of Auger D-parameter for sample GA1.

Fig. 11. Auger D-parameter for non irradiated PR-25-PS and blank samples.
4. Conclusion

Radiation induced graft copolymerization is a method to modify materials with many advantages. The goal of the present study was to investigate the use ionizing radiation for functionalizing carbon nanofibers with several monomers. The experiments were set up in order to determine the optimum radiation dose and inhibitor content required for this process to take place using the existing irradiators.

Characterization of the physical properties of the nanomaterials is still a challenge. The small size and complexity of nanoscale structure make the use of characterization technique more challenging than ever and require extremely sensitive instrumentation and this has been an issue during the process of this investigation.

In this study, direct process of radiation grafting showed better results, however more research should be done to optimize this process. The samples that were added to a solution of acrylic acid with 6% of inhibitor and were direct irradiated with electron beam and gamma source at 100 kGy dose presented higher oxygen content and better dispersion. The Auger D-parameter for the the samples direct grafting irradiated ranged between 17.0-17.7 indicated that these samples had less sp² and more sp³ bonding characteristics compared to unirradiated samples. This can be an indication of C=C bond breaking leading to the formation of new sp³ carbon atoms on CNF surface with oxygen functional groups.
As an immediate next step we intend to manufacture nanostructured composites with this modified carbon nanofiber to assess the impact of these modifications on macroscopic properties and evaluate the adhesion between these modified nanofibers and polymeric matrix.

References


RADIATION CURING OF COMPOSITES FOR ENHANCING THEIR FEATURES AND UTILITY IN HEALTH CARE AND INDUSTRY (CANADA)

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1.3 Effect of hema and silane monomers using gamma radiation on the mechanical and barrier properties of methylcellulose-based films.

Part-II Mechanical and barrier properties of carbon nanotube (CNT)-reinforced polycaprolactone (PCL)-based composite films: effect of gamma radiation.

Part-III Micro-fluidization and irradiation treatment for better dispersion of nano fibers in suspension: Develop a methodology to encapsulate antimicrobial compounds.

Part IV – Develop a protocol for measuring the control release.

Part V- Develop a methodology to encapsulate antimicrobial compounds (essential oils or their mixtures) and probiotic bacteria in the biopolymeric films and combination with irradiation.

General conclusion.
PART I
1.1 MODIFICATION AND CHARACTERIZATION OF BIODEGRADABLE METHYLCHELULOSE FILMS WITH TRIMETHYLOLPROPANE TRIMETHACRYLATE (TMPTMA) BY GAMMA RADIATION: EFFECT OF NANOCRYSTALLINE CELLULOSE

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Key Words: Methylcellulose; Trimethylolpropane Trimethacrylate, Biodegradable Films, Nanocrystalline cellulose; Packaging materials.

Abstract
Methylcellulose (MC)-based films were prepared by solution casting from its 1% aqueous solution containing 0.25% glycerol. Trimethylolpropane trimethacrylate (TMPTMA) monomer (0.1-2% by wt) along with the glycerol was added to the MC solution. The films were cast and irradiated from a radiation dose varied from 0.1-10 kGy. Then the mechanical properties such as tensile strength (TS), tensile modulus (TM), elongation at break (Eb); and barrier properties of the films were evaluated. The highest TS (47.88 MPa) and TM (1791.50 MPa) of the films were found by using 0.1% monomer at 5 kGy dose. The lowest water vapor permeability (WVP) of the films were found to be 5.57 g·mm/m²·day·kPa (at 0.1% monomer and 5 kGy dose) which is 12.14% lower than control MC-based films. Molecular interactions due to incorporation of TMPTMA were supported by FTIR spectroscopy. A band at 1720 cm⁻¹ was observed due to the addition of TMPTMA in MC-based films which indicated the typical (C=O) carbonyl stretching. For the further improvement of the mechanical and barrier properties of the film, 0.025-1% nanocrystalline cellulose (NCC) was added to the MC-based suspension containing 1% TMPTMA. Addition of NCC led to a significant improvement in the mechanical and barrier properties. The novelty of this investigation was to graft insoluble monomer using gamma radiation with MC-based films and use of biodegradable NCC as the reinforcing agent.

1. Introduction
Cellulose is an organic compound with the formula (C₆H₁₀O₅)n, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units. Cellulose is the most abundant organic polymer in the biosphere. It is the main constituent of plants; moreover, it is lightweight, biodegradable, and available natural resources. The interest in using cellulosic materials as the main components in the manufacture of biodegradable packaging materials is increasing day by day. Methylcellulose (MC) is a derivative of cellulose and can be produced from cotton cellulose, wood and annual plant pulps. It is
produced by chemical treatments via alkali cellulose using concentrated sodium hydroxide (NaOH) solution followed by the treatment with methyl halide (or dimethyl sulfate). MC has been widely used for many years to produce gels and fine chemicals in pharmaceuticals, foods, construction, paints, ceramics, detergents, agriculture, polymerization, adhesives, and cosmetics. According to their physicochemical properties, MC can be also employed as emulsifiers, medicine constituents, colloidal stabilizers, viscosity and flow controllers. MC is a hydrophilic white powder in pure form and dissolves in cold water, forming a clear viscous solution or gel. (1-6). Because of various potential uses, modification of MC was considered worthwhile to give materials with improved properties. The modification of polymers using crosslinking and grafting methods is an important commercial process for the purpose of improving the physico-chemical properties of these materials (7-9). Generally, polyfunctional monomers are added to achieve a high degree of crosslinking and to accelerate the crosslinking process. Trimethylolpropane trimethacrylate (TMPTMA), containing three reactive methacrylic acid residues of equal reactivity, has found wide acceptance as a crosslinking agent in poly(vinyl chloride) (10-12), polyethylene (13), ethylene vinylacetate (14), and various peroxide curable elastomers (7). TMPTMA is also acted as a good plasticizer. It produces a high yield of radicals to facilitate grafting reaction. It is particularly effective in promoting the high-temperature creep resistance for products of polymers (7). TMPTMA also helps to improve crosslinking efficiency and physical properties of electron beam-irradiated polyethylene (13).

Cellulose nanocrystals (termed as nanocrystalline cellulose or NCC) are obtained by controlled acid hydrolysis of cellulose sources such as bleached wood pulp. The less-dense amorphous regions along the cellulose microfibril are more susceptible to acid attack during hydrolysis and cleave to give cellulose nanocrystals (15-16). These crystals are rod-like in shape with an aspect ratio which varies from 20 to 100 depending on the cellulose source. Softwood cellulose nanocrystals used in this study had an average length of 120–170 nm with a cross-section of 3–5 nm. The use of sulfuric acid to produce NCC suspensions imparts sulfate ester groups to the NCC surfaces during hydrolysis. The NCC particles are therefore negatively charged and aqueous NCC suspensions are electrostatically stabilized (17). Cellulose nanocrystals are recognized as being more effective than their microsized counterparts to reinforce polymers due to interactions between the nanosized elements that form a percolated network connected by hydrogen bonds, provided there is a good dispersion of the nanocrystals in the matrix (13). A considerable amount of research has been done on the isolation of these nanostructures from plants for use as fillers in biocomposites. It is predicted that NCC reinforcements in the polymer matrix may provide value-added materials with superior performance and extensive applications for the next generation of biodegradable materials (18-19).

Gamma radiation is a high frequency electromagnetic radiation with very short wavelength. As the use of gamma radiation offers several advantages, the application of gamma radiation is becoming more widespread every year. Gamma radiation has several advantages, such as continuous operation, minimum time requirement, less atmospheric pollution, etc. Since gamma radiation is one type of strong ionizing radiation, it can produce ions for cross-linking in polymers in absence of water or any solvents (20-21). When cellulosic materials are subjected to gamma radiation, radicals are produced on the cellulose chain by hydrogen and hydroxyl abstraction. Gamma radiation also ruptures some glycosidic bonds leading to a decrease of the cellulose chain length by random depolymerization (20). Gamma radiation
produces three types of reactive species in cellulose-based polymers. These are ionic, radical, and peroxide. The peroxide species are produced when polymers are irradiated in the presence of oxygen. The effect of gamma radiation on organic polymers produces ionization and excitation, resulting in some free radicals (21). Over the past few decades, there has been a continuous and significant growth in the development and application of radiation techniques. The development of innovative products based on high efficiency and easy process control could be achieved with the help of this radiation technique. A logical extension of this technology was also found in the field of polymer composites (22-23).

The objective of the present research was to evaluate the effect of TMPTMA grafting using gamma radiation on the mechanical and barrier properties of MC-based biodegradable films. Films were exposed to gamma radiation from the range of 0.1-10 kGy to initiate the crosslinking of TMPTMA into MC-based films. The mechanical properties of the films were measured to evaluate their tensile strength (TS), tensile modulus (TM), and elongation at break (Eb%). Water vapor permeability (WVP) tests were carried out to investigate the moisture barrier properties of films under specified conditions. Molecular interactions of components due to the incorporation of TMPTMA in MC-based films were examined by fourier transform infrared (FTIR) spectroscopy. Then, NCC was incorporated into MC-based films along with TMPTMA (followed by irradiation) to verify the potentiality of NCC as reinforcing agent in MC-grafted films. The innovation of this investigation will be the grafting of TMPTMA monomer with MC-based insoluble films by gamma radiation followed by reinforcing NCC to improve mechanical and barrier properties.

2. Materials and methods

2.1. Materials

MC (powder form; viscosity of 400 cP for a 1% solution at 20 °C) and monomer TMPTMA were purchased from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada). Nanocrystalline cellulose (NCC) was produced in FPInnovations pilot plant NCC reactor from a commercial bleached softwood kraft pulp according to a procedure modified from the literature (Pointe-Claire, QC, Canada). Glycerol was purchased from Laboratoire Mat (Beauport, QC, Canada).

2.2. Methods

2.2.1. Film preparation

MC suspension (1%, w/w) was prepared in an ice bath using deionized water with continuous stirring. Then monomer TMPTMA (0.1-2%, w/w) and 0.25% glycerol (as a plasticizer) were added to the MC suspension. The mixture was homogenized using an IKA T25 digital Ultra-Turrax disperser (IKA Works Inc., Wilmington, NC, USA) at 45°C and 24,000 rpm for 1 min. Films were then cast by applying 15 mL of the suspension onto Petri dishes (100mm×15mm; VWR International, Ville Mont-Royal, QC, Canada) and allowed to dry for 48 h, at room temperature and 35% relative humidity (RH). Aqueous NCC (0.025-1%, w/w) suspension was prepared at 60°C and sonicated for 30 min at room temperature. The NCC suspension was added to MC-based formulation containing TMPTMA and glycerol. Then the films were cast in the same process as described above. Dried films were peeled off and stored in polyethylene bags prior to characterization. The composition of the films in dry weight basis is given in Tables 1-2.
TABLE 1. CONCENTRATION OF TMPTMA IN MC-BASED (1% MC+ 0.25% GLYCEROL) FILMS

<table>
<thead>
<tr>
<th>TMPTMA concentration in film formulation (wt%)</th>
<th>Concentration (wt%) of film components after casting (in dry film)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MC</td>
</tr>
<tr>
<td>0</td>
<td>80</td>
</tr>
<tr>
<td>0.1</td>
<td>74.07</td>
</tr>
<tr>
<td>0.25</td>
<td>66.66</td>
</tr>
<tr>
<td>1</td>
<td>44.45</td>
</tr>
<tr>
<td>2</td>
<td>30.76</td>
</tr>
</tbody>
</table>

TABLE 2. CONCENTRATION OF NCC IN TMPTMA GRAFTED MC-BASED (1% MC + 0.25% GLYCEROL + 0.1% TMPTMA) FILMS

<table>
<thead>
<tr>
<th>NCC concentration in film formulation (wt%)</th>
<th>Concentration (wt%) of film components after casting (in dry film)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MC</td>
</tr>
<tr>
<td>0</td>
<td>74.07</td>
</tr>
<tr>
<td>0.1</td>
<td>68.96</td>
</tr>
<tr>
<td>0.25</td>
<td>62.50</td>
</tr>
<tr>
<td>0.5</td>
<td>54.05</td>
</tr>
<tr>
<td>1</td>
<td>42.55</td>
</tr>
</tbody>
</table>

2.2.2. Irradiation

Irradiation of films was conducted with γ-rays generated from a $^{60}$Co source at room temperature, at a dose rate of 17.878 kGy/h (0.3578 kGy/min) in an Underwater Calibrator-15A Research Irradiator (Nordion Inc., Kanata, ON, Canada).

2.2.3. Mechanical properties

Tensile strength (TS), tensile modulus (TM), and elongation at break (Eb%) of the films were evaluated by Universal Tensile Machine (UTM) (Tinius-Olsen Inc., USA, Model H5K) using a 1 KN load cell, with a crosshead speed of 1 mm/s at a span distance of 25 mm. The dimensions of the test specimen were (ISO 14125): 60×15×0.050 mm$^3$.

2.2.4. Water vapor permeability (WVP)

The WVP test was conducted gravimetrically using a modified procedure from ASTM test 15.09: E96 (24). Films were mechanically sealed onto Vapometer cells (No. 68-1, Twingham-Albert Instrument Company, West Berlin, NJ, USA) containing 30 g of anhydrous calcium chloride (0% RH). The cells were initially weighed and placed in a Shellab 9010L controlled humidity chamber (Sheldon Manufacturing Inc., Cornelius, OR, USA) maintained at 25°C and 60% RH for 24 h. The amount of water vapor transferred through the film and absorbed by the desiccant was determined from the weight gain of the cell. The assemblies were weighed initially and after 24 h for all samples and up to a maximum of 10% gain. Changes in weight of the cell were recorded to the nearest 10$^{-4}$ g. WVP was calculated according to the combined laws of Fick and Henry for gas diffusion through coatings and films, according to the equation:
WVP (g·mm/m²·day·kPa) = Δw·x/A·ΔP \hspace{1cm} (1)

where Δw is the weight gain of the cell (g) after 24 h, x is the film thickness (mm), A is the area of exposed film \((31.67 \times 10^{-4} \text{ m}^2)\), and ΔP is the differential vapor pressure of water through the film \((ΔP = 3.282 \text{ kPa at 25°C})\). The value of ΔP=3.282 kPa was obtained directly from the Handbook of Chemistry and Physics (25) that indicates vapor pressure (partial pressure) of water in function of temperature. Data (in kPa) were obtained by deducing directly from the table of the vapor pressure at 25°C for a volume fraction of 0.6 (corresponding to 60% of relative humidity.

2.2.5. FTIR spectroscopy

FTIR spectra of the films were recorded using a Spectrum One spectrophotometer (Perkin-Elmer, Woodbridge, ON, Canada) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high-linearity lithium tantalate (HLLT) detector. Spectra were analyzed using Spectrum 6.3.5 software. Films were stored at room temperature for 72 h in a desiccators containing saturated NaBr solution to ensure a stabilized atmosphere of 59.1% RH at 20°C. Films were then placed onto a zinc selenide crystal, and the analysis was performed within the spectral region of 650-4000 cm\(^{-1}\) with 64 scans recorded at a 4 cm\(^{-1}\) resolution. After attenuation of total reflectance and baseline correction, spectra were normalized with a limit ordinate of 1.5 absorbance units. The resulting FTIR spectra were compared to evaluate the effects of glycerol, TMPTMA grafting, and NC grafting, based on the intensity and shift of vibrational bands.

2.2.6. Statistical analysis

All experiments were conducted in duplicate and each measurement was performed in triplicate. Analysis of variance was performed using the PASW Statistics Base 18.0 software (SPSS Inc., Chicago, Illinois, USA) and mean’s comparison between each treatment was based on Duncan’s multiple range tests \((p \leq 0.05)\).

2.3. Results and discussion

2.3.1. Mechanical properties

The TS values of TMPTMA containing MC-based films were studied as a function of gamma radiation dose and the results are presented in Figure 1. The TS of MC-based films were found to be 38 MPa. Addition of TMPTMA (denoted as 0 kGy in the figure) in the MC-based films, the strength of the films decreased \((p \leq 0.05)\) significantly. MC-based films containing 0.1, 0.25, 1 and 2% TMPTMA, the TS values were found to be 36.00, 30.20, 20.45, and 6.88 MPa respectively. Films became soft at 2% TMPTMA containing films. TMPTMA is a low boiling point monomer \((7-10)\), so addition of monomer had no positive effect on the strength of MC-based films. Moreover, our aim was to fabricate MC-based insoluble films by grafting with insoluble monomer TMPTMA. MC-based films were readily soluble and TMPTMA containing films were also not stable in aqueous medium. Moreover, TMPTMA containing films had a typical smell of monomer. Gamma radiation was used to have reacted TMPTMA with MC. Actually monomer TMPTMA did not react with MC in absence of gamma radiation. But with the exposure of gamma radiation \((0.1 \text{ to } 10 \text{ kGy})\), MC-based films were stable in aqueous medium. The values of TS of the irradiated films changed. The TMPTMA
concentration in the films varied from 0.1-2% by wt (in film formulation). For different monomer concentrations, the TS values increased up to 5 kGy of radiation dose and then decreased (at 10 kGy). The highest TS values were observed at 0.1% monomer concentrations which are 37.94, 44.70, 45.13, 47.88 and 46.20 MPa for 0.1, 0.5, 1, 5 and 10 kGy doses, respectively. With further increase of monomer concentration, the TS values decreased significantly ($p \leq 0.05$). The highest TS value (47.88 MPa) was observed at 0.1% monomer concentration at 5 kGy radiation dose. It is to be noted here that 5 kGy dose was considered as the optimal because at this dose the films had no smell of monomer and indicated complete conversion of monomer into polymer (poly-TMPTMA). Though, the difference between 1 and 5 kGy was not much higher. The monomer TMPTMA might be reacted with MC molecules and thus TS of the films increased. But at higher monomer concentration, homopolymer (TMPTMA+TMPTMA) could form and the TS values of the film decreased (26). Reactive sites could be initiated in the monomers when they were irradiated which enhances the possibility of creating chemical reaction between MC and TMPTMA. The increase of grafting lead to the improvement of the TS values with increased gamma radiation. But at higher doses, the polymer degradation could happen and leading to the reduction of strength of the films (23).

**Fig. 1.** Tensile strength of TMPTMA containing MC-based films against total radiation dose.

**Fig. 2.** Tensile modulus (TM) of the TMPTMA added MC films are cited in Figure 2 against total radiation dose as a function of different monomer concentrations. The TM of MC-based films were found to be 1640 MPa (not shown in Figure). Addition of TMPTMA in MC-based films (not irradiated, at 0 kGy), the TM values of the films decreased significantly ($p \leq 0.05$). Addition of 0.1, 0.25, 1, and 2% TMPTMA, the TM values of MC-based films decreased to 1400, 1060, 457 and 122 MPa respectively. When TMPTMA containing MC-based films were irradiated, the TM values increased with the increase (up to 5 kGy) of radiation dose and then decreased. But the TM values decreased at higher monomer concentrations similarly for TS values (Fig.1). For 5 kGy dose, the TM values were found to be 1792, 1552, 818 and 470 MPa for 0.1, 0.25, 1 and 2% TMPTMA concentrations, respectively. The 0.1% monomer containing films performed better TM values. The MC films containing 0.1% TMPTMA at 5 kGy dose showed the highest TM values. Monomer addition followed by irradiation treatment
increased the TM values due to the cross linking reaction between the monomer and the MC. But at higher monomer concentration, the TM values decreased as the monomer recombination leads to homo-polymerization reaction. Again, with the increase of gamma radiation dose, the TM values increased since more free radicals were initiated with the ionizing radiation which leads to the enhanced cross linking between TMPTMA and MC (27).

**Fig. 2. Tensile modulus of TMPTMA containing MC-based films against total radiation dose.**

Flexibility and elasticity of the films are essential parameters that are considered during the application of the polymer. These two phenomena are related to the elongation at break of the film. Results of Eb values of TMPTMA containing MC-based film as a function of gamma radiation is plotted at Figure 3. The Eb value of MC-based films was found to be 14%. Addition of TMPTMA (denoted as 0 kGy in the figure) in the MC-based films, the flexibility of the films increased \((p \leq 0.05)\) significantly. MC-based films containing 0.1, 0.25, 1 and 2% TMPTMA, the Eb values were found to be 16.40, 29.50, 34.23, and 44.21%, respectively. Films became very soft at 2% TMPTMA containing films. For 0.1 and 0.25% TMPTMA, the Eb values increased up to 5 kGy doses then decreased. On the other hand, for 1 and 2% TMPTMA containing MC-based films gained higher Eb values at 1 kGy dose then found to decrease rapidly. The decrease of Eb values at higher doses could be related to the radiation degradation of the film (28). For 5 kGy, the Eb values of the films were found to be 24.71, 29.84, 39.17 and 9.41% respectively for 0.1, 0.25, 1 and 2% TMPTMA concentration. Thus the highest Eb value (39.1%) was observed at 1% monomer concentration and at 5 kGy dose. When monomer was used, it might be graft copolymerized with the MC molecules. When the films were irradiated, hydroxyl group of MC could react with the acrylate group of TMPTMA resulted a cross-linked network. At low monomer concentrations (0.1 to 0.25%), the Eb values were increased due to inter- and intra-molecular cross-linking of MC with TMPTMA but at higher monomer concentrations (1 to 2%), the flexibility of the films was lowered because of the homo-polymer formation (poly-TMPTMA) or radiation degradation (breakage of the polymeric bonds) of the films. As a result, at 2% TMPTMA, the Eb values decreased significantly after 1 kGy dose. At 10 kGy, all films showed significantly lower Eb values than other doses (26).
2.3.2. Water vapor permeability (WVP)

The WVP of MC-based films (1% MC plus 0.25% glycerol) films was found to be 6.34 g·mm/m²·day·kPa. Figure 4 shows the effect of TMPTMA on the WVP of MC-based films as a function of gamma radiation. WVP is a measure of ease of the moisture to penetrate and pass through a material. Just addition of monomer TMPTMA (without irradiated, termed 0 in the figure) in MC-based films showed an increase of WVP. Incorporation of 0.1, 0.25, 1, and 2% of TMPTMA, the WVP of MC-based films reached to 5.24, 5.92, 7.90, and 11.35 g·mm/m²·day·kPa. A monotonous increase of WVP indicated poor barrier to water vapors through the film. When 0.1% TMPTMA containing films were irradiated from 0.1 to 10 kGy, the WVP decreased up to 1 kGy (5.27 g·mm/m²·day·kPa.) then increased, and reached to 5.57 g·mm/m²·day·kPa. Similarly, for 0.25, 1 and 2% TMPTMA containing films, the minimum WVP was found for 1 kGy. After 1 kGy, the WVP values again increased with the increase of irradiation dose. The maximum WVP were observed for 2% TMPTMA content. At higher radiation doses (5 and 10 kGy), WVP values increased significantly which might be responsible for radiation degradation of MC molecules (24).
2.3.3. FTIR analysis

The FTIR spectra of (a) pure MC films (b) MC-based (with glycerol) films (control), (c) MC-based films containing 0.1% TMPTMA, and (d) MC-based films containing 1% TMPTMA are presented in Figure 5. This analysis attempted to characterize the incorporation of TMPTMA into the MC-based film matrix and distinguish the IR bands and vibrations shifts related to TMPTMA interactions. The absorption peaks of the MC film spectrum (a) are mainly assignable to the stretching vibrations of O-H at 3200-3600 cm⁻¹, overlapping symmetric and asymmetric C-H at 2870-2960 cm⁻¹, and bound water vibration at 1600-1800 cm⁻¹. The pure MC (no glycerol) (a) and MC-based films (with glycerol) (b) shows almost similar absorption peaks. Other bands at 1160, 1110, 1055, 1030, and 950 cm⁻¹ are attributed to typical cellulosic compounds and are assigned to C-O, C-C, and ring structures, in addition to external deformational vibrations of CH₂, C-OH, C-CO, and C-CH groups, as already described (29). Some differences can be observed in the whole IR region (for c-d) after addition of TMPTMA into film matrix. Indeed, a strong absorption band was observed at 1720 cm⁻¹ after TMPTMA addition for all concentrations, related to the typical (˃C=O) carbonyl stretching from TMPTMA structure. The band at 1638 cm⁻¹ is due to the carbon-carbon double bond (˃C=C˂) stretching of the vinylidene group (c-d). The other peaks observed after TMPTMA addition at 1320, 1293 and 1148 cm⁻¹ is mainly due to the deformation vibration of –CH₃ group, in plane deformation of -CH=CH₂ group and CH₂=C(CH₂)COOR group, respectively (30). In our previous studies (24), a detailed FT-IR discussion on the addition of NCC in MC-based films was carried out. Similar type of peaks appeared for NCC addition in this film also.

Fig. 4. Water vapor permeability of TMPTMA containing MC-based films against total radiation dose.
2.3.4. Effect of NCC on the mechanical properties of TMPTMA grafted MC-based films

It was observed that a noteworthy improvement occurred in the mechanical properties when NCC (0.025-1%, w/w in aqueous solution) was added to TMPTMA containing MC-based films. The results are presented in Figure 6. It was reported above (Fig. 1) that the highest TS values of the films were observed at 0.1% TMPTMA concentration and at 5 kGy radiation dose. So, NCC was added to these films to find out its potentiality as a reinforcing agent. It is to be noted here that the TS values of MC-based, MC-based with 0.1% TMPTMA (un-irradiated), and MC-based with 0.1% TMPTMA (irradiated at 5 kGy) films were found to be 38, 36 and 47.88 MPa respectively. From the figure, it is clear that the TS values increased significantly with the increase of NCC concentration. But the TS values seemed to reach a plateau after 0.25% NCC. The TS values increased up to 5 kGy dose and then decreased. The TS values of the 0.25% NCC added films were found to be 55, 61, 68, 69 and 67 MPa for 0.1, 0.5, 1, 5 and 10 kGy dose, respectively which are 46, 37, 53, 44 and 46% higher than the TS values of the MC-based films grafted (5 kGy) with 0.1% TMPTMA films for the same radiation dose. The TS values seemed to reach a plateau after 0.25% NCC content in MC-based films. From this investigation, this is clearly reflected the significant effect on the mechanical properties of NCC in MC-based films. Thus, the NCC acted as a reinforcing agent in MC-based films and is responsible for the higher TS values of the films. Similar observations were reported by Azeredo et al. (31). They mentioned that the mechanical properties, except elongation, were improved significantly by the addition of cellulose nanofibers to mango puree edible films.
Fig. 6. Effect of NCC on the tensile strength of TMPTMA grafted MC-based films against total radiation dose.

Similar trend was observed for the TM of the TMPTMA grafted MC-based films when NCC was added to it which is shown in Figure 7. For 0.25% NC addition the observed TM values were 1979, 2072, 2149, 2202 and 2132 MPa for 0.1, 0.5, 1, 5 and 10 kGy doses, respectively. Thus there were a 37, 29, 38, 23 and 40% improvement in the TM values for 0.25% NCC as compared to the only TMPTMA grafted films for 0.1, 0.5, 1, 5 and 10 kGy doses, respectively.
Figure 8 shows the change in Eb values of TMPTMA grafted MC-based films as a function of gamma radiation when NCC is added. The Eb values increase up to 0.025% of NCC content and then decrease. Sometimes with the increase of reinforcing agent, both strength and elongation may rise. NCC is composed of nano-crystals (similar to nano-rod or -fiber). These nano-crystals can form network with the polymer matrix and can improve elongation. Similar phenomenon is reported elsewhere (24). Thus the highest Eb values were observed for 0.025% NCC content which is 20, 32, 24, 22 and 19% for 0.1, 0.5, 1, 5 and 10 kGy of radiation dose, respectively. At higher levels of NCC, which acts as a reinforcing filler, the material tends to become somewhat more brittle. This is a common observation in nanocomposites as well as conventional composite materials. Here, NCC is acting as a reinforcing agent, so higher amounts of NCC can make the films stiffer. The decreased Eb values may be related to the increased stiffness of the films by the addition of NCC (28).
Fig. 8. Effect of NCC on the elongation at break (%) of TMPTMA grafted MC-based films against total radiation dose.

2.3.5. Effect of NCC on the barrier properties of the TMPTMA grafted MC-based films

The effect of NCC content on the water vapor barrier properties of the TMPTMA grafted MC-based films is presented in Table 3. The WVP values decreased with the increasing of NCC content. On the other hand, at low gamma radiation doses (up to 0.5 kGy), the WVP values reduced but at higher doses (from 5 kGy) all the samples showed higher WVP values. It is to be noted that the WVP value of MC-based films was found to be 6.34 g·mm/m²·day·kPa, but all the TMPTMA grafted films found lower WVP values than that of the MC-based films. There was a 24% reduction in the WVP values upon 1% NCC addition at 0.5 kGy radiation dose. The presence of crystalline fibers in NCC is thought to increase the tortuosity in the MC-based films, leading to slower diffusion processes and, hence, to a lower permeability (31). In the present study, the interactions of NCC with MC-based films components (mainly cellulose) as well as the interactions between nanofibers may have enhanced the water vapor barrier properties (24).

| TABLE 3. EFFECT OF NCC AND GAMMA RADIATION ON THE WATER VAPOR PERMEABILITY (WVP) VALUES OF TMPTMA GRAFTED MC-BASED FILMS |
|-----------------|----------------|----------------|----------------|----------------|
| **Material**    | **Radiation Dose (kGy)** | **WVP (g·mm/m²·day·kPa)** | **0.1** | **0.5** | **1** | **5** | **10** |
| MC+0.1% TMPTMA  | 5.69±0.2c       | 5.3±0.1c        | 5.27±0.3b   | 5.57±0.2b   | 5.89±0.3b |
| MC+0.1%TMPTMA+0.025%NCC | 5.77±0.1c       | 5.48±0.1c       | 6.00±0.2c   | 6.34±0.1c   | 6.55±0.2c |
| MC+0.1%TMPTMA+0.1%NC  | 4.75±0.1b       | 4.42±0.2b       | 5.51±0.1b   | 5.88±0.1b   | 5.97±0.2b |
3. Conclusions

In summary, the aim of the present study was to evaluate the combined effect of the monomer TMPTMA, NCC and gamma radiation on the mechanical and barrier properties of MC-based biodegradable films. The MC is an excellent natural polymer which could be implied to various potential uses. The highest TS (47.88 MPa) and TM (1791.50 MPa) values were found at 0.1% monomer concentration at 5 kGy dose. The lowest WVP was also observed at 0.1% monomer concentration. For the further improvement of the mechanical and barrier properties of the film, 0.1-1% NCC was added to the optimal formulation. It was observed that NCC containing films significantly improved the mechanical and barrier properties of the films. This investigation has significant relevance to the application of packaging sectors. The prepared MC-based films are biodegradable and readily soluble in aqueous media. To protect the film from aqueous media, water insoluble monomer was grafted using gamma radiation. Further improvement of the properties of films was carried out using NCC. This research opens a new door of preparing more hydrophobic biodegradable films for packaging applications. The novelty of this research was to fabricate insoluble films using TMPMA monomer in MC-based films followed by gamma radiation, and use of biodegradable reinforcing agent NCC.

References


PART I
1.2 EFFECTIVENESS OF SILANE MONOMER AND GAMMA RADIATION ON CHITOSAN FILMS AND POLYCAPROLACTONE (PCL)-BASED COMPOSITES

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Abstract

Chitosan films were prepared by casting from its 1% (w/w) solution. Tensile strength (TS) and tensile modulus (TM) of chitosan films were found to be 30 MPa and 450 MPa respectively. Silane monomer (3-aminopropyl tri-methoxy silane) (0.25%, w/w) was added into the chitosan solution (1%, w/w) and films were casted. Then films were exposed to gamma radiation (5-25 kGy) and mechanical properties were investigated. It was found that at 10 kGy, the values of TS and TM were improved significantly. Silane grafted chitosan film (5-30%, w/w) reinforced poly(caprolactone) (PCL) based composite films were prepared by compression molding. The values of TS and TM of the silane composites were found to be 21 and 410 MPa, respectively which is significantly higher (40% TS and 34% TM) than control composites. Surface of the films were investigated by scanning electron microscope (SEM) and found better morphology for silane grafted films.

Keywords: Chitosan, Poly(caprolactone), Gamma radiation, Silane, Composite.

1. Introduction

The invention of biodegradable packaging films using biopolymers is a major interest for researchers. In the market, most of the packaging materials are from petroleum-based synthetic polymers because of their excellent thermo-mechanical properties. These materials are also comparatively cheaper than biopolymers. Unfortunately, these synthetic packaging materials are not biodegradable. Hence, research is in progress to develop alternative packaging materials that are environmentally friendly, cheap, possess good thermo-mechanical properties, and provide a good barrier to moisture and gas. Currently, few biodegradable packaging films are being explored, developed, and marketed. In this regard, biopolymers like chitosan, alginate, cellulose, gelatin, etc. are taken into considerations. Biodegradable films made of these materials do not pose a threat to the environment and are also cost-effective. However, the disadvantages of these films include poor thermo-mechanical properties and a strongly hydrophilic nature. Therefore, many studies are now attempting to overcome these drawbacks to approach physicochemical attributes analogous to those of petrochemical polymers (1-4).

Chitosan, the second most abundant natural biopolymer after cellulose, composed mainly of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units. It is the major component of the shells of crustacean such as crab, shrimp, lobsters, and crawfish. Chitosan contains a large number of hydroxyl and amino groups. These two functional groups provide several possibilities for grafting of desirable bioactive groups. Chitosan could be used to prepare biodegradable packaging materials (5-7).
Poly(caprolactone) (PCL) is a typical aliphatic polyesters, and is fully biodegradable, biocompatible, and nontoxic to living organisms. PCL has good resistance to water, oil, solvent, and chlorine. PCL is prepared by ring opening polymerization of ε-caprolactone using a catalyst such as stannous octanoate (8-10). The unique properties of PCL render its potential in biomedical fields, and it has been used in the development of controlled drug delivery systems, as well as in surgical sutures and other resorbable fixation devices. PCL is partly crystalline with a degree of crystallinity of about 50% and a melting point of about 60°C. The PCL films are strongly water-resistant. One of the main commercial applications of PCL is in the manufacture of biodegradable bottles and films (11).

Silane coupling agents belong to a class of organo-silane compounds having at least two reactive groups of different types bonded to the silicon atom in a molecule. These materials are used as promoters, dispersing agents, cross-linking agents, surface modifiers etc. Alkoxysilanes such as 3-aminopropyl trimethoxysilane (APS) are used for coupling agents to organic polymers thus improving properties of the products. As cross-linking agent it is used in various polymers like polyethers, polyurethanes, polyesters, etc. When used in thermoplastic and thermostetting resin such as phenol aldehyde, polyester, epoxy, polyamide, carbonic ester, it can greatly improve strength, and other physical mechanical properties (7).

Over the past few decades, there has been a continuous and significant growth in the development and application of radiation techniques, primarily in the coating and adhesive industries. As this technique continues to develop innovative products based on high efficiency and easy process control, a rational extension for this technology is found to be in the field of polymer composites. The use of gamma radiation offers several advantages, such as continuous operation, minimum time requirement, less atmospheric pollution, curing at ambient temperatures, and increased design flexibility through process control (1, 12).

The objective of the present research was to evaluate the effect of gamma radiation on chitosan, silane containing chitosan, and PCL-based composite films. To improve the mechanical properties of chitosan films, silane monomer was added in chitosan followed by irradiation for grafting of silane with chitosan. In order to fabricate insoluble films, chitosan film was reinforced in PCL matrix by compression molding. The PCL-based biodegradable and insoluble composite films were fabricated using both chitosan and silane grafted chitosan films to investigate the effectiveness of silane in composite film. The major advantage of chitosan reinforced PCL-based composite will be the use of biopolymer (chitosan) inside synthetic biodegradable polymer (PCL). The composite is expected to get higher strength with complete insolubility in water. The mechanical properties of the non-irradiated and irradiated chitosan films, silane grafted chitosan films, and PCL-based composites were measured. Surface morphologies of films and composite interface were investigated by scanning electron microscope (SEM).

2. Materials and Methods

Materials

Chitosan (Kitomer, Mw 1600 kDa, 85-89% deacetylation degree) was obtained from Marinard Biotech Inc. (Rivière-aux-Renards, QC, Canada). Silane monomer (3-Aminopropyl tri-methoxy silane) and PCL (granules form, molecular weight: 70,000-80,000) were purchased from Sigma-Aldrich (Canada).
Film preparation

Firstly, 1% chitosan solution (w/w) was prepared using 2% (w/w) acetic acid solution. Films of chitosan were prepared by casting at room temperature and at 35% relative humidity (RH). Then 0.25% (w/w) silane was added to chitosan solution and films were casted. The thickness of the films was around 25 µm. Dried films were peeled off and stored in polyethylene bags then samples (inside bag) were placed inside a desiccator for 3 days before characterization.

Irradiation

Irradiation of chitosan and silane added chitosan films were conducted with γ-rays generated from a $^{60}$Co source at room temperature, at a dose rate of 59.63 Gy/s in an Underwater Calibrator-15A Research Irradiator (Nordion Inc., Kanata, ON, Canada).

Composite fabrication

To make PCL films, granules of PCL (0.5 g) were taken into two steel plates and placed in the heat press (Carver, INC, USA, Model 3856). The press was operated at 80°C. Steel plates were pressed at 1-3 bar pressure for 1 min. The plates containing PCL were then cooled using ice bath for 1 min. The resulting PCL films (20-50 µm) were cut into the desired size for composite fabrication. The thickness of PCL films was varied by varying the consolidation pressure from 1-3 bar. The purpose of variation of thickness of PCL was to fabricate the different percentages of chitosan content in PCL-based composites. The composites were prepared by sandwiching one layer of chitosan film between two layers of PCL films. The resulting sandwich construction was then heat pressed at 80°C for 1 min at 3 bar pressure. The plates containing composite were then cooled in ice bath for 1 min. The chitosan weight fractions in the composites varied from 5-30% by weight. The final thickness of the composite films varied from 50-70 µm depending on the weight fraction of chitosan. For the variation of chitosan content in PCL-based composites, the thickness of chitosan films (thickness was around 25µm) was maintained constant but varied the thickness of PCL films. The thickness of PCL films was varied from 20-50 µm depending on the weight fraction of chitosan in the composites. The resulting composite films were cut into the desired size for mechanical testing.

Mechanical properties

Tensile strength (TS) and tensile modulus (TM) of the films and composites were measured by Universal Tensile Machine (UTM) (Tinius-Olsen Inc., USA, Model: H5K) using a 1 kN load cell, with a crosshead speed of 1 mm/s at a span distance of 25 mm. The dimensions of the test specimen were (ISO 14125): 60 mm × 15 mm × 0.025 mm.

Scanning electron microscopy (SEM)

Film samples (5 × 5 mm) were deposited on an aluminum holder and sputtered with gold-platinum (coating thickness, 150-180 Å) in a Hummer IV sputter coater. SEM photographs were taken with a Hitachi S-4700 FEG-SEM scanning electron microscope (Hitachi Canada Ltd., Mississauga, ON, Canada) at room temperature. The working distance was maintained between 15.4 and 16.4 mm, and the acceleration voltage used was 5 kV.
3. Results and Discussion

Effect of gamma radiation

Figure 1 represents the effect of gamma radiation on TS values of chitosan films (without silane) and silane (0.25% w/w) grafted chitosan films (with silane). For chitosan films (control), the TS was found to be 30 MPa. When chitosan films were exposed to gamma radiation, the strength of the films improved significantly up to 5 kGy (33 MPa) then decreased (19 MPa at 25 kGy). But all silane grafted films showed significantly higher TS values than the control sample. The highest TS value (44 MPa) was observed at 10 kGy. At 25 kGy, the TS of the films reached at 41 MPa which is still significantly higher than that of the control sample. Thus, it is clearly observed that the TS of the silane grafted chitosan films improved significantly with gamma radiation.

The silane coupling agent used here has the formula \( \text{H}_2\text{N}(-\text{CH}_2\text{)}_3\text{-Si}(\text{OC}_2\text{H}_5)_3 \). The ethoxy groups (\(-\text{OC}_2\text{H}_5\)) are hydrolyzed in presence of aqueous media. The hydrolyzed silane then undergoes a condensation reaction with the naturally occurring hydroxyl group on the chitosan, which eventually improved the TS values. Cross-linking and chain scission occurred when polymers are irradiated using gamma radiation. Thus, with higher radiation dose there was more possibilities of grafting between silane and chitosan. As a result, the TS values of the silane containing films increased. Higher radiation doses were responsible for the degradation of the films and hence the decrease of the TS values was observed (7).

![Figure 1. Tensile strength of chitosan and silane grafted chitosan films against gamma radiation](image)

Figure 2 showed the effect of gamma radiation on TM values of chitosan and silane grafted chitosan films. The TM of the chitosan films was found to be 450 MPa. The irradiated chitosan films reached to 478 MPa at 5 kGy dose then found to decline but silane coupled chitosan films gained significantly higher TM values compared to control sample. The highest TM values were found to be 590 MPa at 10 kGy for silane grafted chitosan films and then slightly decreased with further radiation dose. Improvement in the TM values of the silane composite films is due to the increased cross-linking between the hydroxyl group of chitosan.
and amino group of silane with applied radiation dose. Our previous results (7) suggested vinyl-trimethoxy silane grafted gelatin films gained higher TM values due to the cross-linking between amino group of gelatin and vinyl group of silane. Silane forms hydrogen bonds between silanol and hydroxyl group of the chitosan and thus improved the mechanical properties (7).

![Graph](image)

**Fig. 2.** Tensile modulus of chitosan and silane grafted chitosan films against gamma radiation.

**Mechanical properties of the PCL-based insoluble composite films**

Figure 3 shows the effect of silane on PCL-based composites. The silane containing chitosan film (0.25% w/w, at 10 kGy) reinforced PCL-based composites (termed as “with silane”) was compared with chitosan film reinforced PCL-based composites (termed as “without silane”). It was found that silane composites gained significantly higher TS values than non-silane composites. At 20% (w/w) chitosan content, the TS value of PCL-based composite was found to be 18 MPa but 22 MPa was observed for the silane composites. The highest TS values were observed at 20% chitosan content. With the increase of chitosan content, the TS values of the composite films showed significant improvement. Improvement in the TS values of the composite films is due to the higher TS value of chitosan (30 MPa) as compared to PCL (12 MPa). So, chitosan acted as a reinforcement agent in the composite films. Again, chitosan is strongly hydrophilic and PCL is strongly hydrophobic, which attributes to the poor interfacial adhesion between them. But, when silane coupling agent was added, the surface of chitosan films are covered by a silane network through oxane bonds with the chitosan surface. This silane bridge improves the adhesion between chitosan and PCL in the silane composite. Thus, silane improves the interfacial adhesion between PCL and chitosan and enhanced the strength of the films significantly.
Fig. 3. Effect of chitosan content on tensile strength of the PCL-based composites. Chitosan films (1%, w/w in aqueous media) reinforced PCL composite is termed as “without silane” and the other one “with silane” indicated composite made of chitosan films containing 0.25% (w/w in aqueous media) silane, irradiated at 10 kGy.

**Scanning electron microscopy (SEM)**

Figure 4 represents the surface morphology of chitosan (4.A), silane grafted (0.25% w/w, at 10 kGy) chitosan (4.B), and interface of chitosan reinforced PCL-based composite (4.C) films. The surface of chitosan films appeared rough and irregular but silane grafted chitosan films revealed a homogenous, smoother and denser film surface with no gross defects. The film was free of bubbles as compared to pure chitosan films. For silane-treated films, a polysiloxane coating formed from silane monomer which may be responsible for the smooth surface. The smooth and homogenous surface of the films is an indicator of the structural integrity of the observed films, and thus good mechanical properties were obtained. It also indicated better solubilization and homogenization of chitosan and silane. The micrograph of PCL-chitosan interface (C) of the tri-layer composite film indicated two (top and bottom) phased of PCL and one (middle) phase of chitosan. The composite film is very typical one which is the combination of tri-layer films (PCL/chitosan/PCL). The interface indicated good adhesion between PCL and chitosan films.
Fig. 4. SEM images of (A) chitosan, (B) silane grafted (0.25% w/w, at 10 kGy) chitosan, and (C) interface of chitosan reinforced PCL-based composite films.

4. Conclusions

Chitosan films were grafted by silane monomer using $\gamma$-irradiation. Mechanical properties of the silane grafted chitosan films were improved significantly. An optimal dose of 10 kGy was observed for silane grafting with chitosan. PCL-based insoluble composite films were prepared by reinforcing silane grafted chitosan films and showed significantly higher mechanical properties than chitosan/PCL (non-grafted) composite films. Silane improved the interfacial adhesion between PCL and chitosan. From this investigation, it is concluded that $\gamma$-irradiation has the potential for silane grafting with chitosan and PCL-based insoluble films.
References


1.3 EFFECT OF HEMA AND SILANE MONOMERS USING GAMMA RADIATION ON THE MECHANICAL AND BARRIER PROPERTIES OF METHYLCELLULOSE-BASED FILMS

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Abstract

Methylcellulose (MC)-based films were prepared by casting from its 1% aqueous solution containing 0.5% vegetable oil, 0.25% glycerol and 0.025% Tween(R)-80. The values of puncture strength (PS), puncture deformation (PD) and water vapour permeability (WVP) of the films were found to be 147 N/mm, 3.46 mm, and 6.34 g.mm/m².day.kPa, respectively. The monomer, 2-hydroxyethyl methacrylate (HEMA) (0.1-1%, w/w) was incorporated into the MC-based formulation and films were prepared by casting. Films were then exposed to gamma radiation (5-25 kGy) and it revealed that 1% HEMA containing films showed the highest PS values (282 N/mm at 10 kGy). Silane monomer (3-aminopropyl tri-ethoxy silane) (0.1-1%, w/w) was also incorporated into the MC-based films and was found to improve the strength of the films significantly. Surface morphology of the grafted films was examined by scanning electron microscopy and suggested better appearance.

1. Introduction

Cellulosic materials are biodegradable and can be the alternative of synthetic polymers (1,2). Methyl Cellulose (MC), a biodegradable polymer, is a modified type of cellulose. MC shows good solubility in water at low temperature, which is produced from cotton cellulose, wood and plant pulps. MC has been widely used to produce gels and fine chemicals in pharmaceuticals, foods, paints, ceramics, detergents, agriculture, polymerization, adhesives and cosmetics for many years (3,4).

The monomer HEMA (2-hydroxyethyl methacrylate), is a vinyl monomer. Poly(HEMA) hydrogels are well known because of their hydrophilicity, softness, high water content, and permeability (5,6). Silane is a monomeric silicon compounds used in a wide range of applications because of their unique ability to chemically bond organic polymers to inorganic materials. When silane monomers are added to these systems, mechanical properties are improved. Silanes also improve adhesion between organic and inorganic phases of a composite by adhering to the individual components, thus bridging the interface (7).

There has been a continuous and significant growth in the development and application of radiation techniques in the coating, adhesive industry and in the field of polymer composites. The use of gamma radiation offers several advantages, such as curing at ambient temperatures, increased design flexibility through process control etc. (8). In this investigation, MC-based biodegradable films were prepared by solution casting, mechanical
and barrier properties of the films were evaluated. Then two monomers (HEMA and silane) were added into the MC-based formulation and then films were prepared by casting. The casted films were exposed to gamma radiation for grafting. The mechanical and barrier properties of the grafted films were compared with the control films. Surface morphology of the films was investigated by scanning electron microscopy.

2. Materials and methods

Materials

Methylcellulose (powder form, viscosity of 400 cP for a 1% solution at 20°C) was purchased from Sigma-Aldrich Canada Ltd (Oakville, ON, Canada). Monomers, 2-hydroxyethyl methacrylate (HEMA) \([\text{CH}_2=\text{C(CH}_3\text{)COOCH}_2\text{CH}_2\text{OH}]\) and 3-aminopropyl triethoxy silane \([\text{H}_2\text{N(CH}_2\text{)}_3\text{–Si–(OC}_2\text{H}_5\text{)}_3]\) were procured from Sigma-Aldrich, Canada. Glycerol and Tween®80 were from Laboratoire Mat (Beauport, QC, Canada). Vegetable oil (Sunflower brand) was obtained from a local grocery.

Film preparation

The MC solution (1% w/w) was prepared in an ice bath using deionized water with continuous stirring. Then 0.5% vegetable oil (hydrophobic agent), 0.25% glycerol (plasticizer) and 0.025% Tween®80 (emulsifier) were directly poured into the MC solution. The mixture was then homogenized using an IKA® T25 digital Ultra-Turrax disperser (IKA® Works Inc., Wilmington, NC, USA) at 45°C and 24,000 rpm for 1 min. Films were then cast by applying 12 mL of the film-forming solution onto Petri dishes (100 mm × 15 mm; VWR International, Ville Mont-Royal, QC, Canada) and allowed to dry for 24 h, at room temperature and at 35% relative humidity (RH). Dried water soluble films were peeled off manually using spatula and stored in polyethylene bags prior to characterization.

Irradiation

Irradiation of films was conducted at the Canadian Irradiation Centre with γ-rays generated from \(^{60}\text{Co}\) source at room temperature, at a dose rate of 17.878 kGy/h in an Underwater Calibrator-15A Research Irradiator (Nordion Inc., Kanata, ON, Canada).

Puncture Strength (PS) and Puncture Deformation (PD)

Puncture strength (PS) and puncture deformation (PD) were measured using a Stevens-LFRA texture analyzer (model TA-1000; Texture Technologies Corp., Scarsdale, NY). Films were fixed between two perforated Plexiglass® plates (3.2 cm diameter), and the holder was held tightly with two screws. A cylindrical probe (2 mm diameter; scale: 0-900 g; sensitivity: 2V) was moved perpendicularly to the film surface at a constant speed (1 mm/s) until it passed through the film. The PS value was calculated using the equation: \(\text{PS} \ (\text{N/mm}) = (9.81F)/x\), where \(F\) is the recorded force value (g), \(x\) is the film thickness (µm), and 9.81 m.s\(^{-2}\) is the gravitational acceleration. The PD value of the films was calculated from the PS curve, using the distance (mm) recorded between the time of first probe/film contact and the time of puncture point.
Water Vapor Permeability (WVP)

The WVP tests were conducted gravimetrically using an ASTM procedure (1) Changes in weight of the cell were recorded to the nearest 10^{-4} g. WVP was calculated according to the combined Fick and Henry laws for gas diffusion through coatings and films, according to the equation:

\[
\text{WVP (g.mm/m}^2\text{.day.kPa)} = \frac{\Delta w}{A.\Delta P}
\]

where \( \Delta w \) is the weight gain of the cell (g) after 24 h, \( x \) is the film thickness (mm), \( A \) is the area of exposed film (31.67 \times 10^{-4} m^2), and \( \Delta P \) is the differential vapor pressure of water through the film (\( \Delta P = 3.282 \) kPa at 25°C).

Scanning Electron Microscopy (SEM) Analysis

Film samples (5x5 mm) were deposited on an aluminum holder and sputtered with gold-platinum (coating thickness, 150-180 Å) in a Hummer IV sputter coater. SEM photographs were taken with a Hitachi S-4700 FEG-SEM scanning electron microscope (Hitachi Canada Ltd., Mississauga, ON, Canada) at a magnification of 40,000\( \times \), at room temperature. The working distance was maintained between 15.4 and 16.4 mm, and the acceleration voltage used was 5 kV, with the electron beam directed to the surface at a 90° angle and a secondary electron imaging (SEI) detector.

Statistical Analysis

For each measurement, five samples in each replicate were tested. Analysis of variance and Duncan’s multiple-range tests were used to perform statistical analysis of all results, using PASW Statistics Base 18 software (SPSS Inc., Chicago, IL, USA). Differences between means were considered to be significant when \( p \leq 0.05 \).

3. Results

Effect of gamma radiation on puncture strength and puncture deformation

The puncture strength (PS) of MC-based films was found to be 147 N/mm. The monomer, HEMA, was added (0.1-1%, w/w) in the MC-based formulation and films were casted then exposed to gamma radiation at 10 kGy dose for grafting. The values of PS were found to be from 182 to 282 N/mm. It revealed that with the rise of HEMA concentration, the PS values of the MC-based films improved significantly (\( p \leq 0.05 \)). The 1% HEMA containing films (solid film contains 36% HEMA) performed the highest PS values (282 N/mm) compared to other HEMA formulations. So, the MC-based formulation containing 1% HEMA was treated as optimized.

To investigate the effect of gamma radiation, different doses (5-25 kGy) were applied to MC-based films containing 1% HEMA.

Figure 1 represented the effect of gamma radiation on PS of MC-based films containing HEMA (1%, w/w). All the HEMA grafted MC-based films showed significantly higher (\( p \leq 0.05 \)) PS values than the control sample. The highest PS values (92% improvement) were
observed at 10 kGy and after that the PS values started to decrease. At 25 kGy, the PS of the film reached to 243 N/mm which is still significantly ($p \leq 0.05$) higher than control sample. The PS value (141 N/mm) of 0 kGy dose in the figure is designated 1% HEMA in MC-based films without irradiation. This film showed significantly ($p \leq 0.05$) lower values of PS compared to control sample (147 N/mm) because HEMA monomer was present in the film which imparted film flexibility and as result strength decreased. During irradiation of the films, both grafting (MC+HEMA) and homo-polymerization (HEMA+HEMA→Poly-HEMA) reactions occurred (Khan et al, 2009b). Grafting improved the PS values of the films. But at higher dose of radiation, homo-polymerization dominated and radiation degradation of cellulose materials started. Thus, after 10 kGy dose, the values of PS started to decrease. Similarly, 1% silane monomer containing films were irradiated and the results are presented in Figure 1. It was observed that the PS values of the grafted films improved significantly ($p \leq 0.05$) with the rise of radiation dose. The maximum PS values (296 N/mm) were observed at 10 kGy and this is 101% higher PS than the PS of MC-based films. It is interesting to note that un-irradiated sample containing silane (0 kGy) showed higher value of PS (165 N/mm) compared to the PS value (147 N/mm) of control sample. It is reported by Plueddemann (9) that all silane coupling agents tend to be effective with all organic and inorganic materials. So, addition of silane monomer in MC-based films improved the PS values. Comparing the effectiveness of HEMA and silane monomers onto the MC-based films, it was observed that silane performed the better results. All the silane treated films showed significantly higher ($p \leq 0.05$) values of PS compared to HEMA films.

![Fig. 1. Effect of gamma radiation on the puncture strength of HEMA and silane containing MC-based films.](image)

Effect of gamma radiation on the puncture deformation (PD) of monomer (HEMA and silane) grafted MC-based films is presented in Figure 2. The PD of the MC-based films was found to be 3.46 mm. When monomers (HEMA and silane) were incorporated (1%) in MC-based films and exposed to gamma radiation from 5-25 kGy doses, all the films showed significantly higher PD values compared to control sample. The highest PD values were observed at 10 kGy for HEMA and 15 kGy for silane then showed slight descending nature. For HEMA and
silane grafted films, the PD values improved to 59 and 45%, respectively over the MC-based films. From above investigation, this is clear that the values of PS and PD improved significantly \( (p \leq 0.05) \) during monomer (HEMA and silane) grafting using gamma radiation. Both strength and deformation nature of the films improved because of monomer grafting with the cellulosic chain of the MC and polymer formation during exposure of gamma radiation. It is reported that HEMA and silane monomers are potential grafting agents using gamma radiation (5, 6, 7).

**Fig. 2. Effect of gamma radiation on the puncture deformation of HEMA and silane containing MC-based films.**

**Effect of gamma radiation on the WVP**

Effect of gamma radiation on the WVP of monomer (HEMA and silane) grafted MC-based films is shown in Figure 3. The MC-based films containing HEMA and silane monomers (1%, w/w) were exposed to gamma irradiation doses from 5 to 25 kGy, and WVP values were measured to evaluate the influence of monomer grafting on barrier properties of the films. The values of WVP decreased significantly \( (p \leq 0.05) \) as the radiation doses increased. The WVP of MC-based films was found 6.3 g.mm/m\(^2\)/day.kPa. For HEMA and silane grafted films (at 25 kGy), WVP values were 5.5 and 4.2 g.mm/m\(^2\)/day.kPa, respectively. Therefore, 13 and 33% reduction of WVP values were obtained for HEMA and silane grafted films. The WVP values of HEMA grafted films were found higher compared to silane grafted films, this is because of strong hydrophilic nature of poly (HEMA). From this investigation, it revealed that gamma exposed films had better barrier properties. During irradiation, grafted complex formed (MC+HEMA and MC+silane) and which is responsible for better barrier properties of the films. It is reported that gamma radiation is effective for improving barrier properties of MC-based films (Khan et al, 2009a).
Surface morphology of the films

The surface morphology of the grafted films (1% monomer containing MC-based films irradiated at 10 kGy) was studied by SEM. The images are shown in Figure 4(a-c). The surface of the HEMA grafted (b) films appeared very clear and smooth compared to the surface of the control films (a) which might be due to the formation of poly(HEMA). During irradiation of HEMA with MC, both grafting (MC+HEMA) and poly(HEMA) formations took place simultaneously (6). It is reported that poly(HEMA) is used in contact lenses and as hydrogels which looks very transparent (5). As a result, HEMA grafted films appeared homogeneous and quite smooth. On the other hand, silane grafted films (c) looks almost similar to the control sample. Compared to the three types of images, HEMA grafted films appeared the best surface morphology. It is reported (6) that HEMA grafted glass fiber surface appeared excellent smoothness.
4. Conclusions

Methylcellulose (MC)-based films were successfully grafted using gamma radiation with HEMA and silane monomers. Mechanical and barrier properties of the monomer grafted MC-based films were improved significantly ($p \leq 0.05$). Surface appearance of the grafted films found better than the control samples. It can be concluded that gamma radiation is a potential source of monomer grafting for MC-based films.

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References


PART II
MECHANICAL AND BARRIER PROPERTIES OF CARBON NANOTUBE (CNT)-REINFORCED POLYCAPROLACTONE (PCL)-BASED COMPOSITE FILMS: EFFECT OF GAMMA RADIATION

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Abstract

Carbon nanotube (CNT) reinforced (0.05-0.5\% by wt) polycaprolactone (PCL)-based composites were prepared by compression molding. Addition of 0.2\% CNT caused a 131\% improvement of tensile strength (TS) of PCL films. The tensile modulus (TM) and elongation at break (Eb) of PCL were also significantly improved with the addition of CNT. The water vapor permeability of PCL was 1.51 g·mm/m\(^2\)·day but 0.2\% CNT containing PCL films showed 1.08 g·mm/m\(^2\)·day. Similarly, the oxygen transmission rate (OTR) of PCL films was found to decrease with the addition of CNT. But, carbon dioxide transmission rate (CO\(_2\)TR) of PCL film was improved due to incorporation of CNT. Effect of gamma radiation on PCL films and CNT reinforced PCL-based composites were also studied. The TS of the irradiated (10 kGy) PCL films gained to 75\% higher than control sample. The TS of the 0.2\% CNT reinforced composite film was reached to 41 MPa at 15 kGy dose. The barrier properties of non-irradiated and irradiated (10 kGy) PCL films and composites (0.2\% CNT reinforced) were also measured. Both PCL films and composites showed lower values of WVP upon irradiation and indicated better water valour barrier. The OTR and CO\(_2\)TR of the irradiated (10 kGy) PCL films and composites were decreased compared to their counterparts. Surface and interface morphologies of the composites were studied by scanning electron microscopy.

1. Introduction

Nanotechnology has gained huge attention to the scientists in recent years because of manipulating materials at the level of atoms and molecules in order to alter the product properties drastically. For packaging sectors, this nanotechnology is of great demand due to its excellent potentiality. For making high performance packaging materials with improved thermo-mechanical and barrier properties, nanomaterials can be used. The important nanomaterials are carbon nanotube (CNT), nanocrystalline cellulose, and chitin/chitosan nanofibers (1-4). In this investigation, CNT was used which is a microscopic carbon cylinder, thousands of times smaller than a human hair. It has generated huge activity in many areas of science and engineering due to their unprecedented physico-chemical properties. The unique properties of CNTs and the technological possibilities that CNT/polymer composites offer, including enhanced thermo-mechanical properties continues to attract global research interest. The CNT have diameters in the nanometer scale, are up to tens of microns long, and can be single- or multi walled. Owing to high aspect ratio (larger than 1000), high strength and stiffness at low density, the CNTs attract attention of the researchers as reinforcing fillers for

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a generation of new high performance low weight polymer-based materials (5-7). Over the last decade, many polymers have been employed as matrices for preparation of CNT/polymer composites (8-10). Biodegradable plastics were also prepared and characterized using CNT and poly(lactic) acid (3). The methods of distribution and dispersion of the CNTs within the polymer matrix plays a vital role on the properties of the final product. Melt-mixing (11), solution-casting (12), and in-situ polymerization (13) have all been employed for CNT polymer composite synthesis.

At present, petroleum-based synthetic polymers are used as packaging materials due to their good thermo-mechanical and barrier properties and also for economic reasons. Unfortunately, these materials are not biodegradable. Thus, efforts are in progress to develop alternative packaging materials, which are environment-friendly. Typical materials under considerations are PCL, poly(lactic acid), poly(glycolic acid) and biopolymer-based materials. Biodegradable films made of these materials do not pose a threat to the environment. Therefore, many studies are now attempting to develop biodegradable films in order to approach physicochemical attributes analogous to those of petrochemical-based polymers (14-15). PCL is a thermoplastic biodegradable polymer resulting from a chemical synthesis from crude oil. It is semi-crystalline, and has a glass transition temperature of about -60°C. PCL belongs to the aliphatic polyester family and it has good water, oil, solvents and chlorine resistance. PCL has a low melting-point (58-64°C) and low viscosity, and it is easy to process. It has been shown that PCL exhibited desirable characteristics as a diffusion-controlled delivery system, including biodegradability, biocompatibility, commercial availability, and affordability. It is produced via the ring opening polymerization of caprolactone monomer. PCL can degrade in water via hydrolysis of its ester linkages. The main commercial application of PCL is in the manufacture of biodegradable bottles and films. This polymer is often used as an additive for resins to improve their processing characteristics and their end use properties. Being compatible with a range of other materials, PCL is mixed with starch to lower its cost and increase biodegradability. It is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives, fully biodegradable compostable bags (16-18).

Gamma radiation is one type of ionizing radiations. The application of gamma radiation is becoming more widespread every year. Over the past four decades, there has been a continuous and significant growth in the development and application of radiation techniques, primarily in the coating and adhesive industry. As this technique continues to develop, innovative products based on high efficiency and easy process control, a logical extension for this technology is found to be in the field of polymer composites. The use of gamma radiation offers several advantages, such as continuous operation, minimum time requirement, less atmospheric pollution, curing at ambient temperatures, increased design flexibility through process control and many more (19-22). The objective of this study was to fabricate CNT reinforced PCL-based composites. Mechanical, barrier (water vapor permeability, oxygen and carbon dioxide transmission rate) and morphological properties of CNT reinforced PCL-based composites were evaluated. Effect of gamma radiation on the PCL films and composites was also carried out.
2. Materials and methods

Materials

Carbon nanotube, multi-walled (purity >90%, diameter 110-170 nm, length range 5-9 μm) and PCL (granular form, molecular weight: 70,000-80,000) were purchased from Sigma-Aldrich Canada Ltd (Oakville, ON, Canada).

Preparation of CNT reinforced PCL-based films by compression molding

PCL films were prepared from its granules by compression molding machine (Carvar, Inc., Indiana, USA, Model 3912) operated at 110°C under a consolidation pressure of 2 tons for 1 min. The mold containing PCL films was rapidly cooled using an ice bath for 2 min. The PCL film was taken out from the mould and kept in the desiccator prior to characterization. PCL were melt-blended with CNTs in a beaker with continuous stirring at 110°C then hot pressed in the same compression molding machine using same parameters.

Film thickness

Film thickness was measured using a Mitutoyo digimatic Indicator (Mitutoyo MFG, Tokyo, Japan) at five random positions around the film, by slowly reducing the micrometer gap until the first indication of contact.

Mechanical properties of the films

The TS, TM and Eb of the films and composites were measured by Universal Tensile Machine (UTM) (Tinius-Olsen Inc., USA, Model H5K) using a 1 KN load cell, with a crosshead speed of 1 mm/s at a span distance of 25 mm. The dimensions of the test specimen were (ISO 14125): 60×15×0.2 mm³.

Water vapor permeability of films (WVP)

The WVP tests were conducted gravimetrically using an ASTM procedure (45). Films were mechanically sealed onto Vapometer cells (No. 68-1, Thwing-Albert Instrument Company, West Berlin, NJ, USA) containing 30 g of anhydrous calcium chloride (0% Relative Humidity). The cells were initially weighed and placed in a Shellab 9010L controlled humidity chamber (Sheldon Manufacturing Inc., Cornelius, OR) maintained at 25°C and 60% RH for 24 h. The amount of water vapor transferred through the film and absorbed by the desiccant was determined from the weight gain of the cell. The assemblies were weighed initially and after 24 h for all samples and up to a maximum of 10% gain. Changes in weight of the cell were recorded to the nearest 10^-4 g. WVP was calculated according to the combined Fick and Henry laws for gas diffusion through coatings and films, according to the equation: WVP (g.mm/m².day.kPa) = Δw.x/A.ΔP, where Δw is the weight gain of the cell (g) after 24 h, x is the film thickness (mm), A is the area of exposed film (31.67 × 10^-4 m²), and ΔP is the differential vapor pressure of water through the film (ΔP = 3.282 kPa at 25°C).

Oxygen transmission rate (OTR)

The OTR was measured using an OX-TRAN® 1/50 (Mocon, Minneapolis, USA) machine. During all experiments, temperature and relative humidity were held at 23°C and 0% relative
humidity. The experiments were done in duplicate and the samples (dimension: 50 cm²) were purged with nitrogen for a minimum of 2 h, prior to exposure to a 100% oxygen flow of 10 mL/min.

**Carbon dioxide transmission rate (CO₂TR)**

The CO₂ transmission rate (CO₂TR) of films was measured using Mocon Permatran-C™ 4/41 (Mocon, Minneapolis, USA). All analysis was carried out under atmospheric conditions, temperature of 23°C and 0% relative humidity. Readings were recorded as cc/m²/day.

**Scanning electron microscopy (SEM)**

Film samples (5×5 mm) were deposited on an aluminum holder and sputtered with gold-platinum (coating thickness, 150-180 Å) in a Hummer IV sputter coater. SEM photographs were taken with a Hitachi S-4700 FEG-SEM scanning electron microscope (Hitachi Canada Ltd., Mississauga, ON, Canada) at a magnification of 40,000×, at room temperature. The working distance was maintained between 15.4 and 16.4 mm, and the acceleration voltage used was 5 kV, with the electron beam directed to the surface at a 90° angle and a secondary electron imaging (SEI) detector.

**Irradiation of films**

Irradiation of films was conducted with γ-rays generated from ⁶⁰Co source at room temperature, at a dose rate of 17.878 kGy/h in an Underwater Calibrator-15A Research Irradiator (Nordion Inc., Kanata, ON, Canada).

**Statistical analysis**

All experiments were done with two replicates. For each radiation dose, three samples per treatment were evaluated. Ten radiation doses were evaluated for each experiment. An analysis of variance was performed using the PASW Statistics Base 18.0 software (SPSS Inc., Chicago, IL), and means for each treatment were comparison with Duncan’s multiple range tests (P ≤ 0.05).

3. Results and discussion

**Effect of CNT on mechanical properties of PCL films**

CNTs were mixed by blending with melted PCL then films were made by compression molding. The TS of PCL was found to be 16 MPa. Addition of minute amount CNT significantly (P ≤ 0.05) improved the TS values of PCL films. Figure 1 shows the effect of addition of CNT on PCL films. With 0.05, 0.1, 0.2 and 0.5 % (by wt) incorporation of CNT, the TS values reached to 20, 29, 37 and 41 MPa respectively. Only 0.2% addition of CNT caused a 131% improvement of TS of PCL films. The drastic improvement of strength of PCL occurred due to the addition of CNT which has very high strength (1-2 GPa). The reinforcing effect of CNTs attributed due to the strong interfacial interaction between polymer matrix and CNTs (5-7).
Similarly, TM of PCL films was also improved by the incorporation of CNT. Figure 2 shows the effect of CNT content on the TM values of PCL films. The TM of PCL films was found to be 156 MPa. The incorporation of CNT into PCL films caused a significant (P ≤ 0.05) enhancement of the modulus. At 0.05, 0.1, 0.2 and 0.5% (by wt) CNT content PCL films, the TM values were found to be 173, 181, 193 and 206 MPa respectively. Thus, by incorporating only 0.2% CNT, the PCL films gained 23.71% increase of TM values. The increased TM values of the CNT reinforced PCL films may be attributed to the increased stiffness of the films by the addition of CNT. Moreover, it indicated better dispersion of CNTs in PCL matrix (7-9). It is to be noted here that TM is a measure of the stiffness of an elastic material and is a quantity used to characterize materials. It is defined as the ratio of the uniaxial stress over the uniaxial strain in the range of stress. In solid mechanics, the slope of the stress-strain curve at any point is called the tangent modulus. The tangent modulus of the initial, linear portion of a stress-strain curve is called TM (or Young’s modulus). It is experimentally determined from the slope of a stress-strain curve created during tensile tests conducted on a sample of the material (23).
The Eb of PCL was found to be 555%. With the incorporation of CNT, the Eb values of PCL films also enhanced significantly ($P \leq 0.05$). Figure 3 represented the effect of CNT on the Eb (%) values of PCL films. With 0.05, 0.1, 0.2 and 0.5% (by wt) incorporation of CNT, the Eb values reached to 760, 910, 1047 and 1215%, respectively. From this investigation, this is clearly revealed that CNTs caused a significant rise of mechanical properties of PCL films. This is a rare combination that all of the tensile properties (TS, TM and Eb) of the PCL films significantly improved with the addition of CNT. During melt blending process, CNTs were dispersed homogeneously with the matrix PCL and as a result strong interfacial interaction occurred between CNTs and PCL. Thus improved the mechanical properties (5-9).
Water vapor permeability (WVP) of the composite films

The WVP of PCL films and CNT reinforced PCL-based composites were measured. The values of WVP for PCL films was found to be 1.51 g.mm/m².day.kPa. Figure 4 shows the effect of CNT content on the WVP of the PCL-based composites. The values of WVP decreased continuously with increase of CNT in PCL-based films. The WVP values of 0.05, 0.1, 0.2 and 0.5% (by wt) CNT reinforced PCL films were 1.40, 1.22, 1.08, and 0.92 g.mm/m².day.kPa respectively. For 0.2% CNT addition in PCL films, the WVP decreased to 39% which indicated better barrier properties. The presence of nanotubes in CNT is thought to increase the tortuosity in the PCL-based composite films leading to slower diffusion processes and hence, to a lower permeability (24). The barrier properties are enhanced if the filler is less permeable and has a good dispersion into the matrix (25). In the present study, the interactions of CNT with PCL may have enhanced the water vapor barrier (26). This can also be explained by the strong hydrophobic character of CNTs. Owing to the higher amount of hydrogen bonds, most of the biodegradable polymeric films are hydrophilic, and that is responsible for poor barriers to water vapor (70). The presence of CNTs in the PCL-based composites is responsible for lower WVP values compared to control PCL films. The WVP values of the composites indicated excellent barriers to water vapor.

Oxygen transmission rate (OTR) of PCL and composites

The OTR of PCL and CNT reinforced composite films was measured. Figure 5 represents the OTR of PCL, and CNT incorporated PCL films. This is clear that CNT containing composite films showed much lower OTR values than that of the PCL films. The OTR value of PCL film was found to be 175 cc/m².day. Incorporation of 0.05, 0.1, 0.2 and 0.5% (by wt) CNT in PCL films decreased OTR values to 160, 152, 136, and 115 cc/m².day respectively. So, 0.2% CNT reinforced PCL-based composites showed a 22% reduction of OTR. The OTR is defined as the quantity of oxygen gas passing through a unit area of the parallel surface of a film per unit time under predefined oxygen partial pressure, temperature, and relative humidity (18).
The transfer of oxygen from the environment to food has an important effect on food quality and shelf life. Oxygen causes food deterioration such as lipid and vitamin oxidation, leading to sensory and nutrient changes. The OTR is very important since oxygen gas influence the rates of oxidation and respiration in the enclosed food, as fruits and vegetables. Generally synthetic polymers (PCL, polypropylene, polyethylene etc.) have higher OTR values (27-30). Addition of CNT in PCL made a barrier to non-polar substances, such as oxygen and as a result the OTR values decreased.

**Fig. 5. Effect of CNT on oxygen transmission rate (OTR) of PCL.**

**Effect of CNT on carbon dioxide transmission rate (CO₂TR)**

The CO₂TR value of PCL film was found to be 1170 cc/m².day. The composite films containing 0.05, 0.1, 0.2 and 0.5% CNT showed 1260, 1430, 1710, and 2240 cc/m².day.kPa. Figure 6 represented the CO₂TR of PCL, and CNT reinforced composite films. This is clear that CNT containing composite films showed higher CO₂TR values than that of the PCL films. Just addition of 0.2% CNT in PCL caused a 46% higher of CO₂TR values. It is to be noted here that modified atmosphere packaging has gained considerable popularity over the last decades as a modern non-thermal method of food preservation. The proper combination of gases (carbon dioxide, nitrogen and oxygen) in the headspace of food packs results in suppression of the microbial flora of perishable foods developed under aerobic conditions and retention of their sensorial attributes. So, the CO₂TR is also very important like OTR. The CO₂TR of biopolymers has low values because of its strong hydrophilic nature but the CO₂TR of synthetic polymers are very high (31). It is reported (32) that the CO₂TR of high density polyethylene is 17470 cc/m².day. This is because synthetic polymers are strongly hydrophobic and thus makes them less barrier to non-polar gases like carbon dioxide. When CNT was added in PCL, the CO₂TR was improved because the composite was more hydrophobic in nature and thus enhanced the CO₂TR.
Effect of gamma radiation on PCL and composites

The PCL films and CNT(0.2%) reinforced PCL-based composites were exposed to gamma radiation from 2-25 kGy. Then TS, TM and Eb of PCL and composite films were measured. The results are presented in Figures 7-9. It was found that gamma radiation had significant influence on the strength of PCL and composites (Figure 7). The TS of PCL film was found to be 16 MPa but 10 kGy irradiated films reached to 28 MPa which is 75% higher than control sample. After 10 kGy dose, the TS values decreased and reached to 22 MPa at 25 kGy dose, which is still higher than control sample. The TS of composite (0.2% CNT reinforced) film was 37 MPa but the strength of the films improved significantly (41 MPa) at 15 kGy (Figure 7). The TS value of the irradiated film improved to 11% which is much less than PCL films (75%).
Similarly, TM values of PCL films improved significantly due to exposure of irradiation. The results are depicted in Figure 8. The highest TM value was observed at 10 kGy. The TM values of composites enhanced up to 15 kGy dose then slightly decreased and reached to 270 MPa at 25 kGy. The irradiated PCL films gained 76% higher TM values at 10 kGy than that of the control PCL films. On the other hand, composites gained 61% higher TM values at 15 kGy dose than their counterpart control composite.

Fig. 8. Effect of gamma radiation on tensile modulus of PCL and composites.

An unexpected result was observed for Eb (%) values. With the rise of TS and TM values, the Eb values of the PCL films and composites were also increased with the increase of radiation dose. The effect of gamma radiation on Eb values of PCL and composites are presented in Figure 8.
Figure 9. Both PCL and composites gained higher Eb values than their control counterpart samples. The maximum Eb values were obtained at 15 kGy dose for PCL and composites.

![Figure 9. Effect of gamma radiation on elongation at break of PCL and composites.](image)

From this investigation, it is clear that gamma radiation had a strong role on the improvement of the mechanical properties of PCL films. The CNT reinforced composites showed positive trend of enhancement of mechanical properties but the intensity is much lower than PCL. The nanotubes from CNT may hinder the cross-linking of PCL and thus reduce the strong influence of irradiation for CNT reinforced composites. It is reported that when polymeric materials are subjected to gamma radiation, radicals are produced on the main chain by hydrogen and hydroxyl abstraction (33-36). Gamma radiation also ruptures some carbon–carbon bonds and produces radicals. Chain scission may also take place to form other radicals. The gamma radiation produces three types of reactive species in polymer during irradiation treatment. These are ionic, radical and peroxide. The peroxides species are produced when polymers are irradiated in the presence of oxygen. In this investigation, irradiation was carried out in presence of oxygen. So, produced peroxides may react with PCL and could produce PCL-diperoxides and PCL-hydroperoxides by a radical chain reaction process. The reaction occurs in three steps: activation, propagation and termination. It is also reported (34) that the effect of gamma radiation on polymers (such as PCL) produce ionization and excitation, as a result some free radicals produce. The polymers may undergo cleavage or scission (i.e., the polymer molecules may be broken into smaller fragment). Subsequent rupture of chemical bonds yields fragments of the large polymer molecules. The free radicals thus produced may react to change structure of the polymer and also the physical properties of the materials. It also may undergo cross-linking (i.e., the molecules may be linked together into large molecules). Gamma irradiation also affects the polymeric structure and can produces active site (37-38). Gamma irradiation of PCL may result in cross-linking which produces higher mechanical properties up to a certain dose. Active sites inside the polymer might be also produced by the application of gamma radiation. But at higher dose of gamma radiation on PCL could cleavage or scission molecules and thus found a decreasing tendency of mechanical properties after a certain dose.
The barrier properties of non-irradiated and irradiated (10 kGy) PCL and composites (0.2% CNT reinforced) were also measured. The water vapor permeability (WVP) of PCL film was found to be 1.51 g.mm/m².day.kPa, but the WVP of irradiated PCL decreased to 1.32 g.mm/m².day.kPa which is 13% less than control PCL film. Similarly, the WVP of 0.2% CNT reinforced PCL-based composites showed 9% lower values due to irradiation at 10 kGy. The values of WVP for unirradiated and irradiated composites were 1.08 and 0.98 g.mm/m².day.kPa. So, gamma radiation improved the water vapor barrier properties by reducing the WVP values. It is expected that during irradiation of PCL and composites, cross-linking of PCL molecules can happen and thus improved the water vapor barriers. It is reported that active sites inside the polymeric matrix might be produced by the application of gamma radiation and as a result more cross-linked structure might form and thus improved the mechanical and barrier properties (39-40). Some researchers found that irradiation improved the barrier properties of the polymeric films because of hydrogen bonding involvement due to irradiation (2,22). So, our results are similar in accordance with the published scientific manuscripts. A dramatic result was observed for oxygen transmission rate (OTR). The OTR of the irradiated (10 kGy) PCL increased to 224 cc/m²/day from 175 cc/m²/day. On the other hand, the OTR of the irradiated (10 kGy) PCL-based composite (0.2% CNT) increased to 152 cc/m²/day from 136 cc/m²/day. Similarly, the carbon dioxide transmission rate (CO₂TR) of irradiated PCL and composites were also improved. The CO₂TR of the irradiated (10 kGy) PCL increased to 1440 cc/m²/day from 1170 cc/m²/day, and the CO₂TR of the irradiated (10 kGy) composite increased to 1830 cc/m²/day from 1710 cc/m²/day. PCL is partly crystalline (16-17), during irradiation treatment a structural changes may occur in PCL. Both oxygen and carbon dioxide are nonpolar in nature but PCL is polar. Active sites can form in PCL during gamma radiation and also chain scission may happen. As a result, crystallinity can decrease and amorphous nature of PCL may improve (41) which may help to passage more oxygen and carbon dioxide.

Surface and interface morphology of the composites

The digital images of the surface of (10.A) PCL, (10.B) 0.05% CNT + PCL, and (10.C) 0.2% CNT + PCL films are presented in Figure 10. The PCL films were white (A) but CNT reinforced PCL films became black (10.B-10.C). Only addition of 0.2% CNT in PCL, the films looked fully black in colour. These digital images clearly indicated the color change due to the addition of CNT in PCL matrix. The surface and interface of the CNT reinforced PCL films were investigated by SEM analysis. Figure 11 shows the SEM images of (11.A) surface and (11.B) interface of CNT (0.2 wt%) reinforced PCL-based composites. CNTs were not appeared at the surface of composite films because only a minute amount of CNTs were added. Moreover, due to pressing at high temperature (110°C), CNTs were penetrated inside the PCL matrix which might be attributed to clear surface. Surface of this film indicated better homogenization of the CNTs with PCL. But at the interface (fracture surface) of the composites, CNTs were clearly visible. CNTs looked like fibers which imparted higher mechanical properties. The length of the CNTs used here was 5-9 µm. The SEM image showed only a fraction of the length of CNT. The remaining part of CNT was inside the polymer matrix. In the image, only 1-2 µm part of CNT is clearly visible. The interface of the composite supported above results discussed for better barrier properties also. It is reported similar types of SEM images for the interface of CNT reinforced polymer-based composites and demonstrated higher mechanical properties (42-43).
Fig. 10. Digital images of the surface of (A) PCL, (B) 0.05 wt % CNT + PCL, and (C) 0.2 wt % CNT + PCL films.

Fig. 11. SEM images of (A) surface and (B) interface of 0.2 wt % CNT + PCL films.

4. Conclusions

An addition of small amount (0.05-0.5 wt %) of CNT caused a significant increase of mechanical properties of PCL films. The values of WVP and OTR of the CNT reinforced composites were reduced compared to PCL and thus indicated better moisture and oxygen barrier properties. But CO₂TR of PCL films was improved by the incorporation of CNT which indicated the possibility of the prepared composite films in modified atmospheric packaging. It was noticed that gamma radiated films had better mechanical and barrier properties over the control counterpart samples. Surface and interface morphologies of the composites were studied by SEM. At the surface, no CNTs were appeared but interface morphology demonstrated the presence of CNTs and which were responsible for higher mechanical and barrier properties. This investigation opens a new door of research for packaging in modified atmospheric conditions.
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PART III
MICRO-FLUIDIZATION AND IRRADIATION TREATMENT FOR BETTER DISPERSION OF NANO FIBERS IN SUSPENSION: DEVELOP A METHODOLOGY TO ENCAPSULATE ANTIMICROBIAL COMPOUNDS

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1. Introduction

Bio-based packaging is defined as packaging containing raw materials originating from agricultural sources, i.e., produced from renewable, biological raw materials such as starch, cellulose and bio-derived monomers. To date, biodegradable packaging has commanded great attention, and numerous projects are under way in this field. One important reason for this attention is the marketing of environmentally friendly packaging materials. Furthermore, use of biodegradable packaging materials has the greatest potential in countries where landfill is the main waste management tool (1,2). Unfortunately, so far the use of biodegradable films for food packaging has been strongly limited because of the poor barrier properties and weak mechanical properties exhibited by natural polymers. For this reason natural polymers are frequently blended with other synthetic polymers or chemically modified with the aim of extending their applications in more special or severe circumstances, so that the biopolymers can compete with the synthetic packaging materials (3). Another way to overcome the weak mechanical and barrier properties of the biopolymers is by adopting innovative technologies such as, nanomaterial reinforcement. Nanocrystalline cellulose (NCC) provides an intriguing and highly potential option in the field of nano-reinforcement.

Chitosan is a cationic biopolymer and is prepared from chitin, which is the second most abundant polysaccharide, found in nature after cellulose Chitosan is a linear polysaccharide and is composed of glucosamine and N-acetyl glucosamine residues with a β-1, 4-linkage. Chitosan has been found to be non-toxic, biodegradable, biofunctional, biocompatible and was reported by several researchers to have strong antimicrobial and antifungal activities (4).

One of the major challenges in the area of nanocomposite is the compatibilization of the nano reinforcements with the polymer matrix to achieve acceptable dispersion levels of the filler within the polymeric matrix. However, in order to achieve a proper dispersion of nanocellulosic materials into the matrix, a high pressure homogenization technique such as microfluidization (figure-1) can be adopted (5).

The objective of this study was to evaluate the effect of different microfluidization pressure and cycles on the preparation of chitosan/NCC nanocomposite films by measuring the mechanical properties such as, tensile strength (TS) of the nanocomposite films and to establish an optimum microfluidization condition (pressure and number of cycles) for the preparation of the nanocomposite films.
2. Materials & Methods

Chitosan (Chitoscience, degree of deacetylation: 82.6-87.5%, viscosity 71-150 mPas) was purchased from Heppe-medical chitosan, Germany. Nanocrystalline cellulose (NCC) was produced in FPInnovations pilot plant NCC reactor from a commercial bleached softwood kraft pulp according to a procedure modified from the literature (Pointe-Claire, QC, Canada).

Preparation of NCC suspension

NCC suspension (2%, by wt.) was prepared by suspending NCC in distilled water for 3h. The suspension was then filtered through a coarse filter paper (Whatman 1) to remove any dust or small debris. Then the NCC suspension was subjected to sonication for 2 min at 60% output on a 500W sonicator (Model Q500, Qsonica LLC. USA).

Preparation of microfluidized chitosan/NCC nanocomposite films

Chitosan (2 wt%) was dissolved in 1% aqueous acetic acid solution. The desired amount of aqueous NCC suspension was added into the chitosan suspension under stirring to obtain a solid content of 5 wt% NCC in the matrix. Then the nanocomposite suspension was
homogenized at 23000 rpm for 2 min by an IKA T25 digital Ultra-Turrax disperser (IKA Works Inc., Wilmington, NC). At first both the chitosan and chitosan/NCC nanocomposite suspension was subjected to microfluidization at a fixed pressure of 20,000 psi (~138 MPa) for 1, 3 and 5 cycles. With the optimized microfluidization cycle the suspension was passed through two different microfluidization pressures (5,000 psi, and 10,000 psi). Films were prepared by casting 10 mL of the suspensions onto Petri dishes (100mm×15mm; VWRInternational, Ville Mont-Royal, QC, Canada) and allowed to dry for 24 h, at room temperature and 40-50% relative humidity.

**Mechanical Properties of the Films**

Tensile strength (TS) and tensile modulus (TM) of the films were measured by using Universal Tensile Machine (Tinius-Olsen, USA, model H5K, with a 1KN load cell). The samples were cut (according to ISO 14125) and the film thickness was measured using a Mitutoyo Digimatic Indicator (Type ID-110E; Mitutoyo Manufacturing Co. Ltd., Tokyo, Japan) with a resolution of 0.001mm, at five random positions around the film.

**Statistical Analysis**

An analysis of variance (ANOVA) and multiple comparison tests of Duncan's were used to compare all the results. Differences between means were considered significant when the confidence interval is smaller than 5% (P ≤ 0.05). The analysis was performed by the PASW Statistics 18 software (SPSS Inc., Chicago, IL, USA).

3. **Results & Discussion**

From figure 2, we can see the effect of microfluidization on the chitosan/NCC nanocomposite suspension. The aggregation of the NCC is clearly visible from the images of chitosan/NCC nanocomposite suspension without microfluidization. Whereas, the chitosan/NCC suspension microfluidized at 20,000 psi for 3 and 5 cycles seems to be transparent, this might be attributed to the dispersion of NCC into chitosan.
Fig. 2. (a) Images of chitosan/ NCC suspension at different cycles of microfluidization and (b) Images of chitosan/ NCC suspension before and after microfluidization (20,000 psi, 5 cycles).

From figure 3, the effect of microfluidization at different cycles (1,3,5 at pressure 20,000 psi) on the tensile strength of chitosan and chitosan/NCC suspension can be observed.

The TS of the chitosan/NCC composite films was found to be 50.9 MPa, which is similar to the TS of pure chitosan (49.4 MPa). So, due to the aggregation of NCC there was no reinforcement. However, the TS of the chitosan/NCC films increased to 63.1 MPa after microfluidization at 5 cycles. TS of the films increased by 27.7% compared to the control chitosan films. So, from the increase of TS it is evident that NCC reinforced with the chitosan matrix and the dispersion of NCC into chitosan is achieved. So, by microfluidization of chitosan/NCC nanocomposite at 20,000 psi and 5 cycles it is possible to disperse the NCC into chitosan and increase the tensile strength of the nanocomposite films.
Fig. 3. Effect of microfluidization on the tensile strength of chitosan and chitosan/NCC films at different cycles (pressure 20,000 psi). Means with same uppercase or lowercase letters are not significantly different, *Optimized microfluidization cycles.

From figure 4, the TS of the chitosan/NCC films increased with the increase of microfluidization pressure. The TS of chitosan/NCC films at 5,000, 10,000 and 20,000 psi was found to be 62.6, 66.5 and 63.1 MPa, respectively. It was found that the TS of the chitosan/NCC films were highest at 10,000 psi (~69 MPa). This could due to that the fact that at high microfluidization pressure (20,000 psi), the TS of the chitosan films (45.6 MPa) decreased as a result of reduction of molecular weight of chitosan at high pressure. So, at 10,000 psi the TS of the nanocomposite films increased by 33% compared to the control chitosan films.
Fig. 4. Effect of microfluidization on the tensile strength of chitosan and chitosan/NCC films at different pressures (5 cycles). Means with same uppercase or lowercase letters are not significantly different, *Optimized microfluidization pressure.

4. Conclusion

The increase of the mechanical strength of the nanocomposite films after microfluidization signifies that NCC reinforced with the chitosan matrix and the dispersion of NCC into chitosan was achieved. So, by microfluidization of chitosan/NCC suspension at 10,000 psi and for 5 cycles it possible to disperse the NCC into chitosan. Microfluidization technique can be used to disperse nanomaterials properly into biopolymeric matrices

References


PART IV
DEVELOPMENT OF A PROTOCOL FOR MEASURING THE CONTROL
RELEASE OF ACTIVE COMPOUNDS FROM A TRILAYER ANTIMICROBIAL
DIFFUSION FILMS (ADFS) BASED ON METHYLCELLULOSE-
POLYCAPROLACTONE COMPOSITES

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Abstract

A novel trilayer antimicrobial diffusion films (ADFs) were developed for food applications. ADFs were composed of two external layers of polycaprolactone and one internal layer of nanocellulose (NCC)-reinforced methylcellulose (MC) matrix. Two antimicrobial mixtures (formulations A and B) were incorporated in MC layer and compared via the evaluation of film properties. Resulting ADFs were inserted as diffusion devices into cauliflowers packages and samples were stored at 4°C for 14 days. Microbiological diffusion assays in presence of ADFs were performed on pathogenic bacteria. The diffusion rate of total phenols (TP) from ADFs was determined by Folin-Ciocalteu’s method and by FTIR analysis. Results indicated a controlled release of antimicrobials into headspace (16.5% for formulation A and 13.4% for B). Good correlations (≥90%) between both methods allowed validating an innovative, accurate, rapid FTIR procedure to quantify the diffusion of TP. Encapsulated antimicrobial formulations induced color changes without affecting visual attributes of films.

1. Introduction

Essential oils (EOs), secondary metabolites of plants, are complex mixtures of volatile substances. They contain large amounts of active compounds such as phenolic acids and flavonoids, which provide strong antimicrobial or antioxidant properties and low toxicity compared with those from synthetic phenolic antioxidants, such as BHT (butylated hydroxytoluene) (7). A screening study of the antimicrobial properties of various EOs against pathogenous bacteria reported their high efficiency as potential food preservatives (2). However, due to their high relative volatility and thereby the difficulty to control their release into food products, the use of EOs may not be fully effective when directly applied on food. Their encapsulation in a polymeric matrix such as packaging films, edible coatings or diffusion films could provide an alternative issue in order to ensure their stability, in such a way that only desired levels of the preservatives diffuse progressively and come into contact with the food (3). Antimicrobial films allow interactions between the film, the product and the environment to increase shelf-life, to improve safety or sensory properties and to maintain the quality of the product without contributing to environmental pollution (4). In migrating approaches, preservatives are introduced into the bulk mass of packaging material, which subsequently allows their controlled release to the food surface. Active compounds immobilized in the films are thereby maintained at an optimal concentration on the food surface, thus increasing the storage time of foods (5).
Polycaprolactone (PCL) is a semicrystalline biodegradable polyester obtained by ring opening polymerization of ε-caprolactone. It provides good water resistance, low melting point, low glass transition temperature and good processability (6). Methylcellulose (MC), one of the most hydrophobic cellulose ethers, possesses high mechanical properties in comparison with other hydrocolloids. MC has been widely used for many years in industry to produce gels and fine chemicals in pharmaceuticals, foods, paints and cosmetics (7). NCC particles (diameter: 2-20 nm, length: a few hundred nanometers) create a percolated network within the matrix, thereby providing mechanical reinforcement into polymer bulk. The aim of the present study was to characterize trilayer antimicrobial diffusion films (ADFs) composed of PCL/MC/PCL, made by casting and compression molding. Natural antimicrobial agents (formulations A and B) were encapsulated into internal MC based-films and compression molding was used to form insoluble ADFs. The diffusion rate of total phenolic (TP) volatiles was evaluated by Folin-Ciocalteu’s method but also by FTIR analysis, via semi-quantification of encapsulated antimicrobials, in order to determine correlations between both methods.

2. Materials

Antimicrobial formulations

Asian (Formulation A) and Italian (Formulation B) EOs mixtures were provided from BSA Ingredients s.e.c./l.p. (Montreal, Quebec, Canada). Mixture of organic acids was from Kerry Ingredients and Flavours (Monterrey, TN, USA). Rosemary extract was from P.L. Thomas and Co., Inc. (Morristown, NJ, USA).

Film ingredients

MC (M_n ~ 40,000; viscosity 400 cP, 2% in water at 20°C) and PCL (M_n ~ 80,000) were from Sigma-Aldrich Canada Ltd (Oakville, ON, Canada). Nanocrystalline cellulose (NCC) was provided by FPInnovations (Pointe Claire, QC, Canada). Glycerol, used as a plasticizer, and Tween®80, as an emulsifier, were purchased from Laboratoire Mat (Beauport, QC, Canada). Vegetable oil (VO) was used as a hydrophobic agent in film-formation process in order to stabilize hydrophobic compounds via emulsion systems and was bought in a local distributor (Metro, Laval, Quebec, Canada).

Reagents

Sodium carbonate (monohydrate), Folin-Ciocalteu’s phenol reagent and gallic acid were from Sigma-Aldrich Canada Ltd (Oakville, ON, Canada).

3. Methods

Preparation of ADFs as trilayer composites PCL/MC/PCL

Trilayer composite films PCL/MC/PCL were fabricated. Each internal and external film weighed around 500 mg. Compression was operated at 120°C for 1 min without compression, then with 1 ton pressure for 1 min before cooling for 2 min. PCL/MC/PCL trilayer films (namely ADF; thickness ~ 225-280 µm) were collected and used immediately for testing.
Evaluation of the antimicrobial properties of films

Antimicrobial assay of pathogenic bacteria

Films were cut into 7.5 mm diameter disks and were placed on Mueller Hinton (Oxoid Ltd, Basingstoke, England) previously streaked with a solution containing $10^9$ CFU/mL of bacteria.

Diffusion rate of antimicrobial compounds

Determination by spectrophotometry

The availability of total phenols (TP) in ADF-A and ADF-B was determined using Folin-Ciocalteu’s procedure, according to a modified method developed by Salmieri and Lacroix (8).

The concentration of TP was determined according to the following equation:

$$TP \ (\mu g \ GAE/film) = \frac{((A_{ADF-A \ or-B}-A_{ADF-control})+b) \times V}{a \times m_{ADF-A \ or-B}}$$  (1)

where:

$A_{ADF-A \ or-B \ or-control} = $ Absorbance of ADF-A or -B or -control.

$V = $ volume of extract.

$m_{ADF-A \ or-B} = $ Mass of ADF-A or -B extracted.

$a = $ slope of the standard curve

$b = $ Y-intercept of the standard curve.

Diffusion rate of TP was deduced from TP availability in film, according to the equation:

$$\text{Diffusion rate of TP} \ (\%) = (1 - \frac{TP}{TP_i}) \times 100$$  (2)

where $A_{ADF-A \ or-B}$ is the initial concentration of TP in films at Day 0.

A 2 periods-moving average regression was used to represent the diffusion rate of antimicrobials from ADF-A and -B in order to smooth out short-term variations and highlight long-term trends over storage, via periodic extrapolation.

Determination by ATR-FTIR spectroscopy

FTIR spectra of the films were recorded using a Spectrum One spectrophotometer (Perkin-Elmer, Woodbridge, ON, Canada) equipped with an attenuated total reflectance (ATR) device for solids analysis and a high-linearity lithium tantalate (HLLT) detector. Spectra were analyzed using Spectrum® 6.3.5 software. Film components, PCL/MC/PCL trilayer films and MC-based films (internal layer), were analyzed for structural characterization and for
evaluating the available content of TP in ADFs during storage. Samples were placed onto a zinc selenide crystal and the analysis was performed within the spectral region of 650-4000 cm\(^{-1}\), with 64 scans recorded at 4 cm\(^{-1}\) resolution. After attenuation of total reflectance and baseline correction, spectra were normalized with a limit ordinate of 1.5 absorbance units. Hence, resulting FTIR spectra were compared i) to identify typical vibration bands related to film components but also ii) to attribute vibration bands assigned to antimicrobial components specifically and their respective peak intensities for estimation of their diffusion rate. Peak absorbance was measured for MC-A and MC-B during storage by determining the height of peaks (with MC-control as a blank) with Spectrum \(^{\circ}\) software. Finally, data obtained by Folin-Ciocalteu’s method and by FTIR were compiled and mathematical correlations were performed between absorbance of FTIR peaks related to antimicrobial volatiles and TP measurements in order to verify the viability and feasibility of FTIR analysis to evaluate the diffusion rate of antimicrobial compounds from ADFs.

**Experimental design and statistical analysis**

Samples were separated into 3 groups: (i) ADF-control; (ii) ADF-A; (iii) ADF-B. All measurements were performed in triplicate (n = 3). FTIR, TP measurements and determination of mechanical properties were done using a 2 x 3 x 3 x 7 factorial design: 2 repetitions, 3 replicates, 3 treatments (ADF, ADF-A, ADF-B), 7 days of storage (0, 1, 2, 6, 8, 10 and 13). Analysis of variance, Duncan’s multiple-range test and Student \(t\) test were performed for statistical analysis by using PASW Statistics 18.0 software (IBM Corporation, Somers, NY, USA). Differences between means were considered to be significant at a 5% level.

4. Results

**Antimicrobial activity of films**

Antibacterial activity of internal films from ADFs is shown in Table 1. Notable inhibitory zones were detected for ADF-A and -B against *E. coli*, *S. Typhimurium* and *L. monocytogenes*. Results showed no significant difference (\(p > 0.05\)) between ADF-A and -B for each bacteria (10.7-12.8 mm for MC-A and 11.5-13.6 mm for ADF-B), suggesting that both antimicrobial films had similar inhibitory efficiency. Also, ADF-A and -B induced similar inhibitory zones against *L. monocytogenes* and *E. coli* (\(p > 0.05\)), with diameter values around 10.7-10.8 mm for MC-A and 11.5 mm for ADF-B.
### TABLE 1. ANTIBACTERIAL ACTIVITY OF ADFS AGAINST E. COLI, L. MONOCYTOGENES AND S. TYPHIMURIUM

<table>
<thead>
<tr>
<th>Type of film</th>
<th>Inhibitory zone (mm) against pathogens $^{1,2}$</th>
<th>E. coli</th>
<th>L. monocytogenes</th>
<th>S. Typhimuriu</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADF-control</td>
<td>ND $^{aA}$</td>
<td>ND $^{aA}$</td>
<td>ND $^{aA}$</td>
<td></td>
</tr>
<tr>
<td>ADF-A</td>
<td>10.7 ± 0.5 $^{bA}$</td>
<td>10.8 ± 0.3 $^{bA}$</td>
<td>12.8 ± 1.2 $^{bB}$</td>
<td></td>
</tr>
<tr>
<td>ADF-B</td>
<td>11.5 ± 0.4 $^{bA}$</td>
<td>11.5 ± 0.3 $^{bA}$</td>
<td>13.6 ± 1.1 $^{bB}$</td>
<td></td>
</tr>
</tbody>
</table>

$^{1}$Means followed by the same lowercase letter in each column are not significantly different at the 5% level.

$^{2}$Means followed by the same uppercase letter in each row are not significantly different at the 5% level.

$^{3}$ND : Non-detectable (no inhibitory zone detected).

**Diffusion rate of antimicrobial compounds by spectrophotometry**

The profiles of diffusion of TP content of MC-A and MC-B internal layers during storage is presented in Fig. 1. The diffusion curve indicated a diffusion rate at Day 2 of 8.7 and 6.8% for MC-A and MC-B films respectively. These data generated slopes of 4.4 and 3.4% TP/day, hence indicating a higher diffusion over this first sub-period. Between Days 2-8, diffusion rates of ADF-A and ADF-B were significantly different (p ≤ 0.05), showing diffusion rates of 19.0 and 10.2% for ADF-A and ADF-B respectively at Day 8. These data generated slopes of 1.7 and 0.6% TP/day suggesting a slower release during this second sub-period. Also, it can be observed that the slowdown of ADF-B diffusion was emphasized with a plateau observed from Day 6 whereas a plateau was noted at Day 10 for ADF-A. As a result, ADF-B films showed the lowest diffusion rate during all storage, which may represent an advantage for long term storage of food. From these results, it could be hypothesized that chemical interactions between antimicrobials and MC matrix could influence the diffusion rate of antimicrobial volatiles, as suggested by previous studies (9). Hence, the different rates obtained for ADF-A and –B could be related to the chemical nature and volatility of major phenolic components in Asian EO (in formulations A) and Italian EO (in formulation B) during diffusion process. Chemical interactions between bioactive molecules and film components, and the resulting diffusion of volatiles, are described below in FTIR analysis.
Fig. 1. Profile of diffusion of TP (%) from ADF-A and ADF-B according to a 2 periods-moving average regression.

**Diffusion rate of antimicrobial compounds by FTIR analysis**

**Identification of bands related to diffused antimicrobials**

The evolution of FTIR spectra of MC-control and MC-B during storage, at Days 0, 2, 6 and 13 is presented in Fig. 3-4.

Note that FTIR spectra of MC-A-based films were not shown since they presented similar evolving peaks as those of MC-B-based films. This analysis focused on the fingerprint region (1800-1200 cm\(^{-1}\)) of MC internal layer in order i) to take into consideration the evolution of the bands ascribed to the hydration of MC matrix (Fig. 3) but also ii) to evaluate the diffusion of antimicrobial volatile compounds (Fig. 4). Spectra were normalized by setting O–H stretching bands up to 1.5 absorbance units (AU) to subtract water absorption in MC matrix. Moreover, the analysis of fingerprint region allowed differentiating the peaks that were associated to antimicrobial compounds. In general, spectra in Fig. 3-4 presented the same evolution in higher frequencies (4000-2400 cm\(^{-1}\)). For each sample (MC-control and MC-B), the O–H stretching vibration at 3600-3200 cm\(^{-1}\) broadened out during storage (Day 0 to Day 13), suggesting hydration of MC matrix, which is in agreement with results obtained for ADFs (Fig. 2) and similar observations have already been reported by Le Tien et al. (10) for cellulose-based films. In the meantime, this band broadening due to hydration was also accompanied by a reduced intensity of C–H stretching vibrations at 2950-2850 cm\(^{-1}\) (hydrophobic groups), as described above (Fig. 2). The fingerprint IR region in Fig. 3 shows that the bound water vibration of MC-control at 1650 cm\(^{-1}\) increased during storage (relatively to hydration effect) while its vibration modes related to degree of order decreased at 1500-1270 cm\(^{-1}\), possibly due to a reduced resonance of methylated groups in MC, as reported by Khan et al. (11).
Fig. 4 shows the evolution of FTIR spectra of MC-B internal films, during storage. In comparison with Fig. 3 (MC-control), the fingerprint region of Fig. 4 indicates the appearance of 3 typical peaks associated with antimicrobial formulation B (containing Italian EO) such as ring stretching modes of aromatic groups at 1600 and 1515 cm\(^{-1}\) and C–O–C anti symmetric stretch mode of esters at 1265 cm\(^{-1}\), which is congruent with observations in Fig. 2. It can also be observed that the intensity of these 3 peaks decreased during storage, thereby indicating a diminution of antimicrobial contents in MC matrix. This profile suggests a diffusion of antimicrobial volatiles towards external environment (headspace), which is in accordance with results obtained for TP quantification (Fig. 1).

Fig. 2. FTIR spectra of composite trilayer ADFs as related to time of storage at Day 0, Day 6 and Day 13. Typical vibration bands of PCL based-external layers, related to water content in the films, are shown in function of time.
Fig. 3. FTIR spectra of MC-control internal films as related to storage time, with focus on fingerprint region (1250-1730 cm⁻¹). Color of spectra indicates the day of analysis: green (Day 0), red (Day 2), blue (Day 6) and black (Day 13).

Fig. 4. FTIR spectra of MC-B internal films as related to storage time, with focus on fingerprint region (1200-1800 cm⁻¹). Color of spectra indicates the day of analysis: green (Day 0), red (Day 2), blue (Day 6) and black (Day 13). Note that FTIR spectra of MC-A films presented exactly the same peaks that evolved in a very similar way.

Correlation between FTIR analysis and TP measurements.

Correlations between TP concentrations and FTIR peak heights were investigated by a simple type of regression to verify linear correlations between the two methods. Calculations allowed concluding it was possible to establish a satisfying correlation (> 0.90) between TP measurements and the absorbance of FTIR peaks at 1600 cm⁻¹ for both antimicrobial films ADF-A and -B. Linear correlation of IR absorbance at 1600 cm⁻¹ vs TP concentration (µg GAE/mg) is presented in Fig. 5 and shows that i) plotting of ADF-A data for ADF-A resulted in a linear equation $y = 0.0063x - 0.0116$ ($R^2 = 0.92$) and ii) plotting of ADF-B data...
generated an equation $y = 0.0063x - 0.0134$ ($R^2 = 0.90$). Consequently, semi-quantitative estimation of peak absorbance at 1600 cm$^{-1}$ (group of aromatic volatiles including phenolic compounds) can offer an accurate, rapid and non-destructive analytical method to evaluate the diffusion rate of TP to the package headspace over storage time.

![Graph showing linear correlation between FTIR absorbance at 1600 cm$^{-1}$ and their availability of TP concentration (µg GAE/mg)](image)

*Fig. 5. Linear correlation between FTIR absorbance at 1600 cm$^{-1}$ of ADF-A and ADF-B and their availability of TP concentration (µg GAE/mg) determined by spectrophotometry, as deduced from data obtained in Table 2 and Table 4.*

5. **Conclusion**

In summary, trilayer ADFs developed in this study showed very satisfactory *in vitro* antimicrobial properties and could further be explored in food applications to prevent pathogenic contamination during storage of ready-to-eat foods. FTIR analysis allowed characterizing the molecular interactions occurring after incorporation of antimicrobials. Moreover, ADFs allowed a slow controlled release of the antimicrobial compounds during storage. This study has also demonstrated that it is possible to follow the diffusion rate of the antimicrobial compounds by FTIR with satisfying correlations (> 90%) compared to standard method.

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PART-V
DEVELOPMENT OF A METHODOLOGY TO ENCAPSULATE ANTIMICROBIAL COMPOUNDS AND PROBIOTIC BACTERIA IN A BIOPOLYMER (FILM AND BEADS) AND COMBINATION WITH IRRADIATION
SECTION 1
EFFECT OF GAMMA RADIATION ON THE PHYSICO-CHEMICAL PROPERTIES OF ALGINATE BASED FILMS AND BEADS

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Abstract

Alginate solution (3% w/v) was prepared from its powder and then dissolved in deionized water. Then the solution was irradiated by gamma radiation. Total radiation dose varied from 0.1 to 25 kGy. Alginate beads prepared from 3% alginate solution (w/v) by ionotropic gelation method in 5% CaCl₂ solution. The size of the beads measured in both wet and dry condition. In wet condition, the bead size was 2-3.5 mm and 0.6-2.0 mm in dry condition. The rate of gel swelling properties was investigated and found that it was improved up to 0.5 kGy. Alginate films from 3% alginate solution (w/v) were prepared by solution casting. The mechanical properties such as puncture strength (PS), puncture deformation (PD), viscoelasticity coefficient (Y coefficient) of the films were also investigated. The values of PS, PD and Y coefficient of the films were 333 Nmm⁻¹, 3.20 mm and 27%.

1. Introduction

Alginate, a linear heteropolysaccharide of D-mannuronic and L-guluronic acid, is found in the cell walls and intercellular spaces of brown algae. Alginate includes a variety of products made up of D-mannuronic acid and L-gluconic acid, which are arranged in regions composed solely of one unit or the other, referred to as M-blocks and G-blocks, and regions where the two units alternate. Both the ratio of mannuronic acid to gluconic acid and the structure of the polymer determine the solution properties of the alginate (1). Alginate has been widely used because of its gel- and film-forming properties. Alginate forms a thermally stable and biocompatible hydrogel in the presence of di- or tri cations. In addition, alginate beads can be easily produced by dropping an alginate solution in a calcium chloride bath (2).

2. Materials and Methods

Materials

Sodium Alginate (powder form: from brown algae, low viscosity) and Calcium Chloride (granules) were purchased from Sigma-Aldrich Canada Ltd. (Oakville, ON, Canada).
**Irradiation**

An aqueous solution containing 3% alginate (w/v) was prepared and then irradiated from 0.1 to 25 kGy in a $^{60}$Co source at room temperature, at a dose rate of 17.878 kGy/h (0.3578 kGy/min) in an Underwater Calibrator-15A Research Irradiator (Nordion Inc., Kanata, ON, Canada).

**Preparation of Alginate Based Beads and Films**

The alginate based films and beads were prepared from native alginate solution (without irradiation) and irradiated alginate solution. Films were cast by applying 10 mL of the film forming solution onto Petri dishes (100mm×15mm) and allowed to dry for 24 h, at room temperature and 35% relative humidity (RH). Dried water-soluble films were peeled off manually using a spatula and stored in polyethylene bags prior to characterization. The beads were produced by dropping through a 20-gauge needle from a 10 mL plastic syringe into a beaker containing CaCl$_2$ solution (1% w/v) under gentle stirring at room temperature. The formed beads were then allowed to harden for 30 min and then rinsed with distilled water.

**Film and Bead Thickness**

Film (thickness ~25 µm) and bead (2-3.5 mm in wet condition and 0.6-2mm in dry condition) thickness were measured using a Mitutoyo digimatic Indicator (Mitutoyo MFG, Tokyo, Japan) at five random positions around the film and bead, by slowly reducing the micrometer gap until the first indication of contact.

**Puncture Strength (PS) and Puncture Deformation (PD)**

Puncture strength (PS) and puncture deformation (PD) measurements were carried out using a Stevens-LFRA texture analyzer (model TA-1000). The film samples were equilibrated in a desiccator containing a saturated sodium bromide solution ensuring 56% RH at room temperature (21°C) for at least 24 h. Films were then fixed between two perforated plexi glass plates (3.2 cm diameter), and the holder was held tightly with two screws. A cylindrical probe (2 mm diameter) was moved perpendicularly to the film surface at a constant speed (1 mm·s$^{-1}$) until it passed through the film. Strength and deformation values at the puncture point were used to calculate the hardness and deformation capacity of the film. To avoid any variation related to the film thickness, the PS values were divided by the thickness of the films. PS was calculated using the equation

$$PS\text{ (N.mm}^{-1}\text{)} = \frac{9.81 \times F}{x}$$  \hspace{1cm} (1)

where $F$ is the recorded force value (g), $x$ is the film thickness ($\mu$m), and 9.81 m.s$^{-1}$ is the gravitational acceleration. PD was calculated from the PS curve, using the equation

$$PD\text{ (mm) } = \frac{d}{8.33}$$  \hspace{1cm} (2)

where $d$ is the distance (mm) recorded between the time of first contact probe/film and the time of puncture point and 8.33 is a corrective factor related to the fixed parameters of the texture analyzer.
The Rate of Gel Swelling

A water uptake apparatus is designed to study the water absorption properties of beads and consequently to determine the rate of gel swelling. Beads are dried at 40° C for 24 h in a drying oven and placed in a 5 mL graduated cylinder (0.2 mL subdivision). Water penetration into beads was measured as a function of time (4). The water uptake is expressed in the rate of gel swelling (percent weight increase).

3. Results and Discussion

Effect of Gamma Irradiation on Puncture Strength and Puncture Deformation

The mechanical properties such as puncture strength (PS) and puncture deformation (PD) of the pure alginate films and irradiated alginate films are given in Figures 1 and 2. The PS and PD of the pure alginate films (0 kGy) were found to be 333 Nmm⁻¹ and 3.2mm respectively. It is found that the PS value increased with the increase of total dose of gamma radiation up to 0.5 kGy. At 0.1 and 0.5 kGy doses, PS of the irradiated films were 365 and 375 Nmm⁻¹ which is about 10 and 13% higher, respectively, compared to the pure alginate film. After that, an increase of irradiation dose decreased the PS values gradually. At 1 and 5 kGy, the PS value goes to 356 and 313 Nmm⁻¹, respectively.

![Graph showing effect of gamma irradiation on puncture strength](image)

Fig. 1. Effect of Gamma Irradiation on Puncture Strength (PS) of Alginate film.

The PD values increased with the increase of gamma radiation and the nature is similar to like that of PS and shown in Figure 2. At 0.1 and 0.5 kGy of doses, the PD values found 4.6 and 4.8mm which is about 44 and 50% higher compared to the pure alginate film. After 1kGy, the PD values decreased gradually.
The increase of mechanical properties of alginate films at low irradiation doses (0.1 to 0.5 KGY) may be attributed to the generation of free radicals and cross-linking of alginate molecules. However, at high irradiation doses (> 1 KGY) both the PS and PD decreased. The decrease in PS and PD may be due to the occurrence of chain scission when polymers are exposed to high gamma irradiation. Alginate, which is a polysaccharide, generally undergoes degradation by the breaking of the glycosidic linkage under high gamma irradiation. It is also reported in the literature that cellulose and alginate molecules also form free radicals in a similar nature when irradiation by gamma source (5).

**Effect of Gamma Irradiation on Rate of Gel Swelling**

Effect of gamma irradiation on the rate of gel swelling of alginate-based beads prepared from irradiated alginate solution is shown in Figure 3. The values of rate of gel swelling improved up to 0.5 kGY. At 0.1 and 0.5 kGY, the rate of gel swelling of 3% alginate beads decreased 18 and 21% (after 10 min) respectively, compared to the pure alginate beads. After that, an increase of irradiation doses increase the rate of gel swelling of 3% alginate beads gradually. At 1 and 5 kGY, the rate of gel swelling found that 58 and 60% (after 10min) which is still lower than the pure alginate bead. This barrier effect improved due the formation of free radicals and this free radical cross-link to each other and makes the polymer matrix more hydrophobic.

Fig. 2. Effect of Gamma Irradiation on Puncture Deformation (PD) of Alginate film.
4. Conclusion

This study was carried out in order to investigate the effect of gamma irradiation on the mechanical and barrier properties of alginate films and beads. From this study it is clear that low gamma irradiation doses (0.1 to 0.5 KGY) increases not only the mechanical properties but also the barrier properties of alginate films and beads. However, at high gamma irradiation doses the mechanical properties decreases. The optimum gamma irradiation dose was found to be 0.5 KGY. So, by applying low gamma irradiation dose we can conveniently improve the mechanical and barrier properties of alginate films and beads.

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References


PART-V SECTION 2
IN SITU EVALUATION OF THE ANTIMICROBIAL PROPERTIES OF BEADS CONTAINING NATURAL ANTIMICROBIAL COMPOUNDS (PRELIMINARY STUDIES)

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Abstract

*L. monocytogenes* is a frequent post-processing contaminant of ready-to-eat (RTE) meat products and has been associated with a number of foodborne illness outbreaks (1). Because of the high mortality rate associated with listeriosis, approximately 20% in susceptible populations, the USDA (US Department of Agriculture) has a “zero tolerance” policy for *L. monocytogenes* in RTE meat products (2). The combined effect of *γ*-irradiation and microencapsulated antimicrobials can increase the radiosensitivity of bacteria, resulting in lower radiation doses required for lethality (3). A variety of antimicrobial agents such as nisin and *Origanum compactum* have been incorporated into edible coatings. The resulting bioactive coatings with microencapsulated antimicrobials microbeads can protect the biological activity of the natural compounds, ensure adequate dispersion of the compounds on the surface of the food and allow a controlled release of the compounds during storage (4). Sodium alginate is the salt of alginic acid, a linear (1–4) linked polyuronic acid extracted from brown sea weed. Alginate has been used as a carrier of nisin and *Origanum compactum* to coat the poultry meat and beef (5).

1. Materials and Methods

Microencapsulation of Antimicrobials

An aqueous suspension containing 1.5% (w/v) alginate (guluronic acid (Eq) or glucuronic (Ax) content ~ 65 - 70%; mannanuronic acid content ~5 - 35% and 5% (w/w) NCC were homogenized using a Ultra-Turrax TP18/1059 homogenizer (Janke & Kunkel, Staufen, Germany) at 23°C and 25000 rpm for 1 min. A 0.5% w/v Lecithin was slowly added to the alginate suspension and heated to 60°C for 30 min. The pH of alginate-lipid suspension was adjusted to 7.5 to 8.0 by using 0.1M NaOH for the proper interaction of alginate and lecithin. Essential oil such as *Origanum compactum*, 0.025% w/v was added to the alginate-lipid suspension and heated to 60°C for 30 min. The pH of alginate-lipid suspension was adjusted to 7.5 to 8.0 by using 0.1M NaOH for the proper interaction of alginate and lecithin. Essential oil such as *Origanum compactum*, 0.025% w/v was added to the alginate-lipid suspension and formed the emulsion. Then the pH of the emulsion was lowered to 5.5-6.0 by using 0.05M lactic acid. A 0.25 % w/v of Nisin (2.5%) was mixed in 0.01M CaCl₂ solution. Then, the antimicrobial gel beads were obtained by addition of 0.01M CaCl₂ containing nisin to the emulsion under vigorous stirring at room temperature.
Bacterial Culture

*L. monocytogenes* HPB five strains (2569, 2558, 2371, 2812 and 1043) were used in this experiment.

Preparation of Ham Samples

Ground lean pork meat was purchased from a local grocery store. Ground ham was cooked with different preservatives such as sodium chloride, triphosphate, erythorbate and nitrite salt for about 1hr at 162.7° C in cooking oven. The ham was removed from the oven, placed at 4° C for 24 hr and sliced. Then, 5 ml of microencapsulated nisin on each side of the ham slice was added. The coated cooked ham slice was then inoculated with ~5 log CFU/g *L. monocytogenes* and vacuum packaged within 24 hr of production. The samples were stored at 4° C up to 35 days.

Microbiological Analysis

Each ham sample was homogenized for 2 min in sterile peptone water (0.1%, wt/vol; Difco, Becton Dickinson) in a Lab-blender 400 stomacher (Seward Medical, London, UK). From this homogenate, appropriate serial dilutions were prepared in 0.1% peptone, and 100 µl of each dilution was spread plated on Palcam (Alpha Biosciences, Maryland, USA), which were incubated for 48 h at 37° C. Bacterial counts were expressed as log CFU/g of ham.

Statistical Analysis

All bacterial counts were log10 transformed prior to statistical analysis. Three samples per day of analysis were used for each group. An analysis of variance (ANOVA) and multiple comparison tests of Duncan’s were used to compare all the results. Differences between means were considered significant when the confidence interval was smaller than 5% (P ≤ 0.05). The analysis was performed by the PASW statistics 18 software (SPSS Inc., Chicago, IL, USA).

2. Results and Discussions

The effect of antimicrobials microencapsulation is represented in Figure 1. The edible coating without (F1) and with (F2) microencapsulated antimicrobials delayed the growth of *L. monocytogenes*. In control ham, the growth of *L. monocytogenes* reached 9.59 log after 35 days of storage at 4° C, whereas the hams coated without microencapsulated and with microencapsulated antimicrobials, *L. monocytogenes* increased less than 0.78 log and 1.69 log after 35 days of refrigerated storage. The growth of *L. monocytogenes* in cooked hams coated with microencapsulated antimicrobials (nisin + *Origanum compactum*) was significantly (P ≤ 0.05) slower than the without microencapsulated antimicrobials.
Fig. 1. Survival and growth of L. monocytogenes on irradiated vacuum packaged cooked ham slices coated with microencapsulated antimicrobials microbeads at 4°C [F-1 represents nisin (0.25% w/v) + *Origanum* compactum (0.025% w/v) without microencapsulated and F-2 represents microencapsulated nisin (0.25% w/v) + *Origanum* compactum (0.025% w/v)]. a) At 0 kGy, b) At 0.5 kGy and c) At 1.5 kGy.

It was reported that the inhibitory effect of the growth of *Staphylococcus aureus* by nisin-containing modified alginate films and beads on beef. The author suggested that the hydrophobic and biodegradable films or beads incorporating various amounts of nisin could be used to control the growth of pathogens or microorganisms responsible for spoilage at the surface of ground beef or other meat products (6). Authors also reported that zein coatings incorporated with nisin, sodium lactate and sodium di-acetate alone or in combination were also shown to be effective inhibitors of *L. monocytogenes* on full-fat turkey frankfurters during a 28-day storage period at 4°C (7). Mytle et al. (8), reported that the use of clove essential oil was inhibited the growth of *L. monocytogenes* on the surface of RTE chicken frankfurters.

3. Conclusion

Microencapsulation of antimicrobials compounds in microbeads was very effective in reducing *L. monocytogenes* in RTE hams during subsequent storage. Antimicrobial ingredient combinations (nisin + *Origanum compactum*) could be used. Next step will be to combined this technology of encapsulation with irradiation at low doses ≤ 1.5kGy applied on RTE ham to inhibit the growth of surviving pathogens during prolonged storage (35days) at 4°C.

**References**


GENERAL CONCLUSION

Objectives that aimed the development of biodegradable polymer grafting by gamma radiation, combined with nanoparticles filling, were reached by characterizing the structure and the rheological (mechanical and barrier) properties of resulting grafted/reinforced films.

The present report described the development and characterization of:

(1) MC-based films grafted with TMPTMA monomer by gamma radiation, in combination with NCC filling,
(2) chitosan-based composites films grafted with silane by gamma radiation, in combination with PCL reinforcement,
(3) Effect of hema and silane monomers using gamma irradiation on the mechanical and barrier properties of methylcellulose-based films,
(4) PCL-based films reinforced by CNT using gamma radiation,
(5) Microfluidisation and irradiation treatment for better dispersion of nanofibers in suspension: Develop a methodology to encapsulate antimicrobial compounds,
(6) Develop a protocol to measuring the control release of active compounds,
(7) Develop a methodology to encapsulate entimicrobial compounds and probiotic bacteria in polymers and combination with irradiation.

The combined effects of TMPTMA, NCC and gamma radiation led to significant improvements of mechanical and barrier properties of MC-based films. Optimal mechanical and barrier properties were obtained by using 0.1% monomer at 5 kGy and molecular MC-TMPTMA interactions were characterized by FTIR analysis. The combined effect of NCC filling enhanced the mechanical properties of grafted films (TS = 67 MPa) and final optimal conditions of treatment were assessed to 4.45% TMPTMA (w/w polymer dry basis), 1 kGy irradiation dose and 1.8% NCC (w/w polymer dry basis) for mechanical improvements. Combined effect of NCC filling also enhanced the barrier properties of grafted films and final optimal conditions of treatment were assessed to 4.45% TMPTMA (w/w polymer dry basis), 0.5 kGy irradiation dose and 42.5% NCC (w/w polymer dry basis) for water vapor barrier improvements. SEM analysis provided typical morphological changes due to NCC filling into polymer bulk. These results suggest that incorporation of NCC allowed reducing irradiation dose (5 to 1 kGy) by greatly improving the physic-chemical properties of films as compared to grafted films alone.

The combined effects of silane and hema, PCL reinforcement and gamma radiation led to significant improvements of mechanical properties of chitosan-based films. Final optimal conditions of silane grafting treatment were obtained by using 25% silane (w/w chitosan dry basis) at 10 kGy irradiation dose (TS = 44 MPa). Silane grafting had also a positive effect on chitosan-PCL insoluble composite films, with significant enhancement of mechanical properties and optimal conditions by using 25% silane (w/w chitosan dry basis) at 10 kGy and 20% chitosan content in composite film. SEM analysis provided morphological changes induced by silane grafting into chitosan bulk, hence demonstrating chitosan-silane compatibilization by gamma radiation and good resulting adhesion between composite components.

The combined effects of hema and MC showed that 1% HEMA containing films (solid film contains 36% HEMA) performed the highest PS values (282 N/mm) compared to other
HEMA formulations. So, the MC-based formulation containing 1% HEMA was treated as optimized. To investigate the effect of gamma radiation, different doses (5-25 kGy) were applied to MC-based films containing 1% HEMA. The highest PS values (92% improvement) were observed at 10 kGy and after that the PS values started to decrease.

Similarly, 1% silane monomer containing films were irradiated. It was observed that the PS values of the grafted films improved significantly ($p \leq 0.05$) with the rise of radiation dose. The maximum PS values (296 N/mm) were observed at 10 kGy and this is 101% higher PS than the PS of MC-based films. Comparing the effectiveness of HEMA and silane monomers onto the MC-based films, it was observed that silane performed the better results.

The combined effects of CNT filling and gamma radiation improved significantly the mechanical and barrier properties of PCL-based films. CNT filling at low concentration (0.2% w/w polymer dry basis) generated high improvements of mechanical and barrier properties of films. Combined effect of gamma radiation also led to significant enhancement of film properties and optimal conditions were reached by using 0.2% (w/w polymer dry basis) CNT filling at 10 kGy. SEM analysis of irradiated CNT-PCL composites showed partial homogenization of CNTs in PCL matrix with higher density of CNTs at the interface structure that possibly conducted to higher mechanical properties of these films.

Overall, these reported investigations emphasize the innovative aspect of polymer compatibilization by radiation grafting and the positive effects of combined treatment of gamma radiation with monomer grafting and nanoparticle reinforcement into polymer bulk. These studies open new issues of preparing functional, insoluble, biodegradable composite films for “green” packaging applications. Further investigations should be carried out in order to determine specific applications of these new functionalized biomaterials.

The tests done on microfluidisation showed an increase of the mechanical strength of the chitosan based films in presence of nanocomposite after microfluidization. A better dispersion of NCC into chitosan was achieved. So, by microfluidization of chitosan/NCC suspension at 10,000 psi and for 5 cycles it is possible to disperse the NCC into chitosan. Microfluidization technique can be used to disperse nanomaterials properly into biopolymeric matrices.

We also have demonstrated that it is possible to follow the diffusion rate of the antimicrobial compounds by FTIR with satisfying correlations (> 90%) compared to standard method.

Irradiation of alginate at low dose of irradiation can improve the mechanical properties of microbeads. Microencapsulation of antimicrobials compounds in these microbeads was very effective in reducing *L. monocytogenes* in RTE hams during subsequent storage. Antimicrobial ingredient combinations (nisin + *Origanum compactum*) could be used.

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Tanzina Huq, Avik Khanh, Ph.D. student, Int. Atomic Energy Commission, Bangladesh.

Nusrat Sharmin, trainee, Int. Atomic Energy Commission, Bangladesh.
WORK PLAN FOR THE NEXT YEAR

Future research

The future research will focus on the development of active compounds using encapsulation technologies to immobilize natural antimicrobial agents into films based on chitosan, methylcellulose, supramolecules polymeric films and grafted films using monomeric compounds. The use of microfluidization of formulations based on nanocomposite will be also done for film developments. Structure-function relationships should be investigated in order to determine the optimal parameters that influence the efficiency of the treatment such as radiation dose, nature of polymer, cross-linking/grafting degree, concentration of active compounds, etc. Bioactive films submitted to gamma radiation will be evaluated for their physicochemical improvement and their capacity to increase the shelf-life of meat (ex: ham) and vegetable products. The antimicrobial efficacy of the films in combination with low dose γ-irradiation will be also investigated in ready-to-eat (RTE) food model against foodborne pathogens like Listeria monocytogenes.

Also, beads will be making with irradiated alginate at the optimal doses of irradiation and the cross-linked polymers will be used to immobilize active compounds (natural antimicrobial compounds and also probiotic bacteria). The antimicrobial efficiency of the beads to protect and to assure a control release of the natural antimicrobial compounds will be evaluated in situ in meat system. The efficiency of the beads to protect the viability of probiotic bacteria will be evaluated during storage time at room and at 4 °C . Finally, combined effect of γ-irradiation and microencapsulated antimicrobials microbeads on cooked ham against L. monocytogenes during storage at 4° C will be evaluated.

Antimicrobial nanocomposite films will be prepared by the incorporation of natural antimicrobial agents such as, organic acids, bacteriocins, spice and fruit extracts, etc.

Scientific papers should result from these applied research works. Also, in order to satisfy the expected research outputs of IAEA packaging concept project, important data should be delivered as related to functional properties of developed bioactive films and their effect on overall food quality, using gamma radiation technology.

List of publications in this CRP


USE OF IONIZING RADIATION TO IMPROVE THE PROPERTIES OF SOME NANO-COMPOSITE MATERIALS FOR POTENTIAL APPLICATION IN PACKAGING AND ENVIRONMENTAL PURPOSES.

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Abstract

Trails were made to improve mechanical and barrier properties of polycaprolactone (PCL) for food packaging purposes. The radiation crosslinking of linear PCL would add an extra possibility to the ways of modifying mechanical and physical properties of PCL. Also, mechanical and barrier properties of PCL might also improved by addition of reinforcing compounds (fillers like graphene oxide). The improvement of PCL using electron beam irradiation in the presence of polyfunctional monomers was studied. The effect of gel content on the physical and biodegradability properties of PCL was investigated. Mixing graphene oxide nano-sheets with PCL to produce poly(caprolactone)/graphene oxide nano-composite films was studied. It was found that the addition of low amount of graphene oxide (GO) or polyfunctional monomer significantly improved both strength and barrier properties of PCL-based films, while the oxygen transmission rate (OT) and water vapor permeability (WVP) decreased significantly with the increment of GO amount in PCL films. Biodegradability of the PCl was not affected by adding GO. Twenty five kGy irradiation dose slightly improved the strength and barrier properties of PCL/GO nano-composite films. PCL- GO films could be used as a high load bearing films in food packaging.

On the other side, polyvinyl alcohol/acrylic acid (PVA/AA) microgels were successfully prepared using electron beam irradiation. To improve the PVA microgel functionality and gel fraction, chains of polyacrylic acid (PAA) were incorporated into PVA microgel by radiation grafting technique. The increase in the acrylic acid content as well as PVA Mwt is accompanied by a mutual increase in the gel fraction and a decrease in the swelling percent. Immobilization of different titanium dioxide (TiO2) concentrations on the surface of the prepared PVA-AA microgel was carried out. The structural changes in the prepared PVA-AA microgel immobilized with TiO2 were investigated using FTIR, EDX and XRD. Photo-degradation efficiency of TiO2/ PVA-AA microgel against metanil yellow dyes was studied. The efficient photo-catalytic ability of PVA/AA–TiO2 composite microgel is reflected in the determined photo bleaching rate of the dye. TiO2/ PVA-AA microgel activity increases with the increase of the amount of TiO2 and results in an increase in the rate of the photo-degradation reaction. Easily recovery and better reproducibility made TiO2/PVA/AA of great important in practice use as a photo-catalytic degradation composite materials for safe treatment of textile wastewater.

1. Introduction

Nanotechnology methods play significant role in producing packaging nano-composites. Research on application of nano-composite materials in packaging products is exponentially increasing. The use of nano-composite materials improves the mechanical and oxidation stability and also the barrier properties [1]. Nano-composite materials are composed of nano-
scale structure that enhances the macroscopic properties of food products. Barrier properties play a vital role in packaging by gaining access into the food products by light, moisture or gases. Other benefit of the use of nano-materials is that they inhibit the growth of spoilage, thus increasing the shelf life and quality. The common nano-composites used in the food packaging industry are (a) Polymer clay nanoclay (b) Silica nano-composites. The effects of nano-clay in polymers are increased stiffness, strength, nucleating agent in foams, and flame retardant. Transparent plastic film containing nano-particles of clay block oxygen, moisture and carbon dioxide from entering into the food particles and also make plastic more durable and heat resistant.

Barrier polymers are in great demand, particularly in packaging industry where they are replacing many traditional materials [2-5]. However in comparison with traditional containers (glass, and metal) plastic packages are more permeable to gases, water vapor, and aromatic compounds. Moreover, in food packaging, where long shelf-life is required, often they fail by allowing oxygen and water vapor to migrate through the wall, enhancing the microbial growth and degrading the organoleptic properties of the food. Therefore improving the barrier to oxygen and water vapor as well as adding antimicrobial activity are both important issues in the current research. In some cases, the best oxygen barriers are typically moisture sensitive, due to their polar hydrophilic nature, and therefore, a good balance is to be considered. Most materials currently used for packaging are non-degradable, generating environmental problems.

Biodegradable plastics offer a promising alternative toward solving these problems. Biodegradable can be classified into natural occurring polymer and synthetic polymers that are produced from renewable raw materials and have advantages over traditional polymers. Recently, aliphatic polyesters like Polycaprolactone (PCL) and Polylactic acid (PLA) have attracted much research interest due to their good properties. Among the commercialized biodegradable plastics, Polycaprolactone (PCL) has received much attention due to its high flexibility and biodegradability as well as its hydrophobic nature and biocompatibility. However, PCL possess poor mechanical and barrier properties together with a high price compared with other composites. These properties limit its commercial applications. Thus, modification of PCL is carrying out using different methods to improve its properties for packaging purposes.

2. Experimental

Preparation of GO

GO is prepared from natural graphite powder according to Hummers and Offeman method. 1.5 g of graphite powder is mixed well with 35 g of H₂SO₄ in 500 ml beaker for 0.5 h and then 0.75 g of NaNO₃ is added to the mixture under stirring. The resulting mixture is cooled to 0 °C and then put into ice bath during the slow addition of 4.5 g of KMnO₄ (solid) under vigorous stirring. Keep stirring for further 2 h after complete addition of KMnO₄. After then, the mixture is warmed to 35 °C and stirred for 0.5 h. 70 ml of water is added slowly under stirring producing large exotherm to 98 °C. Keep this temperature for 15 min by external heating then cool the mixture to room temperature and add another amount of water (250 ml) and 3 ml of 30% H₂O₂ producing another exothermic and yellowish brown dispersion of GO is obtained. GO is isolated and washed many times with 5% HCl to remove SO₄²⁻ ions.
ultrapure water to remove Cl\textsuperscript{−} ions. Successively by centrifugation at 4000 rpm for 45 min and the drying at 60 °C for 3 h.

**Preparation of the Gel**

Commercial PVA was grinded using electric grinder to obtain a very fine powder. Appropriate weights of AAc wetted polymer powders were put in polyethylene bags (the thickness of the bags filled at powder was 3mm) and irradiated at different doses at an electron accelerator in air atmosphere. The parameters of the accelerator were electron energy, 1.45 MeV; electron beam current, 4 mA; scanner width, 90 cm; and conveyor speed at 20 kGy, 3.6 mmin\textsuperscript{−1}. After irradiation, powders were dehydrated for 2 h in absolute ethanol, dried at 37°C for 24 h and stored in vacuum oven at 45 °C for 12 h before use. The wetted PVA was obtained by mixing an appropriate amount of water/AAc with the dry powder before electron beam irradiation.

**TiO\textsubscript{2} Immobilization**

In a typical synthetic procedure the gel presoaked in anhydrous methanol alcohol (Analar) for 48 h to ensure the gel complete dehydration. This is followed by the swelling of microgel in 5ml of different volumes of TiCl\textsubscript{4}. The gel was then washed for several times by distilled water until the pH 7 is maintained, to ensure the complete conversion of TiCl\textsubscript{4}, and then dried in oven overnight.

Titanium tetrachloride is inorganic compound that undergo rapid hydrolysis in contact with water. This goes through a two stage process. First, it forms compounds known as the titanium oxychlorides and hydrogen chloride. It can be described as follows:

\[
TiCl\textsubscript{4} + H\textsubscript{2}O \rightarrow TiOCl\textsubscript{2} + 2HCl \quad (1)
\]

Titanium oxychloride

or

\[
TiCl\textsubscript{4} + H\textsubscript{2}O \rightarrow Ti(OH)\textsubscript{n}Cl\textsubscript{x} + HCl \quad (2)
\]

These oxychlorides are also particles, and they continue to react with water to form hydrogen chloride.

\[
TiOCl\textsubscript{2} + H\textsubscript{2}O \rightarrow TiO\textsubscript{2} + 2HCl \quad (3)
\]

**3. Results and Discussion**

Trails were made to improve the mechanical and -barrier properties to be used as good packaging materials taking into a consideration that the PCL biodegradability property should be kept unchanged as much as possible. A number of ways have been reported to improve the physical properties of PCL among them; variation of copolymer composition and the polymerization or processing conditions and crosslinking of linear PCL which would add an extra possibility to the ways of modifying its mechanical and physical properties. Poor
mechanical and barrier properties of PCL may also improved by adding reinforcing compounds (fillers).

![Graph showing gel fraction of PCL as a function of irradiation dose (kGy) at different concentrations of A-TMPT (Wt/Wt). A-TMPT concentration: 1% (●), 2% (○), 4% (▼), 6% (Δ).](image)

**Fig. 1.** Gel fraction of PCL as a function of irradiation dose (kGy) at different concentrations of A-TMPT (Wt/Wt). A-TMPT concentration: 1% (●), 2% (○), 4% (▼), 6% (Δ).

**Preparation of graphene oxide**

GO is layer-structured compound and can be obtained by the oxidation of natural graphite. GO is a typical two-dimensional solid in the bulk form, with strong covalent bonding within the layers. Figure 2 shows the change in color and structure of graphite when converted in graphene oxide. It was found that the structure changed from three-dimensional to two-dimensional structure and the black colour became yellowish brown one as the graphite converted to GO.
Thermal analysis of GO

The DSC thermogram of the GO shows an exothermal peak at 220 °C. This can be ascribed to the decomposition of labile oxygen functional groups. Pristine graphite does not give peaks under 500 °C Figure (3).

TGA study of prepared GO was studied. No weight loss is observed below 600 °C for pristine graphite due its compact structure. But for GO there are three stages for weight loss: about 25% of GO sample weight is lost at 150 °C, which can be ascribed to the removal of adsorbed water and about 60% of GO sample weight is lost at 220 °C due to the decomposition of labile oxygen functional groups and libration of gases. The remaining weight is almost completely decomposed and lost at 600 °C.
Preparation of PCL-Go composite films

PCL was dissolved in dimethylformamide (DMF) and mixed with different amount of highly dispersed Go in DMF. The mixture solution was ultra-sonocated and poured in Petri dish and left to dry at 90°C for 2 days. The color of prepared nano composite films is change from colorless to yellowish brown. By increasing GO content in PCL, the color of the film becomes deep brown Figure5. Generally some functional groups, such as hydroxyl and carbonyl groups, embedded in the carbon sheets in the GO lamellae make GO easy to interact with polymers to form composite materials. There were strong intermolecular forces between GO and the polymers, such as hydrogen bonding and Coulomb forces. Also, an incorporation of GO into the polymers may improve the thermal stability and electrical and mechanical properties of the polymers.

Thermal properties and nucleating effect of GO on crystallinity of PCL

Thermal properties and nucleating effect of Go filler on PCL crystallinity were investigated Table 1. The Tc values of all of the PCL composites increased compared with that of pure PCL. This was due to the nucleating effect of GO on the PCL crystallization. The degree of crystallinity of PCL in PCL/GO, decreased continuously with increasing volume fraction of
the GO filler. All PCL/GO composites showed slightly increasing in melting temperature. The decrease in $\Delta H_c$ and $\Delta H_m$ and the increase in the Tm observed for the PCL composites could be probably attributed to the fact that the PCL/GO composites formed an intercalated or exfoliated structure. After intercalation of the PCL chain into the layer of GO in the composites, the mobility of the PCL chain was restricted by the GO layer so that it was hard for it to crystallize between the GO layers. As a result the crystallinity of PCL was reduced.

### TABLE 2. THERMAL PROPERTIES AND NUCLEATING EFFECT OF GO ON CRYSTALLINITY OF PCL

<table>
<thead>
<tr>
<th>PCL Composition</th>
<th>$T_m$</th>
<th>$T_c$</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta H_{mrc}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>58</td>
<td>28</td>
<td>59</td>
<td>55</td>
</tr>
<tr>
<td>PCL + 0.5% GO</td>
<td>57.5</td>
<td>29.5</td>
<td>58</td>
<td>55.3</td>
</tr>
<tr>
<td>PCL + 1% GO</td>
<td>58.3</td>
<td>31.5</td>
<td>57.6</td>
<td>53</td>
</tr>
<tr>
<td>PCL + 2% GO</td>
<td>58.9</td>
<td>32.9</td>
<td>57.1</td>
<td>52</td>
</tr>
<tr>
<td>PCL + 2.5% GO</td>
<td>59.2</td>
<td>32.7</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>PCL + 3% GO</td>
<td>59.5</td>
<td>33.9</td>
<td>54.9</td>
<td>51.2</td>
</tr>
<tr>
<td>PCL + 5% GO</td>
<td>59.6</td>
<td>35.7</td>
<td>52</td>
<td>49.2</td>
</tr>
</tbody>
</table>

### Water-Vapor Permeability of GO / PCL Nano-Composite Films

The barrier property of non-irradiated and 25kGy irradiated PCL/GO nanocomposites of different GO contents was investigated. The WVP of PCL/GO films decreases as the GO content in the film increases. 25kGy irradiated PCL and PCL/GO nano-composites showed slightly improved if compared with non-irradiated ones. The WVP of PCL was found to be 1.95 g mm/m$^2$ day, but the WVP of PCL/GO film containing 2% GO was 1.1 gmm/m2 day. The oxygen transmission of non-irradiated and 25kGy irradiated PCL/GO nanocomposites of different GO contents was also investigated. The oxygen transmission decreased significantly with the rise of GO in PCL films.

### TABLE 3. WATER-VAPOR PERMEABILITY OF GO / PCL NANO-COMPOSITE FILMS

<table>
<thead>
<tr>
<th>PCL/GO composition</th>
<th>Water permeability WVP (g.mm/m$^2$.day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-irradiated film</td>
</tr>
<tr>
<td>PCL</td>
<td>1.95</td>
</tr>
<tr>
<td>PCL + 0.5% GO</td>
<td>1.75</td>
</tr>
<tr>
<td>PCL + 1% GO</td>
<td>1.33</td>
</tr>
<tr>
<td>PCL + 2% GO</td>
<td>1.1</td>
</tr>
<tr>
<td>Compositions</td>
<td>$k_1$</td>
</tr>
<tr>
<td>--------------</td>
<td>--------</td>
</tr>
<tr>
<td>PCL + 2.5% GO</td>
<td>0.9</td>
</tr>
<tr>
<td>PCL + 3% GO</td>
<td>0.8</td>
</tr>
<tr>
<td>PCL + 5% GO</td>
<td>1.1</td>
</tr>
</tbody>
</table>

**Photo-catalytic Degradation of Metanil Yellow Dye using TiO$_2$ polyvinyl alcohol/acrylic acid microgel**

Titanium dioxide is one of the most popular and promising materials as a photo-catalyst because it is stable in various solvents under photo-irradiation, commercially available, and easy to be prepared in the laboratory. However, its practical application seems to be limited for different reasons such as the difficulty to separate these fine photo-catalysts from solution after reaction.

Although immobilization technique can improve the TiO$_2$ separation efficiently, it usually decreases the overall photo-catalytic activity comparing to the dispersed TiO$_2$ due to lowering of the surface-to-volume ratio and partial loss of the active surface sites of photo-catalysts. Therefore, it is necessary to develop a novel synthesis approach to prepare TiO$_2$ photo-catalysts, which not only have highly photo-catalytic activity, but also can be steadily separated after photo-catalytic reactions. Since the photo-catalytic activity was confined to the surface of the photo-catalytic material, its surface area must be increased to maximize the photo-catalytic efficiency. Micro and nano-spheres are small and have large surface-to-volume ratio and could be readily separated from the solution by filtration or sedimentation.

Since TiO$_2$ photo-catalytic degradation requires high surface area, attempts is made to design TiO$_2$-immobilized PVA/AA microgel of high surface area prepared by electron beam irradiation. Exposure of PVA/AA to electron beam irradiation aids to create microgel with crosslinking network structure. The formation of crosslinking network hinders the PVA/AA microgel matrix to dissolve and enhances its resistivity towards degradation during the dye photo-degradation process. On the other hand, the presence of PVA/AA – microgel does not only act as a carrier for TiO$_2$, but it also acts as dye absorber materials. The entrapment of both TiO$_2$ and mono azo dye: Metanil Yellow onto PVA/AA – microgel accelerates the degradation rate of the latter.

**PVP/AAc- prepared by ionizing Radiation**

Crosslinking of PVA in the dry form requires much higher doses if compared with that required for crosslinking of PVA in solution form. One of the reasons for the high gelation doses required in the dry state is that the radiation-chemical yields of the radicals is usually lower than that in aqueous solution. Also, the restricted motion of the radical bearing chains limits the effectiveness of crosslinking. Therefore, chains of polyacrylic acid (PAA) were incorporated into PVA microgel by radiation grafting technique to improve the functionality and gel fraction of PVA microgel. Different amount of (AA /H$_2$O) (50:50) was absorbed by PVA microgel and exposed to electron beam irradiation at dose of 20kGy. The gel fraction of irradiated samples was determined and is shown in Figure. (6). As it can be seen from the Figure, the increase in the AA content is accompanied by a mutual increase in the gel fraction. When PVA entrapped AA/H$_2$O mixture exposes to ionizing radiation, it creates radicals localized on AA and the main chains of PVA. The free radical contents on AA increased by
radiation and consequently, tended to recombine and graft with PVA macro-radicals, as a result, crosslinked graft copolymer with high gel fraction was obtained.

To ensure the grafting copolymerization of the AA onto the PVA backbone, FTIR of the PVA and PVA/AA gel was investigated. EB irradiated PVA shows a bands at 3340 cm\(^{-1}\) for OH-stretching, 1596 cm\(^{-1}\) and 1461 cm\(^{-1}\), for C=C, and C=O, respectively. These bands still present after the incorporation of AA grafted copolymer chains onto PVA. In addition, a new peak at 1715 cm\(^{-1}\) related to the presence of the carboxylic group of AA appears.

![Fig. 6. Gel content% of different PVA (Mwt 1400) and PVA/(AA:H\(_2\)O) (50:50) compositions; prepared at 40 kGy.](image)

Immobilization of TiO\(_2\) on the surface of the prepared PVA/AA microgel of composition (90:10) AA–H\(_2\)O (50-50) was investigated. The structural changes and photo-catalytic efficiency of the prepared TiO\(_2\)/PVA-AA microgel were studied.

FTIR spectrum of PVA/AA-TiO\(_2\) catalysts showed, the appearance of absorption peaks at 456-654 cm\(^{-1}\) confirming the immobilization of TiO\(_2\). On the other hand, FTIR spectra of PVA/AA and PVA/AA-TiO\(_2\) showed a small red shift (from 1715 to 1730 cm\(^{-1}\)) of the absorption peak of the AA carbonyl groups (C=O) indicating that the oxygen atoms in AA interact with titanium ions.

Generally XRD is carried out to confirm the TiO\(_2\) polymorphs and their crystalline phases. XRD of PVA/AA and PVA/AA-TiO\(_2\) microgel was measured. A strong diffraction intensity peaks at 20=25° (101), 38° (004) and 62° (204) for PVA/AA-TiO\(_2\) indicated the presence of TiO\(_2\) in Anatase phase which responsible for the photo-catalytic degradation process.

**Evaluation of catalytic performance of PVA/AA- TiO\(_2\) as photo-catalysts**
The catalytic efficiency of the developed PVA/AA-TiO₂ microgel catalysts was evaluated by the photo-degradation of an azo compound. Metanil Yellow (C₁₈H₁₄N₃O₃SNa) M.W. 375.391 is a water soluble anionic monoazo dye with a sulfonate group pH value of its aqueous solution is 2.5. It has been used in solution with other smaller molecular weight yellow acid dyes to increase the intensity of staining. Moreover, it is used as a colorant in wool, nylon, silk, paper, detergent, and biological staining. This dye has been known by its toxicity and carcinogenic nature as well as its presence in wastewater of several industrial wastes such as textile, tannery, soap, cosmetics and polishes etc. The chemical structure of Metanil Yellow is characteristic by the conjugated structure constructed via azo bond that appears at wavelength of 448 nm.

![Chemical formula of Metanil Yellow.](image)

In order to determine the optimal amount of the immobilized TiO₂ catalyst for Metanil Yellow photo-catalytic degradation process, a series of experiments with varied amount of TiO₂ photo-catalyst have been conducted. The amount of the TiO₂ photo-catalyst was varied between 0.1 and 0.5 g/L and compared with P25 standard TiO₂. Dye degradation rate was found to be relatively high in the presence of P25. Almost complete dye degradation was observed after 180 min when PVA/AA- TiO₂ (0.1 g/L) was used as shown in Figure 8. Meanwhile, it takes 85 min when P25 is used at the same concentration. In spite of the relatively high dye-degradation rate in the presence of P25, but the easily recover, low deactivation of the catalyst surface, the by-products, and reusability lie in favor of PVA/AA- TiO₂.

At the beginning of the experiment, the solution without any catalysts was irradiated under UV light to determine to what extent the dye is degraded by UV irradiation in absence of TiO₂. Thereafter, the TiO₂ immobilized catalyst was subsequently dispersed in the metanil yellow solution under vigorous agitation in dark for 2h. Then the mixture was UV irradiated and separated via centrifugation. The supernatant liquid was measured using UV–vis spectrophotometer Figure 9.

Figure 10 shows the effect of the concentration of TiO₂ immobilized into PVA/AA microgel on the dye degradation %. The use of UV/Vis irradiation and TiO₂ free PVA/AA microgel resulted in negligible effect on discoloration of the dye solution. This indicated that the TiO₂ has a significant role as a photo-catalytic reagent where photo-chemical and degradation processes can be occurred. It is clear from Figure (9) that the degradation of dye using PVA/AA microgel immobilized TiO₂ increases by increasing irradiation time for all TiO₂ photo catalyst concentration. The degree of de-colorization of dye solution increases by the increase in the amount of photo-catalyst, reaching the higher value at catalyst loading of concentration 0.5 g/L. The degradation ratio (%) could be calculated using the equation (4):
\[ D = \left[ \frac{(C_0 - Ct)}{C_0} \right] \times 100 \] (4)

Where, D is degradation ratio, \( C_0 \) and \( C_t \) are the concentration of dye solution before and after irradiation, respectively.

Fig. 8. Photo of Metanil yellow color fading with irradiation time (0-180min).
Fig. 9. UV–Vis spectra evolution of Metanil Yellow solution as a function of uv-irradiation time, TiO$_2$ concentration 0.5 g/L in PVA/AA microgel prepared at composition of (90/10) AA:H$_2$O (50-50)

The most effective decomposition of metanil yellow (90%) was observed with the catalyst amount equal to 0.5g/L. The excess of the immobilized TiO$_2$ may cause shielding effect and reduces the penetration of the light in the solution after exceeding the optimal amount.
Reproducibility of (PVA/AA)-TiO$_2$

Easily recovery and reusability are advantages for (PVA/AA)-TiO$_2$ photo-catalytic degradation composite, this is very important in practical applications. The reproducibility of the photo-catalytic degradation activity on (PVA/AA)-TiO$_2$ was performed with a constant of metanil yellow concentration ($8.8 \times 10^{-4}$) and (PVA/AA)-TiO$_2$ of concentration (0.3 g/L) in each cycle. The regeneration of the catalyst is done by following a simple way. After the photo-catalytic degradation of the dye solution, the suspension was filtrated with a stainless steel 40 mesh screen, and the suspended matter was dried at 60°C for 1 h, a recovered (PVA/AA)-TiO$_2$ microgel was obtained and reused in the next cycle. It is observed that the discoloration rate decreases from $0.159 \times 10^{-1}$ to $0.1 \times 10^{-1}$ min$^{-1}$ after three cycles. The decrease in activity is attributed to the deactivation of the catalyst surface by the by-products of the dye degradation and/or polymer degradation by the deposited titanium. After reproducibility for 3 times, The gel content of (PVA/AA)-TiO$_2$ microgel was calculated. The gel content was reduced by 13% from the original gel content value. This means that the crosslinking network of (PVA/AA)-TiO$_2$ is slowly degraded.

Conclusion

Polycaprolactone /Graphen oxide nano-composites were prepared to be used as packaging films. Low amount of GO significantly improved the strength and barrier properties of PCL-based films. The oxygen transmission and water permeability decreased significantly with the rise of GO in PCL films. Biodegradability of the PCl does not affect by in the presence of GO. Irradiated films slightly improved the strength and barrier properties of PCL films.
PCL- GO films could be used for high load bearing packaging films. On the other hand, microgel from PVA/AA was successfully prepared using electron beam irradiation. The proper gel content and swelling properties of the prepared microgels qualified their utilization in dye adsorption from waste water. TiO$_2$ supported microgel was prepared and investigated for metanil yellow photo-degradation. The efficient photo-catalytic ability of PVA/AA- TiO$_2$ microgel is reflected in the determined photo bleaching rate of the dye. The practical advantages of direct and ease of removal of the pollutant dyes from the environment by adsorption on the microgel, as well as a better reproducibility of photo-catalytic degradation; makes it a viable technique for the safe treatment of textile wastewater.

References


DIAGNOSIS AND FOR ELABORATING COHESIVE INTERFACES BETWEEN CARBON FIBRE AND MATRIX IN RADIATION-CURED COMPOSITES

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Summary

The influence of surface functions present at the surface of carbon fibres utilized for high performance radiation curable composites was investigated. The inhibiting effect of aromatic hydroxyl groups as well as the sensitizing effect of thiol groups were evaluated by comparing the dose dependence of butyl acrylate samples submitted to EB irradiation in the presence of various additives. We propose sulfur-based surface modification and/or sizing application to carbon fibers for inducing the formation of cohesive interfaces.

1. Introduction

Cross-linking polymerization initiated by high energy radiation is a very attractive technology for the fabrication of high performance composite materials. The method offers many advantages compared to conventional energy- and time-consuming thermal curing processes [1]. Free radical and cationic polyaddition chemistries have been investigated in some details by various research groups along the last years. A high degree of control over curing kinetics and material properties can be exerted by adjusting the composition of matrix precursors as well as by acting on process parameters [2].

However, the comparison with state-of-the-art thermally cured composites revealed the lower transverse mechanical properties of radiation-cured composites and the higher brittleness of the radiation-cured matrix. We have investigated several points related to these issues, and particularly the reduction of the matrix shrinkage on curing, the wettability of carbon fibres, the design of fibre-matrix interface and the use of thermoplastic toughening agents. A drastic enhancement of the K\text{IC} value exceeding 2 MPa.m^{1/2} was also obtained for acrylate-based matrices toughened with high glass transition temperature T_g thermoplastics [3].

Improving fibre-matrix adhesion and upgrading polymer network toughness are thus two major challenges in this area. Particular attention was paid on the functional groups present at the surface of carbon fibres.

2. Experimental

The aromatic epoxy acrylate resin (Ebecryl 600) was supplied by Cytec. Butyl acrylate (BuA, Aldrich) was purified and rendered free from phenolic stabilizers by elution over a porous organic resin with basic properties. The samples were polymerized by EB irradiation with an industrial 10 MeV accelerator (CIRCE II, 20 kW). Various types of sized, unsized and acid-oxidized carbon fibres (intermediate modulus grade) were used for preparing unidirectional
composites for mechanical testing. The same carbon fibres were analyzed by XPS (R 4000, VG Scienta).

Polymerization was monitored by infrared spectroscopy for multifunctional aromatic monomers (Bruker Alpha FTIR spectrometer in transmission mode) or by size exclusion chromatography chain PL-GPC50 with autosampler PL-ASRT (Polymer Laboratories) including a set of three PLgel columns 5 µm (2 mixed type-C and 1 type-100) with tetrahydrofuran as the eluent (1 mL.min⁻¹) and with differential refractive index detector. Dynamic mechanical analysis was done on a DMA Rheometrics Analyzer RSA II (operating frequency 1 Hz, heating rate +5°C.min⁻¹). The transverse flexural properties were characterized by 3 point bending tests using an Instron 4400R mechanical testing machine.

3. Results and Discussion

The free radicals generated by a cascade of reactions following the primary ionization processes affecting the matrix precursors initiate quite efficiently the crosslinking polymerization. Typical formulations are based on aromatic diacrylates that enable the formation high \( T_g \) networks when monomer conversion is driven to a sufficiently high level (Fig. 1).

![EB-irradiation](image)

**Fig. 1.** EB-induced formation of high \( T_g \) networks by free radical polymerization of epoxydiacrylate prepolymers.

The parameters controlling the progress of the polymerization in the pure matrix have been studied in some details. The spatial distribution of the absorbed dose, the instant dose rate and the fractionation of the dose are influential parameters that need being controlled to ensure the build-up of the network. The temperature profile during irradiation is a key issue since mobility restrictions can early affect the progress of reaction in the material undergoing gradual vitrification [4].

The good intrinsic properties of a matrix improved by appropriate toughening agents need being relayed by excellent fiber - matrix adhesion for inducing appreciable benefits in terms of transverse properties of a composite structure. The adhesion between carbon fibers and the matrix is generally rather weak in EB-cured composites based on acrylate or on epoxy resins, independently of the type of chemistry and on the presence of commercial sizings may be more compatible with epoxy resins.
A representative SEM picture of fracture profile of an EB-cured (50 kGy) unidirectional carbon-fibre reinforced aromatic epoxyacrylate composite reveals the presence of regular cylindric channels from which nude fibers can be extracted with limited mechanical strain, hence producing adhesive failure at the interfaces and brittle failure in the matrix (Figure 2).

Various approaches have been tested during the recent years, including reduction of volume contraction upon curing and surface treatment of fibers.

Fig. 2. SEM micrograph showing a fractured EB-cured carbon fibre composite with poorly interacting aromatic diacrylate matrix.

The volume shrinkage associated with polymerization is possibly affecting negatively adhesion between carbon fibres and matrix. EB-curable acrylate formulations have higher cure-induced shrinkage (in the range of 3 to 7% for high performances formulations) compared to thermally cured epoxy amine systems used for similar applications (commonly around 2 to 3 %). The introduction of thermoplastic additives as poly(vinyl acetate) soluble in the prepolymer was tested. This approach allowed to propose formulation with a decrease of the cure-induced shrinkage from 6 to 4.5 % of the initial volume. Such an improvement without significant decrease of network’s $T_g$ opens an interesting path for upgrading transverse properties, but the first attempts failed to give significant improvements of the fracture properties of standard EB-cured composites [5].

Wetting issues have also been considered. The static contact angle of a droplet of resin coated on a glassy carbon plate exhibiting a surface atomic composition similar to the carbon fibres considered for the application was typically $\theta = 20^\circ$. The spreading of the prepolymer formulation surface composition was shown to be reduced to some extent by formulating with various types of silicone or fluorinated surfactants ($\theta < 5^\circ$). Though carbon fibre impregnation was somewhat easier when using such resins, the mechanical properties of the resulting EB-cured composites were not significantly enhanced. Paragraphe utile ?

The chemistry occurring at the carbon fibre matrix interface during irradiation was also considered. The surface composition of the carbon fibres was analyzed by X-ray photoelectron spectroscopy (XPS). A typical analysis of an unsized commercial fibre allows to determine the atomic composition of the surface and to orient the investigation towards particular functional groups suspected to be present on the basis of the high resolution analysis of the binding energies (Figure 3).
In a representative experiment, we have measured the relative amounts of C, O and N atoms, 83, 15 and 2 % respectively, together with a decomposition into resolved contributions that can be assigned to various aromatic and hetero-atomic functions.

![High resolution decomposition of selected domains (C1s, O1s, N1s) of the XPS spectrum of a representative unsized carbon fibre.](image)

**Fig. 3.** High resolution decomposition of selected domains (C1s, O1s, N1s) of the XPS spectrum of a representative unsized carbon fibre.

Analysis of the data on the basis of current literature allowed to conclude, besides the base graphite aromatics, to the likely presence of the following functional units: phenols, ethers, ketones, carboxylates, amines, amides, imines, nitriles, nitro [6].

In order to examine the influence on free radical processes of the presence of these various functional groups at the surface of the carbon fibres, the efficiency of the polymerization of model acrylate monomers under electron beam was assessed and quantified by spectroscopic (FTIR and $^1$H NMR) as well as by size exclusion chromatography.

A series of aromatic compounds (Fig. 4) bearing the reactive functions possibly present at the carbon fibre surface was thus introduced at various concentrations in the purified acrylate (e.g. n-butyl acrylate).
Selected examples of model molecules added to n-butyl acrylate for evaluating the possible inhibiting effects on free radical processes

Not surprisingly, the results clearly demonstrate the strong inhibiting behavior of the phenolic and amino-aromatic functions [7]. A representative example is illustrated by the plots of Figure 5 showing revealing the inhibiting effect of 9-phenanthrol.

The absence of adhesion shown by the micrograph of Figure 2 can therefore be explained by the inhibiting effect of such functional groups detected by XPS analysis of the typical commercially available carbon fibres. The complete inhibition or even the retardation of the free radical polymerization could then lead to poorly cohesive interfaces as consequence of the volume contraction in the bulk matrix. The sketch of Fig. 6 illustrates the current interpretation of the phenomenon.
In an attempt to overcome this inhibiting effect, we have used the same experimental approach for selecting functional organic additives possibly acting as sensitizers, by amplifying in a positive manner the formation of active free radicals upon irradiation. Various potentially sensitizing agents were tested among which thiols were found to be good candidates for counteracting the inhibiting effects in the vicinity of the carbon fibres. In addition, the thiol groups are known to undergo transfer reactions that can be exploited for coupling the network under formation to the fiber or to some reactive sizing located around the fibres. [5].

In one of its variants, the technological process inspired by the approach on model systems involves the treatment of the carbon fibers with thiomalic acid and an epoxy type sizing that yields a reactive coating particularly adapted to matrices curable by EB-initiated free radical mechanism, as depicted in Fig. 7 [8].

![Fig. 6. Schematic representation of the influence of inhibiting functional groups at the carbon fibre surface.](image)

![Fig. 7. Sketch representing the chemical modification of epoxy functions at the carbon fibre surface by reaction with thiomalic acid.](image)
Significant improvements were achieved on the transverse stress at break, as measured via a three point flexural test, by applying original surface treatments on the fibres so as to induce chemical coupling with the matrix (Fig. 8).

![Fig. 8. Measurement of the transverse properties of carbon fibre reinforced composites revealing the degree of interfacial cohesion with the EB-cured aromatic acrylate matrix.](image)

Covalent bonds between carbon fibers sizing and matrix are indeed created with a high efficiency, as a result of chain transfer reactions between grafted thiol groups and growing polymer network. Transverse properties are drastically enhanced and exhibit values over 70 MPa, whereas the same test applied to samples without coupling agents break when submitted to a strain of 29 MPa.

The effect of the presence of thiol functions was further demonstrated by EB-curable adhesives interacting with thiomalic acid treated epoxy materials prepared in the form of blocks and assembled by a radiation cured aromatic acrylate adhesive. The obtained results illustrate the remarkable efficiency of covalent coupling induced by this type of chemistry (Figure 9). In the absence of treatment based thiol-containing carboxylic acid, adhesive breaking is observed at low strain ($\sigma = 4.5$ MPa), whereas between the epoxy blocks and the EB-cured acrylate adhesive layer, whereas using the thiol-containing coupling agent produces a cohesive break in the acrylate joint at a much higher strain ($\sigma = 9.5$ MPa) [9].

![Fig. 9. Optical micrographs showing the fracture surface between two epoxy blocks: a, top) adhesive breaking observed in the absence of a treatment with thiomalic acid ; b, bottom) with thiomalic treatment, highly resistant EB-cured joint with cohesive fracture in the underlying epoxy material.](image)
4. Conclusions

A variety of technological issues concerning EB-curing have been addressed through a basic approach of radiation physics, radiation chemistry and materials science. Advanced studies aimed at the improvement of matrix toughness, at the reduction of the matrix cure induced shrinkage, and at the design of fiber-matrix interface were addressed. Solutions for matrix toughening with higher processability and compatible with environmental considerations are under development. A next step will consist in aggregating the technological solutions developed for improving isolated aspects of curing, examined from the viewpoints of processing, of curing kinetics, polymer network performances and fiber-matrix interactions [10]. Technological demonstrators with demanding specifications are currently being prepared and further tested. Encouraging results allow envisioning mass production of structural composites as well as functional materials by means of a reliable, cleaner and more productive out-of-autoclave manufacturing.

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References


IMPROVED PROPERTIES OF ACRYLATE-BASED NANOCOMPOSITES BY 172 NM IRRADIATION

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1. Introduction

For surface patterning of polymeric materials, different patterning strategies such as photo-, electron beam- and nanoimprint-lithography, have arisen and represent the increasing scientific and commercial interest in complex structured surfaces [1].

UV-activated cross-linking reactions of photosensitive organic materials are in particular suitable for the fabrication of such complex micro- and nanostructured surfaces. However, most of the sophisticated techniques of surface design are far away from large-scale manufacture until now except the generation of wrinkled microstructures on the surface of UV curable acrylate formulations by monochromatic 172 nm excimer irradiation, i.e. UV induced matting [2].

The appearance of mattness is closely related to diffuse light reflection especially controlled by surface roughness [3]. Whereas for solvent-borne coatings the addition of microparticles (matting agents) to the varnish and the generally high shrinkage during drying/curing easily yield rough surfaces, UV-curable 100% acrylate systems undergo shrinkage during radiation curing to a lesser extent and are commonly regarded as being less effective in producing super matt finished coatings [4].

However, micro-structured surfaces of such UV-curable acrylate formulations can be obtained photochemically by short-wavelength vacuum UV (VUV) irradiation, e.g. a monochromatic 172 nm (Xe²⁺) excimer lamp [5]. Due to the short penetration depth in the range of less than 0.5 µm for such high-energy photons (wavelengths \(\lambda < 210\) nm), only surface-near layers of the acrylate coating are subjected to polymerization reactions and transformation into wrinkled structures. This wrinkled surface texture, especially in combination with the presence of nanoparticles in the varnishes, has already been industrially used to produce scratch and abrasion resistant coatings with matt surfaces for furniture, wood panel, and flooring applications [6]. Schubert et al. [7] studied simultaneously the kinetics of acrylate photopolymerization and the kinetics of the formation of wrinkled surface pattern by 172 nm photons. The authors observed that the on-set of VUV induced matting requires a certain degree of acrylate curing and that this delay of matting depends on the particular acrylate used. In addition, an increased microhardness was measured for micro-structured acrylate coatings, but no explanation of these findings has been given.

Recent studies on 172 nm excimer irradiation concerns in particular the photodegradation of substances [8] and polymer surfaces [9]. The self-initiating of acrylate photopolymerization by high-energy 222 nm and 172 nm photons has impressively shown by Scherzer et al. [10] using real-time (ATR) FTIR spectroscopy. However, it was assumed that photoinitiator-free
C=C polymerization reactions are limited to the maximum penetration depth (< 1 µm) of short-wavelength UV radiation.

In the present study, real-time (ATR) FTIR spectroscopy has been applied to elucidate the effect of the wavelength of UV radiation (polychromatic mercury arc lamp or monochromatic 172 nm excimer lamp) on the excitation of acrylic C=C and C=O bonds and, thereby, to explain the self initiation of acrylates by 172 nm irradiation as well as the improved surface properties of the VUV cured coatings such as microhardness, surface energy, and chemical resistance.

2. Experimental

2.1. Materials and preparation of polyacrylate nanocomposites

For the preparation of nanocomposite materials, nanosized silica Aerosil 200 and OX 50 (all from Evonik Degussa AG), microcorundum powder F400 (Treibacher Schleifmittel GmbH), various surface modifiers, e.g., methacryloxypropyltrimethoxysilane (MEMO) and vinyltrimethoxysilane (VTMO), and aliphatic urethane acrylate resins, e.g., EB1290 and EB5129, tetrahydroxyethylpentaerythritol tetraacrylate (SR 494), as well as reactive diluents such as 1,6-hexanediol diacylate (HDDA, all purchased from CYTEC Surface Specialties) were intensively stirred at 60-75 °C using a combination of dissolver and high-performance ball mill (VMA Getzmann, Germany). All chemicals were used as received.

Typical nanocomposite formulations contained 15-35 wt.% nanosized silica, 15 wt.% microcorundum (10 µm), and 2 wt.% photoinitiator (Darocur 1173 (BASF)). Using a roll coater, films up to 100 µm were prepared on parquet and polymer plates. The wet coatings were typically cured with the aid of a conventional medium pressure Hg lamp (120 W·cm⁻²). For 172 nm irradiation, an excimer lamp (Heraeus Noblelight) having an irradiance of 5 - 25 mW·cm⁻² was used. To enhance the efficiency of radical polymerization and to avoid ozone formation by 172 nm photons, all UV lamps have been purged with nitrogen in order to achieve an oxygen content <100 ppm.

2.2. Equipment

UV-induced real-time (ATR) FTIR measurements were performed on a Digilab FTS 6000 spectrometer equipped with a liquid-nitrogen-cooled MCT detector. Using the attenuated total reflectance (ATR) technique (“Golden Gate”, Graseby Specac), FTIR spectra were obtained in the wavenumber range of 600-4000 cm⁻¹ with a spectral resolution of 16 cm⁻¹ and a temporal resolution of 21 ms. For the determination of the signal intensity of C=C and C=O bonds, peak integration between 1375-1425 cm⁻¹ and 1650-1800 cm⁻¹, respectively, has been applied. Using a doctor blade, thin acrylate layers were applied to the (diamond) ATR unit. A rough estimation of the film thickness includes peak integration of CHₓ groups between 2700-3100 cm⁻¹ and assuming a thickness of 1.0 µm for the maximum peak area according to the Harrick approximation.

For the UV irradiation attached to the ATR unit, a polychromatic mercury arc lamp (100 mW·cm⁻², Müller Elektronik-Optik GmbH, Germany) and a monochromatic 172 nm excimer lamp (15 mW·cm⁻², Xeradex Radium GmbH, Germany) has been applied. The UV irradiance has been measured right on the ATR unit using a VUV radiometer from...
Gerus mbH (Germany). UV spectra of acrylates dissolved in acetonitrile or spin-coated on quartz plates were recorded with a Shimadzu 2101 UV-vis spectrometer.

The microhardness of the composite materials was determined with a Fischerscope H100C hardness tester (Helmut Fischer GmbH, Germany) according to the technical standard ISO 14577. Contact angle measurements of ultra-pure water and diiodomethane were performed using a G2 contact angle meter from Krüss GmbH (Germany). The static contact angles were measured five times for each sample and the method of Owens-Wendt-Rabel and Källble was used to calculate the surface energy. The gloss (at 60°) of the coatings was taken using a micro-Tri-glossmeter (Byk-Gardner). Optical images were obtained with an Olympus BX60 light microscope using reflected light.

3. Results and discussion

3.1. Matting of UV curable coatings by a dual UV lamp system

For flooring and furniture applications, the decision "glossy or not glossy" is not only a matter of consumer's preference but corresponds among other things to the coating's sensitivity to soiling. Highly glossy coatings with a mirror-like surface (Fig. 1a) tend towards displaying greasy contamination and fingerprints. Such gloss levels of >60 units (at 60º) can easily be obtained by typical curing with a polychromatic mercury UV lamp. By contrast, clear coats on wood with a matt or semi gloss appearance (Fig. 1b, gloss levels of <15 units at 60º) represent an advantage of displaying the natural optical appearance of wood grains without any interfering reflections.

![Specular and diffuse reflection](image)

*Fig. 1. Reflectance behavior of a nanocomposite material on laminate cured by (a) a mercury arc lamp and (b) the combination of 172 nm excimer and (Hg) UV lamp (having gloss levels at 60° of 87 and 4 units, respectively.)*

Because of the short penetration depth of 172 nm photons in acrylates, only a thin surface layer is crossed-linked, forming a solidified skin on the still wet coating. The formation of
wrinkled structures (background of Fig. 2) can be explained by swelling of the cured skin. Hence, temperature and viscosity of the coating during the UV curing step have an impact on the magnitude and shape surface wrinkles [7]. To avoid any relaxation processes of the wrinkles formed, these flexible microstructures must be consolidated by immediate curing of the whole lacquer by typical (Hg) UV or electron beam radiation. The described dual lamp set-up allows to obtain gloss levels at 60° down to 0.5 units depending on the acrylate formulation and the curing conditions [2].

![Diagram of UV matting](image)

**Fig. 2.** Scheme of UV matting using a combination of short-wavelength VUV lamp and polychromatic mercury UV lamp for surface and through cure, respectively. (Background: Microscopic image of the surface roughness.

Because of the short penetration depth of 172 nm photons in acrylates, only a thin surface layer is crossed-linked, forming a solidified skin on the still wet coating. The formation of wrinkled structures (background of Fig. 2) can be explained by swelling of the cured skin. Hence, temperature and viscosity of the coating during the UV curing step have an impact on the magnitude and shape surface wrinkles [7]. To avoid any relaxation processes of the wrinkles formed, these flexible microstructures must be consolidated by immediate curing of the whole lacquer by typical (Hg) UV or electron beam radiation. The described dual lamp set-up allows to obtain gloss levels at 60° down to 0.5 units depending on the acrylate formulation and the curing conditions [2].

In addition to matting, there is an effect of the supplementary 172 nm excimer irradiation on the coating’s surface properties such as hardness, chemical resistance, and hydrophilicity [11]. As summarized in Table 1, microhardness measurements and swelling studies (using iodine dissolved in ethanol) revealed that matted surfaces are typically harder and more resistant against chemicals or solvents than glossy ones, respectively.
To explain these findings, a reasonable assumption could be a higher acrylate conversion in surface-near layers induced by higher radical formation during 172 nm excimer irradiation. But, both FTIR microscopy with about 10 µm resolution and (ATR) FTIR spectroscopy (diamond and germanium crystals having IR penetration depths of about 3 µm and 0.5 µm, respectively) showed a similar degree of curing irrespective of the wavelength of UV irradiation [11]. In other words, the absorption of 172 nm photons (having penetration depth in acrylates in the range of less than 0.5 µm) by both the photoinitiator and the acrylate matrix should be certainly higher than that of photons from a mercury lamp and yield higher radical concentrations in surface-near layers. Consequently, short-wavelength UV irradiation is assumed to result in higher acrylate conversions. But, our findings do not support the assumption of higher degree of conversion of acrylic bonds by the highly energetic 172 nm photons and, thereby, other additional cross-linking reactions have to be accountable for improved surface properties of UV matted coatings (see below).

3.2. UV curing of acrylate coatings (172 nm excimer irradiation vs. mercury arc lamp)

Previous investigations [11] showed that UV matt-finished coatings, i.e. supplementary irradiation of their surfaces by short-wavelength VUV, have enhanced hardness and improved chemical resistance compared to glossy ones. Because no dependence of the degree of curing on the wavelength of UV radiation (172 nm excimer lamp or polychromatic mercury arc lamp) was observed, real-time (ATR) FTIR spectroscopy has been applied for both monitoring the radiation-initiated curing process [12] and finding out crucial differences between these two different UV irradiations.

For a photoinitiator-containing acrylate formulation, the vibrations of unsaturated C=C bonds at 1410 cm⁻¹ show a characteristic decrease during both polychromatic mercury and 172 nm excimer UV irradiation (Fig. 3). The kinetic conversion profiles calculated from the decay of this absorption band by integration of the peak area are given in Fig. 4.
Fig. 3. Real-time (ATR) FTIR spectra of an acrylate formulation (2 wt.% photoinitiator) during UV curing by (a) polychromatic mercury arc lamp and (b) monochromatic 172 nm excimer lamp.

For the different UV lamps, a similar degree of conversion as well as a comparable kinetic behaviour during photopolymerization can be observed. But, a more precise comparison of the polymerization rate ($R_P$) has to be considered on the basis of the kinetic scheme,

$$R_P = \frac{k_P}{k_t} [M] \cdot (\Phi_{PI} \cdot I_0 (1 - \exp(-2.303 \cdot \varepsilon \cdot [PI] \cdot d)))^{0.5}$$  

including the rate constants of propagation ($k_p$) and termination ($k_t$) as well as the monomer concentration ($M$), various parameters such as the initiation quantum yield of the photoinitiator ($\Phi_{PI}$), the intensity ($I_0$) of the incident UV light, the molar extinction coefficient ($\varepsilon$) at the irradiation wavelength, the photoinitiator concentration ($PI$), the optical pathlength of the light corresponding to the thickness of the sample ($d$), temperature, inertization, etc.

Whereas the concentration of monomer and photoinitiator as well as the thickness of the sample are identical for the experiments, significant differences in the light intensity, the initiation quantum yield, and the molar extinction can be taken granted between polychromatic mercury and 172 nm excimer UV irradiation. However, the higher light intensity of the (Hg) UV lamp is doubtless compensated by higher initiation quantum yield and molar extinction using the 172 nm excimer lamp. Thus, the kinetic curves of the acrylate formulation (shown in Fig. 4) can be used for a realistic comparison of the photopolymerization rate even though obtained for different UV lamps. Hence, the wavelength of UV irradiation was found to have no significant impact on polymerization rate and acrylate conversion provided the presence of a photoinitiator and the absence of oxygen inhibition.
As Fig. 3 evidently reveals, a significant difference between the (Hg) UV lamp and the 172 nm excimer lamp resides in the fact that the C=O band at 1720 cm\(^{-1}\) decreases during short-wavelength UV irradiation whereas it can be considered as an invariant IR band in the former case. And that means, the highly energetic 172 nm photons are absorbed by acrylic C=O bonds too. Compared to reactivity of C=C double bonds by 172 nm irradiation, the conversion of C=O bonds is significantly lower. Nevertheless, the activation of C=O bonds by short-wavelength UV radiation establishes new reaction pathways during radiation curing of acrylates.

3.3. Photoinitiator-free curing of acrylate coatings (172 nm excimer irradiation vs. mercury arc lamp)

The typical photopolymerization of acrylates requires the addition of a photoinitiator for the generation of radicals initiating polymerization reactions. The photons emitted by the widely-used medium pressure mercury arc lamps have usually longer wavelengths (\(\lambda > 250\) nm) than required for a direct activation of acrylate molecules which strongly absorb at wavelengths \(\lambda < 230\) nm. Therefore, (Hg) UV irradiation leads to an electronic excitation of the photoinitiator molecule followed by the generation of radicals which can start the polymerization reaction. For 172 nm photons (which approximates 7.2 eV), it can be assumed that their absorption generates highly excited acrylate species resulting in the formation of radicals. Thus, photoinitiator-free polymerization of acrylates using 222 nm (KrCl\(^{+}\)) excimer irradiation has successfully been shown by Scherzer et al. [13].

Needless to mention, the absorption spectrum of the acrylate matrix which acts actually as photoinitiator has to match to the emission spectrum of the UV source. The UV absorption spectrum of a typical acrylate, e.g. tripropylene glycol diacrylate (TPGDA), and the corresponding emission spectrum of the monochromatic 172 nm excimer lamp [8] are plotted in Fig. 5.
Fig. 5. Comparison of the UV spectrum of tripropylene glycol diacrylate (TPGDA) and a DFT calculated spectrum of an acrylate with the emission spectrum of the monochromatic 172 nm excimer lamp.

Acrylates strongly absorb radiation with a wavelength shorter than about 220-240 nm, but UV spectra with wavelengths $\lambda < 190$ nm are difficult to obtain because the VUV region is out of the range of conventional UV spectrometers. Therefore, it is very convenient that UV-VIS spectra are included in the quantum chemical calculations of the electronic structures for the ground and singlet states of acrylates (Fig. 5). The spectral matching of UV light emission and acrylate absorption in the region between 160 nm and 190 nm guarantees for high extinction and the possibility that acrylate molecules can be directly excited to generate radicals when exposed to 172 nm irradiation. While radical formation and self initiation of acrylates is limited to the penetration depth of 172 nm photon, please note that radical polymerization reactions, i.e. chain propagation, go beyond the mere surface-near layers. Using the described dual UV lamp set-up, through cure of photoinitiator-free acrylate formulations of about 60 µm thickness has been performed. Hence, intense short-wavelength UV irradiation provides a really alternative opportunity for the initiation of photo-polymerization.
Fig. 6. Real-time (ATR) FTIR spectra of tripropylene glycol diacrylate (TPGDA) during photoinitiator-free curing by (a) polychromatic mercury arc lamp and (b) monochromatic 172 nm excimer lamp.

The time-resolved ATR-FTIR spectra of acrylate nanocomposites during photoinitiator-free curing are shown in Fig. 6, from which it can be clearly seen that both the monochromatic 172 nm excimer and the polychromatic (Hg) UV irradiation have obvious influence on the photopolymerization of acrylic C=C double bonds. As expected, their conversion under mere (Hg) UV irradiation is insufficient for any practical application but radical generation takes place. By contrast, 172 nm excimer irradiation yields high conversion (>85 %) of C=C double bonds without any photoinitiator (even for a film thickness of 20 µm). Figure 7 reveals evidently this dependence of the self initiation and, thereby, of the rate of acrylate photopolymerization on the wavelength of UV light used.

Fig. 7. Photoinitiator-free photopolymerization of tripropylene glycol diacrylate (TPGDA). Comparison between (Hg) UV irradiation and 172 nm excimer irradiation.
Analogous to the real-time (ATR) FTIR studies with photoinitiator, the C=O band at 1720 cm\(^{-1}\) can not be considered as an invariant IR band in the case of 172 nm excimer irradiation (Fig. 6b). Please note that the polymerisation reactions, i.e. the solidification of a wet acrylate formulation, might affect the extinction coefficient of the C=O band (a possible reason for the small increase in intensity at the start of UV curing, Fig. 8) in addition to the observed shift of the acrylic C=O stretch mode (1720 cm\(^{-1}\)) to higher frequencies (1725 cm\(^{-1}\)) as well as the \(^{13}\)C NMR shift of carboxyl groups from 166 ppm to 174 ppm during UV curing of acrylates.

**Fig. 8. Dependence of the photoinitiator-free conversion of the C=O bonds of TPGDA on the thickness of the layers during 172 nm excimer irradiation.** (For comparison: photoinitiator-free conversion of C=C bonds).

The absorption of highly energetic 172 nm photons by C=O bonds most likely yield (via radical formation and H-abstraction) OH groups (spectra not shown). As Fig. 8 reveals, the photochemical reactivity of C=O bonds is small compared to C=C double bonds and seems to be limited to the penetration depth of 172 nm photons, i.e. sub-μm region. This means that the radical formation via excitation of C=O bonds does not start chain propagation of C=O bonds (in contrary to the polymerisation reactions of C=C bonds) but rather results preferably in radical recombination after radical transfer reactions. All these findings confirm that the enhanced surface hardness and improved chemical resistance of UV matt-finished coatings can be explained by a higher network density attributed to 172 nm excimer irradiation.

In conclusion, the avoidance of any photoinitiator in the acrylate formulation would be beneficial since a large amount of photoinitiator residues and/or photoinitiator fragments remaining in the cured lacquers can cause several problems in respect to the application properties of the coating such as release of volatile organic compounds and extractability of fragmentation products (especially in food packaging), limited long-term stability and discolouration (in particular in outdoor applications). Finally, high-priced photoinitiators contribute significantly to the total costs of a coating formulation.
4. Conclusions

The effect of short-wavelength UV irradiation on the curing kinetics of acrylates has been studied by real-time (ATR) FTIR spectroscopy. Providing the presence of a photoinitiator as well as the absence of oxygen inhibition, both the 172 nm excimer lamp and the mercury arc lamp yielded a similar degree of acrylic C=C bond conversion, i.e. the wavelength of UV irradiation was found to have no significant impact on acrylate conversion. However, the strong absorption of highly energetic 172 nm photons by acrylic C=C bonds makes radical formation and self initiation of the photopolymerization possible, i.e. photoinitiator-free curing of acrylate coatings (in contrast to polychromatic mercury UV irradiation).

Furthermore, excitation of C=O bonds by 172 nm excimer irradiation results in additional radical formation and, thereby, in cross-linking reactions within surface-near layers. This radical formation of C=O bonds by VUV radiation may also occur at the surface of thoroughly cured films yielding a higher network density via radical recombination reactions. As a consequence of all the additional cross-linking reactions by VUV irradiation, acrylate coatings matted by a dual UV lamp set-up consisting of a monochromatic 172 nm excimer lamp and a polychromatic mercury UV lamp show enhanced surface hardness and improved chemical resistance. In addition, UV matt-finished nano/micro-hybrid composites provided a very natural optical appearance, pleasant haptics, and seem to be suitable for durable flooring applications.

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References


RADIATION EFFECTS ON POLYCHLOROPRENE-ETHYLENE-PROPYLENE DIENE MONOMER-MULTIPLE WALLED CARBON NANO TUBE NANOCOMPOSITES: CROSSLINKING AND MECHANICAL PROPERTIES

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Abstract

Varying compositions of Polychloroprene rubber (PCR) Ethylene-propylene diene monomer (EPDM) 50:50 blend containing Multiple Walled Carbon Nanotube (MWNT) as nanoparticulate filler (0.5-10%) were prepared and their efficacy for radiation crosslinking was analyzed by gel-content, Charlesby-Pinner parameter and crosslinking density measurements. Gel content measurement indicated insensitivity of the PCR/EPDM to radiation on incorporation of MWNT into the matrix. The elastic modulus increased while elongation at break decreased with radiation dose. The reinforcing mechanism of nano-composites was studied by various micromechanics models which predicted higher modulus than the experimentally observed results, indicating agglomeration in the nano-composites. The thermal stability and $T_g$ of the PCR and EPDM were not significantly affected by MWNT introduction into the blend matrix.

1. Introduction

Blending of two or more components offers an economically viable and versatile way to produce new engineering materials with the desired properties [1-4]. Blends of rubber with other rubbers [5-7] or with plastics have been a subject of study specially in developing new methods of blending and characterizing new blends. The blends of EPDM (non polar) with PCR (polar) have evinced special interest because incorporation of suitable amount of PCR is expected to impart oil resistance, heat resistance and better adhesion characteristics to parent unsaturated matrix [8-9]. EPDM rubber and PCR are usually reinforced with carbon black, silica and other microscopic fillers and are chemically vulcanized to produce a crosslinked-network [10-12]. There is, however, an emerging interest in the development of elastomeric composites filled with nano-particulate fillers as incorporation of even small quantity of these nano-fillers may lead to superior physical and mechanical properties than their conventional analogs [13,14]. Radiation processing of nano-composites using high energy radiation is expected to provide uniformly crosslinked networks in comparison to conventionally vulcanized network [15,16]. The low operation cost, additive free technique and room temperature operations are among the added advantages of radiation crosslinking over the existing crosslinking techniques [17]. Our earlier studies have highlighted some unique characteristics of the radiation processing of PCR/EPDM system in terms of its dependence on morphology, composition, and radiation sensitizer related factors [9,18].

The present work is an extension of our work on the radiation processing of PCR/EPDM system, where the effect of MWNT addition on the radiation vulcanization and physico-mechanical characteristics of PCR/EPDM 50:50 blend was investigated. There are many reports on the development of radiation processed elastomeric nano-composites and the analysis of their mechanical and physical properties [19-21], however not much information is available on the radiation crosslinking behavior of such nano-composites with special
reference to the nature, type and concentration of nano-particulate filler present in the parent polymer matrix. The present paper reports a detailed investigation on the effect of MWNT addition on the radiation induced crosslinking behavior of PCR/EPDM/MWNT nano-composites. Attempt has been made to critically understand such effects in the light of various microscopic and macroscopic changes taking place in PCR/EPDM during nano-composite formation as well as during irradiation.

2. Experimental

2.1. Methods

A series of nano-composites of PCR/EPDM 50:50 blends containing different amounts of MWNT was prepared by initially mixing the two components in Brabender plasticodar. The homogeneous mix was cut into small pieces and compressed into sheets of size 12x12 cm$^2$ of different thicknesses in range 1-4 mm using compression-molding machine at 150 kg/m$^2$ pressure for 2 minutes at 130°C. Irradiation was carried out under aerated condition using a gamma chamber 5000 (GC-5000) having Co-60 gamma source supplied by M/s BRIT India. The gel content determined by Soxhlet extraction with xylene. The swelling study was carried out in toluene.

2.2. Gel Content

The Gel content was determined by refluxing the samples with xylene for 24 hrs. The remaining insoluble portion was rinsed with methanol and dried in vacuum oven at 60°C to a constant weight. Gel content was evaluated using following relationship (Equation 1).

$$\text{Gel content} = \left( \frac{W_g}{W_i} \right)$$  

(1)

Where $W_g$ and $W_i$ are the weight of insoluble fraction and initial weight respectively.

2.3. Mechanical properties

For tensile strength measurements at least five dumbbell shaped specimens were cut from nano-composite sheets using a steel die of standard dimensions. The thickness of the samples were determined to the nearest of 1 mm. The tensile strength and elongation at break were measured by INSTRON universal testing machine using crosshead speed of 100 mm/min at room temperature.

2.4. Thermo gravimetric analysis

Thermograms of samples were recorded on Q50 thermal analyzer at heating rate of 10°C/min in the temperature range RT-600°C under dynamic N$_2$ atmosphere.

2.5. DSC studies

DSC (DSC-822 from M/s Mettler) was used to observe glass transition temperature of the blends. All DSC thermograms were recorded at heating rate of 10°C/min, under inert atmosphere. Prior to DSC run, the instrument was calibrated for temperature and heat flow.
using high-purity indium standard. The mid point of the slope change of heat capacity plot of second scan was taken as the glass transition temperature.

3. Results and Discussion

3.1. Gel content of the nano-composites

Figure 1 shows the change in the gel content of PCR/EPDM/MWNT nano-composites on irradiation. Un-irradiated samples were found to be easily soluble in hot xylene, however nano-composites irradiated to a dose >50 kGy were partly insoluble due to the formation of a three-dimensional network. In order to quantitatively evaluate crosslinking and chain scission yields of irradiated PCR/EPDM/MWNT nano-composites, plots of $S + S^{1/2}$ vs $1/(\text{radiation dose})$ from the Charlesby-Pinner equation (Equation 2) for the different blend compositions were drawn (Fig. 2).

$$ S + \sqrt{S} = \frac{p_o}{q_o} + \frac{1}{q_o p_o D} $$

(2)

where $S$ is the sol fraction, $P_n$ the number averaged degree of polymerization, $D$ radiation dose, $p_o$ & $q_o$ are fraction of ruptured and crosslinked main-chain units per unit dose (proportional to the radiation chemical yields of degradation and crosslinking). From Fig. 2, it is clear that gel fraction is independent of MWNT fraction present in the nano-composites. No significant change in the $p_o/q_o$ values of the nano-composites suggests that that radical-radical interactions in polymer nano-composites is neither inhibited nor enhanced in the presence of MWNT, as observed in other systems investigated by us [22-23]. This observation clearly indicates that, in some matrices, even though MWNT reinforces the system and reduce the overall free volume, these effects do not necessarily translate into higher gel fraction values.

Fig. 1. Gel fraction of nano-composites on irradiation at a dose rate of 3.5 kGyh⁻¹.
Fig. 2. Charlesby-Pinner plot for different nano-composites.

3.2. Crosslinking density of radiation processed nano-composites

In order to gain further insight into radiation crosslinking of the PCR/EPDM/MWNT nano-composites, crosslinking density measurements were carried out. The key parameters that determine the amount of solvent absorbed by crosslinked network are the crosslink density and the extent of polymer-solvent interaction that is reported as the value of Flory-Huggins parameter $\chi$. The diffusion into solid samples depends on the availability of appropriate molecular size holes in the network, however, it may be mentioned that the kinetic response which includes solvent sorption rate, the rate of approach to equilibrium and the transport mechanism controlling the solvent sorption may also depend upon additional factors like history of the samples and its composition. The molecular weight between cross-links ($M_c$) has been estimated using the following relation, based on the theory initially proposed by Flory and Rehner.

$$M_c = -V_1 \rho_p \frac{\phi_p^{1/3} - 1/2 \phi_p}{1/n(1-\phi_p)+\phi_p+x\phi_p^2}$$

(3)

Where, $V_1$ is the molar volume of the solvent, $\rho_p$ is the polymer density, $\phi_p$ is the volume fraction of the polymer in the swollen matrix and $\chi$ is the Flory–Huggins interaction parameter between solvent and polymer which can be calculated using following relation

$$\chi = \beta + \frac{V_i}{RT} (\delta_s - \delta_p)^2$$

(4)

where $\delta_s$ and $\delta_p$ are the solubility parameters of the solvent and the polymer, $\beta$ is the lattice constant, $R$ is the universal gas constant and $T$ is absolute temperature. The behavior of crosslinking density ($1/2M_c$) with MWNT weight fraction and with radiation dose is plotted in Figure 3.
Fig. 3. Crosslinking density of nano-composites on irradiation at a dose rate of 3.5 kGy h$^{-1}$ for different compositions of (a) EP$\_$_NT00 (b) EP$\_$_NT05 (c) EP$\_$_NT1 (d) EP$\_$_NT3 (e) EP$\_$_NT5 (f) EP$\_$_NT10.

It can be seen from the graph that extent of crosslinking in nano-composites increases with the increase in MWNT fraction and with radiation dose, and the crosslink density of NT$\_$_10 is significantly higher than NT$\_$_00 particularly at highest dose studied. Comparing the profiles of figure 1 and 3 the different behavior of gel fraction and crosslink density can be easily understood in view of the fact that though the gel content may not increase after a certain dose, the crosslinking density of the system may still continue to increase with dose due to further increase in inter and intramolecular radical-radical combinations and other rearrangements. The, crosslinking density followed the order EP$\_$_NT00 < EP$\_$_NT05 < EP$\_$_NT1 < EP$\_$_NT3 < EP$\_$_NT5 < EPS$\_$_NT10 in the entire dose range studied, indicating predominantly crosslinking behavior of nano-composites on irradiation and enhancement in the crosslinking density with the incorporation of MWNT.

3.3. Mechanical properties of the nano-composites

Figure 4 shows the relationship between elongation at break and radiation dose for different samples. The elongation at break decreased with dose for all nano-composites due to more crosslinked structures produced in the sample matrix, which prevents the structural organization during drawing and brings about a decrease in internal chain mobility and elongation. The rapid decrease of elongation at break with the increasing MWNT loadings, which is observed in many composite systems, is believed to be caused by the premature failure starting at the MWNT aggregates. This reduction in the elongation at break with the addition of MWNT is not unusual for polymers and indicates that interfacial interactions between the elastomer and MWNTs were not sufficient to induce any positive effect on bulk elongation properties.

To understand the nano-composite characteristics, it is essential to compare the experimental results with standard micro-mechanical models developed for such systems. In this study, additive law, Guth model and Halpin-Tsai (HT) equations are used to predict the bulk properties of the carbon nanotube composites. Additive law has been described as

$$E_c = (n_1 n_0 E_f - E_m)V_f + E_m$$  \hspace{1cm} (5)
where, $E_c$, $E_f$ and $E_m$ are the elastic modulus of composite, MWNT and blend respectively. $V_f$ is MWNT’s fraction, $\eta_0$ is the orientation efficiency factor and $\eta_1$ is the length efficiency factor. $a$ is described as

$$n_1 = 1 - \frac{\tanh(a(l/d))}{a(l/d)}$$  \hspace{1cm} (6)

Where, $l$ and $d$ are length and diameter of MWNT, and $a$ is described as

$$a = \sqrt{\frac{-3E_m}{2E_f\ln(V_f)}}$$ \hspace{1cm} (7)

The Halpin-Tsai (HT) and Halpin-Kardos (HK) equations are a set of empirical relationships that are used to predict the final properties of composite materials in terms of the properties of the matrix and reinforcing phases together with their proportions and geometry. The Halpin–Kardos equation is suitable for randomly oriented short fibers can be expressed as

$$\frac{E_c}{E_m} = \frac{3}{8} \left[ \frac{1+2(l/d)\eta L V_f}{1-\eta L V_f} \right] + \frac{5}{8} \left[ \frac{1+2\eta_T V_f}{1-\eta_T V_f} \right]$$ \hspace{1cm} (8)

Guth proposed another model based on the aspect ratio and volume fraction of filler, which has been widely used to account for the change in modulus in filled elastomers.

$$\frac{E_c}{E_m} = 1 + 0.67(l/d)V_f + 1.62(l/d)^2V_f^2$$ \hspace{1cm} (9)

Fig. 4. Elongation at break of nano-composites on irradiation at a dose rate of 3.5 kGyh⁻¹ (a) EP_NT00 (b) EP_NT05 (c) EP_NT1 (d) EP_NT3 (e) EP_NT5 (f) EP_NT10.
The MWNT diameter, length, and Young’s modulus of 20 nm, 50 μm and 400 GPa were used in the calculations. The additive rule and Guth model were found to be inadequate in expressing the modulus behavior of PCR/EPDM/MWNT nano-composites as the values calculated were much higher than the experimental and HK values. Though HK results shows slightly lower values than the additive rule, the values were still significantly higher than the experimental results. The deviation of experimental results from the above mentioned models indicates that assumptions, such as homogeneous distribution and efficient transfer of tensile load to the MWNTs, made to derive these equations do not hold good for these nano-composites. Thus, these models were modified by applying boundary conditions for the elastomers systems and by varying apparent aspect ratio of MWNTs in the elastomer matrix. Figure 5 represents the fitting of Guth and Halpin-Tsai model to modulus variation with volume fraction of MWNT in the dose range studied. While the fitting using Guth model departs from the experimental results at lower filler loadings, the Halpin-Tsai model shows good agreement within the experimental data obtained. It was interesting to observe that though the aspect ratio estimated using both the models was almost the same but it was much less than the actual aspect ratio of MWNT. This finding clearly indicates the presence of agglomerates in the matrix. It has been reported that \( \frac{dE}{dV_f} \) can be a good measure of reinforcing efficiency of MWNTs as it takes into account both magnitude of the modulus increase and the amount of MWNTs required to achieve it, therefore the magnitude of \( \frac{dE}{dV_f} \) was estimated for nano-composites. The increase in magnitude of \( \frac{dE}{dV_f} \) (measure of reinforcement) with radiation indicates that there is improvement in load transfer effect on irradiation and an interface link between MWNTs and elastomer matrix is established after radiation treatment. It is reported that, radiation induced cross-linking in the rubber-phases enhances the polymer-filler interaction such an effect can also contribute to the observed dose dependent increase in the reinforcement (\( \frac{dE}{dV_f} \)). These results support our justification that higher crosslinking yield of nano-composites containing higher fractions of MWNTs is due to physical crosslinking assisted free volume reduction in the nano-composite matrix.

3.4. Kraus plot

Polymer–filler interactions in PCR/EPDM/MWNT nano-composites were examined using Kraus plot.
\[ \frac{V_{ro}}{V_{rf}} = 1 - m \left( \frac{\phi_f}{1-\phi_f} \right) \tag{10} \]

where \( V_{ro} \) is the volume fraction of the polymer in the swollen rubber, \( V_{rf} \) volume fraction of the polymer in the swollen filled (elastomers+MWNT) system and \( \phi_f \) is the volume fraction of the filler in the filled nano-composites. Swelling of filled polymers was suppressed in presence of MWNT.

**Fig. 6.** Kraus plot of nano-composites on irradiation at a dose rate of 3.5 kGyh\(^{-1}\) for 300 kGy.

The polymer-filler interaction parameter \( C \) (Kraus constant) was calculated using the Kraus equation given by equation.

\[ C = \frac{m - V_{ro} + 1}{3(1 - V_{ro}^{2/3})} \tag{11} \]

Where, \( m \) is the slope obtained from the linear plot of equation 10. Figure 6 shows the Kraus plots for the nano-composites irradiated to 300 kGy. The experimental values were not found fit into Kraus equation, however the negative slope of graph implied positive polymer filler interaction and reinforcement of the matrix. The \( C \) value, determined from the linear region of the Kraus plot, was found to be 3.66 for the system.

### 3.5. Thermogravimetric analysis

The thermal stability of PCR/EPDM/MWNT nano-composites was determined thermogravimetrically and the results are plotted in Figure 7. Weight loss in first step may be attributed to dehydrochlorination of PCR. As clear from the thermograms there was not significant shift in onset or peak temperature of dehydrochlorination on radiation treatment or MWNT addition. The second stage of decomposition, comprises of two diffused steps of a broad peak and a hump. The broad peak may be due to decomposition of EPDM along with partial decomposition of the polyene formed by the dehydrochlorination of PCR followed by complete degradation of complete matrix. A marginal increase in the decomposition temperature of the nano-composites with addition of nanotubes and radiation treatment was 168
observed in the second step. For crosslinking type of polymers, the thermal stability of the matrix is expected to improve due to the formation of more compact three-dimensional crosslinking networks, which is more stable against formation of gaseous products on heating due to slower ingress of air. Thus observed marginal improvement in the thermal stability on irradiation supports our earlier conclusion on the significant increase in crosslinking density of the matrix with the addition of MWNT and irradiation. The slight improvement in thermal stability of un-irradiated nano-composite is probably due to the presence of nanotube agglomerates that can act as barriers to air ingress.

**Differential scanning calorimetry**

The effect of specific interactions between the nano-composite segments (PCR, EPDM and MWNT) on the physical properties of the nano-composites was studied by measuring the glass transition temperature ($T_g$). The value of $T_g$ for all specimens was determined from the midpoints of the corresponding glass-transition region. The DSC thermograms recorded for different nano-composites are shown in Figure 8. The $T_g$ of EPDM and PCR at $-49^\circ$C and $-34^\circ$C respectively was slightly affected by MWNT loading. There was a small increase at low MWNT loading and small decrease at higher MWNT loading. Such an observation can be explained on the basis of the variation in the MWNT dispersion with increase in MWNT fraction. At lower concentration the nano-composites are expected to be well dispersed and effective interactions between the elastomers chains and MWNT leading to better reinforcement of the parent blend and hence increase in $T_g$. On the other hand, at higher filler loadings, because of the agglomeration and hence poor reinforcement $T_g$ may decrease.

![Fig. 7. TGA thermograms of nano-composites.](image)
Fig. 8. DSC Thermograms of (a) $E_{PT00}$ (b) $E_{PT05}$ (c) $E_{PT1}$ (d) $E_{PT3}$ (e) $E_{PT5}$ (f) $E_{PT10}$

4. Conclusion

Radiation sensitivity of PCR/EPDM (50:50) blends was not significantly enhanced on addition of MWNT. However the crosslinking density was found to increase with dose and MWNT fraction. This observation was attributed to the contribution from physical crosslinking induced by MWNT and to the difference in the mechanism of the gel formation and crosslinking. The elastic modulus increased with the radiation dose while elongation at break decreased with dose. The Halpin-Tsai model fitted better into the experimentally observed modulus values and predicted low aspect ratio of MWNT in the matrix, indicating the agglomeration of MWNTs. The slope of Kraus plot indicated high reinforcement of PCR/EPDM 50:50 blend on MWNT addition. Thermogravimetric analysis indicated two step decomposition of the nano-composites with no significant enhancement of thermal stability of the blends on introduction of MWNT in the blend. DSC studies indicated higher influence of MWNT presence on the mobility of the PCR chains.

References


RADIATION-CLEAVABLE MICROPARTICLE CHAPERONES FOR DURABILITY-CONTROLLED NANOCOMPOSITE BIOPLASTICS

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Abstract

Xyloglucans are a major class of structural polysaccharides found in the primary cell walls of higher plants. They are particularly interesting raw materials for their excellent film forming properties, thermal stability and an hydroxyl rich, highly branched molecular structure, which controls their hydrophilicity and solubility characteristics and thereby temperature or solvent responsiveness. If the branching degree and molecular weight are properly controlled, from semi-dilute aqueous solutions nanoparticles can be obtained. These nanoparticles can be considered ideal candidates to incorporate, protect and disperse different actives in polysaccharide-based films. \(^{60}\)Co \(\gamma\) irradiation has been here applied to decrease molecular weight and polydispersity of a partially degalactosylated xyloglucan. Aqueous solutions of the irradiated materials were characterized by both dynamic light scattering measurements at different temperatures and gel filtration chromatography. The aggregation kinetics at 37°C were studied by dynamic light scattering measurements to confirm the temperature-responsive behavior of this polymer when dispersed in water at low concentration after \(\gamma\)-irradiation. Chemical modification of xyloglucan with nitrocinnamic acid was performed in order to graft nitrocinnamate pendant groups to induce reversible photocrosslinking.

1. Introduction

It is forecast that traditional polyolefins will be gradually, but steadily substituted by biodegradable, natural source polymers in the mass production of packaging films due to the environmental concerns related to the post-use of non-degradable, oil-based plastics. At the same time, it is also acknowledged that solvent and chemical resistance, as well as the mechanical properties of polyolefines, in terms of strength, flexibility, deformation at break and tear resistance, will be hardly paralleled. Notwithstanding that, several different polysaccharides and their blends are under investigation as potential alternatives in the film and packaging industries. A wide range of film properties can be obtained due to the diversity of available polysaccharides [1]. In particular, edible and biodegradable films can be obtained from natural biopolymers, such as starch, gelatin, etc. [2–6]. Biopolymer films can benefit from the incorporation of a wide variety of additives, such as antioxidants, antifungal agents, antimicrobials, drugs, colours, nutrients etc. [7], as a way to control the degradability and/or provide further functionality and perceived value. Incorporation and efficient dispersion of actives and bioactives in bioplastics is not trivial. Polysaccharide micro/nanoparticles, incorporating stabilizers (natural antioxidants), pro-degrading agents (such as enzymes or metal oxide nanoparticles) or other active ingredients, can be considered ideal chaperones to introduce various and heterogeneous substances into polysaccharide films in virtue of their structural affinity. In particular, the
possibility of obtaining biodegradable nanoparticles from xyloglucan has been here investigated.

Xyloglucans are a major class of structural polysaccharides found in the primary cell walls of higher plants, thus they are abundant, non-food feedstock materials. Xyloglucan skeleton is formed by β-(1,4) D-glucan, partially substituted by α-(1→6)-linked xylose units. Some of the xylose residues are β-D-galactosylated at the O-2. Depending on the source, there are variants possessing also fucose units attached in the lateral branches. This high degree of substitution is the main reason for water solubility of xyloglucans, when compared with cellulose. [8-10]

Xyloglucan from the tamarind kernel possesses excellent film-forming properties, especially in blends with chitosan or starch [11]. When it is partially degalactosylated (Deg-XG), it becomes a temperature-responsive polymer. Degalactosylation is achieved with β-galactosidase, which strips the (1→2)β-D-galactose side groups. Depending on the degree of degalactosilation and polymer concentration in water, Deg-XG can form physical, reversible gels with temperature variations: a first “sol to gel” transition occurs at relatively low temperatures (20-40°C) and a second “gel to sol” transition occurs at higher temperatures (80-120°C). While macrogels have been already investigated for several biomedical applications[12], there is paucity of information relatively to temperature induced aggregation phenomena in the low concentration regime: it is expected that thermal treatments at moderate temperature would drive the aggregation of these macromolecules in the form of nanoparticles. In order to control the size and the size distribution of the nanoparticles, control on molecular weight can be beneficial.

As most of the other polysaccharides, xyloglucans are likely to be characterised by a wide molecular weight distribution. For other natural source biopolymers, such as cellulose [13], starch [14] and chitosan [15], irradiative methods have been often applied to reduce the molecular weight and, possibly, also the polydispersity. At the best of our knowledge there are only two studies on the effect of γ-irradiation on molecular weight of a non-degalactosylated xyloglucan variant [16,17], while no studies are reported on the degalactosilated variants and therefore no information is available on the impact that irradiation induced degradation may have on the temperature responsiveness of the polymer, which provided motivation for this initial study.

Scoping experiments have been also carried out to introduce nitrocinnamate groups, through a well-known esterification reaction between the hydroxyl groups of xyloglucan and nitrocinnamic acid, in order to confer reversible crosslinking properties to the polymer in the absence of initiators or catalysts [18,19].

2. Experimental

2.1. Materials and irradiation experiments

Xyloglucan extraction from tamarind kernel powder, purification and partial degalactosylation was performed according to an in house developed protocol. A degalactosylation degree of about 40% was achieved. The polymer was subjected to further extensive purification consisting in (i) deionised water dissolution at low concentration, (ii) autoclaving at 120°C for 20 minutes, (iii) centrifugation at 8000 rpm for 15 min, (iv) extensive dialysis against deionised water and (v) freeze drying. The polymer recovered after
this procedure is named after “P”. Aqueous xyloglucan solutions at 0.1, 0.25 and 0.5 wt% were prepared both from the “as extracted” polymer (NP) or the “purified” polymer (P), by homogenization in water at 5°C for 5 hours at 13500 rpm and stored at 5°C. The influence of centrifugation at 8000 rpm for 45 minutes on the “as received” material (NP-C) or autoclaving at 120°C for 20 min, both on the “as received” (NP-A) and “purified” polymer (P-A) was investigated. Samples subjected to γ-irradiation were used after dissolution in cold water and homogenization as described before and centrifugation at 8000 rpm for 45 minutes. Irradiation of Deg-XG powder was carried out in air at room temperature using a 60Co source (Gamma Chamber 5000, Institute of Nuclear Chemistry and Technology, Warsaw, Poland) at 8 kGy/h and irradiation doses of 10, 20, 40 and 60 kGy.

2.2. Chemical modification

Trans-4-Nitrocinnamic acid (100mg) was dissolved in dimethyl sulfoxide (DMSO). To this solution, 100 mg of Deg-XG was added followed by 4 mg of 4-dimethylaminopyridine (DMAP) and 96 µl of diisopropylcarbodiimide (DIC). The mixture was reacted for 20 h at 50°C. Purification was achieved by dialysis against water for seven days.

2.3. Dynamic Light Scattering Measurements

The hydrodynamic radius ($R_h$) of particles dispersions was measured by dynamic light scattering (DLS) using a Brookhaven Instruments BI200-SMgoniometer. The influence of temperature was investigated in the range 15-37°C. Intensity autocorrelation function at the scattering angle of 90° and time autocorrelation function were measured by using a Brookhaven BI-9000 correlator and a 100mW solid-state laser (Quantum-Ventus MPC 6000) tuned at $\lambda = 532$ nm. All samples were analyzed after filtration with 5 µm cellulose acetate (Millipore) syringe filters to remove gross contaminants. When samples showed a monomodal distribution, DLS data were analyzed by the method of cumulants, which provides information on the mean value and standard deviation of the distribution of nanoparticles hydrodynamic size [20].

2.4. Gel filtration chromatography

Estimation of molecular weight was performed using two Shodex SB HQ columns in series (806 and 804) thermostated at 15°C with an Knauer oven, connected to a HPLC device (LC-2010 AT Prominence, Shimadzu, Kyoto, Japan) equipped with a 50 µl sample loop. All samples were eluted with 0.02% sodium azide solution at 0.5 ml/min; the refractive index was recorded with a Smartline RI detector 2300 Knauer. The calibration curve was obtained with injection of dextran and pullulan standards.

2.5. FTIR analysis

FTIR analysis was carried out with Perkin Elmer-Spectrum 400 apparatus by dispersing either freeze dried polymers or the trans-4-nitrocinnamic acid in potassium bromide and compressing into pellets. Spectra were recorded at 30 scans per spectrum and 1 cm$^{-1}$ resolution in the 4000-400 cm$^{-1}$ range.
3. Results and Discussion

3.1. Influence of preparation conditions on Deg-XG aqueous solutions

The preparation of aqueous solutions of Deg-XG is a complicated task due to the strong intermolecular interactions, which impair solubilization in the form of individual polymer chains[21]. For the specific degalactosylation degree (40%) a LCST of about 30 °C and an UCST of about 100°C is expected. For this reason, the preparation of aqueous xyloglucan solutions was carried out with prolonged homogenization at 5°C. Notwithstanding that, precipitation of an insoluble sediment upon storage at 5°C is observed even at a relatively low concentration of polymer in water, such as 0.1 wt%. In order to estimate the average size of the polymer particles, aqueous solutions of Deg-XG at three different nominal concentrations were prepared by cold homogenization (5°C) for 5 h and immediately characterized by DLS measurements at 15°C. Average particles size and standard deviation are reported in Figure 1.

The hydrodynamic diameter in water increases significantly with polymer concentration, which suggests a strong tendency to aggregation. Centrifugation at 8000 rpm for 45 minutes induces phase separation of a deposit, which is about 5 wt% of the initial weight and after centrifuging the formation of a deposit is no longer observed, even after prolonged storage at 5°C. The hydrodynamic size of polymer coils in the supernatant phase is significantly smaller.

![Hydrodynamic diameter of polymer particles at the variance of concentration, before and after centrifuging.](image)

**Fig. 1.** Hydrodynamic diameter of polymer particles at the variance of concentration, before and after centrifuging.

A further purification process was introduced to remove impurities which were evidenced as dark shadows in the transmission microscopy imagetsaken on thin films of the non-purified (non-centrifuged) xyloglucan (here not presented). The purification, which follows a low concentration, cold dissolution step, performed as described above, also includes an autoclaving step, a prolonged dialysis and a final freeze-drying stage. The “P” system is prepared from the freeze-dried polymersimilarly to the “NP”. A loss of 25-30 wt % of the material results. After purification, the dark shadows in casted thin films are no longer visible. Dispersion stability of polymer in water is achieved by this further purification and a sediment
upon storage no longer forms, but no significant effects on the hydrodynamic size of xyloglucan in water are observed.

In consideration of the specific features of Deg-XG/water phase diagram [22], which shows an UCST at ~100°C for a galactose removal ratio of 40%, a beneficial effect of an autoclaving treatment at 120°C on the average size of macromolecular clusters is to be expected. Data reported in Figure 2 indicate that autoclaving causes a reduction of the aggregates’ size except for the centrifuged system. From this preliminary investigation it can be concluded that for both the purified and non-purified polymer the measured hydrodynamic diameters soon after cold dispersion in water are likely affected by supramolecular Deg-XG aggregates, the size being strongly dependent on the polymer concentration. The autoclave treatment improves “solubility” whereas freeze-drying has a detrimental effect on it due to the strong inter-chain interactions, which establish in the dry state and are not easily reverted by water. It should be also emphasized that the purification protocol, the prolonged centrifugation process and the autoclaving process, also when individually considered, are effective in order to obtain stable colloidal dispersions of xyloglucan nanoparticles.

Fig. 2. Hydrodynamic diameter of polymer particles dispersed in water at 0.1 wt% polymer concentration, for centrifuged and purified systems before and after autoclaving.

3.2. Effect of gamma-irradiation on aqueous Deg-XG hydrodynamic size and molecular weight distribution

Gamma irradiation of the solid powder (non-purified) was performed in air at doses ranging between 10 kGy and 60 kGy. The irradiated polymer was then dispersed in water by cold homogenization and subjected to centrifugation at 8000 rpm for 45 min as described above. DLS measurements on the irradiated Deg-XG dispersions were performed at 15°C in order to evaluate both the average hydrodynamic diameter and relative standard deviation as function of the irradiation dose. Data are shown in Figure 3. It is interesting to observe that the average hydrodynamic size of the polymers in water does not significantly vary as a result of the irradiation treatment. Variations are in fact always within the standard deviations of the average diameters measured. GFC measurements were also performed at 15°C on the same
systems to gather information on the molecular weight distributions of both non irradiated and irradiated systems. Data are shown in Figure 4. Values of Mw are to be considered for comparative purposes only, as they come from a calibration curve with linear pullulans, while branching a distinctive feature of xyloglucan.

The molecular weight distribution of the non irradiated system is quite broad, as expected. A main peak is at about 1.5 MDa with a broad shoulder below 1 MDa, which suggests the presence of minimum two main populations of macromolecules or clusters. A progressive shift toward the lower molecular weights for the overall curve, as well as a gradual variation of the two relative populations in favor to the lower molecular weight one are also clearly evident. The two populations have closer peaks and comparable heights for xyloglucan irradiated at 40 kGy. Therefore, gamma irradiation induces polymer chains degradation. Under the light of this evidence, a more exhaustive light scattering analysis will be performed, both in static and dynamic conditions and at the variance of the angle, to evidence eventual differences in the internal organization of macromolecular chains in the nanoparticles.

Fig. 3. Hydrodynamic diameter of polymer particles dispersed in water at 0.1 wt% : non irradiated XG (γ0); irradiated at 10, 20, 40 and 60 kGy (γ10, γ20, γ40 and γ60, respectively).
3.3. Kinetics studies performed by DLS measurements

In principle, chain-scission reactions may involve either the backbone or the lateral grafts. In the latter case, changes in water solubility and above all on the temperature-responsiveness is to be expected.

Deg-XG solutions prepared with the irradiated polymer were subjected to repeated DLS measurements runs at 37°C to study the aggregation kinetics. Figure 5a-b shows the scattered light intensity for the irradiated samples as function of the time. A comparison between the kinetics at 15°C and 37°C is reported for the non-irradiated polymer (Figure 5a), as reference. While at 15°C there is no influence of time on the light scattering intensity, at 37°C an increase of intensity is observed. This also stands for all the irradiated systems. An increase of intensity can be related to an increase of particle size, provided that the density has not changed. The fact that kinetics are observed, although indirectly, supports a prevalence of main chains ruptures rather than lateral grafts. It is also evident that irradiation affects the rate of these observed kinetics, with a maximum for the 20 kGy irradiated system, which probably gets the best compromise between molecular size and chain flexibility, which results to faster aggregation dynamics. Gamma irradiation may be also considered a tool to control the temperature responsive behavior of these polymers.
3.4. Synthesis of the Xyloglucan-Nitrocinnamate Macromer

For the purpose of the present project we designed a photo-crosslinkable macromer based on derivatisation of the hydroxyl rich branched polymer with nitrocinnamate as grafted group. Photocrosslinking of cinnamate groups is well known in the field of photolithography and it has been also reported as a tool to induce photocrosslinking to PEG. [18,19]

The possibility to reinforce the xyloglucan physical networks with chemical crosslinks may increase the stability and solvent resistance of nanoparticles. Furthermore, in virtue of the reversible nature of the isomerization of the cinnamate group, which is at the basis of the crosslinking reaction, a photoscissile crosslinking can be used as a strategy to incorporate and release on demand additives and active ingredients from the crosslinked micro/nanoparticles.

The success of the synthetic approach is confirmed by Fourier transform infrared and UV spectrosopies. In order to quantify the degree of modification of xyloglucan with nitrocinnamate groups 1H-NMR spectroscopy is undergoing.

FTIR spectra of the starting polymer and monomer and of the polymer-monomer adduct or macromer show the appearance of a strong vibrational frequency at 1703 and 1608 cm$^{-1}$ on the Xyloglucan-NC, that is not present in XG, which confirms the ester linkage formation. The carbonyl bond in the FTIR spectrum of nitrocinnamic acid appears at 1687. Few more other distinct bands appear. A dispersion of XG-NC was prepared in 1,4 dioxane and a clear UV-vis absorption band at about 250-300 nm is evident. The process of photocrosslinking and photo cleavage are now under investigation.
4. Conclusions

During the first part of this CRP we have selected a natural biopolymer, xyloglucan, as elective material to produce polymer nanoparticles which will incorporate, in the development of the project, specific additives to control the durability of bioplastics or to introduce specific functionality into polysaccharide-based films and coatings. This approach will preserve the full biodegradability of the nanocomposite material. The highly branched hydroxyl-rich structure of xyloglucan and the possibility to tailor the branching degree through an enzymatic reaction, coupled with its abundance in nature and low cost makes it a very interesting raw material for a variety of applications that span from the packaging and coating industry to the biomedical and electronic fields.

Depending of the degalactosylation degree xyloglucan can be readily water-soluble or only partially water soluble. In this last case, they show a reversible aggregation induced by an increase of temperature from below ambient (15°C) to body temperature (37°C). Gamma irradiation in air of the solid polymer has proved to be an effective methodology to modify molecular weight and temperature-induced aggregation kinetics.

A modified XG-CN adduct, which can undergo reversible photocrosslinking, has been synthetized. The success of the reaction has been confirmed through UV vis and FTIR spectroscopies and a more quantitative estimation of the derivatisation degree is undergoing. The responsiveness to UV irradiation of XG-CN micro/nanoparticles and thin films will be investigated.
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Collaborative Research Activity

Gamma irradiation has been performed at in collaboration with Prof. G. Przybytniak at the Centre for Radiation Research and Technology, Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland.

A training programme for Ms. Noha Deghiedy from 04/03/2012 to 04/03/2012 has been provided, aimed to the synthesis and characterization of polyaniline-coated polyolefin films with induced surface electrical conductivity. In particular polyolefin films, produced, radiation grafted with acrylic acid and primed with a variety of difunctional coupling agents at the National Center for Radiation Research and Technology Atomic energy authority, Cairo Egypt, have been fully characterized at the University of Palermo through FTIR, UV and XPS spectroscopies, then used as substrates for in-situ polymerization of polyaniline. The surface coated films were subjected to spectroscopic, morphological (SEM), electrochemical (CV) and electric (Impedance Spectroscopy) characterizations.

References


RADIATION CURING OF NANOMPOSITES FOR COATING APPLICATION

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Abstract

Composite materials combine properties of the individual components in a synergetic manner to produce a variety of materials in an efficient and cost effective manner. Thus, composite materials are being used in various applications from automotive to furniture industries. Materials reinforced with nanoscale components are adding new dimensions to composite materials and enable further major improvements in functional and structural properties. The incorporation of only a few percent of nano-sized particles can make dramatic property changes that may result in enhancing physical and mechanical properties of the resulting composite. Several major issues need to be addressed to utilize the full potential of such nanofillers i.e. incompatibility or weak interfacial bonding between the matrix and the nanoscale component, and agglomeration of nanosized component during processing resulting in inhomogeneous distribution. UV/EB technology offers a way of overcoming these challenges by grafting of monomers/polymers including natural polymer onto the nanofiller surface thereby fixing their morphology and at the same time making them compatible with the host polymer.

1. Introduction

Recently, there has been a strong and increasing demand for scratch and abrasion resistance composite materials that can be applied to various substrates such as plastic and wood products. For example, plastics have been widely used as motor vehicle parts, optical lenses etc. due to their characteristic features such as lightness, toughness, easy processing and low production costs. However, they are vulnerable to scratch and abrasion resistance. Another application is in the furniture and panels industry where the industry needs high scratch and abrasion resistant coating materials especially for table top and parquets.

Over 90% of all wooden furniture made in Malaysia is exported and paint companies involved in this lucrative export market must adapt to changes in global trade patterns and technology trends to survive. The wood coatings industry is attracting a lot of interest in Asia lately due to its high growth potential. In Malaysia, with a market size of over US$60m, this is an important segment in overall coatings market. Coatings suppliers have to comply with international standards to be competitive in this market. The wood coatings market in Malaysia comprises mainly of nitrocellulose based coatings, acid cured coatings and polyurethane coatings. UV/EB curing and waterborne wood coatings are also present but have a relatively small share. In general, solvent-based wood coatings (which include acid-cured) are likely to lose share to waterborne and UV/EB curing coatings worldwide as the latter are more environmental friendly. The stringent regulations against volatile organic compound (VOC) in developed regions like Europe are forcing the industry to move towards use of environmental friendly coatings in furniture exported from Malaysia. In Malaysia, there are about 750 furniture suppliers and over 15 wood coatings suppliers. In order to meet the expectations of their customer base, maintain their market share and conform to
environmental legislation, the manufacturers need access to a low solvent-based solution. Therefore, there is a need for research and development work in this area to replace the conventional solvent technology. The instant cure of the coating materials by UV/EB and the ease with which the technology fits into highly automated production processes is seen as a great commercial advantage.

At present, coating materials without reinforced filler (nanoparticles) are used to provide a highly glossy and luxurious finish to specific products. In this research work, the incorporation of nanoparticles into coating materials is aimed at improving scratch and abrasion resistant properties while retaining transparency and glossiness. Mineral charges such as silica and alumina nanoparticles can be introduced into UV/EB curable resins to get hard and abrasion resistant materials, which can be used as clear coatings and fiber reinforced plastics. From the structural point of view, the role of inorganic filler, usually as particles or fibers, is to provide intrinsic strength and stiffness while the polymer matrix can adhere to and bind the inorganic component so that forces applied to the composite are transmitted evenly to the filler. UV/EB curable nanoparticles can be prepared and synthesized by heterogeneous hydrolytic condensation technique using acrylated oligomers such as epoxy acrylates and urethane acrylates including palm oil polyols (natural polymers) with the incorporation of nanoparticles.

In conventional composite materials, filler and the polymer are combined on micronic scale, which often leads to insufficient adhesion between the organic matrix and the reinforcing filler. Composite materials that exhibit a change in structure and composition over nanometer length scale (< 100nm) have been proven in imparting remarkable property enhancement with respect to stiffness and strength, heat resistance and gas barrier properties. Several major issues need to be addressed to utilize the full potential of such nanofillers can be realized, among them, (i) weak interfacial bonding between the matrix and the nanoscale component, and (ii) agglomeration of nanosized component during processing resulting in inhomogeneous distribution.

The proposed radiation curing technique by free radical polymerization using UV light or electron beam as the source of radiation is the most suitable process and it offers several advantages including curing process can be done at ambient temperature. Other benefits of this technique are (i) a solvent free-formulation, with essentially no emission of volatile organic compounds to the environment and user friendly i.e. green technology; (ii) an ultra-fast curing by free radical polymerization reaction and using the highly reactive acrylate based resins; (iii) operations at ambient temperature particularly suitable for heat sensitive substrates such as plastic and wood based products; and (iv) improved productivity and increased product performance

2. Experimental

All chemicals were used as received. The prepolymer such as epoxy acrylate (EB600) was obtained from Cytec Specialty Chemicals, Belgium. Monomer such as acrylated pentaerythritol with 3–4 functional group (PETIA) was also obtained from the same manufacturer as above. The chemical structures of the compounds used in this study are shown in Figure 1.
4-hydroxyanisole or 4-methoxyphenol was of gas chromatography (GC) grade quality and used as a stabilizer. Meanwhile, maleic anhydride was of analar grade quality and used as a catalyst in the heterogeneous condensation reaction. Both chemicals were obtained from Sigma-Aldrich Chemical Company Limited, UK.

All the nanoparticles of silicium dioxide such as AEROSIL OX50 used in this work were obtained from Degussa-Hüls AG, Germany. They were normally used as fillers for polymer reinforcement and scratch resistant coatings. Meanwhile, the silane such as VTMOS was obtained from the same manufacturer and used as coupling agent.

Finally, most of the photoinitiators such as DC1173 and IC500 used in the ultraviolet (UV) curing were obtained from Ciba Specialty Chemicals, Switzerland.

![Chemical structures of the compounds used in this study.](image)

3. Preparation of silico-organic nanoparticles

Siloxane methacrylate nanoparticles from the silica/acrylate systems were synthesized in a small batch reactor. Maleic anhydride, dissolved in water, was introduced in a mixture of several acrylates and 4-methoxyphenol. The coupling agent such as VTMOS was added within 30 minutes. Finally, nano-sized silica particles were dispersed under intensive stirring during 1–2 hours using a Dispermat dissolver. The process for preparing these nanoparticles is proton catalyzed and efficiently proceeds at 60–65°C. Thereafter, the product was immediately cooled to room temperature.
4. Preparation of polymeric nanocomposites by UV curing

The polymeric nanocomposite materials were prepared basically from several acrylates and AEROSIL OX50 as shown in Table 1. These materials were coated on different types of substrates such as lamination paper, polyvinyl chloride (PVC) and glass panel using automatic film applicator. They were cured using a low energy electron beam (EB) accelerator and UV irradiator. Furthermore, in spite of relatively high nanopowder content in the nanodispersions, UV induced polymerization with the aid of conventional mercury lamps proved to be an efficient alternative to EB curing. During irradiation, the chambers were degassed by inert gas such as nitrogen. Films of these UV/EB cured nanocomposites were characterized by several methods such as scratch test and Taber abrasion test.

5. Results/Discussion

Silico-organic nanoparticles have relatively large surface areas than microparticles, therefore modification effects from the polymerization activity should have a great influence to the properties of the composites. In these investigations, we use radiation such as ultraviolet and electron beam to initiate polymerization and interaction at the interface between the nanoparticles and the monomeric materials. These polymerization active nanoparticles were obtained by heterogeneous hydrolytic condensation of the silane to the silanol groups of the AEROSIL particles.

The above reaction could be verified by the application of FT-Raman spectroscopy (intensity measurements of the C=C vibration band at 1640 cm$^{-1}$) and gel permeation chromatography to show that the polymerization activity of the nanoparticles imparts to the silico/acrylate dispersion$^{11}$. In the curing process, the nanoparticles form cross-linkages to produce radiation cured polymeric composites with improved scratch and abrasion resistance.

After soxhlet extraction, all the coated materials show very high gel content (see Table 2). These coating materials also show high pendulum hardness property as shown in Table 3. In Table 4, the weight loss of the UV/EB cured materials significantly reduced when the amount of silica particles increases i.e. up to 30% of SiO$_2$. These nanoparticles improve the abrasion property of the coating materials.
TABLE 2. GEL CONTENT UV CURED MATERIALS.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Gel Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lack 1</td>
<td>96.4</td>
</tr>
<tr>
<td>Lack 2</td>
<td>96.7</td>
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<tr>
<td>Lack 3</td>
<td>97.3</td>
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<tr>
<td>Lack 4</td>
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<td>98.4</td>
</tr>
<tr>
<td>Lack 7</td>
<td>98.6</td>
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</table>

TABLE 3. PENDULUM HARDNESS OF UV/EB CURED MATERIALS.

<table>
<thead>
<tr>
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<th>Pendulum Hardness (%)</th>
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<tr>
<td></td>
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<tr>
<td>Lack 4</td>
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<tr>
<td>Lack 5</td>
<td>73.7</td>
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<tr>
<td>Lack 6</td>
<td>74.0</td>
</tr>
<tr>
<td>Lack 7</td>
<td>72.9</td>
</tr>
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</table>

TABLE 4. ABRASION RESISTANT OF UV/EB CURED MATERIALS.

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<thead>
<tr>
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</thead>
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<tr>
<td>Lack 2</td>
<td>28.2</td>
</tr>
<tr>
<td>Lack 3</td>
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<tr>
<td>Lack 4</td>
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<td>9.4</td>
</tr>
<tr>
<td>Lack 7</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Finally, the performance of these composites is also related to other factors such as resistance to scratch. Two types of needles were used for determining the resistance of a single coat system of the composites to penetration by scratching i.e. using diamond tip and steel ball (spherically tipped needle). The method used was by applying increasing loads to the needle to determine the minimum load at which the coating was penetrated. The nanoparticles added into the coating materials improve the scratch property of the composite materials as shown in
Table 5 whereas in Table 6, most of the composites exhibit excellent resistance to scratch property including Lack 1.

<table>
<thead>
<tr>
<th>Formulations</th>
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</tr>
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<tr>
<td></td>
<td>UV</td>
<td>EB</td>
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<td>0.7</td>
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<tr>
<td>Lack 4</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Lack 5</td>
<td>2.0</td>
<td>3.5</td>
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<tr>
<td>Lack 7</td>
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TABLE 5. SCRATCH RESISTANT OF UV/EB CURED MATERIALS USING DIAMOND TIP WITH 90°

<table>
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<tbody>
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<td>UV</td>
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<td>Lack 6</td>
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<td>&gt;10</td>
</tr>
<tr>
<td>Lack 7</td>
<td>&gt;10</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>

TABLE 6. SCRATCH RESISTANT OF UV/EB CURED MATERIALS USING STEEL BALL TIP WITH DIAMETER 1 MM

6. Conclusions

Polymerization active silico-organic nanoparticles could be prepared by heterogeneous condensation (in situ reaction) and formed crosslinking in the polymeric substrates. With a relatively high nanopowder content of the nanodispersions, these coating materials could still be cured by UV light and electron beam (EB) to produce excellent polymeric composites. These coating materials show better resistances toward scratch and abrasion properties compared to pure acrylates.

Furthermore, investigations of the UV/EB curing and properties of waterborne urethane acrylate nanodispersions have also been carried out in collaboration with the Institute of Surface Modification (IOM), Germany.

Acknowledgment

The author would like to thank the International Atomic Energy Agency (IAEA) and the Government of Malaysia for funding the above project.
References

INVESTIGATIONS OF THE UV/EB CURING AND PROPERTIES OF WATERBORNE URETHANE ACRYLATE NANODISPERSIONS

U. Decker, A. Prager, I. Reinhard & E. Bilz, IOM Leipzig in collaboration with Mohd Sofian Alias & Nik Ghazali Nik Salleh, Malaysian Nuclear Agency

Polyurethanes become more and more important for the applications in green (waterborne) coating technologies because of their wide variability of physical and chemical properties and they can additionally be modified by adding different particles, pigments and other additives [1-3].

To optimize the coatings we are trying several samples of Bayhydrol (Bayer Material Science) under different aspects:

— The drying kinetics and the UV-curing were followed by real-time infrared spectroscopy (rt-ir) at different temperatures.
— Dynamic mechanical analysis (DMA) and microhardness measurements were done with cured (EB & UV) and uncured samples to get information about cross-linking by the radiation.
— Different concentrations (0-15%) of SiO₂ nano particles (Köstrosol 03550[Chemiewerke Bad Köstritz] unmodified and modified with Dynasilan Glyeo) were added

Fig. 1. Drying of Bayhydrol UV 2317 200μm neat at different temperatures monitored at 2900cm⁻¹.

From this (Figs.1, 2) one can estimate the polyurethane content in the coating and the optimum time of removing the water. The 200μm wet coatings become of about 70μm solid polyurethane foil which seems good for the EB (160keV/100kGy) & UV (1200mJ/cm²) and also for the mechanical measurements. The uncured dry samples could be measured only in shear modus with thicker samples (~0.5mm- DMA).
Fig. 2. Spectra of Bayhydrol UV 2317 before and after drying at 30°C.

Fig. 3. Temperature dependence of double bond decrease of Bayhydrol UV 2317+1%IC819.

The conversion was calculated by measuring the acrylic double bond concentration (with IR at -810cm⁻¹) during irradiation or on both sides of sample (penetration deep of the ATR unit ~ 2-3µm).

After the drying process, UV light (1200mW/cm²) is applied under inert atmosphere (2min N₂), different concentrations (0.5%, 1%, 2% per weight of urethane) of photo-initiator Irgacure 819 (BASF) are tested.
Fig. 4. Spectra of Bayhydrol UV 2317+1%IC819.

The investigations with REM show, that the sphere structure holds for the solid non- and irradiated coatings (Fig. 5).

Fig. 5. REM of Bayhydrol UV XP 2690+10%SiO2 irradiation with UV at 30°C.

The modified nanoparticles are about 60nm and the unmodified tend to give bigger aggregates and so the coatings become slightly turbid. The radiations improve the crosslinking between the dispersed particles and so the mechanical properties as E-module and micro hardness increased more than one order of magnitude.

The maximum of tanδ of uncured sample was moved from 44°C to 84°C (Tg) by the irradiations (Fig. 6), but the measurements can till now not clearly say, are the modified particles really bonded or not to give a higher networkdensity especially at high nanoparticle concentrations.

It is also not clear, what is happening to the dispersed particles in urethane acrylate, because the crosslinking will be hindered. Further work has to be investigated.
Fig. 6. E-Module and tan σ versus temperature of Bayhydrol UV 2317 unirradiated, UV-irradiated and EB-irradiated.

Bibliography


SYNTHESIS AND ANTIMICROBIAL PROPERTIES OF CHITOSAN/ZN(II) COMPLEX USING IRRADIATED CHITOSAN

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Advanced Polymer Laboratory, Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, P.O. Nilore, Islamabad, Pakistan.

Abstract

The combined effect of molecular weight of chitosan and zinc oxide on antimicrobial properties was carried out in this study. Chitosan having molecular weight in the range of 220 kDa to 73 kDa was extracted from crab shell using various conditions. The molecular weight of obtained chitosan was further lowered by gamma radiation in various environments. Chitosan in dry, wet and solution form was exposed to gamma rays in the dose range of 15 to 150 kGy. The effect of gamma radiation on the molecular weight of chitosan was characterized using viscometry, infrared spectroscopy and X-ray diffraction. The results showed that the physical state of chitosan and radiation dose greatly affect the molecular weight. At given dose, lowest molecular weight chitosan was obtained from chitosan in solution form. The antibacterial response of the radiation degraded chitosan was studied against gram-positive and gram-negative bacteria. In order to enhance the antibacterial property, chitosan was mixed with ZnO.

The influence of chitosan molecular weight and Zn(II) content on the structural and antimicrobial properties of the complexes was also envisaged. The FTIR and XRD analysis of the complexes revealed the formation of different molecule structure with different zinc content. The in-vitro antimicrobial studies of the chitosan and chitosan/Zn (II) complexes were evaluated against Pseudomonas aeruginosa, staphylococcus CNS, Escherichia coli, Staphylococcus aureus 28 and Staphylococcus aureus ATTC using wells assay diffusion method. The complexes showed wide spectrum of effective antimicrobial activities, which were further improved by using low molecular weight chitosan. The complexes had an excellent antifungal activity and no growth of Aspergallious fumigatus and Fusarium solani were observed after two weeks.

Keywords: chitosan, γ-radiation, hydrogen peroxide, degradation

1. Introduction

Chitin (poly-β-(1-4)-linked-2-acetamido-2-deoxy-D-glucopyranose) is one of the most abundant and renewable biopolymers present in crustacean shells and fungi. It is second abundant biopolymer present on earth after cellulose [1]. The deacetylation of chitin gives chitosan (poly-β-(1-4)-linked-2-amino-2-deoxy-D-glucopyranose). Chitosan is structural analog of cellulose and it is copolymer of glucosamine and N-acetylglucosamine linked by β-1-4 glycosidic bond [2]. Chitosan has many inherent properties of natural polymers such as: nontoxic, biocompatible, and biodegradable. Moreover, the presence of easily modified amine and hydroxyl groups made this polymer more versatile [3]. Presently, chitosan has been used...
widely in healthcare, agriculture, biotechnology, wastewater treatment, medical products, food and textile industries [4].

The chitosan obtained after the deacetylation of chitin has very high molecular weight and low solubility in most of solvents. This limits the direct utilization of chitosan mostly in medicine and food industry. Efforts have been made to lower the molecular weight of chitosan to increase its solubility and varieties of methods have been reported in the literature. The degraded chitosan has shown to possess improved physicochemical and biological properties as compared to parent chitosan [5-6]. Some interesting physiological activities of degraded chitosan have been investigated such as antitumor [7], antibacterial [8], antifungal [9], and elicitor activity for plants [10]. Different degradation processes have been developed to reduce the molecular weight of chitosan, without changes in its chemical structure [11]. These degradation methods include acid hydrolysis [12], oxidative [13] enzymatic degradation [14] and radiation [15]. In acid hydrolysis different acids such as: hydrochloric acid [16] hydrofluoric acid [17] sulfuric acid [18] phosphoric acid [19], nitrous acid [20] have been used. These acids are hazardous and the control of degradation process is also difficult. In oxidative degradation of chitosan, hydrogen peroxide, sodium nitrite and potassium persulfate were investigated. But hydrogen peroxide has long been used for degradation of chitosan because of its availability, control on degradation and environmental friendly nature [21]. Radiation degradation has many advantages including the formation of chemically pure product free from initiators and side products. Moreover, compared with the conventional degradation processes, radiation degradation is simple, environment friendly and can be used for large scale production [22].

Keeping in view this fact, an effort has been made to investigate the degradation of chitosan using gamma radiation. The use of ionizing radiation for the modification of polymers is safe and environment friendly [23]. It has already been used for the preparation of oligochitosan [24]. In this study, chitosan in three forms namely: dry, wetted with few drops of water and solution in hydrogen peroxide was exposed to gamma rays in the range of 15 to 150 kGy. The effect of degradation on the molecular weight and structure and antibacterial properties was monitored using infrared spectroscopy, X-ray diffraction, viscometry and antimicrobial studies. To further enhance the antimicrobial properties of chitosan, complexes based on chitosan and ZnO were prepared. The physicochemical and antimicrobial properties of chitosan/Zn(II) complexes were also investigated.

2. Experimental

2.1. Materials

Chitosan having deacetylation of 73% and molecular weight of 220 kDa was obtained from chitin, using standard procedure. Analytical grade sodium hydroxide, hydrochloric acid, acetic acid and hydrogen peroxide were purchased from Sigma-Aldrich. Zinc oxide was prepared by co-precipitation method using zinc acetate and sodium hydroxide precursor solutions.

2.2. Sample preparation and irradiation

Chitosan was irradiated using gamma rays in three conditions namely: (I) Powder, (II) powder wetted with water and (III) solution (chitosan dissolved in acetic acid and 1% H₂O₂ was
added. Irradiation is performed at Pakistan Radiation Services using $^{60}$Co gamma irradiator (Model JS-7900, IR-148, ATCOP, in air at room temperature and the dose rate was 1.02 kGy/h. The absorbed dose was ranging from 25 to 150 kGy. After irradiation, the samples were taken out and powder and wet forms were dried directly in the oven at 50°C under vacuum. The irradiated solution was treated with ammonia solution to precipitate the chitosan, filtered and then dried in oven at 50°C.

2.3. Synthesis of CS-Zn complex

Chitosan (0.5 g) was dissolved in 30mL of 1 % (v/v) acetic acid solution with constant stirring until clear solution is obtained. Simultaneously, appropriate amount of ZnO powder was dissolved in 20 mL of 1 % (v/v) acetic acid. The molar ratio of ZnO is varied from 0 to 2 in the complexes. A silane compatibilizer was added in film solution. Subsequently, the transparent solution was casted into films of complexes after drying.

2.4. Characterization

The dried samples were characterized by FT-IR, viscometry using Ubbelohde, X-ray diffraction and Antibacterial activity using standard procedure.

3. Results and Discussion

The effect of gamma radiation on the structure of chitosan was studied by FTIR spectroscopy. Figure 1 shows the IR spectra of chitosan before and after radiation degradation. No bands were observed in the range of 1900-1660 cm$^{-1}$ confirming the absence of oxidative groups such as, aldehyde and carboxylic groups. The absorption band at 873 cm$^{-1}$ shows the presence of pyranose ring. This further confirmed that the ring opening of pyranose ring did not take place during degradation of chitosan. The bands at 1655 and 663cm$^{-1}$ are related to the binding vibration of –NH$_2$, and the band at 1054 cm$^{-1}$ relates with stretching vibration of C-N. This show that -NH$_2$ group could not destroy during degradation of chitosan.

![Fig. 1. FT-IR spectra of chitosan and chitosan irradiated at different doses.](image)

The effect of radiation on molecular weight of chitosan in different sets has been analyzed by viscometry and the results are shown in Figure 2. This figure shows that in all three sets, the increase in absorbed dose lowered the molecular weight of chitosan. In set-1, a sharp decrease in molecular weight is observed upto 25 kGy. Further increase in absorbed dose showed a gradual decrease in molecular weight with increase in radiation dose. The TGA analysis of the dried samples showed that ~ 8 % of absorbed water was present in the chitosan. These water molecules exposed to radiation are converted into free radicals and start degradation of 198
chitosan polymer chains by abstraction of hydrogen atom from C1 or C4 carbon of the chitosan chain and then chain scission had occurred.

In set-II, few drops of water were added into chitosan and irradiated. The results revealed that the increase in absorbed dose lowered the molecular weight of chitosan. The degradation rate in wetted chitosan is slightly higher as compared to dried one.

In set-III, chitosan solution was prepared in acetic acid and H₂O₂ (1%) was also added. This set showed the combined effect of radiation and H₂O₂ on soluble chitosan macromolecules. It can be seen from the figure that as the radiation dose increased, molecular weight of chitosan decreased drastically. A very sharp decrease in molecular weight of chitosan was observed upto 15 kGy and then changes in molecular weight become slower at higher radiation dose. The trend is similar but here the rate of degradation of chitosan is much greater as compared to the previous two sets. In this case, both water and hydrogen peroxide also play their role to enhance the degradation of chitosan. The overall trend of radiation doses on the molecular weight is as follow:

Chitosan solution + H₂O₂ > Wet chitosan > Dried chitosan

Fig. 2. The effect of irradiation dose on the molecular weight of chitosan.

Fig. 3 shows the XRD patterns of the unirradiated and irradiated chitosan. The unirradiated chitosan shows two characteristic peaks at 2θ = 10.3 and 19.8, which were almost similar to the results reported by [25]. The irradiated chitosan exhibited additional peaks indicating the high degree of crystallinity of irradiated chitosan.
The FTIR spectra of chitosan/Zn(II) complex is shown in Figure 4. In CS/Zn(II) complexes (CZ), the stretching vibration of –NH₂ and –OH groups in the range of 3450-3100 cm⁻¹ was further split into peaks. The bending vibration of –NH₂ group at 1617 cm⁻¹ is shifted towards higher wavenumber and the band at 1089 cm⁻¹ (–OH group) showed a significant shift toward lower wavenumber. This indicated that both the –NH₂ and OH groups of chitosan were involved in complexation with Zn. Wang et al. also observed this phenomena in their complexes as well. Some new bands were also observed in the spectra of CZ complexes [26]. These new bands were at 534 cm⁻¹ and 475 cm⁻¹, which were assigned to stretching vibration of N–Zn and O–Zn [26].

The XRD diffraction patterns of CZ complex is shown in Fig. 5. Two strong peaks were observed in the diffractogram of chitosan at 2θ = 10.3° and 19.8°, indicating the presence of crystallinity in chitosan. These peaks were also present in CZ complex. Peaks observed in irradiated chitosan were not found in the diffractograms of CZ complex containing irradiated chitosan.
Fig. 5. XRD diffractrogram of chitosan/Zn(II) complexes.

The antibacterial property of chitosan is well established. It is a macromolecule which was unable to enter the outer membrane of bacteria because the membrane was impermeable towards macromolecules [27]. Therefore, chitosan could not directly access into the intracellular parts of the cells. The proposed antibacterial mechanisms of CS was suggested as: the protonated form of the amino group at C-2 formed polycationic structure which were interacted with the predominantly anionic lipopolysaccharides components of the microorganisms. As a result, the structure of outer membrane was either altered or ruptured which in turn released the major proportion of proteinaceous material from the cells and caused ultimate death of the cell [28-29].

The antimicrobial activities of the chitosan and two CZ complexes were compared in Table 1. It can be observed that the antimicrobial activities of CZ complexes enhanced with increasing chelate ratios. It can be seen from this table that the antimicrobial activities of CZ complexes were enhanced with increasing chelate ratios. The CZ complex showed broad spectrum of antimicrobial activities against bacteria and fungi, although differences existed among different kinds of microorganisms. Generally, the complexes had different antibacterial activity and variable response was observed for different gram-positive and gram negative bacteria. When chitosan chelated with Zn ions, the positive charge on the amino group of CS was further strengthened. A synergism was observed between chitosan and Zn ions at having ratio 1:1. This complex exhibited higher inhibitory activities as compared to 2 : 1. The antibacterial result showed that the antibacterial activity of CZ complexes can be controlled either by the amount of Zn salt or by the molecular weight of the chitosan.

<table>
<thead>
<tr>
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<td></td>
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<table>
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### Set III

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<tr>
<td>Chitosan : Zn(II) is (2:1)</td>
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### Set IV

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### Set V

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</tr>
<tr>
<td>Chitosan : Zn(II) is (2:1)</td>
<td>24</td>
</tr>
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* CC = unirradiated chitosan; C25 = 25 kGy irradiated chitosan; C50 = 50 kGy irradiated chitosan; C75 = 75 kGy irradiated chitosan; C100 = 100 kGy irradiated chitosan.

### 4. Conclusions

The degradation of chitosan can be tailored using various methods. Ranges of molecular weight were obtained using gamma radiation and/or hydrogen peroxide. The degraded chitosan retained the pyranose structure and degradation reaction occurred at glycosidic linkage (C-O-C). The decrease in intrinsic viscosity and reduction in molecular weight of chitosan subjected to gamma radiation had been occurred in the following order: chitosan solution + H$_2$O$_2$ > wet chitosan > dry chitosan. From this order, it can be concluded that much better degradation and molecular weight distribution had been taken place in chitosan solution with hydrogen peroxide as compared to wetted and powder chitosan.

### References


RADIATION SUPPORTING SYNTEHISIS AND CURING OF NANOCOMPOSITES SUITABLE FOR PRACTICAL APPLICATIONS

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Abstract

The effect of metal ions on the structure of constructed from acrylic acid and acrylamide copolymers was investigated. Ag\(^+\) and Cu\(^{2+}\) cations introduced to the matrix influence density of 3D network. Absorbed doses determining crosslinking efficiency and acidity of aqueous solutions are the other factors which control diffusion of low molecular weight molecules. Copper ions are coordinated predominantly by carboxylic groups what was confirmed by EPR spectroscopy.

Silver agglomerates were synthesized and stabilized in molecular sieves. The main goal of the study was to investigate the structure of paramagnetic particles produced in γ-irradiated synthetic sodalites with different guest anions by using EPR spectroscopy. The size of paramagnetic agglomerates depended on the geometry of environment, hydration, nature of anions present in sieve cages and temperature.

Silver haloids in track-etched membranes applied as templates have been synthesized and investigated. The appropriate procedure of chemical replacement reaction for obtaining such structures has been developed and optimized. Microrods in the pores and micrograins on the surfaces of membranes were deposited. Scanning electron microscope with X-ray microsonde was used for determining morphology and stoichiometry of the samples (AgCl, AgBr).

1. objective of the research

Gamma-radiation has proven to be a powerful tool for synthesis and modification of many materials. This is a very effective method to construct three-dimensional polymer network offering advantages over conventional physical or chemical methods of network formation: mild reaction conditions, negligible formation of by-products, fast gelation and no need for using catalysis. Radiation induced gels might coordinate metal ions whose presence influences their structure.

The reported studies were focused on (1) interaction between inorganic-organic components in a hybrid system, (2) radiation induced aggregation of silver in the pores of well-defined molecular sieves and (3) crystallization of inorganic materials in rod forms inside polymer track membranes.

The products obtained might be potentially used for heterogeneous catalysis purposes or as indicators of high energy quanta.
2. Introduction

2.1. Interaction between inorganic and polymeric components in a hybrid system

Functional groups of polymers are able to coordinate metal ions through ionic bonds, coordination bonds, and ion dipole interactions to form organometallic hybrids having specific features. Such structures might play a role of simuli responsive polymer gels used to produce smart catalysts combining high selectivity with advantageous of homogenous catalysts. The catalytic function of polymer-metal complexes depends on their structure. \( \text{Cu}^{2+} \) and \( \text{Ag}^{+} \) are considered as metal ions of high catalytic activity.

Copper compounds play a valuable role in both synthetic and biological chemistry. Copper catalyzes a vast array of reactions, primarily oxidation-reduction reactions. Copper (I) has a \( \text{d}^{10} \) electronic configuration with no unpaired electrons, making it undetectable by EPR. The \( \text{d}^{9} \) configuration of \( \text{Cu}^{2+} \) makes the ion paramagnetic and detectable by EPR spectroscopy which is a useful tool for both structural and mechanistic studies. Copper (II) centers typically have tetrahedral, or axially elongated octahedral geometry. Their spectra are anisotropic and generally give signals of the axial or orthorhombic type. The structure of complexes might be postulated on a basis their EPR signals.

Contrary to silver atoms monovalent silver ions are diamagnetic. The influence of the metals on crosslinked polymeric matrices was studied.

2.2. Paramagnetic silver clusters in sodalites

Ultrasound metal particles have attracted considerable interest as a distinct state of matter with unique physical and chemical properties. One of the methods to avoid problems with size and shape distribution of clusters is to produce metal agglomerates inside well-defined cages and channels of molecular sieves. During the past three decades silver agglomeration in molecular sieves reduced by hydrogen or ionizing radiation was extensively studied mostly by electron paramagnetic resonance (EPR). Both silver isotopes \( ^{107}\text{Ag} \) and \( ^{109}\text{Ag} \) have nuclear spin 1/2 and large magnetic moments. The nuclearity \( N \) of cationic silver clusters can be easily calculated from the number \( n \) of EPR lines: \( N = n-1 \). It should be stressed that only paramagnetic silver clusters can be studied by EPR.

Generally, two types of pathways of silver agglomeration are described. The first one was observed in \( \gamma \)-irradiated AgNaCs-rho zeolite, where agglomeration process is initiated by radiolytic formation of silver atoms \( \text{Ag}^{0} \) and involves the reaction between silver atoms and \( \text{Ag}^{+} \) cations followed by the reactions between paramagnetic silver clusters and \( \text{Ag}^{+} \) cations, leading to the successive formation of silver dimers \( \text{Ag}_{2}^{+} \), trimers \( \text{Ag}_{3}^{2+} \) and tetramers \( \text{Ag}_{4}^{3+} \) [1].

The second pathway of silver agglomeration was observed in dehydrated zeolite A with high silver loadings (Ag\(_{x}\)Na-A, \( x \geq 6 \)). In this case, directly after irradiation at 77 K a seven-line EPR multiplet, assigned to a silver octahedral hexamer \( \text{Ag}_{6}^{2+} \), is recorded [2,3]. As the mobility of the silver species at such low temperatures is negligible, it was postulated that paramagnetic hexamer is formed from diamagnetic hexamer by electron capture during radiolysis at 77 K. The proposed mechanism assumes that silver agglomeration is initiated by
autoreduction of Ag\(^+\) and proceeds by the reaction of Ag\(^0\) atoms with Ag\(^+\) cations until a diamagnetic hexamer is formed.

Formation of silver octamer cluster Ag\(_8\)^{7+} was observed according the same mechanism in high-temperature synthesize sodalite crystals with hydroxyl guest anion \[4\].

The main goal of our study was to investigate by using EPR spectroscopy the structure and stability of silver clusters stabilized in \(\gamma\)-irradiated synthetic sodalites with different guest anions.

### 2.3. Template deposited microstructures of silver haloids

Nowadays materials of micro-/nanoscale are widely investigated due to their unusual physicochemical properties. Template synthesis in pores of different kinds of membranes for receiving materials having assumed dimensions (length and diameter) among others silver halides is widely applied \[5\text{-}12\].

At the Institute of Nuclear Chemistry and Technology (INCT) investigations concerning micro-/nanostructures of silver haloids deposited in track-etched membranes (TMs) as templates have been conducted. The membranes might be manufactured in a cyclotron generating swift heavy ions which passing through a thin polymer film (usually polyester or polycarbonate) forming a set of latent tracks. After UV sensitization and chemical etching, membranes with precisely determined pores (of diameters in the range from 0.2 up to 2.5 µm) were produced. It is possible also to use TMs with pore diameters smaller than 0.2 µm.

The influence of 10 MeV EB radiation and 366 nm UV on the membranes with deposited silver halides microstructures was studied.

### 3. Materials and Methods

#### 3.1. Interaction between inorganic and polymeric components in a hybrid system

The presented study provides insight into designing polymeric catalysts based on the understanding of the effect of molecular interactions between radiation induced polymer network and metal complexes \[13\]. In the reported series of experiments matrix was synthesized from acrylic acid AAc and acrylamide AAm aqueous solutions polymerized during irradiation with \(\gamma\)-rays.

Petri dishes were filled with appropriate amounts of aqueous solution and irradiated in a gamma source (Gamma Chamber 5000) to a dose of 20 kGy. Then the samples were heated for 24 h at 30°C in vacuum, washed with water and dried in an oven at 60°C. In this way monolithic films were obtained by solution cast in a teflon-lined plate.

The complexation of Cu\(^2+\) and Ag\(^+\) ions with the gels was carried out by the batch equilibrium method. Dried gels were placed in 16 mM AgNO\(_3\) or CuCl\(_2\) solutions and allowed to equilibrate for 24 h. Subsequently the samples were exposure to gamma-rays, dried and studied by spectroscopic and thermal methods.
3.2. Paramagnetic silver clusters in sodalites

Sodium class B sodalites, in which only some cages are filled with different guest anions, were synthesized under mild hydrothermal conditions at 150°C and autogenous pressure for 7 days. Additionally sodalite with oxalate anion was synthesized from gel at 95°C.

Silver cations were loaded into the framework cages by room temperature cation exchange with AgNO₃ solution kept in dark. After exchange the samples were repeatedly washed with distilled water and dried in air. The stoichiometry compositions were calculated based on the results of inductively coupled plasma (ICP) analysis and were: Ag₄Na₄-SOD (for OH⁻ i CO₃²⁻ anions) and Ag₃Na₅-SOD (for C₂O₄²⁻ anion). The AgNa-sodalites were degassed at room temperature or dehydrated at 250°C in vacuo.

All samples were γ-irradiated in a ⁶⁰Co-source at liquid nitrogen temperature (77 K) with a dose of 4 kGy. The EPR spectra were recorded with an X-band Bruker ESP-300E spectrometer equipped with variable temperature Bruker unit operating in the temperature range 100-350 K.

3.3. Template deposited microstructures of silver haloids

TMs made of polyethylene terephthalate (PET) film (10 μm thick) and irradiated in the Joint Institute for Nuclear Research, Dubna, Russia, have been used as a template. In such a way the cylindrical pores with diameters of 0.2, 0.4, 0.7, 1.2 or 2.3 μm were formed.

In order to obtain desired particles an appropriate procedure of chemical synthesis has been applied. A sample of TM was compressed in the two-part mould (Fig 7) and contacted with the various aqueous solution simultaneously from both sides. 1 N AgNO₃ solution was introduced on one side of the mould and 1 N NaCl or NaBr aqueous solution on the opposite side thus in the pores and on the surfaces of membrane a replacement reaction was carried out. The process was performed for 1 up to 10 min and subsequently the solutions were removed, the sample was washed in distilled water and finally dried.

Scanning electron microscope (SEM) was used for studying surface morphology of the sample. The membrane fractures were examined by a DSM 942 Zeiss-Leo, Germany. Elemental analysis of the obtained structures was carried out using an X-ray microanalysis (Quantax 400 Bruker, Germany).

4. Results and discussion

4.1. Interaction between inorganic and polymeric components in a hybrid system

The effect of mono- and divalent metal ions on the structure of P(AAc/AAm) copolymers has been investigated by EPR spectroscopy. An example of typical spectrum recorded for Cu(II) in P(AAc-AAm) matrix at various temperatures is shown in Figures 1A and B. From the anisotropic signal the coordination geometry of Cu²⁺ might be suggested.

The resolved parallel hyperfine features of the monomeric Cu²⁺ are as follows: A_H = 14.0 mT and g_H=2.37 and correspond to a distorted molecular tetrahedral geometry. Such values are characteristic for oxygen containing ligands. Kruczala et al. [14] reported that two types of
monomeric Cu(II)-poly(acrylic acid)s are formed in which Cu$^{2+}$ was coordinated by one or two carboxylic acid groups on the polymer chains. The parameters are changing if the sample is annealed to ambient temperature as $A_{II}$ decreases to 12.3 mT whereas $g_{II}$ increases indicating modifications in metal ion coordination. It seems that in this case the amine group contribution as a ligand might be taken into consideration.

A triplet at $g=2.0030$ was attributed to the organic radical generated in the matrix. The same spectrum was found for the system Ag/P(AAc/AAm) at 240 K. It seems that at 240 K relaxation of the metal centre surrounding leads to the configuration corresponding Cu/P(AAc/AAm) system as under cryogenic conditions only a broad singlet was confirmed. The triplet was assigned to the $-\text{CH}_2\text{C}^\bullet\text{R}-\text{CH}_2$ radical where $R = -\text{COOH}$ or $-\text{CONH}_2$ when two $\beta$-protons show hyperfine splitting about 2.5 mT whereas two other protons weak splitting is the linewidth.

![EPR spectra](image)

*Fig. 1. EPR spectra of irradiated P(AAc/AAm) in the presence of Cu$^{2+}$ (A and B) and Ag$^+$ (C and D)*
Fig. 2. Swelling of AAc/AAm gels at pH=7 and pH=4 in the presence of Cu$^{2+}$ and Ag$^+$.  

The decrease in swelling capacity in the presence of mono- and divalent metal ions is mainly due to the screening effect. However, the decrease in swelling results also from complexation of the ions by ligands presented as functional groups in macromolecules, which increases apparent cross-link density. Metal ions also affect characteristic for the copolymer dependence between pH and swelling.

Fig. 2. demonstrates that the sorption effect of gels is predominantly related to the acidity of aqueous solutions. For pH below pK of AAc the swelling is low, whereas after deprotonation degree of swelling significantly increases. Additionally, in the presence of metal ions the diffusion of molecules is limited not only by intramolecular bonding network but also by the coordination of metal ions by functional group of polymeric chain. Such additional nodes increase density of network diminishing water penetration.

On the other hand, after exposure to gamma-radiation (5kGy) the ordered surrounding of metal centres inhibits development of crosslinking as the diagrams of swelling versus time revealed higher swelling values in the presence of the cations. The cations might facilitate oxidative degradation catalyzing redox reactions.

Summary: For P( AAc/AAm) matrices the rate of swelling and its equilibrium level decrease significantly with increasing network density. These results show that the interior space is filled up by water molecules, and the process develops fast from surface inwards. Additionally, 3D polymer networks containing acrylic acid and acrylamide were characterized.
by completely different features in the non-ionized state (low pH) than in ionic form (high pH). Coordinated silver and copper ions introduce to the polymeric material additional nodes restraining diffusion.

4.2. Paramagnetic silver clusters in sodalites

Materials with sodalite structure, while not generally consider as belonging to the family of zeolites, are nonetheless very closely related. The building block of the sodalite structure is cubo-octahedron of corner-connected tetrahedra or sodalite cage, which is also a component of zeolite A, X and Y (Fig.3). The unit cell of sodalite consists of two cages with single cage stoichiometry $Na_4X(AlSiO_4)_3 \times 2$ H$_2$O, where X represents a negative ion (e.g. OH or halogen) and has tetrahedral coordination with four sodium cations as nearest neighbours.

![Fig. 3. The framework structure of sodalite.](image)

The sodalite structure is chemically highly adaptable in terms of substitution in both the framework and cubo-octahedral interstices (ionic sites). The center of sodalite cages can be occupied by halides, chalcogenides and oxyanions which can be surrounded by alkali metal cations but also Ag$^{+}$, Ca$^{2+}$, Cd$^{2+}$ and other metal.

The EPR spectra of silver sodalites synthesized at 150°C with different guest anions (hydroxyl, oxalate and carbonate anions) dehydrated at 250°C and recorded at 110K were complex and consist of anisotropic doublet due to divalent silver cations Ag$^{2+}$, silver atoms and 9-line, near isotropic multiplet with $g=1.997$ and hyperfine coupling $A=8.2$ mT (Fig.4). The multiplet was assigned to silver octamer Ag$_8^{m+}$ with postulated charge +7. After thermal annealing above 270 K all signals decay. The silver octamer is more stable than similar cluster in high-temperature synthesized microcrystal sodalite, which decays at 200 K [4].
The EPR spectra of hydrated samples recorded at 110 K showed mainly signals due to divalent silver cations \( \text{Ag}^{2+} \), silver atoms \((A_{iso}= 54.0 \text{ mT}, g_{iso}= 2.002)\) and overlapped various signals from silver clusters and radiation-induced framework defects (Fig.5). During thermal annealing till 240K weak signals due to \( \text{Ag}_8^{19+} \) appeared. Only the spectrum of sodalite with \( \text{CO}_3^{2-} \) anion differed and showed more complicated multiplet. We postulate that due to interaction with water one silver atom is nonequivalent and interacts with seven atom cluster. The best fit was obtained for \( g=2.002, A_1(7 \text{Ag})=6.9 \text{ mT}, A_2(1 \text{Ag})=3.4 \text{ mT}. \)

The agglomeration pathway in dehydrated sodalite sample synthesized from gel with oxalate anions at 95°C is significantly different than previous one. The EPR spectrum recorded at 110K shows signals due to \( \text{Ag}^{2+} \) anions and silver atoms \( \text{Ag}^0 \). After thermal annealing to 280K \( \text{Ag}^{2+} \) and \( \text{Ag}^0 \) disappeared and new signal gained its importance. It is almost isotropic sextet with \( A_{iso}=9.2 \text{ mT}, g_{iso}=1.976 \) and was tentatively assigned to \( \text{Ag}_5^{19+} \) cluster (Fig.6).
Because the initial silver concentration in both samples were the same, we suppose that difference in agglomeration processes are due to different sizes of sodalite crystalities. In sodalite synthesized at 150°C crystalites are size of 5 μm, whereas in sample from 95°C the size is only 0.5 μm. Smaller crystal sizes allow silver cations to diffuse to surface and local concentration of silver is lower and leads to smaller cationic silver cluster inside sodalite cages.

Summary: In sodalite with different guest anions silver agglomeration occurs directly after irradiation at liquid nitrogen temperature, when silver atoms and cations are not mobile. It requires preliminary arrangement of silver cations during thermal dehydration process. We postulate that Ag₈⁷⁺ octamer is formed by trapping radiolytically produced electron by a set of eight silver cations located in the same cage. Silver agglomeration process in sodalites is controlled first of all by water molecules located inside sodalite cages. The higher degree of dehydration the larger amount of empty cages inside which migration of the reduced silver species is easier. The type of guest anion plays rather secondary role. On the other hand, the nuclearity of silver clusters stabilized in sodalites depends also on the size of sodalite crystallites.

4.3. Template deposited microstructures of silver haloids

In the first stage silver halide particles were formed via AgNO₃ + NaCl → AgCl reaction. The product images are shown in Fig 8. The images demonstrate covered with micrograins surfaces of TMs having a pore size either 0.4 or 0.7 μm. It is worth noting that on the AgNO₃ solution side there is a very small amount of micrograins of dimension 0.4 μm and smaller. On the other hand, on the NaCl solution side, the amount of the micrograins is greater and their size also is larger than on the surface which was in the contact with AgNO₃ (from about 0.5 μm up to 4 μm). Fig. 8 shows also fractures of the samples with deposited microstructures whose size corresponds to the diameter of membrane pores. One can observe characteristic „mushroom” arrangements when microrods and micrograins create one structure.
Microrods in the pores and micrograins on the membrane surfaces were investigated by an X-ray microanalysis. The data presented on Fig. 9 made possible to determine weight contribution of Ag/Cl elements for both sides of the sample. It was confirmed that AgCl of stoichiometric participation of elements was deposited into the membrane pores and on the membrane surfaces.
In the second series of experiments the microparticles were deposited in TM pores and on membrane surfaces using the AgNO$_3$ + NaBr system, Fig 10. Surfaces and fractures of the selected samples with a pore size of 0.2 μm are presented on Fig. 10A. Micrograins having a size of 0.4 – 5 μm are seen only on the surfaces previously being in contact with NaBr solution.

Fig. 9. Results from X-ray microanalyzer for deposited microstructures resulted from reaction: AgNO$_3$ + NaCl.
Fig. 10B shows effects of AgBr deposition in TM pores of diameters either 1.2 or 2.3 μm. Inside pores there are microrods constructed from grains of 130-200 nm size. On the membrane surfaces AgBr micrograins are seen only at the side of NaBr solution. Their size is 2-4 μm and 5-8 μm for TMs having pore diameters 1.2 or 2.3 μm, respectively.

The membranes comprising AgCl structures have light-violet color whereas the samples containing AgBr structures – light-yellow color. Colors of the samples practically do not change in scattering visible light contrary to the AgCl or AgBr compounds prepared in bulk which becoming dark due to precipitation of silver macroparticles.

Fig. 10. A - Microstructures of AgBr deposited in TMs with pore size 0.2 μm. Left column – membrane sides at AgNO₃ solution; right column - membrane sides at NaBr solution. B- Surfaces of TMs with deposited AgBr microstructures. Upper line – pore size: 1.2 μm; lower line - pore size: 2.3 μm. Left column – membrane sides at AgNO₃ solution; right column - membrane sides at NaBr solution.

TM with deposited silver halides microstructures were irradiated by UV (366 nm) or by 10 MeV electron beam (28 kGy and a multiple thereof: 56 and 84 kGy). In the last case a linear electron accelerator Elektronika 10-10 at the Centre of Radiation Research and Technology, INCT, was applied. After exposure to EB darkening of the samples was observed for all applied doses. To register the extent of the changes a photometric method was used and the exemplary results are shown on Fig. 11A.

After irradiation the membranes were examined by SEM and selected results for AgBr deposits in TMs having a pore size of 0.2 μm. Each row of the microphotographs presents selected SEM magnification of 1000, 5000, or 10000x. The left column of the images shows the non-irradiated samples. It seems that after irradiation with UV or EB, middle and right columns respectively, the morphology of surfaces was modified as previously separated micrograins are combined into larger structures.
Fig. 11. A - Photometric measurements of irradiated AgBr microstructures in TM. B - Surfaces of TMs (0.2 μm pore size) with AgBr micrograins at different SEM magnification (from upper line respectively: 1000, 5000, 10000x). Left column – the reference: non-irradiated sample; middle column – the sample exposure to UV (366 nm) for 45 min; right column – the sample irradiated with EB (10 MeV) with a dose of 84 kGy.

Summary

— It was confirmed that silver halides microrods in membrane pores and micrograins on membrane surfaces were deposited.
— Migration of silver cations through track membrane is more intensive than chloride/bromide ions.
— Color of the silver haloids microstructures practically does not change in scattering visible light what is in contrast with darkening of silver halides prepared in bulk.
— The microstructures darkened after exposure to UV (366 nm) and EB (10 MeV) what was confirmed by a photometric method. The effect results from changes in micrograins morphology identified by SEM.
— It seems that silver halide microstructures can be used as indicators of UV or ionizing radiation.

Acknowledgments

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References

Abstract

The research activities in Serbia are related to radiolytic synthesis of nanocomposites with Ag-nanoparticles (Ag NPs) incorporated in polymer matrix composed of chitosan (CS) and/or poly(vinyl alcohol) (PVA). The obtained results indicate the good stability of Ag NPs as well as uncrosslinked Ag-CS/PVA nanocomposites over a long period of time. It was found that the composition of CS/PVA matrix affects the size of the obtained Ag NPs, as well as the parameters such as density, molar concentration and the effective surface area. Spherical Ag NPs with the average diameter around 13 nm and face centered cubic structure were stabilized through interaction with –OH and –NH₂ groups of the polymers. Moreover, it was confirm that gamma irradiation method is suitable for formation of crosslinked PVA/CS polymer networks, which can serve as a matrix for further radiolytic in situ incorporation of Ag NPs, in order to obtain crosslinked nanocomposites.

1. Introduction

The major challenges in designing of polymer nanocomposites are the ability to control the size and the morphology of nanoparticles, as well as to achieve their homogeneous distribution through the polymer. Several methods for the preparation of polymer nanocomposites are known, but they are mostly based on in situ polymerization in the presence of nanoparticles [1] or on incorporation of previously synthesized nanoparticles in the polymer [2]. However, by these methods, sometimes it is too difficult to achieve homogeneous distribution of nanoparticles and prevent their agglomeration in the polymer. Therefore, the method of in situ synthesis of nanoparticles within polymer matrix was investigated in many studies [3-5].

The gamma irradiation induced reduction of metal ions in polymer solutions i.e. radiolytic in situ synthesis of metal nanoparticles in the presence of polymers such as chitosan (CS) and poly(vinyl alcohol) (PVA) or other bio- and synthetic polymers, is particularly suitable for preparation of nanocomposites based on Ag-nanoparticles (Ag NPs) incorporated in polymer matrix. The advantage of in situ radiolytic method, over the other methods, is possibility to obtain a homogeneous distribution of synthesized Ag NPs within the polymer matrix as well as to control their size by changing the experimental conditions. The obtained material is clean and sterilized at the same time, which is very important in the case of their potential biomedical applications. The presence of polymer molecules during the radiolytic in situ synthesis of Ag NPs significantly suppresses the process of their agglomeration and further growth, by interaction of polymer’s functional groups with a high affinity for the metal with atoms on the surface of metal clusters [6-9].
In this study, the CS and PVA were used as capping agent for stabilization of Ag NPs, during their in situ gamma irradiation induced synthesis. Chitosan is a linear polysaccharide primarily composed of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of b-(1,4)-linked 2-deoxy-2-acetamido-D-glucopyranose units. It is prepared by the deacetylation of chitin, the most abundant natural polymer after cellulose. Chitin is not easily soluble in any solvent. Nevertheless, unlike chitin, chitosan is dissolved in aqueous solutions of some organic and inorganic acids and becomes cationic polymer because of protonation of amino groups present on the C-2 position of the pyranose ring. Chitosan consists of a large number of functional amino groups and hydroxyl groups. Since chitosan is non-toxic and biocompatible with the human physiological system, it has been investigated as biomaterial in the fields such as biomedicine, pharmacology and biotechnology, and has already been used in agricultural, food, industrial and medical fields [10]. In addition, the antibacterial properties of chitosan are suitable for use as wound dressings, and further improvement of wound healing is achieved by incorporation of Ag NPs, which also exhibit antibacterial properties. Chitosan can also be applied in the process of reducing radiation damage to the radiation workers or radiation cured patients as well as in other areas of oncology [11]. Poly(vinyl alcohol) is a vinyl type polymer, produced by free radical polymerization of vinyl acetate monomers. The degree of hydrolysis, i.e. the content of acetate groups in the polymer, has a comprehensive impact on its physico-chemical properties. Poly(vinyl alcohol) is non-toxic, water soluble, biocompatible and biodegradable polymer that is widely used in biochemical and biomedical applications [12,13].

On the other hand, many nanomaterials such as titanium dioxide, zinc oxide, magnesium oxide or copper exhibit significant antibacterial properties, but nanocrystalline silver has proved as most effective antimicrobial agent. Ag NPs exhibits strong antimicrobial activity and a wide biocide inhibitory spectrum against microbes, both bacteria and viruses, and even euakaryotic microorganisms, in vitro and in vivo. In addition, Ag NPs have high optical absorption efficiency, which is very suitable for biomedical diagnostics, biosensors and heat absorption in special devices [14].

Moreover, the radiolytic method has been recognized as highly suitable tool to aid in the formation of hydrogels. Hydrogels are hydrophilic bi- or multi-component systems consisting of three-dimensional network of polymer chains and liquid that fills the space between macromolecules. It is characteristic that hydrogels have possibility to absorb large amount of water or biological liquids and, as a consequence, swell i.e. increase its mass and volume, but not dissolved. Due to this property they are biocompatible and similar to biomaterials, which is the main reason for their wide use in medicine and pharmacy. The radiation process has various advantages, such as easy process control, the possibility of joining hydrogel formation and sterilization in one technological step, the lack of necessity for initiators and crosslinkers, which are possibly harmful and difficult to remove. These qualities make irradiation the method of choice in the synthesis of hydrogels. On the other hand, limited studies have been reported concerning the radiolytic formation of metal nanoparticles in hydrogel matrix (template synthesis). Hydrogels in the swollen state provide free spaces within the network, which can also serve for nucleation and growth of nanoparticles. In this way, the carrier-hydrogel system acts as a nanoreactor that immobilizes nanoparticles and provides easy handling, giving a new hybrid nanocomposite systems. Therefore, highly stable and uniformly distributed nanoparticles with predetermined dimensions and size-dependent properties have been achieved by a very delicate balance between the reaction conditions, the composition
and the structure of hydrogel templates, and the concentration of nanoparticles [15]. Nanocomposite based hydrogels synthesized by gamma irradiation have attracted great attention due to their various applications in biomedicine, pharmaceutics, optic, photonics, and catalysis.

Ag NPs in systems based on CS and PVA, as a stabilizer, can be obtained by reduction of Ag$^+$ ions by using sodium borohydride or by using the functional groups of polymers themselves (–COOH, –NH$_2$, –OH) [1,16]. In this study, Ag NPs were in situ synthesized by gamma irradiation, using CS/PVA blends as a capping agent. Reduction of Ag$^+$ ions was performed by radiolytically formed reduction species. The influence of composition of CS/PVA blends on optical and structural properties of obtained Ag-CS/PVA nanocomposite systems was investigated. Moreover, the crosslinking of PVA in the presence of CS was performed in order to obtain PVA/CS polymer networks as a matrix for further in situ incorporation of Ag NPs. The swelling properties of PVA/CS polymer networks were investigated in deionized water at 25±1 °C.

2. Experimental part

Poly(vinyl alcohol) (PVA) with molecular weight 72 000 g/mol and 99% of minimal degree of hydrolysis, silver nitrate (AgNO$_3$) and 2-propanol ((CH$_3$)$_2$CHOH) were products of Merck. A medium molecular weight chitosan (CS) with 200-800 cP viscosity (1% solution in 1% acetic acid) and 75-85% degree of deacetylation was obtained from Sigma-Aldrich, while acetic acid (CH$_3$COOH) was product of Zorka Pharma. All chemicals were commercial products of analytical grade and were used without additional purification. Water from Millipore Milli-Q system was used in all experiments, while the high purity argon gas (99.5%) from Messer Tehnogas was used for removing the oxygen from solutions. The irradiations were performed at room temperature using $^{60}$Co gamma source.

The aqueous solutions of PVA (5% (w/w) and 10% (w/w)) were prepared by dissolving PVA at 90 °C under the constant stirring for 6 h and 24h, respectively. The solution of CS (2.5% (w/w)) was prepared by dissolving the CS in aqueous solution of CH$_3$COOH (5% (v/v)), at room temperature under the constant stirring for 3 h.

Preparation of uncrosslinked Ag-CS/PVA nanocomposites. Solutions of CS (2.5% (w/w)) and PVA (5% (w/w)) were used to prepare solutions in which the mass ratios of CS/PVA were 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100. In all prepared solutions, AgNO$_3$ and (CH$_3$)$_2$CHOH were added up to the concentration of 5 mM and 0.2 M, respectively. In order to remove oxygen, solutions were bubbled with Ar for 30 min, and then exposed to gamma-rays to the absorbed dose of 8.5 kGy for reduction of 5 mM Ag$^+$ ions, at a dose rate of 6 kGy/h. After solvent evaporation from obtained Ag-CS/PVA colloids, at room temperature, the uncrosslinked Ag-CS/PVA nanocomposites (10-30 µm thick films) were formed.

Crosslinking of PVA in the presence of CS. PVA (10% w/w) and CS (2.5% (w/w)) solutions were used to prepare solutions with the different PVA/CS mass ratios (100/0, 97/3, 95/5, 93/7 and 90/10), and constant total weight of polymers in the systems (7% (w/w)). Solutions were bubbled with Ar for 30 min to remove oxygen, and exposed to gamma-rays to the absorbed dose of 25 kGy, at a dose rate of 0.5 kGy/h. The obtained crosslinked PVA/CS polymer networks were immersed in an excess of deionized water, changed every 12 h for 3 days, to remove uncrosslinked polymer, and dried at room temperature.
Methods of characterization. The optical properties of obtained Ag-CS/PVA colloids and nanocomposites were investigated by UV-Vis absorption spectroscopy. Absorption spectra were recorded using Thermo Fisher Scientific Evolution 600 Spectrophotometer, in the wavelength range of 300-800 nm. Theoretical calculations of the size of Ag-nanoparticles were made using software “MiePlot V.3.4”. Scanning electron microscopy (SEM) analysis of Ag-CS/PVA nanocomposites was performed on JEOL JSM-6610LV instrument, operated at an accelerating voltage of 20 kV. Prior to the analysis of surface morphology, the samples were coated with thin layer of gold (around 15 nm). Microstructural properties of Ag-CS/PVA nanocomposites were investigated by X-ray diffraction (XRD) measurements performed on Bruker D8 Advance Diffractometer (Cu Kα1 radiation, λ = 0.1541 nm). FTIR spectra of CS, PVA and Ag-CS/PVA nanocomposites were recorded using Thermo Electron Corporation Nicolet 380 Spectrophotometer, working in ATR mode (Attenuated Total Reflection Mode). Swelling studies of obtained crosslinked PVA/CS polymer networks were performed using dry gels (xerogels). Hydrogels were cut in the form of discs (diameter \(d\) = 10 mm, thickness \(\delta\) = 4 mm), dried to the constant weight, and then used in swelling investigations. The xerogel discs were immersed in an excess of deionized water to obtain equilibrium swelling at 25±1 °C. Process of swelling was monitored gravimetrically by measuring weights of swollen hydrogel at predetermined time intervals.

3. Results and discussion

Uncrosslinked Ag-CS/PVA nanocomposites

The ions of noble metals can be reduced by exposing their aqueous solutions to gamma irradiation in order to obtain metal nanoparticles. To prevent clusters collision and their growth into bigger nanoparticles during formation, the polymer molecules with functional groups that have a great affinity for metals were added. In the case of CS and PVA, the amino (–NH₂) and hydroxyl (–OH) groups interact with the atoms on the surface of metal nanoparticles and thus stabilize them, preventing their further growth (Fig. 1a) [7,17,18].

After the gamma irradiation, the yellow colored Ag-CS/PVA colloids were obtained (Fig. 1b), which is characteristic of Ag NPs. These colloids are transparent and stable for a long period of time. By absorption spectroscopy it was confirmed that the optical properties of the synthesized Ag-CS/PVA colloids does not change for 9 months (results not shown), which clearly indicates that there is no agglomeration of Ag NPs. Moreover, even after evaporation of solvent from the Ag-CS/PVA colloids and formation of transparent Ag-CS/PVA nanocomposites the agglomeration of Ag NPs was not observed, and the nanocomposites retains the same yellow color as starting colloids (Fig. 1c).
Fig. 1. Proposed mechanism of stabilization of Ag NPs (a) and photographs of Ag-CS/PVA: colloid (b) and nanocomposite (c).

Fig. 2. UV-Vis absorption spectra of Ag-CS/PVA colloids.

Fig. 2 depicts the absorption spectra of synthesized Ag-CS/PVA colloids, which clearly indicates the presence of surface plasmon resonance (SPR) bands of Ag NPs, with the characteristic maximum of absorption at about 410 nm. Such intensive absorption occurs as consequences of collective oscillations of conductive electrons, caused by interaction of metal nanoparticles with electromagnetic radiation. The precise position, intensity and width of the SPR band depends on a number of compositional attributes, including nanoparticle size, shape and surface structure and medium dielectric constant, refractive index and temperature, within three discrete size domains, namely quantum (< 2 nm), intrinsic (2-20 nm) and extrinsic (> 20 nm) regimes. For nanoparticles in the extrinsic regime, information concerning the precise nanostructure can be inferred from the relative position of the SPR band, with larger nanoparticles resulting in a red shift to lower energies (shift to higher $\lambda_{\text{max}}$ in absorption spectra), while for particles smaller than 20 nm the situation becomes more complicated [19]. In this case, the average radius of the nanoparticles can be determined by the width of their corresponding SPR band. Their symmetry can be estimated by fitting to the experimental absorption spectrum to a simulated one calculated using a theoretical model considering different shapes for the nanoparticles. The simplest exact theoretical model is given by Gustav Mie, and it describes the effect of light on a spherical metallic nanoparticle embedded in a dielectric medium. The classical theory developed by Mie [20] predicts that the SPR wavelength should be independent of the particle size when the mean particle diameter is smaller than the incident wavelength. For Ag NPs with radii ($r$) in the range 1-10 nm, the $1/r$ size dependence of the FWHM (full width at half maximum) of the SPR band was observed,
and the quasi-static approximation of the Mie theory can be applied. In this size regime, the relation \[ r_{\exp} = \nu_f / \Delta \omega_{1/2} \] can be used, where \( r_{\exp} \) is the particle radius, \( \nu_f \) is the Fermi velocity of the metal, and \( \Delta \omega_{1/2} \) is the FWHM for the SPR band in units of angular frequency [21]. The calculated mean particle radii of Ag NPs by this method are given in Table 1.

Assuming that the silver bulk density is \( 5.86 \times 10^{22} \) atoms/cm\(^3\) it is possible to determine the average number of atoms \( N_{av} \) belonging to spherical nanoparticles in metallic phase and the nanoparticles density \( (D) \) in the sample as a first approximation [22]. The average number of atoms in Ag NPs was calculated using equation \[ N_{av} = \rho(\text{Ag}) V_{sf} \], where \( V_{sf} \) is volume of the nanosphere. Dividing the total amount of Ag atoms \( (N_{tot}, \text{equivalent to the initial amount of silver salt added to the reaction solution}) \) by the average number of atoms in each nanoparticle, a density for the Ag NPs in the colloid can be estimated. In addition, the molar concentration of the Ag NPs in colloids were calculated by \[ C = N_{tot} / (N_{av} V_N) \], were \( V_N \) is the volume of the reaction solution and \( N_A \) is the Avogadro’s constant [23]. The theoretical effective surface area \( (S.A.) \) of Ag-nanoparticles was also calculated by \( S.A. = 6 / D_{sf} \rho \), were \( D_{sf} \) is the diameter of Ag NPs and \( \rho \) is the theoretical density of silver \( (10.5 \text{ g/cm}^3) \) [24]. The obtained values for the parameters of Ag NPs: the average number of atoms \( (N_{av}) \), the density in colloids \( (D) \), the molar concentration in colloids \( (C) \) and the theoretical effective surface area \( (S.A.) \) are listed in Table 1.

**TABLE 1. THE OBTAINED VALUES FOR THE PARAMETERS OF AG NPS STABILIZED BY CS/PVA BLENDS: THE RADIUS \( (r_{\exp}) \), THE AVERAGE NUMBER OF ATOMS \( (N_{av}) \), THE DENSITY IN COLLOIDS \( (D) \), THE MOLAR CONCENTRATION IN COLLOIDS \( (C) \) AND THE THEORETICAL EFFECTIVE SURFACE AREA \( (S.A.) \).**

<table>
<thead>
<tr>
<th>CS/PVA</th>
<th>FWHM (nm)</th>
<th>( r_{\exp} ) (nm)</th>
<th>( N_{av} )</th>
<th>( D ) ( \text{(NPs/cm}^3) )</th>
<th>( C ) ( \text{(mol/dm}^3) )</th>
<th>S.A. ( \text{(m}^2/\text{g}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>91.3</td>
<td>6.74</td>
<td>74961</td>
<td>4.02 \times 10^{12}</td>
<td>6.67 \times 10^{-9}</td>
<td>42.39</td>
</tr>
<tr>
<td>80/20</td>
<td>91.2</td>
<td>6.73</td>
<td>74666</td>
<td>4.03 \times 10^{12}</td>
<td>6.69 \times 10^{-9}</td>
<td>42.45</td>
</tr>
<tr>
<td>60/40</td>
<td>90.8</td>
<td>6.70</td>
<td>73858</td>
<td>4.08 \times 10^{12}</td>
<td>6.77 \times 10^{-9}</td>
<td>42.64</td>
</tr>
<tr>
<td>40/60</td>
<td>83.8</td>
<td>6.18</td>
<td>58024</td>
<td>5.19 \times 10^{12}</td>
<td>8.61 \times 10^{-9}</td>
<td>46.23</td>
</tr>
<tr>
<td>20/80</td>
<td>80.1</td>
<td>5.91</td>
<td>50694</td>
<td>5.94 \times 10^{12}</td>
<td>9.86 \times 10^{-9}</td>
<td>48.34</td>
</tr>
<tr>
<td>0/100</td>
<td>74.8</td>
<td>5.52</td>
<td>41203</td>
<td>7.31 \times 10^{12}</td>
<td>12.10 \times 10^{-9}</td>
<td>51.76</td>
</tr>
</tbody>
</table>

Taking into account the calculated values for the Ag NPs radii (Table 1), the corresponding theoretical optical extinction spectra are simulated using the software “MiePlot v.3.4” [25], which algorithm is based on Mie’s theory i.e. on scattering and absorption cross sections of isolated spherical nanoparticles in solution. Program “MiePlot v.3.4” calculates efficiencies \( (Q_{ext} \text{ - extinction, } Q_{abs} \text{ - absorption, } Q_{sca} \text{ - scattering}) \) as functions of wavelength. Basically, light absorption dominates in the extinction (extinction = absorption + scattering) spectrum for particles relatively small radius \( (< 20 \text{ nm}) \), and light scattering becomes the dominant process for large particles [26]. Fig. 3 shows the optical extinction spectra of Ag-CS/PVA colloids which are experimentally obtained (solid line) and obtained by simulation according to the Mie theory (dashed line). The values of average Ag NPs radii obtained by the fitting to experimental spectra are also given in Fig. 3.
In general, a good agreement between experimentally and theoretically obtained optical extinction spectra was observed, with a better adjustment for larger Ag NPs. For all samples, the experimental spectra present a shift from 7 nm to 15 nm in the position of SPR band towards longer wavelengths with respect to the simulation. These red shifts have been observed previously [22], and they are probably result of the increasing density of nanoparticles ($D$) with decreasing of particle size. The density of Ag NPs increase from $4.02 \times 10^{12}$ NPs/cm$^3$ in the sample CS/PVA (100/0) ($r_{exp} = 6.74$ nm) up to $7.31 \times 10^{12}$ NPs/cm$^3$ in the sample CS/PVA (0/100) ($r_{exp} = 5.52$ nm) (Table 1). Also, the shifts on the SPR band can be affected by different atomic parameters in very small particles compared to those used in the calculations, corresponding to the Ag bulk material. Furthermore, the calculations based on the Mie theory depend on the radius of the nanosphere and on the refraction indexes of the matrix and the metal, and is the reason why these shifts also can be related to differences in the dielectric constants (Peña et al., 2007). As already mentioned, the absorption of light is dominant over the scattering for very small nanoparticles, as confirmed by simulation (Fig. 4). The simulation results also show that contribution of scattering in extinction spectra increases with increasing the size of Ag NPs from 6.51 % for sample Ag-CS/PVA (0/100) ($r_{sim} = 6.75$ nm) up to 11.94 % for sample Ag-CS/PVA (80/20) ($r_{sim} = 8.46$ nm).
According to the values of Ag NPs radii, calculated from experimentally obtained UV-Vis absorption spectra (Table 1) as well as from Mie’s simulation (Fig. 3), it can be observed that smaller nanoparticles were produced when the PVA content in the blend is greater than 50%. Theoretical studies have shown that the compatibility of CS and PVA in the blend is greater in the systems with the PVA content less than 50% [27]. In the case of greater compatibility of CS and PVA, probably the better interactions of blend components caused the weaker stabilization during synthesis i.e. the formation of larger Ag NPs as a consequence.

The UV-Vis absorption spectra of synthesized Ag-CS/PVA (40/60) colloid, corresponding nanocomposite and colloid obtained by dissolving the nanocomposite are presented in Fig. 5. For all investigated systems, the red shift in the position of SPR band of nanocomposite (red curve), in comparison with starting colloid solution (black curve), was observed. This red shift can be mainly explained by the change of the dielectric constant of surrounding medium in which particles are dispersed. Namely, in the case of nanocomposite Ag-nanoparticles are dispersed in the polymer ($n_{\text{PVA}} = 1.53$; $n_{\text{CS}} = 1.55$), whereas in the case of colloid they are dispersed in water ($n_{\text{H2O}} = 1.33$). The increasing on refractive index of surrounding medium causes the shift of SPR band towards longer wavelengths. In addition, the long-wave shift of SPR band of nanocomposite compared to starting colloid solution can be consequence of charge particle redistribution at the particle-matrix interface [28]. To exclude any possibility that observed changes in position of SPR band are consequence of agglomeration of Ag-nanoparticles upon formation of nanocomposite, the Ag-CS/PVA nanocomposite was dissolved in water and absorption spectrum (green curve) was compared with absorption spectrum of starting colloid (black curve). Absorption spectrum of the dissolved nanocomposite has SPR band at 409 nm, and it is almost identical to the absorption spectrum of starting colloid (407 nm) indicating that observed optical changes are not the consequence of agglomeration of Ag NPs. These small differences of SPR band position are caused by the formation of a thin polymer layer-shell on nanoparticles surface [3,5].
Fig. 5. UV-Vis absorption spectra of Ag-CS/PVA (40/60) colloid, corresponding nanocomposite and colloid obtained by dissolving of nanocomposite.

Fig. 6. SEM micrograph of Ag-CS/PVA (40/60) nanocomposite and size distribution of Ag NPs (inset). Morphological properties of Ag-CS/PVA nanocomposites were examined by scanning electron microscopy (SEM). The obtained micrograph of Ag-CS/PVA (60/40) nanocomposite and particle size distribution of synthesized Ag NPs are shown in Fig. 6. The average size of Ag-nanospheres was found to be 12.7 nm, estimated from the histogram by subtracting the size of the gold layer of 15 nm.

The X-ray diffraction pattern of Ag-CS/PVA (60/40) nanocomposite is shown Fig.7. Diffraction maxima at 2θ angle values of 38.0°, 44.2°, 64.4° and 77.6° correspond to Bragg's reflections from the crystal planes (111), (200), (220) and (311), which are characteristics of the face centered cubic crystal structure of Ag NPs. The crystalline domain size, calculated by Scherrer's formula, was found to be 13 nm, which is in a good agreement with average diameter of Ag-nanoparticles estimated by SEM and UV-Vis spectra [3,7]. The results of optical (UV-Vis), morphological (SEM) and structural (XRD) analysis show that the obtained Ag NPs are less than 20 nm in diameter, i.e. they are within the intrinsic regime [19].
Fig. 7. XRD pattern of Ag-CS/PVA (40/60) nanocomposite.

Fig. 8. FTIR spectra of pure CS, Ag-CS/PVA nanocomposites and pure PVA.

The interaction of CS and PVA macromolecules with incorporated Ag NPs, and nature of particle stabilization was investigated by infrared spectroscopy. In Fig. 8, the FTIR spectra of pure CS, pure PVA and Ag-CS/PVA nanocomposites are presented. It can be clearly seen that there is no formation of new bands neither as a consequence of mixing of CS and PVA, or as a consequence of formation of nanocomposites with Ag NPs.

In the range of 3000 to 3600 cm\(^{-1}\) the band intensity decreases from pure CS (Graph 1) up to Ag-CS/PVA (40/60) nanocomposites (Graph 3). In this area, the wavenumbers of CS are corresponding to the following vibrations: 3445-3455 cm\(^{-1}\) O–H stretching vibrations of hydrogen bond; 3380-3420 cm\(^{-1}\) intermolecular OH...3 and CH\(_2\)OH hydrogen bonds, 3250-3260 cm\(^{-1}\) intermolecular C(21)NH...O=C(73) hydrogen bonds; 3140-3150 cm\(^{-1}\) intermolecular C(61)OH...HOC(62) hydrogen bonds; 3270-3290 cm\(^{-1}\) N–H stretching vibrations. In the case of PVA, the band at 3250 cm\(^{-1}\) corresponds to stretching vibration of –OH groups, linked by intermolecular and intramolecular hydrogen bonds, and it is very
The decrease of band intensity in this area from pure CS (Graph 1) or PVA (Graph 4) to CS/PVA (40/60) can probably be related to the changes in the compatibility of CS and PVA. Namely, according to molecular modelling simulations it was predicted that compatibility of CS and PVA blends is greater for the content of PVA less than 50% [27]. Therefore, better stabilization of Ag NPs was achieved by the less compatible blend system, in this case CS/PVA (40/60) resulting in the stronger interaction between the Ag NPs and polymers, decreasing particle radius, increasing density (\(D\)) and higher molar concentration (\(C\)) of Ag NPs, as well as larger effective surface area (S.A.), as shown in Table 1. This is in accordance with previous studies which show that the interaction between polymer and nanoparticles increases with decreasing size of nanoparticles. Table 2 shows the wavenumbers of characteristic bands and corresponding assignments for CS and PVA. The results are in agreement with data for CS and PVA found in the literature [28-30].

**TABLE 2. WAVENUMBERS OF CHARACTERISTIC BANDS FOR THE FTIR SPECTRA OF CS AND PVA**

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3445-3455</td>
<td>O–H streching</td>
</tr>
<tr>
<td>3380-3420</td>
<td>Intermolecular OH…3 and CH(_2)OH hydrogen bonds</td>
</tr>
<tr>
<td>3250-3260</td>
<td>Intermolecular C(2,1)NH…O=C(7,3) hydrogen bonds</td>
</tr>
<tr>
<td>3140-3150</td>
<td>Intermolecular C(6,1)OH…HOC (6,2) hydrogen bonds</td>
</tr>
<tr>
<td>3270-3290</td>
<td>N–H streching</td>
</tr>
<tr>
<td>2873</td>
<td>C–H streching</td>
</tr>
<tr>
<td>1643</td>
<td>C=O–NH–CH(_3) streching (amide I band, (\alpha)-chitin, (\beta)-chitin, and partially deacetylated chitosan)</td>
</tr>
<tr>
<td>1630</td>
<td>N–H bending of NH(_2)</td>
</tr>
<tr>
<td>1550</td>
<td>Amide II band</td>
</tr>
<tr>
<td>1380</td>
<td>C–H bending and C–CH(_3) deformation mode</td>
</tr>
<tr>
<td>1320</td>
<td>Amide III band</td>
</tr>
<tr>
<td>1151</td>
<td>Glucose linkage/C–O–C bridge (asymmetric (antisymmetric) stretching)</td>
</tr>
<tr>
<td>1070</td>
<td>C–O–C streching</td>
</tr>
<tr>
<td>1020</td>
<td>C–O–C streching</td>
</tr>
<tr>
<td>890</td>
<td>C–O–C bridge (gluosidic linkage)</td>
</tr>
<tr>
<td>PVA</td>
<td></td>
</tr>
<tr>
<td>3250</td>
<td>–OH from the intermolecular and intramolecular hydrogen bonds</td>
</tr>
<tr>
<td>2944</td>
<td>C–H from alkyl groups</td>
</tr>
<tr>
<td>1750-1735</td>
<td>C=O of vinyl acetate groups</td>
</tr>
<tr>
<td>1411</td>
<td>–OH in-plane</td>
</tr>
<tr>
<td>1325</td>
<td>Coupling of the O–H in-plane with C-H wagging</td>
</tr>
<tr>
<td>1142</td>
<td>Symmetric C–C stretching mode</td>
</tr>
<tr>
<td>849</td>
<td>–CH out-of-plane</td>
</tr>
</tbody>
</table>

**Crosslinked PVA/CS polymer networks as a matrix for in situ incorporation of Ag NPs**

In the second part of our work, crosslinking of PVA in the presence of CS was investigated, in order to obtain crosslinked PVA/CS polymer networks as a matrix for further \textit{in situ} formation of Ag NPs. The different amounts of CS were added to PVA (PVA/CS weight ratios were 100/0, 97/3, 95/5, 93/7 and 90/10) to investigate the influence of CS concentration
on network parameters and swelling behavior in water, as well as to determine diffusion properties of hydrogels.

When a xerogel is brought into contact with a solution, the solution diffuses into the network and volume phase transition occurs, resulting in the expansion of the hydrogel. Diffusion involves the migration of fluid into pre-existing or dynamically formed spaces between the hydrogel chains. The capacity of swelling is one of the most important parameters for evaluation the properties of hydrogels. Fig. 9 (left) depicts the swelling curves of the investigated crosslinked PVA/CS polymer networks in deionized water at 25 °C. As can be seen, the swelling isotherms are similar in shape, but introduction of large quantities of CS has influence on the swelling properties as well as on characteristic network parameters. The obtained values for gel fraction (Gel(%)), xerogel density (ρxg), average molar mass between the network crosslinks (Mc), pore size (ξ) and equilibrium swelling degree (SDeq) are listed in Table 3.

To obtain a more quantitative understanding of the nature of the sorption kinetic in crosslinked PVA/CS polymer networks, the initial swelling data were fitted to equation

\[
\frac{M_t}{M_{eq}} = k t^n
\]

were \(M_t\) is the amount of absorbed water in time \(t\), \(M_{eq}\) is the maximum absorbed amount, \(k\) is a kinetic constant, incorporating characteristics of macromolecular

![Swelling curves of crosslinked PVA/CS polymer networks in deionized water at 25 °C (left) and the best linear fits of linear parts of swelling curves ln SD/SD_{eq} vs. ln t (right).](image)

**TABLE 3. CHARACTERISTIC NETWORK PARAMETERS FOR CROSSLINKED PVA/CS SYSTEMS AND PARAMETERS OBTAINED FROM SWELLING MEASUREMENT IN WATER AT 25°C: GEL FRACTION (Gel(%)), XEROGEL DENSITY (ρxg), AVERAGE MOLAR MASS BETWEEN THE NETWORK CROSSLINKS (Mc), PORE SIZE (ξ), EQUILIBRIUM SWELLING DEGREE (SD_{eq}), INITIAL RATE OF SWELLING (V_{in}), KINETIC CONSTANT (k), DIFFUSION EXponent (N) AND DIFFUSION COEFFICIENT (D).**

<table>
<thead>
<tr>
<th>PVA/CS</th>
<th>Gel (%)</th>
<th>ρxg (g/cm³)</th>
<th>Mc (g/mol)</th>
<th>ξ (nm)</th>
<th>SD_{eq} (%)</th>
<th>V_{in} (%/min)</th>
<th>k (1/min)</th>
<th>n</th>
<th>D (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>88.9</td>
<td>0.89</td>
<td>9432</td>
<td>15.4</td>
<td>430</td>
<td>2.9</td>
<td>0.028</td>
<td>0.55</td>
<td>1.01∙10⁻⁷</td>
</tr>
<tr>
<td>97/3</td>
<td>88.2</td>
<td>0.91</td>
<td>10474</td>
<td>16.4</td>
<td>448</td>
<td>8.6</td>
<td>0.025</td>
<td>0.70</td>
<td>2.35∙10⁻⁷</td>
</tr>
<tr>
<td>95/5</td>
<td>87.2</td>
<td>0.91</td>
<td>13997</td>
<td>19.6</td>
<td>513</td>
<td>11.0</td>
<td>0.023</td>
<td>0.73</td>
<td>2.63∙10⁻⁷</td>
</tr>
<tr>
<td>93/7</td>
<td>86.0</td>
<td>0.92</td>
<td>14643</td>
<td>20.2</td>
<td>524</td>
<td>16.1</td>
<td>0.044</td>
<td>0.60</td>
<td>2.64∙10⁻⁷</td>
</tr>
<tr>
<td>90/10</td>
<td>83.6</td>
<td>0.88</td>
<td>15108</td>
<td>20.7</td>
<td>539</td>
<td>22.2</td>
<td>0.049</td>
<td>0.60</td>
<td>3.05∙10⁻⁷</td>
</tr>
</tbody>
</table>
network system and the penetrant, $n$ is the diffusion exponent, which is indicative of the transport mechanism. This equation is valid for initial stage of swelling i.e. for the first 60% of the normalized solvent uptake. The characteristic constants $n$ and $k$ were calculated from the slope and intercept, respectively, of the linear parts of logarithmic form of kinetic equation of swelling. The obtained results are presented in Table 3, and indicated that hydrogel systems show non-Fickian or anomalous diffusion ($0.5 < n < 1$) when the rates of diffusion and polymer chain relaxation are comparable. The study of diffusion phenomena of water in hydrogels is important because that clarifies the polymers behavior. For hydrogel characterization, the diffusion coefficients ($D$) can be calculated by using the equation $D^n = \frac{k}{4} \left( \frac{\pi}{r^2} \right)$, were $r$ is the radius of gel disc. As can be seen from Table 3, the values of diffusion coefficients increase with an increase in CS content, indicating the easier diffusion of water molecules into PVA/CS polymer network, giving the greater capacity of swelling ($SD_{eq}$).

4. Conclusions

Obtained results indicated that gamma irradiation is suitable for in situ synthesis of Ag NPs in CS/PVA matrix as a capping agent, with different ratio of polymers, in order to obtained uncrosslinked nanocomposites. Ag$^+$ ions are reduced and protected from agglomeration by interaction with the polymer molecules, and all obtained nanosystems were stable over a long period of time. UV-Vis absorption spectra of Ag-CS/PVA colloids showed SPR band having $\lambda_{\text{max}}$ around 410 nm, which confirms the formation of Ag NPs. It was found that the composition of CS/PVA system affected the size of the obtained Ag NPs, as well as the parameters such as density, molar concentration and the effective surface area, calculated from the experimentally obtained UV-Vis absorption spectra and spectra obtained by simulation according to the Mie theory. Spherical morphology of Ag NPs is confirmed by SEM micrograph, and the average diameter of the particle is around 13 nm. Microstructural analysis of synthesized Ag-CS/PVA nanocomposite was performed by XRD measurement, and obtained results indicate that Ag NPs have face centered cubic structure, with the crystalline domains around 12 nm. The results of FTIR spectroscopy showed that the stabilization of Ag NPs occurs through their interaction with $-\text{OH}$ and $-\text{NH}_2$ groups of the polymers, and that the interaction increases with increasing of PVA content in the blends.

Moreover, it was confirm that gamma irradiation method is suitable for formation of crosslinked PVA/CS polymer networks, which can serve as a matrix for further in situ incorporation of Ag NPs. Swelling properties of synthesized PVA/CS hydrogels were investigated in the deionized water at 25 °C and obtained results show that the increasing of CS content influenced the swelling properties of hydrogels. The investigation of diffusion properties of PVA/CS hydrogels indicate that systems showed non-Fickian diffusion ($0.5 < n < 1$) when the rates of diffusion and polymer chain relaxation are comparable.

References


PREPARATION AND CHARACTERIZATION OF PLA-STARCH BIODEGRADABLE COMPOSITES VIA RADIATION PROCESSING

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Abstract

This research aims to modify starch surface to make it more compatible with polylactic acid (PLA) as well as to find an optimum condition for crosslinking of PLA by gamma radiation. The surface modification of starch granules was carried out using L-lactic acid. While working on the modification of starch surface, pure PLA was used to find the optimum condition for its radiation-induced crosslinking. The mixture of PLA and a crosslinking agent was irradiated by gamma radiation at different doses. The gamma irradiation was done in two atmospheres; in air and in vacuum. Gel fraction and differential scanning calorimetry (DSC) were used to determine crosslinking efficiency. Results showed that the presence of a suitable crosslinking agent enables PLA to undergo crosslinking induced by gamma radiation. The optimum condition for radiation-induced crosslinking of PLA was; TAIC at 3 phr, gamma irradiation at 60 kGy and samples irradiated in vacuum. The results from both gel fraction and DSC experiments confirmed that the presence of oxygen molecules in air atmosphere induced oxidative degradation of PLA molecules, whereas the absence of oxygen molecules in vacuum atmosphere led to the dominance of crosslinking between PLA molecules. TMA results also confirmed the prevalent crosslinking as well as higher thermal stability of PLA samples irradiated in vacuum in the presence of TAIC.

1. Introduction

Poly(lactic acid) or polylactide (PLA) is a compostable thermoplastic obtained by ring-opening polymerization of lactide monomers which can be derived from renewable resources [1], such as starch or sugarcanes. In recent years, PLA has been receiving a great deal of attention, essentially due to its degradability. For this environmental-friendly profile, along with a highly transparent appearance, similar to that of polyethylene terephthalate (PET), PLA has undoubtedly become one of the most promising alternatives to non-biodegradable synthetic polymers conventionally derived from petroleum-based chemicals. Nonetheless, two of the most important factors that prevent PLA from being commercially and widely used are its low thermal stability [2-3] and high cost, compared to commercial plastics such as polyethylene (PE) or PET commonly used in packaging materials. Renewable resources such as starch are relatively inexpensive and therefore able to offer a competitive commercial strategy. The proposed blending between PLA and starch derivatives is designed to combine the processability and PET-like properties of PLA with the high thermal stability of starch derivatives. This work intends to utilize radiation processing as a means to overcome the aforementioned shortcomings associated with PLA, by blending PLA with starch derivatives and using radiation-induced cross-linking to improve thermal stability of the blends and their composites.
Chen et al. [4] developed a new method for the surface modification of starch by esterification reaction of the hydroxyl groups on starch molecules with lactic acid. The surface modified starch was then used as a macromolecular initiator for the ring-opening polymerization of L-lactide to synthesize the starch grafted PLLA copolymer (St-g-PLLA). The amphiphilic character of St-g-PLLA showed good adhesion between the two components and therefore was a good compatibilizer for bleeding hydrophobic PLA with hydrophilic starch by melt blending.

When subjected to radiation, PLA undergoes degradation process [5]. However, a number of researchers [6-9] have discovered that, with a suitable crosslinking agent, electron beam can induce crosslinking between PLA molecules. The beginning part of this research aims to modify starch surface to make it more compatible with PLA as well as to find an optimum condition for crosslinking of PLA by gamma irradiation, in the presence of a crosslinking agent.

2. Experimental

2.1. Materials

Commercial cassava starch was obtained from Siam Quality Starch Co., Ltd. Lactic acid was purchased from Merck. Polylactic acid (PLA 2002D) was purchased from Nature Works® (USA). Triallyl isocyanurate (TAIC) was supplied by Aldrich (USA). Chloroform (Lab Scan) was used as received.

2.2. Surface Modification of Starch Granules by Lactic Acid

30 g of cassava starch was dispersed in 100 ml of THF. 30 g of lactic acid was gradually dropped into the suspension. The mixture was stirred and heated to 60 °C and maintained at constant temperature for 30 min. The THF solvent was removed by evaporation and 150 ml of toluene was added into the mixture. The mixture was heated to 150 °C and kept for 10 h under stirring. The water formed was removed by azeotropic dehydration with toluene. The mixture was washed five times with THF and ethyl acetate, respectively, to remove non-grafted lactic acid. It was then filtrated and dried in vacuum oven at 60 °C for 24 h to remove the residual solvent.

2.3. PLA Samples Preparation and Irradiation

PLA pellets were dried in a vacuum oven at 75°C for 24 h. A co-current twin-screw extruder (Lab Tech, LTE16-40, Thailand), equipped with segmented screw of 16 mm diameter and L/D ratio of 40, was used to mix PLA with TAIC at different concentrations: 0, 1, 3 and 5 phr (hereafter referred to as T0, T1, T3 and T5, respectively). The temperatures of barrel heating zone I, II, III, IV and of the die of the extruder were set to 155, 175, 185, 195, and 200°C, respectively. The TAIC-containing PLA pellets were then compressed by a compression molder (Lab Tech, Thailand) to form 150 mm x 150 mm x 0.2 mm films. The pellets were pre-pressed and full-pressed at 200°C for 8 and 2 min, respectively, followed by cold-pressing at room temperature for 2 min.
The film samples were irradiated at the Office of Atoms for Peace (OAP) using a Co-60 gamma irradiator (GammaCell® 220 Excel, Nordion, Canada) at 0, 20, 40, 60, 80 and 100 kGy, in both air and vacuum.

2.4. Gel Fraction Measurement

After irradiation, the film samples were dissolved in chloroform (CHCl3) for 48 h to determine gel fraction using the following equation,

\[ W_0 - Wg \]

where \( W_0 \) is the initial weight of dried sample before the gel fraction test and \( Wg \) is the remaining weight of dried samples after the gel fraction test.

2.5. FTIR and DSC Measurements

Chemical characterization of the samples was done using a Fourier Transform Infrared Spectrometer from Bruker (Tensor 27). Spectra were collected with 16 co-added at a resolution of 4 cm\(^{-1}\). Thermal properties of the film samples were characterized by a Differential Scanning Calorimeter (DSC 822e from Mettler Toledo, Thailand), from 25°C to 225°C under nitrogen atmosphere at a heating rate of 10°C/min.

2.6. TMA Measurement

A Thermomechanical Analyzer (Mettler Toledo, TMA/SDTA 841\(^{e}\)) was used to study the thermo mechanical properties of the samples. Sample films (thickness 0.2mm) were fixed to the sample holder under a constant load of 0.5 g (0.004 Newton) and heated from 0°C to 260°C at a heating rate of 10°C/min. Deformation (%) against the temperature was recorded.

3. Results and Discussion

3.1. The Surface Modification of Starch by Lactic Acid

Figure 1 shows the reaction for the surface modification of starch by lactic acid. After azeotropic dehydration of the starch with toluene, the hydroxyl groups on the surface of starch granules reacted with lactic acid to form starch carboxylate bonds. FTIR spectra of starch and surface modified starch are shown in Figure 2. The FTIR spectrum of cassava starch shows the following characteristic absorption bands: 3200-3600, 2932, 1155, 1078, 1016 and 927 cm\(^{-1}\), while that of surface modified starch shows similar pattern with an additional peak at 1740 cm\(^{-1}\) due to C=O stretching vibration. This additional peak confirms the presence of carboxylate bonds and thus the surface modification of starch by lactic acid.
Fig. 1. The surface modification of starch with lactic acid.

Fig. 2. FTIR spectra of starch (bottom) and surface modified starch.

3.2. Crosslinking of TAIC-containing PLA by Gamma Radiation

FTIR was used to confirm the presence of TAIC in TAIC-containing PLA samples. Chemical structures of PLA and TAIC are shown in Figure 3.

Fig. 3. Structures of PLA (left) and TAIC (right).

Figure 4 shows the FTIR spectra of T0 and T5 samples. The FTIR spectrum of T0 sample shows characteristic peaks of PLA with three strong peaks at 1750, 1180 and 1080 cm\(^{-1}\) corresponding to C=O stretch in ester, C-O-C antisym stretch in ester and C-O-C sym stretch in ester, respectively. T5 sample shows similar FTIR spectrum with an additional peak at approximately 1690 cm\(^{-1}\) which corresponds to C=O stretch in tertiary amide, confirming the presence of TAIC in T5 sample.
Figure 5 shows gel fraction of the film samples irradiated in air and under vacuum as a function of TAIC concentration and radiation dose. For both atmospheres, gel fraction was 0% for all T0 samples, implying that, without TAIC, gamma radiation cannot induce crosslinking between PLA molecules. For both atmospheres, T1 samples showed relatively low or even 0% gel fraction, suggesting that TAIC at 1 phr was too low to induce crosslinking. For T3 and T5 samples, in both atmospheres, gel fraction increased with increasing TAIC concentration, confirming the ability of gamma radiation, in the presence of TAIC, to induce crosslinking between PLA molecules. Moreover, T3 and T5 samples showed similar gel fraction, which were relatively high, compared with those of T1 samples. The gel fraction of T3 and T5 samples increased with increasing dose up to 60 kGy, after which the gel fraction started decreasing. This trend was quite obvious for the samples irradiated in the presence of air. This is due to the fact that, during irradiation, the energy transferred to polymer chains can induce alterations in chemical and molecular structures. The two major effects are crosslinking and degradation, which can occur simultaneously, depending on the
chemical structure and dose. At low doses, radiation can promote crosslinking over degradation reactions, whereas at high doses, radiation can induce intensive chain scissions, ultimately leading to the dominance of degradation reactions over crosslinking. A comparison between two atmospheres showed that T3 and T5 samples irradiated in vacuum showed higher gel fraction than those irradiated in air. This stems from the fact that, in air, oxygen was also irradiated generating highly reactive free radicals that can induce oxidation reaction and/or oxidative degradation of PLA molecules, thus reducing the efficiency of crosslinking. Gel fraction results implied that the optimum dose for the maximum gel fraction was 60 kGy.

3.3. Thermal Properties

Figures 6 shows the DSC thermograms of T0, T1, T3 and T5 samples irradiated at different doses, in air and vacuum, respectively. The unirradiated T0 sample showed three peaks at roughly 62, 120 and 150°C, corresponding to glass transition (T_g), recrystallization (T_c) and melting temperature (T_m) of PLA, respectively.

For T0 samples irradiated in air, T_m peaks separated into double peaks, while T_c peaks shifted to lower temperatures. Moreover, their T_g decreased with increasing dose, from roughly 62°C at 0 kGy to approximately 59°C at 100kGy. These results agreed very well with the results from the gel fraction test, indicating the oxidative degradation of PLA molecules irradiated in the presence of oxygen and the absence of a crosslinking agent. These oxidation and/or oxidative chain scission reactions finally brought about the introduction of irregularities. These irregularities, such as random degradation of crystalline regions, led to degraded PLA molecules that have a lower heat of fusion than crosslinked PLA molecules, thus resulting in doublet T_m peaks with one peak shifting to a lower temperature (Nugroho et al., 2001). The shift to lower temperatures of T_c was also caused by introduction of these irregularities, due to the presence of degraded crystalline components. DSC thermograms of T1 samples irradiated by gamma radiation in air showed similar patterns to those of T0 samples, with T_m peaks splitting into doublets and T_c peaks shifting to lower temperatures.

For T3 samples, their DSC thermograms also showed three peaks similar to those of T0 and T1 samples, displaying both the split of T_m into double peaks as well as the shift of T_c to lower temperatures. However, T3 samples irradiated in air additionally exhibited a split of T_g peaks into double peaks. The major difference between T0 and T3 samples was the presence of TAIC in T3 samples. Hence, the split of T_g peaks is most likely a result of the presence of both degraded and crosslinked PLA molecules in T3 samples, due to oxidative degradation in the presence of oxygen and crosslinking reactions in the presence of TAIC, respectively. The first T_g located at a lower temperature is possibly associated to degraded PLA molecules, whereas the second one located at a higher temperature is likely correlated to crosslinked PLA molecules. The fact that the split of T_g was not observed in T1 samples substantiated the results from the gel fraction test that TAIC concentration at 1 phr was too low to effectively induce crosslinking between PLA molecules. DSC thermograms of T5 samples were similar to those of T3 samples. However, the split of T_g in T5 samples became even more evident at high doses.
Fig. 6. DSC thermograms of T0, T1, T3 and T5 samples irradiated in air at 0, 20, 40, 60, 80 and 100 kGy, from bottom to top, respectively.

The DSC thermograms of PLA samples irradiated by gamma radiation under vacuum as a function of irradiation dose and TAIC concentration are shown in Fig. 7. The DSC thermograms of T0 and T1 samples irradiated by gamma radiation under vacuum were basically similar to those of T0 and T1 samples irradiated by gamma radiation in air. In contrast, major differences were noticeably evident in T3 and T5 samples. The DSC thermograms of unirradiated T3 and T5 samples were not largely different from those of unirradiated T0 and T1 samples. However, for TAIC-containing T3 and T5 samples subjected to gamma radiation under vacuum, their Tc and Tm peaks disappeared almost completely. These results affirmatively confirmed the crosslinking between PLA molecules which hindered their chain mobility, thus eventually restricting them from undergoing recrystallization as well as melting processes. The disappearance of Tc and Tm peaks of T3 and T5 samples irradiated at radiation dose as low as 20 kGy obviously demonstrated the high penetrating capability of gamma radiation.

Additionally, T3 and T5 samples irradiated by gamma radiation under vacuum did not show a split of Tg into a doublet but exhibited an increase in Tg with dose. This result implied that T3 and T5 samples irradiated by gamma radiation under vacuum did not undergo oxidation or oxidative degradation, but rather undertook crosslinking reactions in the absence of air and the presence of the crosslinking agent. Nevertheless, their Tg increased with increasing dose only up to 80 kGy. This result was, once again, in agreement with the results from the gel fraction test, confirming that, at high doses of gamma irradiation, degradation was more influential than crosslinking.
Fig. 7. DSC thermograms of T0, T1, T3 and T5 samples irradiated in vacuum at 0, 20, 40, 60, 80 and 100 kGy, from bottom to top, respectively.

3.4. Thermo mechanical Properties

Figures 8 shows the TMA thermograms of T3 samples irradiated at 0, 40, 60 and 80 kGy in both air and vacuum. T3 samples irradiated in air at 40 and 80 kGy elongated significantly at 60°C and broke soon after. T3 samples irradiated at 0 and 60 kGy started their initial elongation slightly after 60°C, continued their gradual elongation to higher temperatures and showed their drastic deformation at approximately 100°C and 190°C, respectively, after which they finally fractured. The significant elongation reflects the softening of the samples. All T3 samples irradiated in vacuum at 40, 60 and 80 kGy also showed initial elongation at around 70°C and continued to show their gradual deformation to higher temperatures. All T3 samples were thermally stable even after 200°C and showed approximately less than 15% of deformation even at 250 °C, without breaking. These results hence, once again, confirmed the radiation-induced of PLA samples irradiated in vacuum as well as the higher thermal stability of the samples irradiated in vacuum, compared with those irradiated in air.
Fig. 8. TMA thermograms of T3 samples irradiated at 0, 40, 60 and 80 kGy in both air and vacuum.

4. Conclusion

For the surface modification of starch, the surface of cassava starch granules has been modified by dehydration reaction of hydroxyl groups with lactic acid. Results from FTIR confirmed the presence of carboxylate groups in the surface modified starch. For the study to find the optimum conditions for the radiation-induced crosslinking of PLA by gamma irradiation, results showed that gamma radiation is able to induce crosslinking between PLA molecules, in the presence of TAIC as a crosslinking agent. The optimum condition for radiation-induced crosslinking of PLA in the presence of TAIC was: TAIC at 3 phr and gamma irradiation at 60 kGy in vacuum. Both gel fraction and DSC results demonstrated that oxygen exposure of samples irradiated in air led to oxidative degradation which decreased crosslinking efficiency. On the contrary, the samples irradiated in vacuum suffered much less degradation and predominantly undertook crosslinking reactions. Thermomechanical properties of radiation-induced crosslinked PLA also confirmed the predominant crosslinking as well as higher thermal stability of PLA samples irradiated in vacuum in the presence of TAIC.

5. Work Plan for Coming Year

The radiation-induced grafting polymerization of L-lactide onto the hydroxyl groups of the obtained surface modified starch will be performed. Starch-grafted-PLLA copolymer and PLLA homopolymer coexisting in the reaction products will be separated by toluene extraction. Starch-grafted-PLLA will be characterized and subsequently used as a plasticizer for blending PLA with starch, with and without clay, to form biodegradable composites. In order to further improve the thermal properties, the blends and their composites will be subjected to radiation to induce crosslinking between the molecules of PLA and starch derivatives. The mechanical, thermal and thermo mechanical properties of the blends and their composites will be analyzed.
References

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Abstract

Polymer/clay nanocomposites were prepared by melt intercalation by using torque rheometer. Poly(ethylene-vinyl acetate) (EVA 18) with 18 % wt. vinyl acetate was used as the base polymer, unmodified clay (Na\(^{+}\) montmorillonite, MMT), commercial organo-modified clays I44 P, I31 PS and clay modified by in-situ radiation polymerization of a charged monomer were used as the filler. Na\(^{+}\) montmorillonite was interacted with charged monomer [2-((Methacryloxy)ethyl]-trimethyl ammonium chloride in presence of water and through ion exchange with Na\(^{+}\) monomer was introduced between the clay plates. This mixture was irradiated to 10 kGy, 20 kGy, 30 kGy to load the clay with polymer. The conversion of monomer to polymer was followed by gravimetric measurements as well as FTIR_ATR spectroscopy. The maximum opening between clay layers was obtained at 30 kGy irradiated clay, which was measured by X-ray diffraction (XRD) analysis.

Structures of nanocomposites were characterized by ATR-FTIR, TEM (Transmission Electron Microscopy), XRD (X-Ray Diffraction) and PALS (Positron Annihilation Lifetime Spectroscopy).

The effect of addition of radiation-modified clay on mechanical properties of EVA 18 was examined by mechanic tests of nanocomposites. When the samples prepared using 30 kGy irradiated modified clay was compared with commercial organo-modified clays, 30 kGy radiation- modified clay gave better results than I44 P and similar with I31 PS.

1. Introduction

Nanocomposites are a new class of materials that are particle-filled composites in which at least one dimension of the dispersed particles is in the nanometer range. The addition of nanoclays to a polymer matrix has been proven to bring large improvement in the mechanical properties, thermal stability, fire resistance, gas barrier properties of starting polymeric materials [1]. Polymer nanocomposites have three components. These are polymers, inorganic nanofillers and compatibilizers. Montmorillonite is the most commonly used smectite-type layered silicates for the preparation of nanocomposites, which uses as a nanofiller. Smectites are a valuable mineral class for industrial applications because of their high cation exchange capacities, surface area/volume ratio, surface reactivity, easy processability and adsorption properties [2]. A number of polymer/clay nanocomposites with different polymer matrices have been prepared and studied by melt-blending since the report of Nylon-6/MMT nanocomposites from the Toyota research group [3]. Ethylene vinyl acetate copolymers (EVA) are one of the important polymers with broad applications, such as wire and cable insulation, hot melt adhesives and packaging. For polymers not containing polar functional groups, it is necessary to use a compatibilizer to increase the interaction between polymers and layered silicates. So, layered silicates are generally modified to obtain an organophilic structure by ion exchange reaction with cationic surfactants including primary, secondary,
tertiary, and quaternary alkylammonium in order to increase the interaction between hydrophobic polymer and hydrophilic layered silicate [4].

Polymer/layered silicate nanocomposites can be classified into three types depending on the level of dispersion and the strength of interfacial interactions between the polymer matrix and layered silicates. These are conventional composites, intercalated nanocomposites and exfoliated nanocomposites. If polymer molecules do not penetrate into the galleries, clay remains unchanged and forms conventional composites. If polymer enters into the galleries, distance between layers increase, but the clay layers remain stacked and forms intercalated nanocomposites. If the clay layers are completely separated from each other to create a disordered array, the composite is said to be exfoliated nanocomposites. The extent of dispersion of layers in polymer matrix depends on the interactions between polymer, clay, modifying agent and processing conditions [5].

In this study, poly (ethylene-vinyl acetate) (EVA18) containing 18% wt. vinyl acetate was used as the base polymer, Na-Montmorillonite (Na-MMT) and commercially available modified clays were used as inorganic nanofiller. Na-MMT was modified to enhance the interaction between EVA polymer and clay. [2-(Methacryloyloxy)ethyl]trimethyl ammonium chloride which is a charged monomer was used to modify clays instead of alkyl ammonium salts. Monomer impregnated clays were irradiated 10, 20, 30 kGy doses to introduce corresponding polymers in between the silicate layers. Nanocomposites were prepared by using melt intercalation method in different compositions. Later, the improvement in mechanical and structural properties of EVA18/clay nanocomposites was investigated.

2. Experimental Part

2.1. Materials

Poly(ethylene-vinyl acetate), containing 18% wt. vinyl acetate (EVA18) was obtained from Innospec Active Chemical, England, with melt flow index (MFI) 12.415±0.045 g/10 min. measured at 2.16 kg/190°C conditions. Unmodified Na-montmorillonite (Na-MMT), with a cation exchange capacity (CEC) value of about 145 meq/100g, was obtained from Nanomer/PGV Company. Commercial organoclays used were; Na-Montmorillonite modified by 3-aminopropyltriethoxysilane and octadecylamine (I31PS) and Na-Montmorillonite modified by dimethyl dialkyl (C14-C18) amine (I44P) were obtained from Nanomer. Clay modifying agent [2-(Methacryloyloxy) ethyl]-trimethyl ammonium chloride, with concentration 80% wt. was obtained from Sigma Aldrich.

2.2. Preparation of Modified Clays

The modified clays were prepared by cation exchange reaction between Na-MMT and [2- (Methacryloyloxy) ethyl]-trimethyl ammonium chloride in aqueous solution. The aqueous suspension solution containing 20 g Na-MMT and 16 ml [2-(Methacryloyloxy) ethyl]-trimethyl ammonium chloride was prepared in 100 ml of distilled water. The suspension was stirred at 25°C for 24 h and nitrogen gas was passed from this solution for 5 min. Then this solution was irradiated to 10 kGy to induce radiation polymerization of monomer inside the clay particles. The modified clay was washed and filtered with distilled water to remove polymers which formed outside the clay particles. Then the product was dried in vacuum oven at 60°C for 24 h. The modified clay was obtained and then was ground with a mortar and
sieved by a Cu griddle with 54 micron. The same preparation method was applied to 20 kGy and 30 kGy irradiated samples.

2.3. Preparation of Nanocomposites

Poly (ethylene-vinyl acetate)/clay mixtures were prepared (1% wt., 3% wt., 5% wt. clay loading) by using torque rheometer (Thermo Scientific Measuring Mixer and Extruder System, Haake Polylab OS). Mixing of EVA18 with clay was accomplished at 140°C, and 100 rpm for 20 minutes. After mixing, the samples were hot-pressed under 100 MPa to form sheets with suitable thickness for 3 min. at 150°C (Brabender, Polystat 200 T). These film samples were cut to dog-bone shape according to ASTM D638 standard and were used for stress-strain tests.

2.4. Characterization of EVA18/Clay Nanocomposites

XRD patterns were obtained by using a Japanese Rigaku D/Max-2200/PC X-ray diffractometer equipped with graphite mono-chromatized CuKα radiation (λ =0. 15406 nm). The scanning range was 2°-15° with a scanning rate of 2°/min.

The microstructures of nanocomposites were imaged using a Tecnai G2 F30 (300 kV) Transmission Electron Microscopy (TEM). The samples for TEM were cut to 200 nm thick sections with a diamond knife microtome (Leica Microsystems, Model EMUC6 + EMFC6).

Mechanical properties were measured using a ZWICK Z010 following ASTM D638 standard. The crosshead speed was 50 mm/min. All tensile data were the average of five independent measurements.

The free volume radia of composites were determined by an ORTEC Positron Annihilation Lifetime Spectrometer using 30 μCi 22NaCl as a positron source in sandwich formation (sample-source-sample). Spectra were analyzed by LT9 program available in the software of the system.

Spectroscopic characterization was made by using a Nicolet iS10 Diamond ATR-FTIR spectrometer. Each spectrum was obtained in the range of 4000-650 cm⁻¹.

3. Results and Discussion

3.1. Spectroscopic Measurements

Unmodified clay was interacted with charged monomer [2- (Methacryloxy) ethyl]-trimethyl ammonium chloride in presence of water and through ion exchange reaction monomer filled the space between the silicate layers. Later, this mixture was irradiated 10 kGy, 20 kGy, 30 kGy for in-situ polymerization of the monomer.

FTIR-ATR spectra given in Figure 1 were obtained for the polymer formed in clays as a result of irradiation. The intensity of peaks due to the polymer obtained by 30 kGy irradiation can be seen to be more intense than 10 kGy and 20 kGy samples indicating directly increasing conversion of monomer to polymer. The formation of polymer inside the MMT silicate layers has also been followed gravimetrically and found that 7.2, 7.7 and 8.1 g polymer formed in 20
g clay after 10, 20 and 30 kGy irradiation respectively. Table 1 shows the amount of polymer in clay and corresponding % weight ratios.

**TABLE 1. THE AMOUNT OF POLYMER FORMED IN CLAY AND % WEIGHT RATIOS**

<table>
<thead>
<tr>
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<th>10 kGy</th>
<th>20 kGy</th>
<th>30 kGy</th>
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<tr>
<td>(g)</td>
<td>7,2</td>
<td>7,7</td>
<td>8,1</td>
</tr>
<tr>
<td>(%)</td>
<td>36</td>
<td>39</td>
<td>41</td>
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**Fig. 1. FTIR spectra of polymers obtained inside the clay irradiated to (a) 10 kGy (b) 20 kGy (c) 30 kGy.**

**3.2. Mechanical Properties**

Binary blends of EVA18/clay were prepared by using EVA 18, and natural montmorillonite, the same modified by 10, 20, 30 kGy irradiation in the presence of the charged monomer and two commercial organo-modified clays I31PS and I44P. The evaluation of stress-strain curves yielded the major mechanical properties such as elastic modulus, tensile strength and elongation at break. The Figures 2-4 show the changes in these mechanical properties as a function of clay composition in the range of 1-5%. All the EVA18/clay nanocomposites exhibited some improvement in both E-Modulus and tensile strength. E-Modulus and tensile strength values for EVA18/30 kGy composite samples show better results than EVA18/10 kGy, EVA18/20 kGy, EVA18/I44P and EVA18/Na-MMT composite samples. When compared with EVA18/I31PS, similar results were obtained for EVA18/30 kGy irradiated modified clay. E-Modulus and tensile strength values of composite samples increased with increasing clay content. The elongation at break values for composite samples were found to be inferior which is an expected result considering the inverse relation between the modulus and elongation. The elongation at break values for composite samples decreased with decreasing clay content. Clay is modified to obtain organophilic structure. Thus, distance between layers increase and the interaction between polymer and clay increases. Intercalated and exfoliated nanocomposites are obtained by using modified clays. Intercalated and exfoliated structures give better results compared to the microcomposites. The results show that observed improvements in the mechanical properties are due to the presence of both intercalated and exfoliated structures.
Fig. 2. Change of E-Modulus of EVA18/clay nanocomposites loaded with different clays.

Fig. 3. Change of Tensile Strength values of EVA18/clay nanocomposites with different type and amount of clay loading.
3.3. Positron Annihilation Lifetime Spectroscopy (PALS) Measurements

Positron Annihilation Lifetime Spectroscopy (PALS) was used to see the changes taking place in the sizes and distribution of free volumes in the EVA18/clay nanocomposites. A typical PALS spectrum recorded for the EVA18-5% 30 kGy composite sample is given in Figure 5. When the master, uppermost curve was deconvoluted to separate the contributions coming from amorphous and crystalline portions of EVA18/clay nanocomposites, respective free volume hole radii were determined for these two domains. The results of data analysis of similar PALS spectra obtained for every EVA18/clay nanocomposites are collected in Table 2. Here, $r_c$ is the hole radius of free volume of crystalline parts and $r_a$ is the radius in the amorphous parts.
Fig. 5. PALS spectrum for EVA18-5% 30 kGy composite sample. Yellow curve is due to crystalline part and grey for the amorphous part of EVA/clay nanocomposites.

The size of the free volume holes in the EVA-modified clay nanocomposites were determined by using the equation given below which was developed by Tao (1972)[6] and Eldrup et al (1981)[7].

\[
\tau_{o-Ps} = 0.5 \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R + \Delta R} \right) \right]^{-1}
\]

In this equation \(\tau_{o-Ps}\) is the lifetime of the \(o\)-Ps in ns, R is the radius of free volume holes in nm, and \(\Delta R\) is a constant whose value is 0.1656 nm.

**TABLE 2. VALUES OF AVERAGE RADIUS OF FREE VOLUMES IN EVA18/CLAY NANOCOMPOSITES**

<table>
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<th></th>
<th>EVA 18</th>
<th>EVA18/ I44 P</th>
<th>EVA18/ I31 PS</th>
<th>EVA18/ 10 kGy</th>
<th>EVA18/20 kGy</th>
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<td>0.185 ±0.003</td>
<td>0.333 ±0.004</td>
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<td>0.328 ±0.004</td>
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<td>% 3</td>
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<td>% 5</td>
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The values of average radius of composite samples are smaller in crystalline parts as compared to amorphous parts. A significant reduction in free volume hole radius was observed from EVA18-5% 30 kGy and EVA18-5% I31PS composite samples. Composite samples, which are prepared by radiation modified clays, are more compatible with polymer and have better distribution. Because of this, decreasing in free volume hole radius is an expected situation.

3.4. Thermogravimetric Analysis (TGA)

The thermogravimetric analyses of the nanocomposites have been carried out to study the effect of the clay and the type of modified clay on the resistance of the various nanocomposites towards thermal degradation. The degradation of poly (ethylene-vinyl acetate) (EVA) takes place in two steps. First, deacetylation is observed between 350 and 400°C from poly(vinyl acetate) moieties, with production of gaseous acetic acid and formation of carbon-carbon double bonds along the polymer backbone. The second step (between 400-500°C) is arising from main chain degradation of polymer. Figure 6 shows TGA derivative curves of EVA 18, EVA 18-% 5 I44 P, EVA 18-% 5 I31 PS and EVA 18-% 5 30 kGy composite samples. When looking closely on derivative curves, both the first and second degradation temperature of composite samples occur at higher temperature compared to EVA18 copolymer. Thermal degradation delay is mainly due to barrier effect and insulator properties of clay, thus polymeric structure becomes more stable. Also, well dispersed modified silicate layers can act more efficiently as diffusion barrier than unmodified silicate layers, inducing a much efficient delay in volatiles evolved from the thermally degraded EVA.

![Fig. 6. TGA derivative curves of EVA 18, EVA 18-% 5 I44 P, EVA 18-% 5 I31 PS and EVA 18-% 5 30 kGy composite samples.](image)
3.5. X-Ray Diffraction (XRD) Measurements

Every composite sample was analyzed by X-Ray Diffraction (XRD) in order to investigate whether intercalation and/or exfoliation occur. The distance between layers of the clays and composite samples were calculated from Bragg’s equation and are given in Table 3. Figure 7 shows the X-ray diffraction (XRD) pattern of Na-MMT and 10, 20 and 30 kGy modified clays. For 10, 20 and 30 kGy modified clays; there are intense peaks at 4.38, 4.18 and 3.84° respectively, which are shifted from the diffraction peak of the Na-MMT at 6.98°. This confirms that polymer, which was obtained from charged monomer by irradiation, intercalated into the layers of the clay and increased the distance between layers.

Figure 8 shows XRD patterns of EVA18/clay nanocomposites using different modified clays. EVA18/Na-MMT composite has the same basal spacing like Na-MMT. This indicates that the chains of EVA could not intercalate into the layers of Na-MMT. Thus, microcomposite structure formed. For EVA18-5% I44P, EVA18-5% I31PS and EVA18-5% 10 kGy composites, there are obvious shifts to lower angles from that of the corresponding I44P, I31PS and 10 kGy modified clays. The peaks of EVA18-5% I44P, EVA18-5% I31PS and EVA18-5% 10 kGy nanocomposites indicate the clay layers remain stacked and distance between layers increased. The structures of these nanocomposites are intercalated nanocomposites. However, for EVA18-5% 20 kGy and EVA-5% 30 kGy composites, there are no peaks. If the clay layers are completely separated from each other, diffraction peaks are not observed in XRD due disordered array. So, these last two composite samples are said to be exfoliated nanocomposites.

![Figure 7. X-ray diffraction (XRD) pattern of Na-MMT and 10, 20 and 30 kGy modified clays.](image-url)
4. Conclusions

We have investigated the effect of radiation-modified montmorillonite on the morphology, tensile and thermal properties of nanocomposites obtained by melt blending of Poly(ethylene-vinyl acetate) (EVA 18) containing 18 wt% vinyl acetate with clay. While nanocomposites, prepared by using commercially available organo-modified clays exhibit intercalated structures, the nanocomposites based on radiation modified clays exhibit both intercalated and exfoliated structures, which were characterized by XRD and TEM. Modification of montmorillonite was achieved by radiation-induced in-situ polymerization of a charged...
monomer namely, [2-(Methacryloxy) ethyl]-trimethyl amonium chloride impregnated within the galleries of silicate layers. Loading of clays with the polymer increases the spacing between the layers from 1.27 nm up to 3.45 nm in intercalated and much higher in exfoliated structures. Incorporation of modified clays into EVA matrix causes an increase in tensile and E-modulus and thermal degradation due to good interaction between polymer and clays. 50% increase in tensile strength for EVA18/30 kGy composite samples was achieved as compared to pure EVA. E-Modulus and tensile strength values of composite samples increased with increasing clay content. Considering the TGA results, the onset of both first and second degradation temperatures of composite samples were found to occur at higher temperatures due to barrier effect and insulator properties of clay. PALS investigation has shown a decrease in the free volume hole radius upon clay loading due to better distribution of clay layers in polymer matrix and consequent compact structure.

References


RADIATION-INDUCED SYNTHESIS OF MAGNETIC NANOCOMPOSITES

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Abstract

We report the preparation and characterization of nanocomposites of magnetite in 2-ethylhexyl acrylate (2-EHA) – acrylic acid (AA) co-polymers as well as ionomers obtained by the reaction of FeCl₃ with such co-polymers. These co-polymers were prepared through gamma and pulsed electron beam irradiation of a mixture of the monomers in an organic solvent. Gamma irradiation was used to measure co-polymer yields at various ratios of 2-EHA:AA and pulse radiolysis was used to follow the buildup and decay of radicals during the formation of the co-polymers.

Co-polymer synthesis and reaction with the iron-containing species was followed by drying of the nanocomposite or by dialysis in the case of the ionomers. The products were characterized by means of FTIR, XPS, SEM-EDS, TEM, chemical analysis and magnetization using a vibrating sample magnetometer (VSM). The results obtained for the magnetite nanocomposites are indicative of a mixed ferromagnetic – superparamagnetic behavior associated with a distribution of particle size where the superparamagnetic behavior is associated with the smaller particles. The magnetization of these nanocomposites is proportional to the concentration of magnetite in the co-polymer up to a level of 10% (on a Fe basis), and at levels of higher concentrations of magnetite.

The magnetization of the ionomers also increases with FeCl₃ concentration. Although the magnetization of the ionomers is much smaller than that of the nanocomposites, it still exhibits hysteresis which is associated with cooperative behavior of the spins. The cooperative behavior is emphasized, as expected, at low temperatures. Again, this cooperative behavior is observed to be combined with superparamagnetic behavior associated with regions where spin-spin interaction is not as extensive. The FTIR spectra confirm the formation of the FeCl₃ ionomers as indicated by the appearance of an absorbance band at 1374 cm⁻¹. The XPS spectra, too, are again indicative of ionomer formation through the observation of a 530.6 eV peak resulting from the interaction between Fe³⁺ ions and the oxygen atoms of the acrylic acid in the co-polymer. The SEM-EDS measurements shows that ionomers are formed fairly uniformly throughout the co-polymer and the TEM, which has a much higher resolution, indicates the possible formation of clusters.

1. Introduction

Magnetic nanocomposites, in which magnetic nanoparticles are encapsulated in polymeric matrices, have important applications in medicine, electronics and mechanical devices. However, the development of processes leading to magnetic nanocomposites with desirable, predictable and reproducible properties has turned out to be a difficult challenge. Attempts to produce magnetic nanocomposites encapsulated in polymeric matrices have often yielded products with large variations in structure and in magnetic properties. The difficulties in
controlling the product are greatly magnified when the particle size is in the nanometer range.¹

One possible approach to the production of magnetic nanocomposites is to aim for incorporation of magnetically active ions or oxide nanoparticles into acrylate co-polymers. The magnetic properties of such structure are expected to be predictable and controllable since they are controlled by the distance between adjacent magnetically active groups along the backbone of the polymeric molecules. Iron, for instance, can be considered for inclusion into a polymeric matrix.

The production of the polymer or co-polymer in which the magnetically active ion is to be encapsulated may be initiated by ionizing radiation. For instance, the polymerization of acrylate esters is known to be initiated by a pulsed electron beam.² Subsequently, such esters may be reacted with an iron salt to form a magnetic ionomer or with fine-particle iron oxide to form a magnetic nanocomposite.

The formation of acrylate polymers and co-polymers and modification of such polymers, e.g., synthesis of acrylate-based ionomers, is of great fundamental as well as applied value. Ionomer-forming systems are of interest because of their unique morphology and physical properties.³ The introduction of functional groups into co-polymers, when followed by reaction with a metal ion, makes it possible to produce ionomers and, at higher concentrations, nanocomposites. The formation of nanocomposites based on the introduction of metallic or semi-metallic (e.g., silicon-based) species into polymeric structures can result in improved mechanical properties, such as higher strength and stiffness, reduction in flammability, and improved effectiveness of the resulting material as a barrier to the transport of gases such as organic vapors (e.g., in fuel tanks) and oxygen (e.g., in food packaging).

The use of ionizing radiation to initiate acrylate polymerization reaction is likely to be advantageous over the use of chemical initiators. Because they occupy sites within the co-polymer, chemical initiators may interfere with the incorporation of the iron species and may form compounds with the iron. Furthermore, such initiators may cause undesirable changes in the oxidation state of the iron.

The study described here was intended to improve the understanding of several inter-related aspects of the polymerization of acrylate esters. One objective was to determine quantitatively the extent of incorporation of the ester 2-ethylhexyl acrylate (2-EHA) and of acrylic acid (AA) into co-polymers formed upon irradiation of binary mixtures of these two monomeric species. Another objective was to determine the kinetics of the formation of acrylic radicals upon irradiation of pure 2-EHA as well as 2-EHA in methanol solutions and in mixtures with AA using pulse radiolysis. This part of the study included measurements of the early nanoscale stages of acrylic ester polymerization. Based on the results of these two parts of the study, synthesis of ionomers consisting of iron-containing 2-EHA/AA co-polymers was

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performed by reacting the co-polymers with iron salts to replace the protons of the AA with Fe(III) ions as well as reacting the 2-EHA/AA co-polymers with magnetite to produce magnetic nanocomposites. Such products formed by neutralization of acrylic acid groups with transition metal ions in general are likely to have useful magnetic properties.

It has been postulated that ionomers form groupings and clusters at high ionic contents. Ion pairs of amorphous random ionomers form ionic aggregates called multiplets. The presence of multiplets in the polymer matrix strongly affects the physical properties and morphology of the polymers. According to the multiplet/cluster model, the polymer chains surrounding the multiplets experience a reduction in their mobility. At low ion content, only a few multiplets are present. As the ion content grows, the restricted mobility regions begin to overlap and, eventually, become a large continuous phase called a cluster region. For acrylic co-polymers, the ion content at which the cluster phase becomes dominant depends on the nature of the species which forms the co-polymer with AA.

Studies of ionomers in co-polymers of styrene and AA have shown that the state of ion aggregation depends on the composition and sequence of the co-polymer. Whereas at a low acrylate content the ions aggregate into multiplets, increasing the acrylate content leads to the formation of clusters, which may further form interpenetrating phases. The sizes and shapes of aggregates also depend on the nature of the metal.

The co-polymer system investigated in this study was the 2-EHA/AA system. The pure co-polymer is very useful in pressure-sensitive applications, in particular for the development of adhesives for use in products such as labels, masking tapes and films. In poly(2-EHA-co-AA) co-polymers, AA provides high cohesive strength while 2-EHA acts as a plasticizer, generating a soft and tacky surface. This combination of properties is useful in products that make use of bonding agents.

We first performed a quantitative analysis of the radiation-initiated formation of the co-polymer. The extent of polymerization of each of the two components of the monomer mixture was studied as a function of total dose and dose rate. The resulting co-polymer structure can affect the subsequent ionomer formation. The progress of the polymerization of mixtures of 2-EHA and AA was quantified using $^1$H NMR to determine the concentrations of the remaining monomers as a function of total dose, dose rate, and the relative amounts of 2-EHA and AA in the mixture.

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The second part of this study was directed towards improving the understanding of the kinetics of formation of radicals upon irradiation of 2-EHA. The effects of methanol solvent and of the presence of AA on the propagation and termination of the radical species were also investigated.

Another point of interest is that most kinetic studies of the radiation-initiated polymerization of acrylic esters have explored time periods of several microseconds and longer following the radiation pulse. In contrast, this study expands the kinetic measurements to include shorter periods in the nanosecond range in order to follow the course of neutral radical formation and the early part of the decay of such radicals. The initiation stage in the homopolymerization of 2-EHA is expected to consist of the scavenging of a thermal electron by the 2-EHA monomer to form a radical anion, which subsequently reacts with a proton to form a neutral α-carboxyalkyl neutral radical.11 The propagation step consists of consecutive head-to-tail additions of 2-EHA monomers to the neutral radical. Termination takes place through the recombination of two polymer chain radicals.12

The study of poly(2-EHA-co-AA) co-polymers also requires understanding of the radiation chemistry of AA.13 AA is introduced in order to provide carboxylic groups that can subsequently be reacted with metal ions to form complexes. The carboxylic group in AA also provides a cross-linking agent for the co-polymer.14 The presence of the AA protons is expected to accelerate the conversion of the initially formed radical anions into neutral radicals. If oxygen is present, peroxides are formed and the polymerization is inhibited, as has been experimentally observed.15 Upon radiolysis of mixtures of the two monomers containing a large excess of 2-EHA over AA, initiation can be expected to take place primarily through the generation of carbon-centered 2-EHA radicals. Propagation is expected to follow via head-to-tail addition of AA and 2-EHA monomers, with the unpaired electron centered on the most highly substituted carbon of the vinyl group of the monomer added to the growing chain. Termination is expected to occur primarily through a bimolecular combination mechanism.16

When 2-EHA/AA mixtures in dilute methanolic solutions are irradiated, \( ^* \text{CH}_2\text{OH} \) radicals are expected to be the predominant species, as in the previously mentioned solutions of pure 2-EHA in methanol. In the mixed solution, these radicals are expected to react with 2-EHA to produce acrylate monomer radicals, which subsequently undergo propagation and termination. AA is expected to provide protons for the conversion of any initially produced 2-EHA radical anions to neutral radicals. AA is also expected to undergo co-polymerization

with 2-EHA during the subsequent propagation stage, as described above in the case of pure 2-EHA/AA system.

As mentioned above, this study had three objectives: (1) to investigate monomer/polymer conversion in 2-EHA/AA mixtures; (2) to investigate the kinetics and mechanism of the formation and decay of transient intermediates by means of pulse radiolysis; and (3) to synthesize and characterize iron-based ionomers in radiation-produced poly(2-EHA-co-AA). Pulse radiolysis made it possible to compare data taken at high dose rates using nanosecond pulses with results obtained at low dose rates with pulse duration of several microseconds. The combination of the observations made under these two sets of conditions was used to shed light on the formation as well as subsequent fate of radiation-produced radical intermediates.

2. Experimental

The work presented in this study involves a synthesis of a co-polymer composed of 2-ethylhexyl acrylate (2-EHA) and acrylic acid (AA) using gamma and pulsed electron beam radiation. The structure and synthesis kinetics of this co-polymer were investigated by \(^1\)H nuclear magnetic resonance (NMR), electron pulse radiolysis with kinetic spectroscopic detection (PR-KSD), and Fourier transform infrared spectroscopy (FTIR). The effects of total dose, dose rate, and acrylic acid content on the polymerization reaction were studied. The conversion of 2-EHA monomer into polymer at a given total dose was found to be enhanced at lower dose rates and higher concentrations of acrylic acid.

2-Ethylhexyl acrylate/Acrylic acid (2-EHA/AA) co-polymers were prepared by mixing together 2-EHA and AA in an Erlenmeyer flask sealed with a rubber septum, bubbling with argon gas to remove oxygen, transferring aliquots of the mixture to glass vials in a glove box and irradiating the vials using either the University of Maryland’s 100 kCi Co-60 gamma source or the University of Maryland’s pulsed electron beam linear accelerator (LINAC).

Iron-poly(2-EHA-co-AA) ionomers were produced by dissolving the irradiated 2-EHA/AA mixtures in THF, mixing with FeCl\(_3\), and performing dialysis by means of a cellulose membrane to remove unassociated ions, such as chloride, from the co-polymer. Chloroform and methanol were used as solvents in the dialysis.

The experimental procedure of the ionomer synthesis is shown in Figure 1 below.
The proposed mechanism of the formation of iron-based monomer in 2-EHA/AA co-polymer is represented in the following schematic diagram (Fig. 2):

Another type of samples is made by reacting the co-polymer (2-EHA/AA) with a suspension of nanoparticulate Fe$_3$O$_4$ in kerosene (Nanocat) as shown in the following figure. The experimental procedure used in the preparation of the magnetic nanocomposites with THF being used as a solvent was identical with the procedure used to make the magnetic ionomers, but the reaction products were directly dried to remove the solvent without using dialysis.
3. Results and discussion

3.1. Magnetic Properties

Several types of magnetism are observed in solids. The types which are relevant to this study are:

— Paramagnetism
  - Individual spins can be oriented in the direction of an external magnetic field
  - Magnetization proportional to field and disappears when field is removed
  - Curie’s Law (or Curie-Weiss’ Law) of temperature dependence

— Ferromagnetism
  - Cooperative behavior of spins within domains of about 100nm
  - Magnetization much stronger, exhibits hysteresis, and saturates at high fields with all spins aligned in direction of fields

— Superparamagnetism
  - Phenomenologically similar to ordinary paramagnetics
  - Observed when grains of ferromagnetic material become smaller than domain size – small number of spins per grain weakens cooperative behavior

Calculation of Particle Size from Magnetic Measurements

Magnetic measurements were performed using a Vibrating Sample Magnetometry (VSM) shown in the following figure (Fig. 4).
General

Ferromagnetic materials are those that consist of particles that have a size that is larger than, or at least equal to, the size of a magnetic domain. A typical domain size is around 100 nm or 0.1 μm.

If the individual particles are smaller, i.e., they are subdomain in size, the observed magnetic behavior is no longer ferromagnetic. Above a certain temperature, called the “blocking temperature (T_B)” (except at very high fields), the magnetization (M) of subdomain particles continues to rise with increasing applied magnetic field and drops to zero, similar to paramagnetic behavior, once the external field is removed. This behavior is called superparamagnetism.

The blocking temperature T_B is the temperature at which the time it takes the spins to flip due to thermal fluctuations becomes comparable to the time of the measurement. T_B depends on the nature of the material, the particle size, and the applied magnetic field H. T_B increases with increasing particle size and with decreasing H. For instance, in the case of magnetite with particle size of \( \geq 100 \) nm and very weak H the limiting value of T_B is 580 °C. For a particle with a size of 5 nm and a field of 500 G, T_B can be as low as 45 K.

Equations (The transition from Ferromagnetic to Superparamagnetic behavior in nanoparticles)

*The Langevin Function*

\[ M_T = M_s + N_{sp}μ\left\{\cosh(μH/kT)/\sinh(μH/kT)\right\} - (kT/μH) \]

where,

\( M_T \) = Total magnetization

\( M_s \) = Saturation magnetization of particles larger than, or close to, domain size
N_{sp} = \text{Number of superparamagnetic particles (much smaller than domain size)}
\mu = \text{Magnetic moment of superparamagnetic particles}

For \( T > T_B \), \( \mu \) can be found from curve fitting.

\( V = \mu/\sigma \)
\( V = \text{Particle volume} \)
\( \sigma = \text{Specific magnetization (materials property)} \)
\( T \) is the temperature of the experiment
\( k \) is the Boltzmann constant (Gas constant/Avogadro's Number)

*The Bean-Livingston equation*

\[ H_C = \left(\frac{2KV}{\mu}\right)\left[1 - 5\left(\frac{kT}{KV}\right)^{1/2}\right] \]

where,
\( K \) = Anisotropic energy
\( V \) = Particle volume
\( H_C \) = Coercive force (magnetic field that has to be applied in the opposite direction in order to reduce the magnetization to zero)

For \( T < T_B \), \( \mu \) can be found by plotting \( H_C \) vs. \( T^{1/2} \) and calculate the slope and intercept.

\( V = \mu/\sigma \)
\( V = \text{Particle volume} \)
\( \sigma = \text{Specific magnetization (materials property)} \)
\( T \) is the temperature of the experiment
\( k \) is the Boltzmann constant (Gas constant/Avogadro's Number)

**How do we decide if \( T < T_B \) or \( T > T_B \)?**

a) We plot the magnetization \( M \) against the applied field \( H \) and obtain the hysteresis curve. We increase \( H \) until \( M \) no longer changes significantly with \( H \), i.e., \( M \) reaches its saturation value. The coercive force \( H_c \) is the field that we have to apply in the opposite direction in order to bring the magnetization back to zero after the sample has reached its saturation magnetization.

b) If \( T < T_B \), \( H_c \) depends on the temperature of the experiment \( T \). If \( T > T_B \), \( H_c \) is independent of the temperature.

**Determination of Particle Size for the case of \( T > T_B \)**

a) Find \( \sigma \), the specific magnetization, of the material in question from the literature or from measurements on large particles.

b) Plot the total magnetization \( M_T \) against \( H \).

c) At high fields, at low fields, \( M \) increases quickly with \( H \), mostly due to the contribution of the large (ferromagnetic) particles. At high fields, the dependence becomes much weaker, because it is only due to the superparamagnetic particles, while the contribution of the large particles to \( M_T \) has become saturated. Thus, it is easy to draw a horizontal line at the level of \( M_T \) where this
contribution becomes constant. This represents the value of the saturation magnetization, $M_s$. The continued weak dependence of $M_T$ on $H$ represents $M_T - M_s$, i.e., the component of the magnetization due to the superparamagnetic (subdomain) particles.

d) Plot $M_T - M_s$ as a function of $\{\cosh(\mu H/kT)/\sinh(\mu H/kT)\} - (kT/\mu H)$. The slope will yield $N_{sp}\mu$. (Actually, we plot $M_T - M_s$ against $H$ at constant $T$ or against $1/T$ at constant $H$ and perform curve fitting to find $N_{sp}\mu$ using Equation (1)).

e) $N_{sp}$ can be found from the number of magnetic moments (based on the number of iron atoms) associated with the superparamagnetic (subdomain) particles. This is obtained by calculating the total number of magnetic moments based on the concentration of the iron species (e.g., magnetite) in the sample on one hand, and the number of unpaired spins per formula unit (e.g., number of unpaired spins per Fe$_3$O$_4$ unit) on the other. From the total number of magnetic moments we subtract the number of magnetic moments associated with ferromagnetic (multidomain) particles, which is obtained by dividing the saturation magnetization, $M_s$, by the specific magnetization (paragraph 4a). The difference corresponds to the number of magnetic moments associated with the superparamagnetic component.

f) Now we can find a value for $\mu$. $\mu = \sigma V$. Since we know $\sigma$ (see paragraph 4a), we can calculate $V$, the particle volume, and from it the diameter $d$ of the particle $R$ [$V = 4\pi(d/2)^3/3$].

Comment: When we are studying nanoparticle dispersions, no large (multidomain) particles are present, and this greatly simplifies the procedure, since $M_s$ is not significant and we can calculate $N_{sp}$ directly without having to subtract the number of magnetic moments corresponding to $M_s$.

**Determination of Particle Size for the case of $T < T_B$**

a) Same as IVa.

b) Plot $H_c$ against $T^{1/2}$.

c) The slope of the line obtained in paragraph V(b) is $S = (-10/\mu)(kKV)^{1/2}$. The intercept ($H_c$ extrapolated to $T = 0$) is $I = 2KV/\mu$.

d) Based on paragraph V(c), $\mu = 50kI/S^2$. Thus we do not need to know $K$.

e) Same as IVf.

**Characterization**

Experimental methods used to perform analysis are as follows:

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- Fourier Transform Infrared (FTIR) Spectroscopy
  - Used to characterize nature of bonds in acrylic co-polymer ionomers

- X-ray Photoelectron Spectroscopy (XPS)
  - Used to characterize the chemical environment of Fe$_3^+$ in ionomers

- Energy Dispersive X-ray Spectroscopy (SEM/EDS)
  - Used to study microstructure and perform quantitative elemental analysis (in particular, Fe) in ionomers and nanocomposites

- Transmission Electron Microscopy (TEM)
  - Used to study nanomorphology of ionomers

- Vibrating Sample Magnetometry (VSM)
  - Magnetic properties

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The observation of the 530.6-eV peak in the XPS spectrum in Figure 4 results from interaction between ferric ions and the oxygen atoms of acrylic acid in the co-polymer.

![XPS spectra comparison](image)

**Fig. 5. X-ray Photoelectron Spectroscopy: O 1s Analysis of Poly(2-EHA-co-AA)/Fe³⁺ Ionomer.**

The FTIR analysis that was performed on the samples along with the experimental procedure is explained in detail below. The FTIR spectra of a mixture of 73 mol% 2-EHA and 24.3 mol% AA before and after irradiation with gamma radiation to 100 Gy at a dose rate of 13 Gy·min⁻¹ are shown in Figure 6.

Different concentrations of the Fe³⁺ ionomer were prepared by using different volumes of FeCl₃ solution in THF. It was observed that it was possible to obtain ionomers with concentrations of FeCl₃ corresponding to as high as (1.00 ± 0.05)% Fe without indications of non-uniformity resulting from exceeding the solubility of FeCl₃ in the acrylic co-polymer. On the other hand, when it was attempted to raise the concentration of FeCl₃ to 2% based on Fe, it was observed that the solubility was exceeded as indicated by the fact that different portions of the sample had widely different concentrations of Fe.

Thus, it was concluded that the solubility of FeCl₃ in the co-polymer, expressed in wt.% Fe³⁺, was between 1 and 2% Fe. A concentration of 1% by wt. of Fe corresponds to a 2.7 mole % Fe in the 3:1 EHA-AA co-polymer. The concentration of Fe in the ionomers was determined by dissolving the samples in a mixture of HCl and HNO₃ and analyzing these solutions using an ICP-AES spectrometer. Evidence for the formation of ionomers was provided by the observation that the FTIR spectrum of the samples, most noticeable in the case of the sample with the highest Fe³⁺ content of 1.00 %Fe³⁺, exhibited peaks which were not observed in the base co-polymer. The most noticeable of these peaks was the one at 1374 cm⁻¹.
Fig. 6. FTIR spectra of 2-EHA-co-AA co-polymers produced by irradiation, and of co-polymers reacted with FeCl₃ to produce a 2.7 mol% Fe ionomer in a 73 mol% 2-EHA/24 mol% AA mixture; — a) co-polymer (after exposure to 100 Gy of Co-60 gamma radiation at a dose rate of 13 Gy·min⁻¹) represented by the pink line; b) 2.7 mol% Fe ionomer in a 73 mol% 2-EHA/24 mol% AA mixture represented by the blue line.

The EDS of both ionomers and nanocomposites shows incorporation of Fe into the co-polymer as seen in figure 7. Based on the similarity between the C and Fe maps, as well as the SEM image, it is concluded that the distribution of Fe throughout the ionomer microstructure is uniform (Figure 7).
Magnetic measurements were performed on the poly(2-EHA-co-AA)/iron samples which are shown in the figures below.

In nanoparticles which are smaller than the domain size but not extremely small, there is a mixed ferromagnetic/superparamagnetic behavior as reflected in the Langevin equation (Figure 9).
The magnetization results for the magnetite nanocomposites show a combination of ferromagnetic behavior (hysteresis) at relatively small magnetic fields with superparamagnetic behavior at large fields. The ferromagnetic behavior can be attributed to the presence of larger nanoparticles and the superparamagnetic behavior to smaller nanoparticles. As expected, the magnetization increases with magnetite concentration up to about 10% Fe (in the form of Fe$_3$O$_4$). Above this concentration, the magnetite apparently no longer forms a uniform suspension in the 2-EHA/AA co-polymer.
Fig. 11. Magnetic Susceptibility vs. Field (Ferric Chloride Ionomer).

Fig. 12. Magnetic Susceptibility vs. Temperature (Ferric Chloride Ionomer).

The observed proportional dependence of the magnetic susceptibility on the inverse temperature is in accordance with Curie’s Law for paramagnetic materials, but our results show a positive deviation from the Curie’s Law dependence at low temperature (high 1000/T). This deviation can be attributed to a mutual spin alignment contribution to the magnetization. In nanoparticulate materials both a superparamagnetic behavior (due to very small particles) and cooperative behavior (due to larger particles) contribute to the total magnetization; such combined effect is indeed clearly visible in our results. The ferromagnetic behavior is expected to be more noticeable at lower temperatures, where thermal motion is least likely to disrupt mutual spin orientation. This is indeed reflected in our results. Note that specific magnetization of the FeCl₃ ionomers is much lower than the one observed with the magnetite nanoparticles. This is to be expected in view of the strong
tendency of magnetite to exhibit ferromagnetic behavior. However, it is remarkable that some mutual spin alignment takes place within the FeCl$_3$ ionomers.

Spectroscopic evidence and magnetic measurements confirm the formation of magnetic nanocomposites. Depending on the chemical nature and size of the nanoparticulate composites, it is possible to obtain different types of magnetic behavior for different applications.

4. Conclusion

Ionomers based on magnetically active ions and nanocomposites based on magnetic oxide nanoparticles were incorporated into acrylate co-polymers using ionizing radiation in the form of Co-60 gamma rays or electron beam irradiation. The applied radiation doses and dose rates affect the 2-ethylhexylacrylate/acrylic acid co-polymerization and, consequently, the size and distribution of the ionomers or nanoparticles throughout the structure formed upon reacting the co-polymer with a salt of the magnetic ion or with a dispersion of oxide nanoparticles. As a result, the irradiation conditions are ultimately responsible for controlling the magnetic properties of the product. This makes it possible to obtain different types of magnetic behavior for different applications by adjusting the irradiation conditions to generate a desired degree of polymerization and a desired distribution of the acrylic acid functionalities. Preparation of the co-polymer through the use of ionizing radiation makes it possible to avoid the use of chemical initiators, which later occupy sites within the structure of the co-polymer and are thus likely to interfere with the formation of the magnetic ionomers and nanocomposites. Radiation-induced synthesis of co-polymers can also be performed without having to use, and later to remove, volatile solvents. Thus, radiation technology offers a highly advantageous pathway for the synthesis of magnetic ionomers and nanocomposites, which are currently attracting much attention because of their potential use in imaging, drug delivery, magnetic storage, and other advanced applications.

5. Future Work

Future work for this project includes the continuation of characterization of the magnetic nanocomposites and ionomers and measurements of magnetic properties over a broad range of concentrations of the magnetic species. Correlations between the spectroscopic observations of magnetic particle size and the supermagnetic and ferromagnetic behavior will also be developed. Detailed characterization of the nanostructure will be performed in order to obtain a clear picture of the distribution of Fe in the co-polymer.

References


## LIST OF PARTICIPANTS

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