IAEA
International Atomic Energy Agency
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REPORT

of the TECHNICAL MEETING on the

"USE OF RADIATION TECHNOLOGIES IN THE DEVELOPMENT OF ACTIVE PACKAGING MATERIALS"

20-24 May 2019

Centre for Energy Research, Hungarian Academy of Science, Budapest, Hungary Budapest, Hungary

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FOREWORD

Packaging is an integral part of food products which besides increasing the shelf life of the food, it also facilitates its storage and distribution. Synthetic packaging materials based on fossil hydrocarbons have been used extensively due to their low cost and good mechanical properties; recently concerns related to their sustainability are increasing. There is therefore an opportunity for development of biodegradable or reusable packaging materials based on natural resources (starch, vegetable oils, cellulose) and their waste (shrimp shells and squid pen for example), with intelligent or bioactive properties. Radiation technology offers a clean and environmental-friendly way for the development of such new packaging materials from synthesis of new to modification of existing materials. In addition, for food that is intended to be irradiated pre-packaged, radiation resistant materials are needed.

To deal with such a complex research, development and application, a coordinated research project (CRP) has initiated. The proposal for CRP F22063 on Application of Radiation Technology in the Development of Advanced Packaging Materials for Food Products was formulated based on the conclusions and recommendations of the Consultants Meeting on Applications of Radiation Techniques in Development of Advanced Packaging Materials for Food Products held at IAEA Headquarters, Vienna, Austria, 14-18 May 2012. The objective of CRP F22063 was twofold: on one hand it is to assess the effects of ionizing radiations (gamma, electrons, and X-rays) on commercial and emerging food packaging materials, while on the other hand, to develop new functional packaging materials based on natural polymers with improved stability, sealability, biodegradability, and recyclability by using radiation techniques.

The CRP F22063 has successfully completed with 60 scientific papers, 102 presentations in international conferences and 17 contributions to book chapters. After the previous CRP, there have been continuous needs from Member States to transfer the knowledge and experience on advanced packaging material development. Therefore, it is necessary to review the status of present-day knowledge of the effects of ionizing radiation on packaging materials, and to revisit the scientific breakthroughs in terms of new concepts likely to incite the development of new materials for active packaging.

This report of the meeting is a collection of the work presented by the project participants of CRP and contributors at the Technical Meeting on Use of Radiation Technology in the Development of Active Packaging Materials, held in 20-24 May 2019 at Budapest, Hungary. This report is divided into two main parts: the first part gives a summary of the talks by the participants, as well as the identified needs and gaps that need to be addressed for potential use of radiation technology for further researches in nanoscience/nanotechnology, followed by recommendations to the IAEA. The second part of the report contains a more detailed contribution by the meeting participants.

BACKGROUND

The world's food supplies need to be increased and protected to meet the demands of the growing global population. The World Summit on Food Security in 2009 reported that by 2050, food production needs would have to increase by as much as 70 % in order to feed the anticipated 9 billion people (FAO 2009). However, improving crop yield is only just one aspect of meeting this increased food supply needs. It is equally important to expand arable lands and protect what is produced. A significant quantity of harvests around the world does not make it to the consumer. It is estimated that the loss between the point of production and consumption constitutes as much as 30-40% of the total amount of food that is produced. Where the food is wasted differs in different parts of the world. In the developing countries majority of the food is wasted at the farm and during shipping and transportation, while in the developed parts of the world such as the US and UK, majority of food waste occurs at the home (Science, 2010).

Plant and animal products are also at risk of microbial pathogen contamination during their journey from the producer to the consumer. Also, processing and prolonged storage can potentially increase food safety risks especially when the food is not adequately packaged and protected from fungal infestation and toxin contamination. The US Center for Disease Control reported 48 million cases of food borne illnesses and 3000 deaths in 2011, while Agriculture Canada reported 13 million cases of food borne illnesses per year (Agriculture Canada, 2006). The Foodborne Diseases Active Surveillance Network (Food Net) of the USA states that in 2007 incidence of infections caused by *Campylobacter*, *Listeria monocytogenes*, *Salmonella*, *Shigella*, *Vibrio*, and *Yersinia* did not decline significantly compared to 2004-2006 data and estimated incidence of Cryptosporidium infections increased by 44% (Imran et al., 2010). The most recent Food Net data point out that Salmonella and Campylobacter contamination of foods continue to be the leading cause of bacterial food borne illnesses. Foodborne illnesses cause immense economic burden due to food recalls and medical treatment costs. According to recent estimates, foodborne illnesses linked to domestic and imported fresh fruits and vegetables cost the US economy over $150 billion per year (Scharf, 2010). The post-process contamination caused by product mishandling and faulty packaging is reported to be responsible for approximately two thirds of all microbiologically related recalls in the USA (Gounadaki et al., 2007). Post-processing protection and active packaging and coatings has been proposed as an innovative approach that can be applied to ready-to-eat products to minimize or prevent the growth of pathogenic microorganisms (Min et al., 2008).

Considerable research and development is being conducted in different Member States to improve and develop new packaging materials and coatings for use in the food sector. These research activities include developing recyclable, biodegradable, bioactive and smart packaging material and food coatings. Ionizing irradiation plays a major role in the development and improvement of packaging polymers as well as in sterilizing packaging material used in aseptic packaging. However, the use of ionizing radiation for pre-packaged foods is a major technology used worldwide to combat foodborne pathogens. However, the behavior of these materials (especially those directly in contact with foods) under ionizing radiation doses needs to be evaluated and quantified in order to obtain regulatory approval prior to their commercial use. Innovative packaging based on natural polymers in conjunction with other technological advanced material modifications (e.g. in nanotechnology) have considerable promise for the future in this field.

Radiation induced degradation of various newly developed polymers and their components including adjuvants, antioxidants, plasticizers, coatings, release agents, stabilizers, and their emerging technologies (for example incorporating nanoparticles, sensing agents, and "intelligent"/bioactive components) also need to be evaluated at the radiation doses recommended for phytosanitary treatment and food safety applications.

The effect of ionizing radiation doses around 10 kGy on packaging materials, and the packaged food in contact with these materials, needs to be evaluated for ensuring the wholesomeness (safety and quality) of food. Likewise, the suitability of packaging materials when used in conjunction with lower doses (≤ 1000 Gy) when used for extending the shelf life, reducing post-harvest losses, and for quarantine applications for trade in agricultural commodities, also needs to be evaluated.

The successful commercialization of new materials for food packaging has to overcome many multidisciplinary barriers (science and technology, safety regulation, standardization, training and technology transfer). In order to ensure that economic and social benefits can occur, research and development in this area should be encouraged and involved with a high degree of multidisciplinary collaboration. The issue of developing and recommending packaging materials for radiation processing of pre-packaged foods therefore needs to be addressed through research networks and coordinated interactions of multidisciplinary expertise. This can be best addressed by means of a coordinated research effort through a CRP. In a similar, but much broader approach to developing sustainable food packaging, a network of 35 Countries and more than 80 research and industrial Institutions is already in place under the EU 7th Framework Project Cost Action FA0904 entitled "Eco-sustainable food packaging based on polymer nanomaterials" (www.costfa0904.eu), with an aim to develop new packaging materials. Collaboration and joint events with this Cost Action have already been taken place, while others are planned.

PURPOSE OF THE TECHNICAL MEETING

After the successful completion of previous CRP (F22063), there have been continuous needs from Member States to transfer the knowledge and experience on advanced packaging material development. Therefore, it is necessary to review the status of present-day knowledge of the effects of ionizing radiation on packaging materials, and to revisit the scientific breakthroughs in terms of new concepts likely to incite the development of new materials for active packaging.

The purpose of this event is to review the status of present-day knowledge of the effects of ionizing radiation on packaging materials, and to revisit the scientific breakthroughs in terms of new concepts likely to incite the development of new materials for active packaging. The Meeting will focus on finalization of the work plan to be implemented during the proposed new CRP keeping in mind the needs of the participating Member States. The final outcome of the meeting will be a concise report providing details of the activities to be implemented in the project.

ACHIEVEMENTS

The Technical Meeting consists of series of presentations to facilitate sharing experiences by:

- discussions of the achievements after the CRP F22063
- sharing the up-to-date information on packaging materials

- discussion the commercialization of developed materials with the industrial sectors.
- discussion of future CRP

1. Discussions

This technical meeting compiled information from the CRP F22063 as well as research developments from additional Member States such as India, Republic of Korea, Serbia and Argentina. The meeting was successful in achieving the development of new packaging materials such as Starch-PVA blends, starch-PVA-nanocellulose blends, PLA blends, bionanocomposites, polypropylene-clay film, sorbic acid grafted polyethylene film, cellulose acetate-clay blend, poly aniline blended PCL film, natamycin and limonene-grafted polyethylene film, anthocyanin-grafted polyethylene film, methyl cellulose-chitosan-alginate blends, PLA-Carboxy methyl cellulose blends.

The meeting was successful in assessing the radiation sensitivity of commercial packaging materials such as PLA, PET, PE, PHBV, nylon. It was able to test the radiation sensitivity of novel packaging materials such as Starch-PVA, starch-PVA-nanocellulose, PE-clay nanocomposites and PLA-PHBV C30B bionanocomposites. It has also developed protocols to functionalize crystalline nanocellulose in order to develop active beads films and coatings.

The participants of this meeting were successful in publishing their research in peer-reviewed literature sources as well as presenting their results in international and regional meetings. There were fruitful collaborations between the participants

Specifically, the Technical Meeting provided an opportunity for participants to discuss

- the trends in biopolymers in terms of volumes being produced, the prices and the potential commercial applications
- the resistance of biopolymers to high energy electron beam, gamma irradiation, and X-ray
- optimization of combined irradiation treatments with active beads, coatings and films
- combining irradiation treatments and essential oils/natural antimicrobial compounds loaded bioactive films and beads
- addition of nanocrystal cellulose in polymer to enhance encapsulation efficiency and assure a control release of active compounds
- irradiation of nanocellulose (crystal, whisker, fibres, bionanocellulose, etc.), clays, TiO_2 to produce functional groups to improve functionality and physical-chemical properties of films, beads and coatings
- The incorporated additives derived from natural products do not negatively affect consumers health.
- Grafting of antimicrobial additives onto a polymer film has been shown to offer potential active packaging material to enhance food safety.
- Bioactive stratified composites and nanocomposites can not only passively protect the food against environmental factors, but they may enhance stability and quality of foods.
- Melt processing requires large amounts of bioactive agents, some of them could deteriorate during melt processing, therefore other method was proposed namely cold plasma or

gamma irradiation activation followed by coating with a bioactive layer. The former method can be applied where no technological changes are possible.

- Starch-PVA blends was shown to have promise to extend the shelf life of guavas.
- Starch-PVA and starch-PVA-nanocellulose blends can be improved by compositional modifications and radiation processing. These have potential for food packaging, in particular for dry food, food with a high content of fat or food covered with fatty layer (including food destined for irradiation processing). Active materials were also obtained.
- The ability to graft a phytochemical such as anthocyanin to polyethylene (as a pH indicator) was shown to have promise
- The grafting of natural food additives (such as Natamycin, Limonene) on PE film and the development of emulsion grafting media. The PE films grafted Natamycin and Limonene have antibacterial/antifungal and antioxidant properties.
- developments and demands in the area of food coating and packaging as well as the regulatory aspects in different countries
- the incorporation of reduced graphene oxide (RGO) by ionizing radiation in EVOH matrix led to obtaining of EVOH/RGO flexible films with the same transparency with light transmittance in the entire visible light of EVOH flexible films, but with better oxygen barrier. After electron-beam radiation treatment, both, mechanical and oxygen barrier properties of EVOH/RGO flexible films were drastically improved
- the extent of exfoliation and dispersion state for the graphene oxide nanosheets in the EVOH matrix and electron-beam radiation treatment is a significant factor for producing high-performance composite film based on EVOH resin for food packaging application including for pre-packaged irradiated foods. The PBAT/PLA blend reinforced with bio-$CaCO_3$ presented tensile properties and penetration resistance close to the commercially available products
- the addition of 5 % (wt. %) of pre-irradiated PLA enhanced the adhesion of the filler in the polymeric blend matrix resulting in better property gains. The BAT/PLA blend reinforced with bio-$CaCO_3$ compatibilized by electron-beam radiation meets requirements to dry food packaging applications
- Stable isotope technique (δO^{18} δH^2) has been found to be a promising technique to detect and quantify leachates from polymeric packaging materials;
- Emerging technologies e.g. encapsulation, immobilization of active compounds in films, beads and coating can be synergistically enhanced by radiation technology;
- The participants acknowledged that majority of their current activities are categorized under R & D stage and they are actively engaged in further development. Some of the products developed have reached level of maturity that the next step would be on upscaling;
- By the final CRP Meeting, there was an extensive amount of collaboration among participants, resulting in student exchanges, visiting scientists, Ph.D. students and joint publications.
- Biodegradable polymers such as PLA and PBS are good candidates for food packaging materials, in terms of their eco-friendliness. Blends of PLA and PBS with natural polymers are also economically interesting. Radiation processing offers potential solutions for these problems either by improving their properties or enhancing their compatibility, while simultaneously preserving their biodegradability.
- Addition of starch or clay greatly improves the barrier properties of cellulose acetate.
- Packaging materials containing polyaniline (PAN), a color conjugated polymer could be used as pH sensitive sensor for detecting food spoilage.
- Incorporation of irradiated CS and chitin increases the antioxidant and antimicrobial activity of PCl and cellulose acetate.

- Development of guar gum-based biodegradable packaging materials having mechanical and barrier properties comparable to commercial cling films, for food irradiation applications.
- Development of nano catalysts which when added to polyethylene films can result in oxodegradation of films.
- Development of PP and PU blends having high thermal and mechanical properties by radiation grafting.
- Development of high porous film having good mechanical properties by radiation technique.
- Development of biomaterials based on polymers from food industry waste in order to improve the values using irradiation.
- Development of PE with silver zeolite for active packaging.
- Information about fresh produce quality when packaged in bioplastics and exposed to e-beam irradiation doses applicable to the fresh produce industry.
- Development of bio-nanocomposites and nano-coatings based on PE and PLA with bioactive compounds such as chitosan, chitin, natural extracts and nanoclays.
- Radiation crosslinking methods for natural and synthetic polymers to enhance the functionalities for applications as packaging materials; gelatine chitosan films incorporating antioxidants; fractionation methods for natural polymers to enhance functionalities as film coating for edible films; methods to measure film thickness using rotating disk technique and development of Mimica™ touch and technology as an indicator for food spoilage based on gelatine films.
- Development of active, smart and biodegradable food packaging materials for dried food and dairy food applications.
- Development of smart packaging materials from hibiscus and PVA for detection of fresh spoilage.
- Use of radiation technology to develop polymers and/or polymer blends with new functionalities, for example surface modification
- The advent of low energy e-beam technology provides a new approach of modifying surfaces and incorporating additional functionalities to biopolymers and polymer blends
- The commercial availability of 3D printing platform allows for rapid prototyping of novel biopolymers and blends for scale-up evaluation

SUMMARY AND ACHIEVEMENTS OF THE PARTICIPATING INSTITUTIONS

ALGERIA

Our challenge was to produce biodegradable primary food packaging materials based on blends of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and poly (lactic acid) (PLA), which withstand to gamma rays without altering the mechanical and barrier properties as well as not resulting in toxicological side-effects during both food storage and usage. Our study showed that the effects of ɣ-irradiation on PHBV/PLA: 50/50 (w/w) blend resulted in strong modifications in the chemical structure after 100 kGy of absorbed dose. Indeed, carbonyl products were formed during degradation, which were responsible for the decrease in the molecular weight of all irradiated samples due to the chain scission mechanism, being however, much more pronounced for the neat polymers, i.e. PHBV and PLA. On the other hand, thermal stability as well as modulus and hardness of PHBV/PLA blend remained almost unchanged during ɣ-irradiation test and an enhancement of these properties was observed in the presence of organo-modified montmorillonite (Cloisite 30B) or (C30B) and (PHBVgrafted-maleic anhydride) (PHBV-g-MA) used as the compatibilizer. Indeed, scanning electron microscopic (SEM) data confirmed the morphological stability of PHBV/PLA/C30B/PHBV-g-MA after 50 kGy compared to non-irradiated one. The results clearly demonstrated that up to 100 kGy, such blend materials are stable and may have some potential applications considering that the regular doses for food irradiation are lower than 10 kGy and for packaging sterilization the doses are lower than 25 kGy. The work was extended to an investigation of the oxidative degradation under eBeam irradiation of neat PHBV, neat PLA and PHBV/PLA blend (50/50 w/w) with and without C30B (3 wt%) at absorbed doses of 1 and 10 kGy. The changes in the chemical structure, the molecular weight, the thermal, mechanical and barrier properties as well as the morphology were evaluated. The data showed that eBeam irradiation of PHBV/PLA blend leads to oxidation reactions involving ester groups in both neat PLA and neat PHBV resulting in the formation of hydroperoxides groups. The presence of C30B in the polymer blend has no influence on the nature of the degradation process. However, the good dispersion of C30B nanoparticles provides more stability to the molar mass and the thermal, mechanical and barrier properties of PHBV/PLA blend. At absorbed dose of 10 kGy, the irradiated samples are completely safe. Furthermore, ecotoxicity testing of both non irradiated and irradiated samples clearly showed no toxicity. In the last part of the work, PHBV/ZnO nanocomposites films were prepared by melt compounding in the presence of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) grafted maleic anhydride (PHBV-g-MA) as the compatibilizer. The effectiveness of PHBV-g-MA on morphology, thermal and mechanical properties of PHBV/ZnO nanocomposites was evaluated at various nanofiller contents, i.e. 1, 2 and 3 wt. %, while the amount of compatibilizer was fixed to 5 phr. The study showed through scanning electron microscopy that the addition of PHBV-g-MA results in a finer dispersion of the ZnO nanoparticles in the PHBV matrix compared to the uncompatibilized one which shows heterogeneous morphology and aggregates. Consequently, improved thermal stability and tensile properties are observed. Furthermore, the crystallinity index (Xc) of the compatibilized nanocomposite is slightly increased. The above results suggest that PHBV-g-MA is promising as compatibilizer for PHBV/ZnO nanocomposites.

ARGENTINA

In response to new agreements and consumers demand for ecofriendly materials, the area of biodegradable and active packaging is becoming more significant. Some studies had been conducted in Argentina on development of films and coating based on natural polymers using resource available in the country. Natural polymers from different sources were evaluated such as whey and soy isolate protein, sub-product from oil and dairy industry, and alginates and chitosan, from fishing industry. Differently strategies were chosen in order to improve mechanical and physical properties of this films, and some antimicrobial and antioxidant compounds were also added and studied. However, the application of this developments to obtain packaging materials based on biopolymers, has not yet been commercially implemented in the country. The production of bioplastics is still low and until now there has been a large amount of theoretical research and little research applied in the semi-industrial scale. In addition, the few experiences of production are mostly in the hands of large companies that use imported raw materials. In this context, it is important to try to highlight all the initiatives that are being carried out in the different spheres of public and private activity and articulate as much as possible between these actors, in order to join efforts in the initial stage and take advantage of resources with the greatest possible efficiency. Irradiation has demonstrated to produce proteins cross-links, improving mechanical strength, water resistance and confer elastomeric properties to the materials. Considering this, our main approach is the development of new packaging materials based on biomolecules using ionizing radiation in order to improve their characteristics, as well as to generate added value to food industry waste that is currently being discarded with negative environmental consequences and significant disposal costs.

BANGLADESH

Current worldwide ecological consciousness boosts the practice of biodegradable materials rather than the dominant tendency of petroleum based synthetic polymers for packaging purpose. The fabrication of biodegradable films from natural polymers has attracted much attention due to the excellent biodegradability, biocompatibility and edibility of the films. Blending of synthetic and natural polymers is one of the useful ways to produce new materials with desired properties. Biodegradable films were prepared by blending chitosan and poly (vinyl alcohol) (PVA). Chitosan-PVA blend films (thickness 0.16 mm) of different compositions were prepared by casting method. Best composition (chitosan: PVA = 1: 4) of the blend film was carefully chosen on the basis of mechanical properties. The tensile strength (TS) and elongation at break (Eb) of the film determined at this composition was 24 MPa and 20 % respectively. Radiation modification of the chitosan-PVA films with monomer, methyl methacrylate (MMA) were carried out using gamma radiation. Monomer concentration, soaking time and radiation dose were varied from 1-7 %, 10-30 min and 10 kGy-40 kGy respectively. Mechanical properties of the radiation modified films were examined. The optimum condition for the radiation modification was 3% monomer concentration, 20 min soaking time and 30 kGy radiation dose. The TS and Eb observed at this condition were 36 MPa and 34 % respectively. Water uptake of the films were investigated that indicates that radiation modification reduced the hydrophilicity of the chitosan-PVA film. Thermo gravimetric analysis (TGA) and dynamic mechanical analysis (DMA) were used to characterize the thermal properties of the films. The TGA displays that the weight loss of chitosan-PVA (both non-irradiated and irradiated) is lower than chitosan below 370 °C and lower than PVA after 370°C. An important outcome of DMA studies is that the 2nd transition temperature (tg) of PVA increased after blending with chitosan. Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used to investigate the molecular interaction and morphological features of the films. FTIR analysis presented that the interaction of blend film with monomer MMA might have occurred through the hydroxyl and carbonyl groups. SEM analysis indicated that the surface of the blend film became smooth and homogeneous after radiation modification.

• Biodegradable films were prepared by blending chitosan and PVA. Different composition of chitosan-PVA blend films (thickness 0.16 mm) were prepared by casting method. Best composition (chitosan: PVA = 1: 4) of the blend film was carefully chosen on the basis of mechanical properties.

• Radiation modification of the chitosan-PVA films with monomer, methyl methacrylate (MMA) were carried out using gamma radiation. The optimum condition for the radiation modification was 3% monomer concentration, 20 min soaking time and 30 kGy radiation dose. The TS and Eb observed at this condition were 36 MPa and 34 % respectively.

• Water uptake of the films presented that radiation modification reduced the hydrophilicity of the chitosan-PVA film.

• Thermal properties of films were characterized by TGA and DMA that revealed improvement of thermal property of the film after blending and radiation modification.

• FTIR and SEM analysis indicated the structural and morphological change after radiation modification.

BRAZIL

Until recently, at the end of the 1990s, protection, hygiene, product quality and convenience were the major drivers of food technology and packaging innovation. The materials used for food packaging consist of a variety of petroleum-derived plastic polymers, metal, glass, paper, and board, or combinations thereof. The use of plastics in the packaging industry is largest and has increased worldwide; more than 90 % of flexible packaging is made of plastics and only 17 % of rigid packaging. In recent years, there has been a rising demand for packaging that offers ease of use, high-quality food to consumers with busy lifestyles and also presents alternative to minimize the quantities of waste material disposed of to landfill throughout the world. In addition, the recent preoccupation with the environment has changed the society habits and makes the using of biodegradable or recyclable materials in the production of food packaging materials a sustainable perfect choice. The renewable nature and the natural origin of materials are guiding the criteria and defining the choice for a particular product. This work presents a review of the development at IPEN, Brazil, in the field of food packaging. The obtaining of fillers from agro-waste, in micro and nano size and its application in food packaging material, have been presented. The results showed that the addition of the smaller amount of nanocellulose, extracted from agro-waste into of the biodegradable or conventional polymers led to obtaining of food packaging materials with superior mechanical properties than neat polymer. Food packaging material prepared with PBAT/PLA foams and bio-$CaCO_3$ from eggshells presented higher tensile and compression properties than neat PBAT/PLA foams. In order to solve the incompatibility between hydrophilic nanoparticles and hydrophobic polymers and to improve the dispersion of the nanoparticles into the polymer matrix, the functionalization of nanoparticles by grafting induced by gamma radiation were studied. Gamma radiation was also used to reduce graphene oxides by modifying their surface in order to obtain graphene nanosheets. The addition of clay and TiO_2 nanofillers grafted with GMA by gamma radiation into EVA flexibles films led to better distributed of nanofillers into matrix than ungrafted ones, higher tensile resistance, and UV-Vis absorption properties. The addition of nanocellulose into flexible films based on biodegradable PBA/PLA blend and EVA polymer matrix, processed by melt extrusion, improved the tensile strength, deformation percentage, the Young modulus and maintained the thermal stability of films. Nanoparticles uniformly distributed in the matrix, absence of agglomerates and particle size less than 100 nm were also observed. The influence of clay addition on the performance of foams based on recycled polymers was also studied. The results showed that clay addition favored bubble formation in the matrix and a degree of foaming of around 46 %. Currently, food packaging has no longer just a passive role in protecting and marketing a food product. Today, it can be seen an increase of interest of consumers for packaging that is more advanced and creative than what is currently offered. The recent development of active and smart packaging is the answer to the packaging segment for this increasingly demanding and enlightened consumer. Given the importance of these new concepts, the relevance of product innovations for the food packaging, and also based on IPEN's group expertise in nanomaterials and development of packaging materials, the IPEN has created a new research line for the development of active and smart food packaging. The present IPEN's research line on active and smart food packaging focuses on the development in two different fronts: Packaging for dry food and Packaging for dairy food.

CANADA

Cellulose nanocrystals (CNCs), highly recognized for its reinforcing properties, are an organic nanosized material extracted from natural cellulose sources. CNCs were used for the development of active films based on chitosan (CH) and methylcellulose (MC). The addition of CNCs to CH and MC based films as reinforcing filler improved the tensile strength of these nanocomposites-based films by 10-23% and decreased their water barrier properties by 6-9%. In situ tests with CH/CNC based bioactive films containing EO emulsion produced a 1-2 log reduction in fungal growth in infected rice during 8 weeks of storage and resulted in insect mortality (Sitophillus oryzae) ranging between 20-43% after a 10 day of storage at 28°C. The combined treatment of γ-irradiation and bio-polymeric diffusion devices encapsulated with plant derived EOs emulsions showed an enhanced antifungal and insecticidal effect and against all tested fungal species. A 4 log CFU/g reduction in fungal growth and a mortality rate of more than 95% was observed. Moreover, the addition of CNCs to chitosan nanocomposite films containing EOs nano-emulsion showed a slower release of volatile component over 12 weeks of storage period. A reduced release of the volatiles from 27% to 41% was observed. The application of the active films and γ-irradiation did not have any detrimental effect on the sensorial properties of rice.

CNCs have a large available surface and this characteristic was explored using γ-irradiation. Irradiation was applied on CNCs in order to verify the production of aldehyde groups on the surface of CNCs under two different atmospheric conditions (nitrogen and nitrous oxide). Irradiation at 80 kGy showed the highest production of aldehyde group and the highest antioxidant property when irradiation was done under nitrous oxide. A production of 358 mmol CHO/kg and an antioxidant property of 50% at 0.1% CNCs was observed as compared to 286 mmol CHO/kg of aldehyde production and an antioxidant property of 32% under nitrogen. The control showed a 12 mmol CHO/kg and no significant antioxidant property. Introduction of irradiated CNCs in active films could have potential applications in food packaging area in order to preserve food components against oxidation. A crosslinked coating by γ-irradiation based on calcium caseinate and containing nanoemulsion was also developed and used to apply on pre-cut carrots. The coated carrots were also irradiated at low dose (0.5 kGy). Irradiation of the polymeric solution under inert atmosphere has permitted to obtained films with higher mechanical properties, and lower water vapor permeability. A synergistic effect was observed between the coating and γirradiation to reduce the total microflora count and to protect the physico-chemical properties of the carrots.

EGYPT

Active packaging films are capable of releasing, antioxidants or antimicrobial preservatives have been prepared. Antimicrobial property of polymers like PCL was enhanced by mixing them with polysaccharides as chitosan or chitin whiskers. The miscibility between the PCL and polysaccharides can be improved by exposing the chitosan to gamma rays at different doses to obtain compatible blends. PCL/polysaccharides films showed good antioxidant and antimicrobial activities which depend on the content and molecular weight of chitosan. Mechanical and barrier properties of PCL could be also improved by adding reinforcing compounds (fillers like graphene oxide). The addition of low amount of graphene oxide (GO) significantly improved both strength and barrier properties of PCL-based films. The oxygen transmission rate (OTR) and water vapor permeability (WVP) decreased significantly with the increment of GO content in PCL films. The strength and barrier properties of PCL/GO nanocomposite films was slightly improved when exposed to 25 kGy. PCL- GO films could be used as a high load packagingbearing films. Bio-active nanocomposite films based starchpolyvinyl alcohol/ zinc oxide (ST-PVA/ZnO) have been prepared by casting technique. The water vapor transportation rate property (WVTR)of (ST-PVA/ZnO) decreases with increasing PVA content. Addition of 0.5wt% of ZnO significantly decreases the oxygen transportation rate (OTR). The antibacterial activity of the nanocomposite films increases with increasing ZnO content. Smart packaging for fish and seafood products was preliminary designed using polyaniline fibers as a sensor. Polyanilinenano-fibers (PANIFS-HCl) were synthesized through interfacial polymerization and then blended with a biodegradable polycaprolactone (PCL) to obtain green colorednano-composite films. Mechanical and physical properties of such films were studied. The green color polyanilines in their protonated conductive form are rapidly interacted with basic solutes or vapors associated with food decay likes amines and changed to blue color neutral non-conductive form. Gamma rays have no significant effect on the green color of PANIFS-HCl /polycaprolactone films as well as their mechanical properties. The prepared smart films could be used as smart material to detect food spoilage.

INDIA

Polymeric food packages, after their use, are disposed as waste causing environmental hazards as they cannot be easily degraded by soil microorganisms. In recent years there has been an increased interest in the use of biodegradable films for packaging to reduce the volume of waste as they can be degraded during composting. Preservation of food by exposure to ionizing radiation, a non-thermal method, has gained considerable interest in recent years. The process involves subjecting pre-packed food to controlled amount of radiation. As packaging is also exposed to ionizing radiation, their premature degradation can impart bad taint and/or odour to the packed food items besides loss in functional properties. Thus, there is a need to develop biodegradable packaging resistant to ionizing radiation. Biopolymer based edible biodegradable films for food irradiation applications were developed using guar gum. India is the largest producer of guar gum (GG), a galactomannan, with share of 80 % of the total world production. The properties of the developed films were compared with functional properties of commercial cling film. Films were also prepared using GG irradiated at various radiation doses (0.25, 0.5, 0.75, 1, 5, 10, 25 & 50 kGy). An improvement in tensile strength by 33 % was observed when the films were prepared with guar gum irradiated at a dose of 500 Gy. To further improve mechanical, barrier and antimicrobial properties various additives such as beeswax, nano clay (nanofil 116), tween-80 and grape pomace extract was added. Concentrations of all these additives were optimized using response surface methodology (RSM) to obtain films with desired properties. At the optimum concentration of the additives, biodegradable films had mechanical and barrier properties comparable to that of commercial PVC cling films. The developed GG based films were found to be stable to radiation processing up to a dose of 25 kGy. Further, GG was chemically modified to methylated GG (MGG) to make it hydrophobic in nature. Films prepared with MGG resulted in 50 % improvement in percent elongation and 40 % reduction in WVTR as compared to control GG films. A novel eco-friendly nano-catalyst based on functionalized nanoclay was also developed. Biodegradable polyethylene based films resistant up to 30 kGy were prepared by incorporating the catalyst.

• Developed GG based films had mechanical and barrier properties comparable to that of commercial PVC films

• The films were found to be stable to radiation processing up to a dose of 25 kGy.

• The newly developed nano catalyst functioned as an oxo-catalyst, when added to polyethylene films. Films were resistant up to a dose of 30 kGy.

ITALY

The main target is the design of food packaging solutions through sustainable processes and recyclable/recoverable/biodegradable/compostable materials, creating a resilient and efficient food chain that contribute: (1). to prevent/reduce food spoilage/damage/waste as it moves from producers to consumers; (2). to maintain/extend food shelf life; (3). to monitor/alert in real time about food quality/safety; (4). to minimize environmental/economic impact related to food and packaging waste, while preserving resources; (5). to meet the consumers demands of food quality/safety; and (6). to balance innovation with cost-efficiency.

This challenge was addressed in an innovative prospective way by synergistically exploiting radiation technology and polymer nanotechnology. Both matrices derived by oil and by renewable resources were analyzed: In particular polypropylene (PP) and poly (lactic acid) (PLA) were tested. PP, derived by oil, is one of the material most used by the packaging market (market share (19%)). This material provide protection for the food they store, but it lacks in both mechanical and barrier properties and gives minimal support to prevent damage. It can be recycled, but it is not biodegradable accumulating in the environment. PLA is a biodegradable polymer obtained by renewable resource: it has been introduced as food packaging materials, aiming at partially solving the ecological problems of plastic waste accumulation. Although this polymer has great commercial potential, some of the properties such as brittleness, low heat distortion temperature, high gas diffusion restricts their use for food packaging While these biodegradable materials are environmentally friendly, the packaging produced from these materials have poor thermo-mechanical and barrier properties compared to the commercial packaging currently in use. Examples of the achievements by using PLA are described below. It has been investigated the effect of ZnO nano/micro particles in PLA film and of gamma irradiation treatment, singularly and combined, on the shelf life of packed ham inoculated with bacteria suspension of L. innocua, E. coli and S. enterica. It was found that the only presence of ZnO on PLA surface film, wrapping the ham, was not sufficient to reduce significantly the bacteria. The combined treatments, instead, induced a higher reduction of bacteria, showing a complete inhibition of S. enterica and E. coli after 5 days of storage. The effect of addition of clay nanoparticles and irradiation on crystallinity of PLA based nanocomposites was investigated using WADX. It was reported, that the pure PLA remains amorphous after irradiation to the doses of 1 kGy and 10 kGy. For the nanocomposites containing clay nanoparticles, however, the X-ray diffraction patterns showed the formation of a crystalline phase. Few crystals of the α- form were observed in PLA nanocomposite containing 1 wt% of clay. Increase of crystallinity was observed for nanocomposites containing 3 wt% and 5 wt% of Dellite D67G. In partcular it was characterized the change of crstallinity that for semicrystalline polymers influences almost all properties of the final manufactured products, including the barrier properties of primary importance for food packaging application. Several questions are still open and need to be studied. Food could potentially become contaminated with RPs formed in the packaging materials when irradiated in contact with food. Moreover, in the case of food packaging based on nanomaterials, the migration of the nanoparticles inside the food must be taken into account. Testing of packaging materials after exposure to irradiation is an integral part of the pre-market safety assessment of packaging materials irradiated in contact with food and is critical to success of irradiation technology for pre-packed food.

KOREA, REPUBLIC OF

The purposes of this paper were to study the role of a nucleating agent and a γ-ray irradiation on the crystallinity and thermal-mechanical properties of a microporous HDPE film. Nucleating agents increase the number of nucleation sites, resulting in an increase in the overall crystallization rate and a decrease in the spherulite size. Both the number and the size of the nucleation sites may affect the crystallization process. Molecular interactions between the polymer and the surface of a nucleating agent must match so as to increase the crystallization rate. The crystallinity of the HDPE films was increased with the amounts of nucleating agent but decreased above the addition of 0.1 wt% of nucleating agent. Also, the porosity of the stretched HDPE films was very similar to the crystallinity trend. The thermal shrinkage behavior decreased with an increasing radiation dose up to 50 kGy. The mechanical characteristics of the HDPE containing nucleating agent films improved with an irradiation dose up to 50 kGy. However, the maximum strength of the membrane irradiated at 75 kGy had the lowest value and its strain at a break was only 20%. The high doses of irradiation induced severe degradation rather than a crosslinking of the materials. However, the optimum dose of an irradiation induced a further crosslinking of the materials. The porosity and pore distribution of the stretched HDPE films after a γ-rays radiation were higher than that of the irradiated HDPE/ nucleating agent films after a stretching due to a crosslinked structure.

MALAYSIA

As technology advances, new and more sophisticated techniques will be developed to meet the consumer's demand for healthier and safer foods with improved quality and shelf life. In addition, foods are expected to be more 'natural' with all the goodness left in and not over processed with less chemical additives being used as preservatives. Whichever method is used, packaging will still be required to protect the food. Recently, active packaging has shown its prominence and is being developed to have antimicrobial functionality because of its potential to enhance food safety compared to traditional packaging. The alternative of generating a surface that is capable of killing microorganisms is of interest for packaging of beverages and where cut surfaces are subsequently subjected to tight-fitting, flexible packaging. Potential applications are cheese, meats, sauces, and particularly beverages, so there has been ongoing interest in generation of plastic surfaces with antimicrobial properties. Japan has historically been a leader in antimicrobial use in food packaging. Allylisothiocyanate, a naturally occurring compound in horseradish and wasabi, is used as an antimicrobial in commercial packaging in Japan. While in Europe, interest in the use of silver as antimicrobials in food processing, foods and pharmaceutical packaging has increased tremendously in the past year, and some commercial uses are being developed. This type of packaging film is yet to be explored in Malaysia. In this study, a non-migrate antimicrobial active packaging film was developed using radiation-induced grafting by electron beam accelerator. Sorbic acid was selected for incorporation onto raw polyethylene (PE) film. Sorbic acid and its mineral salts are antimicrobial agents (AM) often used as preservatives in food and drink to prevent the growth of mould, yeast and fungi. Sorbic acid, or 2,4-hexadienoic acid, is a natural organic compound used as a food preservative. Sorbic acid is highly active against fungi as well as a wide range of bacteria, especially catalase-positive organisms.

This acid also among the preservatives listed in Malaysian Association of Standards Users and is safe to be used for consumption in Malaysia. At the end of the research the following outcomes has been achieved: • The optimum condition for enhancing grafting yield were found at the following conditions: absorbed dose of 60 kGy, SA concentration of 10%, reaction temperature and reaction time of 60 °C and 3 hours. • Physico-chemical studies on the effects of surface modification on grafted antimicrobial film were performed. • The result of microbial analysis showed that total plate count (TPC) was lower for bread wrapped with grafted film proved that the developed antimicrobial film successfully protected the food against spoilage microorganism like yeast and mould. • Comparison study on shelf-life study of freshly baked bread packed with grafted antimicrobial film with regard to their moisture content, changes in color, and hardness.

POLAND

The studies were focused on optimization of methodology of preparation the composite packaging materials based on starch – PVA system. This concerned modification of the composition of the basic polymers (the starch and PVA specimens, the starch:PVA ratio, plasticizer content, etc.) and introduction of cellulose/nanocellulose fibres or particles or the selected small molecular components. Moreover, the experiments dealing with grafting of the selected monomers onto the films were carried out and the films were subjected to treatment with chosen salts solutions. Alteration of composition was followed by irradiation with Co60gamma rays (in vacuum or in nitrogen) or with fast electrons (in air). The doses in the range 1 - 25 kGy were applied, however some experiments were done with a use of doses till 70 kGy.

The studies of the irradiation influence were performed in relation to improvement the films properties. However, these studies were connected also to the search for the newer biodegradable materials resistant to irradiation that might be applied for packing the products predicted for radiation decontamination.

In the result of these studies the films with the improved functional properties were obtained directly after the synthesis as well as after further irradiation. The effect of irradiation on the properties of the films depends on the sample composition and on the condition applied during the films synthesis and storage. Appropriate alteration of the films composition enabled at least to stabilize the polymer against non-desired effects of irradiation. Some films appear resistant to irradiation with an absorbed dose as high as 25 kGy. However, irradiation might additionally improve the films properties. For example, hydrophobic films with improved mechanical properties were obtained due to appropriate introduction of nanocellulose followed by irradiation.

Moreover the safety of the obtained materials for food was studied in relation to the potential use as packaging for food. Accordingly, migration processes with participation of these materials were examined in contact with the selected food simulants.

The trials were initiated forward active packaging materials. Several antioxidant or antimicrobial agents were tested, and some materials with strong antioxidant properties were obtained due to introduction of the selected component into the film composition in the last stage of the project. These properties could be modified due to action of ionizing radiation.

Basic studies dealing with the modification occurring under influence of irradiation were carried out applying several physico-chemical methods alike: Electron Paramagnetic Resonance (EPR), gas chromatography, differential scanning calorimetry (DSC), thermogravimetry (TGA), ATR-FTIR spectroscopy, Diffuse Reflectance Spectroscopy, UV-VIS spectroscopy, NMR spectroscopy, Scanning Electron Microscopy (SEM) etc..

- Optimization of the methodology for preparation of the starch:PVA films was done. This concerns modification of the films composition as well as the action of gamma or electron radiation carried out on the particular step of the films preparation.

- Addition of nanocellulose, thymol and selected monomers supported by irradiation appeared especially beneficial for improvement of the functional properties of the films.

- Safety of the materials for some types of food was proved. The appropriate compositions can be applied for preparation of the packaging materials for dry food and the food with a high content of fats.

- The materials resistant to ionizing radiation were obtained. The appropriate compositions can be applied for preparation of the packaging materials for the products that are predicted for radiation decontamination.

- The material that reveal strong antioxidant properties was obtained and the effect of ionizing radiation on these properties was discovered.

- Degradation is the major process induced by irradiation, however it is accompanied by crosslinking. Moreover, grafting of the selected monomers on the films can be supported by ionizing radiation. The changes in the films properties due to irradiation can be attributed to modification of the surface properties of the films (in particular surface oxidation) and to their modified microstructure/nanostructure.

PHILIPPINES

Commercially available packaging films made up of LAMI PET12/FOIL7/PE100, LAMI VMPET12/PE70, LAMI NY15/PE100, LAMI PET12/PE 70, PET12/CPS40 were studied for the determination of leachates after irradiation at 10 kGy using gamma radiation. Stable isotope technique (SIT) analysis via isotope ratio – mass spectrometry (IR-MS) and liquid chromatography – mass spectrometry (LC-MS) were performed to analyze the samples for the presence of leachates using food irradiation dose. Likewise, Gel Permeation Chromatography (GPC) was also performed on the samples. Stable isotope analysis showed that there was a significant enrichment after irradiation on LAMI PET12/PE 70, LAMI NY15/PE100, and PET12/CPS40 based on the δ2H and δ2O values before and after irradiation, indicative of possible formation of radiolytic products or leachates. Minimal enrichment was observed for LAMI PET12/FOIL7/PE100 and LAMI VMPET12/PE70. These results were confirmed by GPC analyses and LC-MS analysis of the water samples which detected the presence of highmolecular weight fragments on the irradiated samples especially for LAMIPET12/PE70. No fragments were detected on LAMI NY15/PE100 which also coincided with the result from SIT. The data would indicate that stable isotope technique for δ18O ‰ and δD ‰ could be a promising methodology to determine possible contamination of leachates from packaging materials even at ppb level.

ROMANIA

The dynamics of packaged food in Romania is dependent on purchasing power of population but significant efforts are made to improve the food quality and to extent the self-life of food products. These were the main objectives of the researches developed in the project titled: "Ionizing radiation and plasma discharge mediating covalent linking of bioactive compounds onto polymeric substrate to obtain stratified composites for food packing". Because of the inert nature of most commercial polymers, they must undergo surface functionalization prior to covalently attach bioactive compounds. Chemical and physical surface functionalization techniques are applied in order to introduce the desired type and amount of reactive functional groups. Bioactive compounds (natural or synthetic) are defined as compounds which catalyze or elicit a specific response within a given biological system. Two physical ways cold plasma gas discharge and gamma irradiation have been applied to activate polymers surface. The main advantage of plasma treatments is that the modification turns out to be restricted to the uppermost layers of the substrate, thus not affecting the overall desirable bulk properties. Its main effects on polymer surfaces are: cleaning, increase of microroughness, production of radicals and finally implementation of various functional groups, the surfaces becoming hydrophilic with acidic, basic or amphyphilic character. The action of high energy radiation as gamma radiation causes changes in bulk properties and even the backbone scissions. These undesirable effects depend on the structure of the polymers, the dose applied, the testing conditions or the presence of additives and can be avoided by optimization irradiation conditions. In the studies performed during project development and further research, the surface modification of synthetic polymers, poly (lactic acid) (PLA) and polyolefins (PO) and natural cellulose-based (CC) materials has been performed. Covalent bonding onto polymeric substrates of some bioactive components (chitosan, vitamin C, vitamin E and various vegetable oily extracts) was achieved by a two steps procedure consisting on: I) ionizing radiation/cold plasma activation plasma, corona or gamma-irradiation as pre-treatment method for surface functionalization and optimization of experimental conditions (Optima conditions were for Corona: frequency 30 kHz, interelectrodes distance 7 mm, discharge power 45 kJ/m^2; for High-frequency plasma: O_2, air or N_2 as discharge gases; 40 Pa; 10, 20 and 30 minutes; interelectrode distance 6.5 cm; 1.3 MHz; discharge power of 100 W; 20-30 mA and for Gamma irradiation: ^{137}Cs source; irradiation doses were 5, 10, 15, 20, 30 kGy absorbed in air, at room temperature, at a dose rate of 0.4 kGy h^{-1}); II) coupling reaction for further coating with active/bioactive compounds like chitosan (CHT), lactoferrin, eugenol and vegetable oils (Tea Tree essential oil (TT), rosehip seeds (RO) and grape seeds oils (GO), Clove (CO), Thyme, Rosemary (R), Argan Oil and Apricot Oil). To obtain stable coatings onto polymeric substrates different coupling agents as: 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS) and carbonyldiimidazole were employed in order to covalently linking of active/bioactive formulations to the preactivated polymeric surfaces. It was found that both PLA and PE plasma exposed, and gamma irradiated samples coated with CHT are efficient as antibacterial materials for meat, cheese and antioxidant for apple juice. Covalent linking prevents the migration of components of coating into food products and also even if the migration occurs these natural additives are not harmful, more they are beneficial for consumers' health as the vegetable oils are recognized for their high therapeutic value. The antioxidant scavenging activity of chitosan is explained by its strong hydrogen donating ability. An increase in thermal stability of materials after surface modification with essential oils proved that they act as a good antioxidant. For PE packaging materials the antioxidant activity varied in the following order: PE/20kGy/EDC+NHS/CHT < PE/30kGy/EDC+NHS/RO < PE/cp air/EDC+NHS/CHT ~ PE/20kGy/EDC+NHS/TT and for the antibacterial character: PE/20kGy/EDC+NHS/TT < PE/30kGy/EDC+NHS/RO ~ PE/20kGy/EDC+NHS/CHT ~ PE/cp air/EDC+NHS/CHT. Covalent bonding of the coatings containing vegetable oils (PE/EDC+NHS/TT) seems to be more efficient for antioxidative effect than physical bonded one. In most cases rosehip seeds oil imparts the best antioxidant and antimicrobial properties. As gamma-irradiation affects also the bulk properties of the selected polymers and for a proper functionalization longer time is needed, it has been concluded that the most efficient procedure is plasma treatment. Natural and synthetic polymeric substrates, plasma activated and/or gamma-irradiated and coated with bioactive compounds, were tested as active-food packaging to improve the shelf-life of fresh curd cheese. The best antioxidant and antimicrobial properties against *Bacillus cereus, Escherichia coli, Listeria monocytogenes* and *Salmonella typhymurium* were found for PE, PLA, cellulose/chitin mix substrate and Kraft cellulose paper modified with CHT and vegetable oils as rosehip seeds oil. The air plasma was a more efficient pre-treatment of the surface functionalization for cellulosic substrate in the modifying reaction than the nitrogen plasma; and for γ-pre-irradiation, best results are obtained when using a dose of 20 kGy. The encapsulation of active (antimicrobial and antioxidant) vegetable oils into chitosan matrix by co-axial electrospinning techniques and emulsion/solvent casting method lead to a significant decrease of Total Viable Counts (TVC) on minced poultry meat, fresh beef meet, fresh curd cheese and apple juice when compared with the PE or PLA substrate plasma pre-treated and surface modified only with chitosan. Use of chitosan/vegetable oils shows synergistic activities. Choosing two biodegradable polymers as functionalizable substrates, the environmental concerns are avoided as they are biocompatible and by their degradation non-toxic compounds resulted. The PLA/CHT stratified composites supported fungal growth of *Phanerochaete chrysosporium* fungus. The gamma irradiated PLA samples show increased degradation by soil burial. Lactoferrin –covalently bonded coating onto PLA showed also high antimicrobial and antioxidant properties. Two laboratory technologies for active packaging have been elaborated and tested at micro-pilot scale at SC ICEFS COM S.R.L. Savinesti - Romania. The micropilot device was based on micro-printing technique involving the deposition of the chitosan/oil mixture onto plasma activated/gamma irradiated PE, PLA Chitcel and Kraft cellulose paper.

SERBIA, REPUBLIC OF

Located at the crossroads between Central and Southern Europe Serbia is one of the largest producers of frozen fruit to the EU (largest to the French market, and 2nd largest to the German market) Serbia is world's second largest producer of plums and second largest of raspberries Other important agricultural products: sunflower, sugar beet, soybean, potato, apple, pork meat, beef, and dairy Capital and largest city: Belgrade is located at the confluence of the Sava and Danube rivers. Over 2 million people. One of the most important prehistoric cultures of Europe, the Vinča culture, evolved within the Belgrade area in the 6th millennium BC. Nearby the archeological site today is localized Vinča Institute

VINČA INSTITUTE OF NUCLEAR SCIENCES Founded in 1948 Vinca Institute of Nuclear Sciences has been the most prominent multidisciplinary research institute in the Republic of Serbia. The research program at the Institute covers the following areas: physics, chemistry, biology, power engineering and technology, radiation and environmental protection, production of radiopharmaceuticals, accelerator science, and nanoscience. Radiation unit at Vinca Institute of Nuclear Sciences has operated since 1978. The facility core is cobalt–60 gamma irradiator with wet storage working in batch mode. Uniplast is a regional leader in the production and distribution of pharmaceutical, medical and cosmetic products. Since 1991, when it was founded, and over 28 years of operation, the company has independently developed over 200 different products. Development of antimicrobial active packaging materials in the food industry based on silver zeolite and polyethylene

The aim of this project is to produce materials for active packaging based on zeolite and silver, with additional gamma irradiation treatment. The plastic is mixed with a zeolite containing silver ions. Zeolite will release silver inside the package. Yoni silver is a potent antimicrobial agent and at very low concentrations destroys most of the pathogenic microorganisms. It is important to note that ions of silver in this concentration do not affect the content of the packaging. However, some microorganisms are resistant to the influence of Ag ions. Therefore, we examined the effects of ionizing radiation on the elimination of all microorganisms from these materials that can be used for food packaging. Basic goals: - Destroying pathogenic microorganisms or stopping them from reproduction - Creating products that are safer for consumers - Extension of the shelf-life without the use of preservatives, which is better for consumers

THAILAND

The first part of the project aims to study the effects of gamma irradiation on commercially available polymers currently being used for food products sterilized by radiation processing at Thailand Irradiation Center (TIC). The chosen product is fermented pork sausages. The effects of gamma irradiation on packaging material of fermented pork sausages were investigated. FTIR results showed that the middle and inside layers of the packaging materials were made of PP. FTIR analysis revealed that the chemical changes of the inside PP, even before irradiation processing, was caused by the high fat content and the direct contact between the inside PP and acidic fermented pork sausages. The results from mechanical tests also implied that the direct contact between acidic fermented sausages and the inside PP led to the premature degradation of the inside PP, whereas irradiation led to further decrease in mechanical properties of both the middle and the inside PP. The second part of the project focuses on the effects of irradiation on a promising biodegradable polymer, poly(lactic acid) (PLA), an emerging biodegradable polymer, poly(butylene succinate) (PBS), as well as their blends with an indigenous natural polymer, i.e. cassava starch, which is quite abundant and inexpensive in Thailand. PLA and PBS are good candidates for food packaging due to their compostability and biodegradability. Results showed that upon irradiation, PLA underwent degradation, while PBS was able to crosslink. However, the dose required for the crosslinking of PBS was rather high. Hence, a food-grade crosslinking agent was used to lower irradiation dose for PBS and ensure that PLA, along with their blends with TPS, will not degrade but rather crosslink upon irradiation, hence resulting in safer products with enhanced mechanical properties, while simultaneously being able to maintain their biodegradability and/or compostability. Results indicated that the crosslinking agents were able to induce crosslinking of PLA and lower radiation doses required to crosslink PBS. For the blends between the PLA or PBS and thermoplastic starch, mechanical properties basically declined with increasing content of TPS, most likely due to poor compatibility between the biodegradable thermoplastic and TPS.

TURKEY

There are synthetic and naturally occurring compounds that may be exploited by the packaging industry. The surface of polymer films can be made antimicrobial by using some compounds which have antimicrobial activitiy. Antimicrobial films can be grouped into two types: those that contain an antimicrobial agent which migrates to the surface of the food and, those which are effective against surface growth of microorganisms without migration. The objective of the present work was to graft some food additives onto commercial packaging film polyethylene (PE) by gamma-irradiation under O2 and N2 atmosphere. With this aim, we tried to graft some food additives (FA) with antimicrobial properties such as fumaric acid (FAc), grafting acrylic acid (AAc) and then loaded natamycin (Nat) onto PE film. We investigated the irradiation dose and concentration of FA on grafting yield. The grafting yield of FAc onto PE film was very low. The antimicrobial activity of FAc grafted PE films was investigated. PE-g-FAc film was antibacterial effect against E.Coli. Although PE-g-AAc/Nat samples were not antibacterial against E.Coli and Staphylococcus aureus, they were antifungal effect against Penicillium aurantiorium and Aspercillus versicolor. The antifungal effect against Aspercillus versicolor is more than Penicillium aurantiorium. The inhibition zone diameter in Aspercillus versicolor is bigger than those of Penicillium aurantiorium. There was no grafting of natamycin onto PE film.

We performed the grafting of acrylic acid (AAc) onto PE films and AAc grafted PE film could be used to bind antifungal and antibacterial agents, such as natamycin, and the antifungal and antibacterial properties of the films were investigated. The experimental conditions and optimum conditions to graft PE films were determined such as the irradition dose, concentration of comonomer, temperature and the time of reaction. The synthesized PE, PE-g-PAAc, PE-g-PAAc/Nat samples were characterized by using X-ray-photoelectron spectroscopy, contact angle studies, swelling studies, thermal and mechanical tests. The grafting of PAAc on PE surface and the loading of natamycin on PE-g-PAAc surface caused to increase in TS and E and a marked decrease in EB, which means that the material becomes less elongable and more resistant. The thermal stabilities of PE-g-PAAc, PE-g-PAAc/Nat were between those of the corresponding PE, PAAc and Natamycin. The thermal stability of these packaging materials was very high. PE-g-PAAc/Nat films can be used for all types of cheese.

To develope the other packaging materials for the other type of foods, the presence of L on the surface of PE film was explained by gravimetric, surface analysis, XPS spectra. To graft D-Limonene on PE film, Emulsion media was developed and optimized by determining some parameters such as amounts of D-limonene, Tw-20, and the other compunds in it. The emulsion had a good physical stability. The grafting of D-limonene on PE was performed by pre-irradiated and mutual emulsion grafting methods. The results of spectroscopic and thermal characterization show that D-limonene graftted on PE. The synthesized PE, PE-g-L samples were characterized by using X-ray-photoelectron spectroscopy, contact angle studies, thermal tests. Although PE film showed the antioxidant property after PE film grafted with D-Limonene. PE-g-L film was not antibacterial effect against E.Coli and S.aureus. PE-g-L films were not also antifungal effect against Penicillium aurantiorium and Aspercillus versicolor.

UK

The Hydrocolloids Research Centre was relocated to the University of Chester in August 2015. We continued to work on the application of natural polymers (Hydrocolloids) as materials for intended applications such as edible film coating, packaging matrix or as indicators in food labels to predict food spoilage (intelligent packaging). In the first RCM meeting we reported our radiation technology to cross link polysaccharides and protein using ionizing radiation in the presence of acetylene gas. The technology was demonstrated to be applicable also to cross-linking natural and synthetic polymers. Subsequently, we worked on active packaging in collaboration with the French group at Burgundy (Prof. Fredreic Debeaufort) on incorporating antioxidants into gelatin-chitosan film (Publication 1). Additionally, our work on developing a method to measure the film thickness of polymer solution which relevant to predict the functionality of film forming ability of protein, polysaccharides and mixtures thereof was also reported (publications 2 and 3). The Centre has been also engaged in developing a method to modify hydrocolloids by fractionation using segregative phase separation (publication 4). This work is particularly relevant to the RCM when dealing with various preparations / formulations for film coating and radiation grafting which requires good understanding of the homogeneity of such formulation. Furthermore, the Centre has been successful in working with a start up company based in London (Mimica Ltd) to work on the development of Mimica Touch as an indicator for food expiry. The technology relies on calibrating the decay (degradation) of gelatin film to correlate with the same rate of food spoilage contained in a package. The design of Mimica Touch is inclusive of people with visual or cognitive impairments where the gel covers some plastic bumps, when the gel is set is solid and the surface is smooth, then an activator is added on top of the gel and it reacts with it breaking down its structure. This reaction changes its rate with the change in temperature or in the environment. When the food is off the gel turns liquid and the bumps underneath can be felt. This work has been supported by the highly prestigious awarding body in the UK (Innovate UK grant) and has also received favorable press coverage in the UK.

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USA

The use of high energy electron beam (eBeam) food processing technology is a safe and useful alternative to the use of radioisotopes such as cobalt-60 for food processing. One of the focus areas of activities at the National Center for Electron Beam Research (NCEBR) is to harness eBeam food processing technology for preserving and possibly enhancing the quality of fresh produce. Our long-term goal is to demonstrate that eBeam technology can not only maintain the quality of fresh produce but also extend shelf life of packaged fresh produce in an environmentally sustainable manner. Extending the shelf-life of fresh produce makes a significant impact on reducing food waste. Using bioplastics will reduce the impact of food packaging on the environment. We are harnessing multiple contemporary food processing technologies such as modified atmosphere packaging (MAP), starch-amended bioplastics and eBeam processing to extend the shelf life in an environmentally sustainable manner. In one of our early studies, the experimental objectives were to evaluate low dose eBeam ($\leq$ 1 kGy) processing alone or along with MAP for red grapes, cherry tomatoes, and strawberries for reducing bioburden, while maintaining sensory attributes and consumer acceptability scores. The results suggested that eBeam at low doses ($\leq$ 1 kGy) alone or in combination with MAP can be a unique approach for developing packaged healthy vending fresh produce items. In on-going studies, we evaluated the use of polyethylene films extruded with varying levels of a proprietary starch resin (0%, 20% and 30%) for packaging baby carrots and cherry tomatoes. Varying eBeam doses (0 kGy, 0.1 kGy, 1.0 kGy and 4.0 kGy) were employed in these studies. The results to date suggest that eBeam in combination with MAP has a significant impact on maintaining quality. The color characteristic, specifically the hue angle of the bioplastics changed depending on the eBeam dose and the % starch resin. The 10% starch resin amended polyethylene exhibited an increase in the hue angle even at 0.1 kGy. However, the 20% and 30% amended polyethylene films showed no changes even at 4 kGy. Results from the objective sensory analyses and the bioburden analysis are currently being analyzed.

CONCLUSIONS

- The previous CRP and this meeting have yielded a significant amount of information on the use of radiation technology in the development of advanced packaging materials for food products
- This meeting is of particular relevance to the recent regulations and consumer demands worldwide for the need to reduce the use of conventional plastics in food packaging. This trend has undoubtedly exerted significant pressure on major food processors and retailers to provide alternative biodegradable and sustainable packaging materials
- The meeting participants presented country specific restrictions and limitations of the use of the plastics in packaging which further justifies additional research and commercialization.
- The meeting participants agree that packaging industry is highly competitive in terms of polymers used, know-how and their path to commercialization. Therefore, there is a heightened need to partner specifically with end-users who ultimately control the adoption of alternative packaging materials.
- The participants reiterated the importance of using of irradiation technology in the development of the polymers as well as in studying the resistance of these biopolymers in food packaging applications.
- It is noted that some of the projects presented to this meeting are close to commercial adoption, for example (a) antimicrobial packaging for bread and ready-to-eat food (b) intelligent indicators using gelatine-based formulations (c) active coatings.

RECOMMENDATIONS

- The results from the previous CRP and this technical meeting should be compiled and published as a TECDOC titled "The use of radiation technology in the development of advanced packaging materials for food products"
- A new CRP should be organized focusing on the use of radiation technology for food packaging and coating that is strategically targeted for commercialization. To do so, approaches may include working and collaborating with commercial stake-holders, utilizing additive manufacturing by 3D printing and directed at research gaps that currently preclude commercialization.
- This new CRP should consider the following: (a) industry stake-holders as observers (b) participation of the Joint FAO/IAEA Division of IAEA (c) consideration of regulatory aspect of the participating countries when choosing appropriate targeted polymer and blends.

ANNEX I

IAEA Technical Meeting on
"Use of Radiation Technologies for Active Packaging Material"
20-24 May 2019, Budapest, Hungary

MEETING AGENDA

Monday, 20 May 2019

09:00 - 10:00	**Registration**	
Session I:	**Introductory Session**	
10.00 – 11:00	**Opening of the meeting by:** **Mr Tamas Belgya, Director, Institute of Energy Security and Environmental Safety** **Mr Bumsoo Han, Scientific Secretary, RPRT (IAEA)** **Ms Erzsébet Takács "Application of ionizing radiation"** **Scope and Objectives of the Meeting, Adoption of the agenda** Election of the chairperson of the meeting, introduction of participant	
Session II:	**Participants' Presentations**	
11:00 – 11:40	Mr Mustapha Kaci (**Algeria**)	The Effects of Gamma Irradiation on Morphology and Properties of Nanocomposites Based on PHBV/PLA Blend and Organo-Modified Montmorillonite
11:40 – 12:00		*Coffee Break*
12:00 – 12:40	Ms Maria Celeste Cingolani **(Argentina)**	Edible Films and Coating Development Based on Natural Polymers in Argentina. A Review.

12:40 – 13:10	Mr Nirmal Chandra Dafader **(Bangladesh)**	Preparation and Characterization of Biodegradable Packaging Film from Radiation Modified Chitosan-Poly (vinyl alcohol) Blend
13:10 – 14:30		*Lunch Break*
14:00 – 14:40	Ms Esperidiana Moura **(Brazil)**	Development of Food Packaging Materials Reinforced with Nanofillers Modified by Ionizing Radiation - A Review
14:40 – 15:20	Ms Monique Lacroix **(Canada)**	Use of Gamma irradiation for the development of active nano-biopolymers and to assure food safety and security
15:20 – 15:40		*Coffee Break*
15:40 – 16:20	Mr Hassan Abdel-El-Rehim **(Egypt)**	Development of active and smart biodegradable based food packaging materials using gamma radiation
16:20 – 17:00	Ms. Jyoti Tripathi (**India**)	Biodegradable packaging materials for food irradiation applications

Tuesday, 21 May 2019

Session III:	**Participants' Presentations**	
09:00 – 09:40	Mr Jong-Seok Park **(Republic of Korea)**	Development of High Functional Polymer Film Using Radiation Technology
09:40 – 10:20	Ms Nor Azwin Shukri **(Malaysia)**	Application of Radiation Technique in Development of Advances Packaging Materials for Food Products
10:20 – 10:40		*Coffee Break*
10:40 – 11:20	Ms Lucille Abad (**Philippines**)	Stable Hydrogen and Oxygen Isotopes as Indicators for Organic Leaching in Irradiated Packaging Materials
11:20 – 12:00	Ms Krystyna Ciesla (**Poland**)	Based on Starch - PVA System and Cellulose Reinforced Packaging Materials. Active Packaging. The Effects of Ionising Radiation.
12:00 – 12:40	Ms Cornelia Vasile (**Romania**)	

		Plasma or Gamma Assisted Active (Nano) Coatings Deposition onto Polymeric Surfaces to Obtain Multifunctional Materials for Food Packaging
12:30 – 14:00		*Lunch Break*
14:00 – 14:40	Mr. Slobodan Masic (**Serbia**)	Development of antimicrobial active packaging materials in the food industry based on silver-zeolite and polyethylene
14:40 – 15:20	Ms Kasinee Hemvichian (**Thailand**)	Development of Natural and Synthetic Polymers as Suitable Packaging Materials for Food Products Sterilized by Radiation Processing
15:20 – 16:00	Ms Dilek Solpan (**Turkey**)	Grafting of D-Limonene onto Polyethylene Films by Gamma Irradiation to Impart Antimicrobial Properties
16:00 – 16:20		*Coffee Break*
16:20 – 17:00	Mr Saphwan Al-Assaf (**U.K.**)	Review of Recent Developments in Smart Packaging
17:00 – 17:40	Mr Suresh Pillai (**USA**)	Harnessing Bioplastic-Based Packaging for High Value Fresh Fruits

Wednesday, 22 May 2019

Session V & VI:	**Discussion on the publication of IAEA TECDOC (ALL PARTICIPANTS)**
09:00 – 10:30	Preparation of the Meeting report: scope/contents/structure of the meeting report
10:30 – 11:00	*Coffee Break*
11:00 – 12:30	Preparation of the Meeting report: conclusions/recommendations
12:30 – 14:00	*Lunch Break*
14:00 – 15:00	Discussion and drafting of the Meeting report:
15:00 – 15:30	
15:30 – 16:00	*Coffee Break*

16:00 – 17:30	Discussion on the future direction of food packaging material
17:30 – 18:00	*Finalize and document the discussion*

Thursday, 23 May 2019

Session VII:	**Finalizing the Preparation of Technical Document (ALL PARTICIPANTS)**
09:00 – 10:30	Discussion and drafting of the publication of IAEA TECDOC
10:30 – 11:00	*Coffee Break*
11:00 – 12:30	Discussion and drafting of the publication of IAEA TECDOC
12:30 – 14:00	*Lunch Break*
14:00 – 15:30	Drafting of the of IAEA TECDOC
15:30 – 16:00	*Coffee Break*
16:00 – 17:30	Drafting of the of IAEA TECDOC
17:30 – 18:00	Review of the Draft IAEA TECDOC

Friday, 24 May 2019

Session VIII:	**Final Review and Acceptance of Meeting Report**
09:00 – 10:30	Review of the Draft Meeting Report
10:30 – 11:00	*Coffee Break*
11:00 – 12:30	Finalizing and Acceptance of the Meeting Report
12:40 – 14:00	*Lunch Break*
14:00 –	*Closing of the Meeting*

ANNEX II

F2-TM-1804857
Technical Meeting on the Use of Radiation Technology in the Development of Active Packaging Materials
Budapest, Hungary
20 to 24 May 2019

List of Participants
(as of 2019-05-07)

S. No.	Authority	Personal Details
1	**IAEA**	Ms Dinara ABBASOVA Vienna International Centre P.O. Box 100 Wagramer Strasse 5 A-1400 VIENNA AUSTRIA Tel: +43 66565210607 Email:D.Abbasova@iaea.org
2	**IAEA**	Mr Bum Soo HAN Vienna International Centre P.O. Box 100 Wagramer Strasse 5 A-1400 VIENNA AUSTRIA Tel: +431260021750 Email:B.S.Han@iaea.org
3	**Algeria**	Mr Mustapha KACI Université Abderrahmane Mira, LMPA, campus Targa-Ouzemmour BÉJAIA 06000 ALGERIA Tel: +213673453151 Email:kacimu@yahoo.fr
4	**Argentina**	Ms Maria Celeste CINGOLANI Comisión Nacional de Energía Atómica (CNEA), Centro Atómico Ezeiza (CAE) Presbitero, Juan Gonzalez Y Aragon N. 15 C 1429 BNP BUENOS AIRES ARGENTINA Tel:+54 (11)41258629/ +54(11)41258403 Email:cingolani@cae.cnea.gov.ar
5	**Bangladesh**	Mr Nirmal Chandra DAFADER Institute of Nuclear Science and Technology (INST); Atomic Energy Research Establishment (AERE); Bangladesh Atomic Energy Commission (BAEC) P.O. Box 3787, Ganakbari, Savar DHAKA BANGLADESH Tel:+880 27789250 Email:nirmaldafader@yahoo.com

S. No.	Authority	Personal Details
6	**Brazil**	Ms Esperidiana MOURA Instituto de Pesquisas Energeticas e Nucleares (IPEN-CNEN/SP) Av. Prof. Lineu Prestes, 2242 Cidade Universitaria 05508-000 SAO PAULO BRAZIL Tel: +551131339336 Email:eabmoura@ipen.br
7	**Canada**	Ms Monique LACROIX Institut national de la recherche scientifique (INRS) Institut Armand-FRAPPIER 531 des Prairies Blv., Laval city Uvebec, H7VIB7 CANADA Tel: +14506875010 ext. 4489 Email:monique.lacroix@iaf.inrs.ca
8	**Egypt**	Mr Hassan ABDEL-REHIM Atomic Energy Authority of Egypt Ahmed El-Zomor P.O.Box 29 CAIRO EGYPT Tel:+20 10 06520 350 Email:ha_rehim@hotmail.com
9	**India**	Ms Jyoti TRIPATHI Food Technology Division Bhabha Atomic Reseach Centre Trombay, Maharashtra 400 085 MUMBAI INDIA Tel:+91 (22)25590560 Email:jsharma@barc.gov.in
10	**Malaysia**	Ms Nor Azwin Binti SHUKRI Malaysia Nuclear Agency Bangi 43000 KAJANG SELANGOR MALAYSIA Tel:+60 389112000 Email:azwin@nm.gov.my
11	**Philippines**	Ms Lucille ABAD Philippine Nuclear Research Institute (PNRI) P.O. Box 213, Commonwealth Avenue, Diliman QUEZON CITY PHILIPPINES Tel: Email:avlucille@pnri.dost.gov.ph
12	**Poland**	Ms Krystyna CIESLA Institute of Nuclear Chemistry and Technology ul. Dorodna 16 03-195 WARSAW POLAND Tel:0048 22 8111313 Email:k.ciesla@ichtj.waw.pl

S. No.	Authority	Personal Details
13	**Republic of Korea**	Mr Jong Seok PARK Advanced Radiation Technology Institute Korea Atomic Energy Research Institute (KAERI) 29, Geumgu-gil JEONGEUP REPUBLIC OF KOREA Tel: 82635703069 Email:jspark75@kaeri.re.kr
14	**Romania**	Ms Daniela PAMFIL Romanian Academy, Physical Chemistry of Polymers Department, Petru Poni, Institute of Macromolecular Chemistry PPIMC 41 A Gr, Ghica Alley IASI ROMANIA Tel:+4 0232 217454 Email:pamfil.daniela@icmpp.ro
15	**Romania**	Ms Cornelia VASILE "Petru Poni" Institute of Macromolecular Chemistry Physical Chemisrty of Polymers Department, 41A Grigore Ghica Voda Alley 700487 IASI ROMANIA Tel: 40232217454 Email:cvasile@icmpp.ro
16	**Serbia**	Mr Slobodan MASIC Vinca Institute of Nuclear Sciences Mike Petrovica Alasa 12-14 P.O. Box 522 11001 BELGRADE SERBIA Tel:+381 (11)3408449 Email:slobodan.masic@gmail.com
17	**Thailand**	Ms Kasinee HEMVICHIAN Thailand Institute of Nuclear Technology 9/9 Moo 7 Saimoon 26120 NAKHON NAYOK THAILAND Tel:6637392944 Email:kasineeh@yahoo.com
18	**Turkey**	Ms Dilek SOLPAN Department of Chemistry Hacettepe University 06800 Beytepe /ANKARA TURKEY Tel: +903122977990 Email:solpan@hacettepe.edu.tr
19	**United Kingdom**	Mr Saphwan AL-ASSAF University of Chester Parkgate Road, Chester, CH1 4BJ CHESTER UNITED KINGDOM Tel:+44 1244511540 Email:s.alassaf@chester.ac.uk

S. No.	Authority	Personal Details
20	**United States of America**	Mr Suresh PILLAI Texas A&M AgriLife Research 600 John Kimbrough Blvd., Suite nr. 512 P.O.Box MS 2142 77843 COLLEGE STATION TX UNITED STATES OF AMERICA Tel:+1 9798452994 Email:s-pillai@tamu.edu