HARMONIZED PROTOCOL for RADIATION-INDUCED GRAFTING

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CONTENTS

1. Introduction

Grafting can be defined as a polymer modification where mostly a different monomer is attached to an existing polymer through a covalent bonding attachment. Thus graft copolymers are branched macromolecules in which the branches are of different molecular structure w.r.t. base polymer [1]. The grafting technique is primarily aimed at synergistically combining properties of two polymers.

Grafting is afree radical process, which can be initiated chemically, photo-chemically and using ionizing radiation. Radiation-induced grafting has the following advantages over conventional grafting methods:

- It is simple, accurate, easy to control and relatively cleaner process.
- Additives or catalysts are seldom required.
- Local heating can be avoided unlike in the chemical method, thus thermally sensitive monomers can be grafted
- Absorption of energy by the polymer substrate initiates free-radical process unlike in the chemical method.
- Zero activation energy process for initiation, as it is a temperature independent step.
- High penetrating ability makes it appropriate for grafting onto solid substrates.
- Possibility exists to perform mosaic grafting (grafting of different monomers in differentportions on the same substrates) on the solid substrate, as grafting canbe directed to the location of interest [2].

Grafting is a well-known technique for several decades and large number of references are available in the literature on the subject. In view of this fact, IAEA initiated RAS/1014 on "Supporting radiation processing for development of advanced grafted materials for industrial applications and environmental preservation". From different activities taken under RAS it has been felt that there is a strong need for harmonizing the existing radiation-induced grafting protocols. The harmonized protocol aims at accumulating, sharing and dissipating the knowledge on radiation-inducedgrafting in a systematic way for the benefit of not only beginners in the field but practitioners who already have been involved in radiation grafting.

The Protocol is divided into 10 Chapters, of which the first six give general information and guidance, while specific protocols can be found in Chapter 7. Important considerations for the scale-up of grafting processesare in Chapter 8, followed by examples of successful technology transfer in Chapter 9. Chapter 10 is devoted to emerging applications.

This protocol draftwas discussed and adopted with minor modifications at the Project Review Meeting held on 23-27 June 2014 in Sri Lanka.

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2. Basic Terms and Definitions

Ionizing radiation: Ionizing radiation is a type of radiation composed of photons/particles like gamma, X-rays, beta and alpha particles or machine accelerated particlesthat individually carry enough kinetic energy to liberate an electron from an atom or molecule with which it interacts.

Radiation sources:Radiation sources are of two types a) Radioactive sources which emit radiation due to their nuclear instability e.g. alpha, beta, gamma radiations b) Machine generated radiation e.g. electron beam, cyclotrons etc.

Units and G-value: The SI unit of absorbed dose is Gray (Gy). 1 Gy = 1 J/kg=100 rads=100 ergs/g. The radiation chemical yield is expressed as G-value and defined as number of events/100 eV. The SI unit of radiation-chemical yield is $\mu mol.J^{-1}$. (*1 molecule/100 eV = 1.036 x 10^{-7} mol.J^{-1} = 0.1036 $\mu mol.J^{-1}$*) [1].

Grafting yield (generally reported in terms of % grafting) and grafting efficiency are defined as follows

$$\% \text{ Grafting} = \{(W_g - W_o) / W_o\} \times 100$$

WhereW_g= Weight after grafting and W_o= Initial weight of the substrate

% Grafting efficiency = (Amount of monomer grafted/Total monomer converted into polymer) x 100

*Grafting rate:*It is the grafting yield per unit time (dW_g/dt).

Free-radical polymerization: Radiation induced polymerization proceeds mainly by a free-radical mechanism. The kinetics of free radical polymerization of a variety of vinyl monomers has been extensively studied leading to better understanding of the mechanism of polymerization reactions. Thus, a number of fundamental reaction steps are involved as in conventional free radical polymerization. In their simplest form, four steps can be distinguished in radiation induced polymerization. This includes free radical formation, initiation, propagation and termination. Free radical polymerization has the ability to polymerize a wide range of monomers, is tolerant to unprotected functional groups, compatible with different reaction conditions, very simple to implement and inexpensive.

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3.Techniques of radiation-induced grafting

Radiation-induced graft copolymerization can be performed using three common methods: i) Grafting by simultaneous or mutual irradiation ii) Grafting initiated by pre-irradiation in vacuum or inert atmosphere and iii) Grafting initiated by peroxidation (pre-irradiation in air). The three grafting methods are suitable for performing graft copolymerization of various monomers onto polymer substrateshaving different forms such as powder, beads, films and fibres. Any free radical polymerization techniques can be employed to carry out grafting.

Grafting by mutual irradiation: In this technique, the polymer substrate is irradiated in presence of reactive monomer which may be present as vapor, liquid or in the form of solution Irradiation leads to the formation of radicals on polymers and/or monomers, resulting in graft copolymerization. Since monomer is simultaneously irradiated during the grafting, homopolymer is formed by radicals from the monomer or polymer fragments. Such homopolymers usually need to be removed by solvent extraction from the graft copolymerprior to any further evaluation. Generally, grafting by simultaneous irradiation technique is preferred for polymer backbones which undergo predominantly degradation[1,2].

*Pre-irradiation technique (Post-irradiation grafting)***:** In this technique, generally a polymer is irradiated in vacuum or in presence of an inert gas. Later the polymer is removed from radiation field and exposed to monomer at an elevated temperature to achieve grafting. Irradiation of the polymer produces relatively stable, trapped radicals. Diffusion of monomer to these active sites produces graft copolymer. Homopolymer is hardly produced by this method. Thus if the initiating radicals are depleted too quickly by decay at elevated temperature, the grafting yield is decreased. Electron spin resonance is a useful tool to confirm the change in the radical concentration during the grafting reaction and after irradiation of polymers.Pre-irradiation method is preferred when using reactive monomers and the reaction is desired to be performed away from the irradiation source as the polymer can be irradiated and stored under sub-ambient temperature [3,4]. It is also suitable for EB irradiation for grafting at industrial scale [5].

*Per-oxidation***:** In this technique the polymer is irradiated in air or oxygen to yield stable peroxides or hydroperoxides. The peroxidized polymers are removed from the radiation source

and stored at room temperature until ready for reaction with monomer in air or vacuum at elevated temperature to obtain graft polymer. The peroxidation method has the same advantages of pre-irradiation method in addition to its convenience in elimination of evacuation and the use of inert gases.

Radiation grafting for controlling chain length (RAFT): In this technique, while maintaining usual advantages of free radical polymerization, the limitations in controlling molecular weight, molecular weight distribution and molecular fine structure are overcome. In the presence of a so-called RAFT agent the free radical polymerization proceeds through an equilibrium state allowing the control of development of molecular weight with conversion of monomer. The polymer obtained at any conversion will not only have a predetermined molecular weight but a narrow molecular weight distribution as well [6,7].

In a grafting reaction in presence of a suitable RAFT agent with mutual irradiation of monomer and substrate it has been shown that the molecular weight of homopolymer formed had the same molecular weight as the grafted chains. The result of this important finding was the application of RAFT graft copolymerization of a number of monomers to different substrates with a perfect control over the molecular weight and distribution of grafted chains. In other words in any RAFT-mediated radiation-induced grafting determination of molecular weight of homopolymer formed at any stage during grafting will give us information about the grafted chains. The molecular weight of the homo- and graft copolymers can be predicted by the following simple equation as a function of conversion of monomer as well as [Monomer]/[RAFT agent] ratio:

$$M_n(\text{theoretical}) = M_{\text{monomer}} \times [\text{Monomer}]/[\text{RAFT}] \times \text{conversion} + M_{\text{RAFTagent}}$$

where $M_n(\text{theoretical})$, M_{monomer} and $M_{\text{RAFTagent}}$ refer to the molecular weights of the polymer, monomer and RAFT agent respectively. Conversion should be taken as the value of percent conversion of monomer into polymer. Square brackets correspond to respective concentrations of monomer and RAFT agent.

In a typical RAFT-mediated, radiation-induced graft copolymerization, the most important step is the selection of proper RAFT agent. There are a number of RAFT agents commercially available for selection from the market. The basic approaches for the selection of the most

appropriate RAFT agent for a particular monomer are available in literature [8-10]. After deciding on a certain RAFT agent, the second step is to preparea solution of RAFT in the monomer at a certain [Monomer]/[RAFT] ratio. The rest of the process follows conventional mutual irradiation with samples taken occasionally from the grafting medium to determine the conversion of the monomer to polymer as well as determination of molecular weight of the homopolymerformed in the medium.

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4. Factors affecting grafting

Grafting, being a chemical reaction, depends on the experimental parameters such as the nature of substrate, type and concentration of monomers, dose and dose rate, presence of additives, temperature, storage conditions and atmosphere [1-3].

Nature of substrate:The physical state and chemical structure of polymer substrates significantly affects the grafting yield. The radiation response of the polymer backbone itself plays an important role in the final properties of grafted material. Crystallinity, orientation, thickness and bulk densityof the polymer backbone affect the extent of grafting and post grafting dimensional changes. Based on the sensitivity of substrates towards radiolytic degradation, polymers can be classified into radiation degrading and radiation resistant polymers. The former undergoes severe chain scission affecting their physico-chemical stability and PTFE is a typical example. Whereas, in the latter, degradation effect is less likely affecting physico-chemical stability as in PE. Radiation degrading polymers are preferred for simultaneous irradiation method while radiation-resistant polymers can be grafted by any grafting methods.

Substrates can be of synthetic or natural origin. When choosing natural polymers as substrates one should keep in mind that they predominantly undergo degradation on irradiation, therefore grafting parameters must be carefully selected (especially dose).When polymer waste is used as substrates for grafting, proper cleaning is required.

Nature of monomer:Radiation grafting is favored if G-radical for polymerbackbone is greater than G-radical for monomer in mutual grafting. Monomers which tend to swell the substrate are likely to enhance bulk grafting. The monomers with smaller size tend to diffuse into the substrate and facilitate grafting. It is important to know whether a monomer is homogeneously or heterogeneously polymerizing in bulk or in solution. In case of heterogeneously polymerizing monomers the control of grafting is very difficult.

Effect of dose and dose rate: Absorbed radiation dose and dose rate are two significant parameters that determine the kinetics and extent of grafting. The former affects the number of radicals generated in the grafting system whereas the latter has a strong impact on the survival of

such radicals and the termination of growing chains. In addition, dose rate favors frequency of the grafted chains (number of chains per unit area) particularly in case of pre-irradiation grafting. The grafting yield increases with increasing dose whereasit often decreases with high dose rates. This is caused by radical recombination reactions and fast termination of the grafted growing chains. Relatively low dose and dose rates are required for simultaneous irradiation to achieve a grafting yield comparable to pre-irradiation method which has to be performed at high doses. High dose rates are to be avoided in case of mutual grafting to reduce homopolymer formation. When grafting is carried out in emulsion state, dose requirement is generally reduced by an order of magnitude compared to solution grafting.

Role of additives

i) *Controllinghomopolymerization:*In aqueous phase grafting, homopolymerization could be inhibited by incorporating ferrous ions, while anions do not affect grafting or homopolymerization. Generally, metal ions such as Fe^{2+}act as reducing agent to decompose hydroperoxides, thereby converting ·OH radicals formed in the thermal decomposition of the hydroperoxides to OH ions. Thus homopolymerization initiated by $^.$OH is suppressed and homopolymer is not formed.

ii) *Enhancing grafting by acid addition:* Addition of mineral acid (0.1-0.5 M) to grafting medium increases the grafting yield. Presence of H^+ results in conversion of solvated electron to H radical which causes abstraction reaction with the backbone to generate more grafting sites. Presence of acid is also reported to enhance the partition of the monomer from the bulk to backbone thereby further promoting the grafting reaction.

iii) *Role of crosslinking agent:* Addition of multifunctional monomers (MFM) enhances grafting yields in some of the cases. However addition of MFM is generally recommended when improvement of the mechanical properties of grafted material is desired.

Effect of grafting medium

i) *Bulk*: When only monomer is used for grafting without any solvent it is called bulk grafting. This is a simple process that was successfully used for grafting of non-woven fabric [4].

ii) *Solution*: This is the most common method of grafting. Monomer is used for grafting after dissolving in some solvents. Suitable solvent is selected in terms of its swelling effect on substrate and radiation response.

iii) *Emulsion*: Water-insoluble monomer is dispersed in water using a surfactant to form stable emulsion. The stability of the emulsion depends on ratio of monomer and surfactant. Stability of emulsion should be maintained during the grafting process. Emulsion grafting improvesgrafting yield. This is an environmental friendly alternative to grafting carried out in organic solvents [5].

Effect of temperature

Irradiation temperature: Irradiation of substrate at sub-ambient temperature is preferred for maintaining the activity of radicals which ultimately contributes to enhanced grafting. The glass transition temperature (T_g) is important property to affect grafting yield of the substrate. Irradiation carried out above T_g will increase grafting compared toirradiation at temperatures lower than T_g [6].

Grafting temperature: Grafting is to propagate another polymer chains from the substrate. Higher temperatures accelerate the grafting rate.However, high temperature also contributes to formation of homopolymer at the expense of grafting.

Effect of atmosphere

Atmosphere during irradiation: Irradiation in air or O_2 atmosphere is preferred for peroxidation grafting. In case of mutual and post-irradiation grafting an inert atmosphere must be provided. Generally, substrates in PE bag with zip are irradiated after inside air is substituted with N_2 gas.

Atmosphere during grafting: Presence of O_2 in grafting medium reduces the grafting yield due to scavenging of radicals by oxygen. N_2 bubbling in bulk monomer, solution and emulsion is effective in displacing dissolved O_2 with N_2. The oxygen free monomer/solution is sucked into evacuated reactor for further grafting. In emulsion grafting, PE bottle with lid can be used as grafting reactor. In this case, the monomer emulsion should be filled in the bottle top and lid put without any space of air in the bottle to avoid the diffusion of O_2 into monomer emulsion [6].

Effect of storage conditions: Substrates irradiated in N_2 should be stored at low temperature (preferably -80 ºC) to maintain the activity of radicals created by irradiation [7].

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5. **Precautions and safety in graftingprocedures**

Basic radiation safety principles should be followed in irradiation facilities. Pocket dosimeters like TLD should be worn by workers in irradiation facility for personal monitoring. Monomers used for grafting are generally toxic and carcinogenic. Information about toxicity should be obtained from Material Safety Data Sheet (MSDS) providedin safety manuals. Graft chambers/hoods should be used for carrying out grafting procedures with protective clothing. Ventilation system should be in place to remove monomer vapors if any. Safe disposal protocols as described in MSD should be used for disposal of unused/left over chemicals.

6. Characterization of grafted materials

Once graft polymerization is completed, the grafted materials should be extracted in suitable solvents in order to remove occluded monomers,homopolymers and other additives. The clean grafted materials need to be dried in vacuum at suitable temperatures(to constant weight) before subjected to characterization. In case of studying hydrophobic and hydrophilic characteristics of the surface of grafted materials, it should be noted that orientation of functional groups on the surface of grafted materials may be influenced by the types of post-grafting treatment.

*Gravimetry:*The main aim of any grafting process is to know the amount of polymer grafted on the substrate. This can be achieved by a simple weighing process. The substrates to be grafted in powder, film or any other forms should be first purified by following the standard purification processes. This is especially important for commercially available samples. Dry weight of the samples before grafting (W_o) should be determined with as high precision as possible. At any stage of the grafting process the grafted substrates to be taken from the grafting medium should be washed, cleaned from any surface contaminations, and preferentially should be solvent extracted via Soxhlet extraction until a constant weight (W_g) is reached. The simple calculation, $(W_g - W_o) \times 100/ W_o$ will give the percentage of grafting.

*FTIR-ATR:*Fourier Transform Infrared Spectroscopy (FTIR)is the most widely used analytical technique in polymer studies. It is very powerful and highly informative tool of non-destructive characterization and measurement of chemical structure of polymers. The qualitative and quantitative information it generates can be related to either macroscopic or molecular interactions. The IR activity depends on the change of dipole moment upon absorption of light. FTIR spectral analysis of grafted polymer is commonly coupled with attenuated total reflectance (ATR) that is a special prism (e.g. ZnS) to which the film is pressed and FTIR is directed through. This results in obtaining of FTIR spectrum from the top layers of the samples, which are in intimate contact with the prism. This method was found to be very useful for obtaining spectra for high absorbing materials. Due to its simplicity and versatility, FTIR is often used to verify grafting and identifying grafted functionality in radiation grafted polymers. This is usually

carried out by comparing the spectra of the ungrafted polymers with that of grafted or functionalized ones. However, in many cases of polymer characterization, the use of FTIR is limited to qualitative analysis due to the difficulty in performing quantitative analysis. This is ascribed to the difficulty in obtaining standards of polymer containing compositions and concentrations similar to the analyzed samples.

Raman spectroscopy:Raman spectroscopy is an analytical tool that can be used to determine the chemical structure of grafted polymers. Raman activity is based on the change in polarizability upon absorption of laser. The Raman spectrum can be interpreted similar to infrared absorption spectrum. Generally Raman spectra are with less interference than mid-IR spectra. Raman spectroscopy is most suitable to measure the bands of symmetric linkages which are weak in infrared spectrum. As in IR spectroscopy, band areas are proportional to concentration, making Raman apt for quantitative analysis. Since Raman bands are sharper than their infrared counterparts, isolated bands are generally present in the spectrum for better quantitative analysis. Raman spectroscopy is also very convenient tool for studying structural properties, water absorption properties and different states in which water can exist in hydrophilic polymers. It is also useful for the characterization of fibres since scattering geometry is very much appropriate for fibrous materials. Since it is based on scattering no tedious sample preparations are necessary, Raman spectra can be taken for bulk solids, liquids and gaseswith almost no sample preparation. The use of Raman is also extended to investigate the degradation of functional grafted polymers.

NMR:Nuclear Magnetic Resonance (NMR) spectroscopy, commonly referred to as NMR has become one of the most important and useful techniques for determining the structure of organic compounds. It is the only spectroscopic technique where a complete analysis and interpretation of the entire spectrum is possible. In a typical NMR analysis the NMR spectrometer should be tuned to a specific nucleus, and in most of the cases this being proton and/or carbon-13 which are ubiquitous in almost every polymer structure. In infrared and UV-Vis spectroscopy the absorption peaks are specifically, uniquely located at certain frequencies or wavelengths. The location of different NMR signals however, is dependent on the external magnetic field strength and the RF frequency. The location of an NMR signal is therefore

reported relative to a reference signal from a standard compound and expressed as 'chemical shift'. In order to take the NMR spectra of a solid, it is usually necessary to dissolve it in a suitable solvent. Deuterium-labeled compounds are widely used as NMR solvents. The intensity of an NMR signal is proportional to the molar concentration of the sample. NMR spectroscopy is therefore a very powerful technique for both qualitative and quantitative analysis of polymers, copolymers. The percentage of grafting for instance can be easily followed by measuring the change in the intensity of an NMR peak specific for the grafted polymer structure.

*XPS:*X-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA) is a non-destructive technique that allows a wealth of information regarding the surface elemental and functional groups therefore composition, structure and properties of polymer surface can be investigated. The XPS results can be analyzed in both qualitative and quantitative modes. Basically, XPS spectrum is obtained by irradiating the sample with monochromatic X-rays. Photons can collide with electrons giving them their energy. Emitted electrons acquire a kinetic energy, which equals the difference between the energy of the incident photon and the binding energy of the electron to the nucleus. The binding energy of the electron in the molecule is measured. The absolute binding energies of electrons in a given element have fixed values and are characteristic of that element. Differences in chemical environment lead to changes in binding energies i.e. chemical shifts, which depends on the electronegativity of the attached groups. XPS can detect atoms to a depth up to 20 atomic layers (0.5-10 nm) through survey scan which makes it most useful for surface analysis. In the second part of the analysis the specific peaks appearing on the survey scan are widened to determine chemical binding energies of the surface elements. From this informationfine structure of the compounds present on the surface is obtained. XPS is a very effective technique for quantitative analysis of elements on a surface and can detect all elements except hydrogen and helium. It is possible to estimate the composition of a surface without extensive calibration. A typical application is to follow changes on the surface chemistry of polymers before and after surface treatment processes, grafting, ageing, oxidation etc.

Contact angle analysis: The contact angle is the result of the interface/surface tensions between liquid and solid surrounded by vapour. From contact angle, interaction between solid

and liquid like wettability, affinity, adhesiveness and repellency can be studied. The most common method for the measurement involves looking at the profile of the drop and measuring two-dimensionally the angle formed between the solid and liquid. Contact angles are characteristic of liquid–solid systems and provide valuable information on the surface energies of solids. The surface free energy components can be determined from the contact-angle data of polar and apolar liquids by using Van Oss–Good methodology. By measuring the contact angle of different liquids on grafted and ungrafted surfaces one can obtain information on the change in the hydrophilicity, hydrophobicity of the substrate upon grafting. The most common type of contact angle measurement is to determine static contact angle, by measuring the angle of a sessile drop shortly after its creation. Contact angle measurements can be used to map surfaces in terms of hydrophilicity, presence of low surface tension components or contaminants, or variations in composition.

SEM-EDX: Scanning electron microscope (SEM) is one of the material research techniques that can be used to study the morphology of the polymer surfaces. It provides a very convenient and simple method to investigate and characterize the superficial properties and the porous structure of polymers. In radiation grafted polymers, the surface modification of the base polymer due to monomer grafting can be examined by SEM which can be also used to study grafting distribution by scanning polymer surface in a transverse (lateral) position. The grafted layers look different from the non-grafted ones in the polymer indicating variation in grafting profiles across the thickness. There are number of steps that have to be considered during the preparation of polymer sample for SEM analysis such as drying and coating of the sample mostly using gold sputtering. SEM application with polymers is generally related to examination of fiber morphology, fracture surfaces, fiber composites, polymer foams, weathering, and surface damage. When used in conjunction with the closely-related technique of energy-dispersive X-ray microanalysis (EDX, EDS and EDAX), the elemental composition of individual componentscan be determined.

*AFM:*Atomic force microscopy (AFM) has become an important tool for studying the surfaces of polymers by imaging their surfaces to atomic level resolution. The main use of AFM is to obtain topographical images by scanning with a sharp tip over the surface. The advantages

of AFM rely on the ability to scan and obtain an image of a non-conducting sample without special sample preparation, which is very essential for SEM and TEM measurements. The success of AFM is based on precise and sensitive measurements of the tip-sample forces by an optical deflection scheme. The tip is attached to the free end of a cantilever and is brought very close to the surface. Attractive or repulsive force resulting from the interactions between the tip and the surface causes a positive or negative bending of the cantilever. The interacting forces causing the bending between the tip and the sample are determined by a cantilever motion which is magnified on the optical detector by a laser beam reflected from the top of the cantilever surface. Basically there are two modes of operation in AFM, contact mode and tapping mode. The difference between the two modes is in the way the tip interacts with the sample surface.

X-ray Diffraction: X-ray diffraction (XRD) is a material research technique that can provide valuable information about the polymer structure including crystalline and amorphous regions. This technique is of particular interest for understanding the nature of changes taking place in polymers as a result of grafting using high-energy radiation. The XRD basically produces diffractograms (curves) in which crystalline regions show coherent scattering patterns in form of sharp peaks, whereas amorphous phases give flat (broad) peaks. In radiation grafted polymers, the incorporation of side chain grafts, which have an amorphous nature, exerts mainly a dilution effect on the grafted film by increasing the amorphous content and consequently reduces the degree of crystallinity.

The degree of crystallinity, X_c can be calculated using equation below

$$X_c = A_c/(A_c+A_a)$$

where, A_c and A_a are the areas of crystalline peak and amorphous halo, respectively.

TGA: Thermal gravimetric analysis (TGA), is one the most important techniques in studying and evaluating thermal stability and thermal decomposition behavior of the polymers via determination of changes in the sample weight, which may result from chemical transformation, as a function of temperature or time depending on the mode of operation (dynamic or isothermal). Vacuum, inert, high pressure, or reactive environments and various heating rates can be applied during the heating run. TGA is often coupled with FTIR and/or mass spectroscopy (MS) to provide a useful technique that can be used to investigate the thermal

behavior of the individual degradation steps of the grafted polymer in correlation with the degree of grafting and eventually understanding the degradation mechanism through the identification of the evolving gaseous products by FTIR or mass spectroscopy. Generally first derivative of weight loss curve is utilized for quantitative analysis. Best TGA results are obtained when samples are dry and in fine powder form.

*DSC:*Differential scanning calorimetry (DSC) is another technique that is widely used to study the thermal behavior and to determine thermodynamic properties of the polymers through detection of physical and chemical changes, which are accompanied by a gain or loss of heat in a sample as its temperature is increased, decreased or held isothermally. The polymer characterization by this technique includes qualitative and quantitative evaluation of phase transformation such as glass transition temperature (T_g), melting (melting temperature, T_m), cyrstallization (crystallization temperature, T_c) and other related data such as heat of melting (ΔH_m) and heat of crystallization (ΔH_c). DSC is mostly used for determination of the degree of crystallinity (X_c) of polymers. The X_c in the grafted polymer is calculated in two steps.

The $X_c$of original polymer is calculated as follows:

$$X_c = (\Delta H_m / \Delta H_{m100}) \times 100$$

where, $\Delta H_m$is the heat of melting of polymer sample and ΔH_{m100} is the heat of melting of 100 % crystalline polymer material.

The weight fraction of polymer in in the graft copolymer (W_p) is calculated using the following equation:

$$W_p = m_p/(m_p + m_g)$$

where, m_p is the weight of polymer and m_g is the weight of the grafted monomer in the grafted polymer. The X_c of the grafted polymer is calculated as follows:

$$(X_c)_{grafted} = (\Delta H_{mgrafted} / \Delta H_{m100}) \times 100$$

where, $(\Delta H_{mgrafted})$is the heat of melting of base polymer fraction in the grafted polymer obtained from DSC curves.

DSC can be also used to determinedifferent types of water, oxygen index etc. For samples with unknown thermal history reliable data can be obtained from second scan of the samples.

Mechanical testing: Mechanical testing is a technique that is performed on polymer specimens to study the mechanical properties such as elastic modulus, tensile strength, elongation at break and toughness from stress-strain curves. Testing the grafted polymer with this technique allows understanding the changes taking place as a result of introducing chemical moieties by grafting. The elastic modulus is obtained from the tangent of the angle of the linear part of the stress-strain curve. The tensile strength (R_M) represents the maximum test force (F_B) per original cross section (A_o) until specimen fails as per the formula:

$$R_M = \frac{F_B}{A_{\circ_\circ}}$$

The elongation at break is obtained by measuring the ultimate length of the sample at break. In the relative form it can be expressed as per the following equation:

$$A = \frac{L_U - L_\circ}{L_\circ} \times 100$$

Where, A is % increase in length at break, L_o is original length and L_U is the length of the sample at break.

The stress-strain curves clearly represent different behavior of the individual polymers and allow classification of polymers. Each polymer has a characteristic pattern of stress and strain which often changes after grafting and from which one can distinguish between the elastic and plastic behavior of the obtained polymer.

DMA: Dynamic mechanical analysis (DMA) is mechanical testing under an oscillatory force. The oscillatory force (stress) is applied to a sample and the resultant dimensional changes (strain) are measured. It is used for characterization of polymeric materials by measuring the modulus or stiffness; softening temperature, impact resistance, T_g and sub-T_g transitions. It is a technique very sensitive to small changes in the mechanical properties of micro-domains. It characterizes visco-elastic properties. Temperature scan at a constant frequency can generate a fingerprint of material's relaxation processes and its glass transition temperature. DMA also has the advantage of measuring side chain and main chain motions of the polymers. DMA is more sensitive in detecting T_g, especially T_g of minor component. This makes DMA a valuable tool in determining the T_g of graft chains as well as substrate in a graft copolymer.

*GPC***:** Gel Permeation Chromatography (GPC), in other words Size Exclusion Chromatography (SEC), is the most important and frequently used technique in the determination of molecular weight averages and distributions of polymers. Although this technique is exclusively used for the determination of molecular weights of homopolymers, it is rather difficult to obtain reliable quantitative information for the copolymers and in particular graft copolymers. As long as the grafted polymer and the substrate are both soluble in the GPC solvent, the molecular weight distribution of the whole sample can be obtained but evaluations are restricted to be more qualitative. In some particular cases where the grafted chains can be cleaved from the substrate without causing any degradation on the backbone, the molecular weight of the cleaved chains that means graft chains can be determined by GPC.

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7. Guidelines for specific applications

The optimum grafting yield depends on the intended applications. For applications like biocompatible surfaces grafting of 2-4 % may be sufficient, for fuel cell and battery separator applications grafting of 20-50% would be desired, whereas for adsorption applications even grafting of 100% would be preferred.

Environmental applications:

Removal of hazardous metal ions and recovery of valuable material

*Polymer scrap based adsorbents:*The radiation response of the polymer does not change whether it is pristine or scrap. Thus the part of the polymer which is otherwise discarded as scrap can be grafted for environmental applications like dye/metal adsorption from industrial effluents. The Teflon scrap obtained after machining, PU waste in form of packaging material and cotton waste from textile industry radiation grafted with suitable monomers have shown significantly fast and high adsorption of dyes/metal ions[1-3]. These grafted matrices have potential application of utilizing a scrap/waste to treat other waste through mediation/intervention of radiation grafting.

A typical protocol for the synthesis of metal ion adsorbent from Teflon scrap is as follows

1.   Immerse Teflon scrap in toluene for a day. Remove scrap from toluene and leave for drying under proper condition. Wash dried scrap with strong soap solution followed by water and leave for dying.

2.   Prepare solution to be used for grafting by mutual irradiation. The grafting solution consists aqueous solution of 20 % (v/v) acrylic acid + 4% Mohr's salt$\{FeSO_4(NH_4)_2SO_4.6H_2O\}$+ 0.5 M Sulphuric acid ($H_2SO_4$).

3.   Take known weight of cleaned Teflon scrap and immerse it completely in known volume of grafting solution in glass tube/bottle and leave it for 1-2 hours.

4.   Irradiate the Teflon scrap dipped in grafting solution (from step 3) for irradiation in the dose range 1-5 kGy.

5.   Soxhlet the grafted Teflon scrap. Determine grafting yield gravimetrically and further characterize the grafted matrices.

Important observations: 1)Grafting is function of thickness of the Teflon scrap. For a given Teflon scrap/Grafting solution volume ratio it increases with decrease in thickness.

2) For a given thickness the grafting increases with Teflon scrap/Grafting solution volume ratio.

Specialty adsorbents: The functional groups having strong affinity for target metal ions are introduced into substrates by graft polymerization and subsequent chemical reaction as shown in Table 1. Substrate such as fiber and nonwoven fabric are better selection for synthesis of adsorbent to realize the large surface area for high efficient contact with metal ions. Glycidyl methacrylate (GMA) grafted matrices are widely used for the synthesis of such adsorbents followed by suitable chemical treatment to desired functional groups such as amines, iminodietanol, iminodiacetic acid, glucamine, sulfonic acid, phosphoric acid etc.

A typical protocol for the synthesis of metal ion adsorbent using GMA is as follows [4-5]

1.   Polyethylene (PE) fibers, 25 μm in diameter, 0.30 g were irradiated with 10 kGy in PE zip bag by using 2 MeV EB at 20 ºC after the air in the bag was substituted with N_2 gas.

2.   Emulsion of GMA was prepared by adding GMA into 0.5 % aqueous Tw-20 (Polyoxyethylene sorbitan monolaurate) until the concentration of GMA became 5%. This emulsion was stirred at room temperature for 1 h.

3.   Emulsion of GMA de-aerated with nitrogen gas was sucked into an evacuated glass ampoule in which the irradiated PE fibers were transferred.

4.   The glass ampoule including irradiated fiber and GMA emulsion was heated at 40ºC in the water bath. Degree of grafting reached 120 % at reaction time of 1 h. Degree of grafting in the range from 100 % to 150 % is suitable for synthesis of metal ion adsorbents.

5.   After grafting reaction, the grafted PE fibers were taken out of the glass ampoule and rinsed twice with distilled water and methanol to remove residual monomer and homopolymer. Degree of grafting was evaluated after drying under reduced pressure.

•   Reaction conditions such as dose, monomer concentration, reaction time, reaction temperature, etc. are optimized since final degree of grafting mainly depend on the kind of substrate material, its crystallinity, grafting medium, O_2 concentration in medium and so on.

•   PE bottle with lid can be used instead of the evacuated glass ampoule in steps 3 and 4. The monomer emulsion is filled in the bottle without any space of air between the surface of monomer emulsion and the lid.

Table 1: Functional groups obtained and selection of monomers

Functional group	Grafting monomer	Chemical reagent	Ref
Amidoxime	Acrylonitrile	Hydoxylamine	6
Amines	Glycidyl methacrylate N-vinyl formamide	Diethylamine Sodium hydroxide	7 8
Iminodiethanol	Glycidyl methacrylate	2,2'-Iminodiethanol	9
Iminodiacatic acid	Glycidyl methacrylate	Sodium iminodiacetate	10
Glucamine	Glycidyl methacrylate	N-Methyl glucamine	11
Sulfonic acid	Styrene Glycidyl methacrylate	Sulfuric acid Sodium sulfite	12 13
Phosphoric acid	Glycidyl methacrylate 2-hydroxyethyl methacrylate phosphoric acid	Phosphoric acid -	14 15

Each functional group in Table has generally affinity against listed ions as follows:

Amidoxime: Cu^{2+}, Au^{3+}, V^{4+}, U^{6+}, Fe^{3+}, etc.

Amine: Cl^-, SO_4^{2-}, etc.

Iminodiethanol: $Sb(OH)_6^-$, $Ge(OH)_6^{2-}$, etc.

Iminodiacetic acid: Hg^{3+}, Cu^{2+}, Pb^{2+}, Fe^{3+}, etc.

Glucamine: BO_3^{2-}

Sulfonic acid: cations (low selectivity)

Phosphoric Acid: Th^{4+}, U^{4+}, Fe^{3+}, etc.

Biomedical applications: Radiation induced grafting has been known to be a useful tool formedical applications. The surface of otherwise incompatible finished productsviz. catheters, implants etc. can be radiation grafted to enhance their biocompatibility. For the purpose of fabricating biocompatible polymers, radiation processing holds advantages over conventional methods including no needs for catalyst or additive. There are many examples of how and where to take advantage of radiation grafting technologies from substrates for tissue culture, biocompatible polymers, antimicrobial polymers and bioassays for biomedical diagnostics to controlled drug delivery.When considering a biomaterial for medical use, the most important requirements are non-toxicity, chemical inertness and acceptability by human body. Medical

devices and their component materials may leach compounds or have surface characteristics that may produce undesirable effects when used clinically. The FDA and ISO guidelines provide a general testing framework to assess device biocompatibility.

Biocompatibility: With the progress of prosthetic surgery, blood-compatible polymers have been increasingly in demand, and a large number of investigations have been carried out. The grafting technology to prevent platelet adhesion was tried by grafting 2,3-epoxypropyl methacrylate with a reactive epoxy group to polypropylene film, and the epoxy group was used as a reactive site for phosphonation reaction. The phosphoric acid group-introduced polypropylene film was found to have good blood compatibility, which increased with the content of the introduced phosphoric acid group [15].

A typical protocol for improving biocompatibility without altering the bulk properties is as follows [16].

Additive-free polypropylene (PP) film with a thickness of 200 mm was used as a substrate for graft polymerization. The PP film was cut into 3.0x5.0 cm pieces and ultrasonically cleaned twice in methanol for 10 min each, and dried.

1. PP films were irradiated by γ-rays from Co-60 sources at an exposure rate of 4.61 kGy/h in the presence of air to a total dose of 30 kGy. After irradiation, PP films were quickly stored in the refrigerator kept at -130℃ before grafting experiments.

2. The grafting reactions were performed in stoppered glass ampoules. Methanol was added first, followed by a monomer to make a total volume of 50 ml. The pre-irradiated PP was immersed into the monomer solution, purged by bubbling nitrogen gas for degassing. For obtaining grafted PP film.

3. The epoxy group of 2,3-epoxypropyl methacrylate-grafted PP film was converted to –PO_3H group by immersing the grafted sample in 85% phosphoric acid aqueous solution at 80℃ for phosphonation reaction, the phosphonated PP film was repeatedly washed with pure water for the removal of phosphoric acid adhered onto the PP film.

4. The grafting was verified by Fourier transforminfrared spectroscopy in the attenuated total reflectancemode (FTIR-ATR) and ESCA.

5. The evaluation of non-thrombogenicity in vitro wascarried out by the formation of a thrombus and theadhesion of platelets onto the phosphonated PP filmsurfaces using human whole blood and PRP(platelet-rich plasma),respectively.

6. The phosphoric acid group-introduced PP film was found to have good bloodcompatibility, which increased with the content of the introduced phosphoric acid group.

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8. Scale-up considerations for industrial applications

Application target of grafting is determined by the needs of the each MS. In the laboratory scale, substrate and monomer can be selected by following the guidelines outlined in this protocol. Optimization of grafting process for scaling up while maintaining the characteristics such as grafting yield and performance should be carried out before planning the specification for scaling up of equipment. After completion of optimization under laboratory conditions and favorable economics design of pilot scale facility should follow. After synthesis of the grafted material on a pilot scale (in collaboration with probable partner from industry)technical feasibility of the process and finally economic viability should be evaluated. Once economic viability is established scaling-up is considered followed by technology transfer to private companies. Additionally, collaboration with a partner-company, which shows special interest in the grafted products, accelerates the technology transfer. New process design and relevant equipment may be needed for each specific application for which no know-how may be available.

9. **Successful industrial applications/technology transfer examples**

Separator membrane for battery: Grafting of acrylic acid onto PE film, 25µm thick, is commercialized as battery separator membrane for button-shaped battery in1985 in Japan [1]. Silver oxide battery has been used in watches, measuring instruments, medical instruments owing to super long-term reliability, small & thin shape, high-energy density (2 times of alkaline button battery), flat discharge characteristics. Its market size reached 100 million dollars in Japan. Graft PE membrane is applied to Ni-Cd battery which has excellent performance of high rate discharge, long service life (12 to 20 years), and superior characteristics against high and low temperature. These characteristics are advantages in the usage of emergency power supplies for trains, power supplies for engine starting of railcars and diesels, uninterruptible power supply. The market size is 10 million dollars in Japan.

Air filter for Large Scale Integrated (LSI) circuit facility: Continuous process for grafting of nonwoven fabric is installed for fabrication of NH_3 gas removal filter for LSI facility. In this plant, substrate is irradiated with 300 keV EB, and is dipped into bulk monomer. The grafting proceeds through impregnated monomer in the reactor [2]. The monomer is completely consumed in the grafting so that removal of residual monomer is not necessary in this process. This technology was transferred in 1997. The maximum production rate is 20 m/min. The graft product can adsorb NH_3 quicker than conventional adsorbents such as charcoals and organic-acid treated charcoal. Its adsorption capacity is 150 times higher than that of charcoal. As a spin-off technology,antimicrobial fabrics were produced by radiation-grafting of N-vinyl pyrrolidone onto polypropylene nonwoven fabric and subsequent adsorption of iodine. These fabrics have been commercialized to produce antimicrobialmasks since 2002.

Metal removal filter in alkaline washing of Si wafer: Emulsion graft polymerization is so efficient that dose required and monomer consumption can be reduced in comparison with grafting in monomer solution. In the case of GMA grafting on PE nonwoven fabric, dose of 200 kGy was reduced to 50 kGy and monomer concentration of 10% to 5% to obtain the degree ofgrafting 250 %. This process has been transferred to private company in 2010. The grafted product is applied as a filter for metal ions such as Ni and Cu in alkaline wash and used for Si

wafer production. This filter can reduce the concentration of metal ions to 1ppb with flow rate of 10 h^{-1} in space velocity. This performance cannot be realized by conventional resins [3].

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10.   **Emerging applications**

In addition to the examples given in the document radiation grafting is presently being investigated to prepare grafted matrices with an aim to synthesize non-reactive/reactive compatibilizer for blends with immiscible components. The introduction of grafted matrices would result in better miscibility of the components and hence in improvement in mechanical properties.

Radiation grafting of elastomers can be easily carried out as elastomers inherently show swelling in most of the organic solvents. The radiation grafting of elastomers have two potential applications as thermoplastic elastomers (TPE) and as non-halogenated oil resistant elastomers. The TPE though consist of backbone of thermosetting type but can be processed as thermoplastics. On the other hand non-halogenated grafted matrices will be flexible but would not swell in oils [1-2].

Polymers sensitive to a particular stimulus have been increasingly employed in biomedical and medicinal applications [3]. Cell sheets grown on NIPAM grafted surface can be collected without damaging the cells network sheet structure. Use of other chemicals and proteolytic enzymes damage the grown structure. These cell sheets have already been successfully used in opthalmology, periodontology, and cardiac cell repair.

One of the important applications of polymeric biomaterials is in the field of surgical sutures. The presence of suture at site of injury can increase the tissue susceptibility to infection. To prepare suture with antibacterial property, radiation grafting has been used. Acrylonitrile monomer was grafted to polypropylene monofilament, followed by hydrolyzation to introduce carboxylic groups, where tetracycline hydrochloride as antimicrobial drug was consequently immobilized [4].

The fabrication of bioassays for various applications including biomedical diagnostics, biomolecular analysis, drug discovery, and environmental monitoring has attracted tremendous attention over the past decade because of their advantages such as fast and high-throughput detection of target molecules.The radiation grafting process which is effective for the immobilization of proteins, which is applicable to quantitative immunoassays was used to detect target biomolecules such as antibodies, antigens, and other protein molecules [5].

Fuel cell application is among the areas where radiation induced grafting techniques has played significant role in developing proton exchange membranes [6-7]. Particularly, this method offers new routes to obtain membranes containing sulfonic acid moieties for proton exchange membrane fuel cells (PEMFCs) [8]. Various strategies involving grafting of new polymer/monomer combinations have been established in order to improve stability by double crosslinking, patterned grafting, single-step grafting and pore-filling of ion-track membranes. New monomers such as 2-chlorovinyl ether, α-methylstyrene, p-methylstyrene, p-tert-butylstyrene and p-styryltrimethoxysilane and monomer combinations such as styrene/acrylonitrile, styrene/methylacrylnitrile, α-methyl styrene/methylacrylnitrile and styrene/(trimethoxysilyl)propyl methacrylate have been successfully grafted onto poly(ethylene-co-tetrafluoroethylene) (ETFE) films and subsequently, functionalized. This was coupled with new polymer substrates such as crosslinked PTFE, engineering plastics, powder followed by thermal treatment. A variety of membranes with excellent combinations of physical and chemical properties suitable for PEMFC and DMFC were obtained. However, majority of these membranes should be tested in PEMFC under dynamic conditions to establish their stability and durability.

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