

Radiation Processing of Polymers and their Industrial Applications

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Abstract

High energy (ionizing) radiation has ability to generate reactive free radicals or ionic species at any temperature in any phase - solid, liquid or gas. Unlike the conventional energy deposition approaches, which mainly involve the translational, rotational and vibrational modes of the molecules, the high energy radiation mainly interacts with the orbital electrons and excites the absorbing molecules to higher excited states that result in the formation of highly reactive ions or radicals. Subsequent reactions of these reactive species form the basis of industrial radiation processing. Polymers, due to their high molecular size are particularly amicable for radiation processing. In past few decades, several applications of radiation processing of polymers have been commercialized in India. The chapter discusses some of the important activities related to radiation processing of polymers carried out at BARC.

Keywords: *Monomer, Polymer, Gamma-radiation, Electron-beam, Cross-linking, Degradation, Grafting*

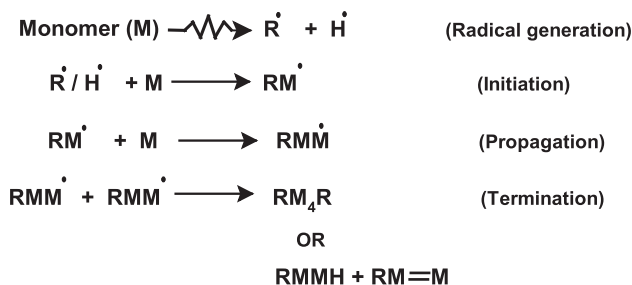
1. Introduction

Conventional addition polymerization involves heat assisted generation of radicals from an initiator for polymerization of monomer. The use of initiator results in residual initiator in final product. The residual initiator reduces the life of the product as well as leaches out from matrix over period of time. Free radicals can be generated without heat assistance using suitable chemical combinations (e.g. Fenton's reagent), through homolytic cleavage of covalent bonds photochemically etc. But all these methods still persist with residual chemical problem. High

energy radiations like gamma and electron beam (EB) are capable of generating free radicals in any system at room temperature and even at sub-room temperature. Their ability to generate radicals in any monomer and polymers can be explored to generate radicals in monomers to cause polymerization and to bring out modification in polymers.

2. Radiation induced polymerization

At room temperature the monomer (M) molecule undergoes radiolysis to generate free radical species (R^\cdot and H^\cdot) or an electron may be ejected from monomer molecule to generate a radical cation $R^{\cdot+}$. The ejected electron may be captured by another molecule to generate radical anion ($R^{\cdot-}$). However it has been established that at room temperature in presence of traces of water the radical cation or anion ultimately lead to generation of radical as initiating species. The radical R^\cdot/H^\cdot ; preferably H^\cdot (as it is smaller atom with higher mobility) can add to another monomer molecule to form a monomer radical and the monomer radical so formed may add to second monomer molecule to form dimer radical so on and so forth on to form long chain radical. This chain reaction (propagation) would cease when two radicals interact to recombine (termination by recombination) or undergo abstraction (termination by disproportionation) (Schematic 1).



Schematic 1: Steps in radiation induced polymerisation

Major advantages of radiation induced polymerization are:

- i) In radiation polymerization No initiators are used hence there is no chance of any residual impurity or undesired groups in polymer matrix.
- ii) The process can be carried out even at sub-room temperatures. So even thermo-sensitive monomers can be polymerized
- iii) Since radiation can also sterilize the products, there is possibility of simultaneous sterilization of polymeric products.

Some unique examples are described in subsequent sections to highlight the role of radiation induced polymerization for polymer synthesis.

2.1 Sub-room polymerization of 2-Hydroxyethylmethacrylate (2-HEMA) for designing control drug delivery (CDD) system

2-HEMA mixed with water was dropped in hexane cooled to dry ice temperature (-78°C) in methanol-dry ice bath to form beads. The water present in the monomer mixture freezes to ice at -78°C and provides a skeletal structure for 2-HEMA monomer molecule to adhere to. The beads so

formed were irradiated in gamma chamber at -78°C leading to polymerization and simultaneous cross-linking of 2-HEMA. On bringing the cross-linked beads to room temperature the water melts out to form porous poly(2-HEMA) beads. These beads were swollen in saturated drug solution of interest to equilibrium swelling and dried to load the drug. The surface drug of the dried beads was dusted-off gently and the drug loaded beads were studied for the drug release in saline solution and the release monitored spectrophotometrically.

**Radiation induced polymerisation at dry ice temperature
(2-HEMA+EGDMA+NVP/MMA)**

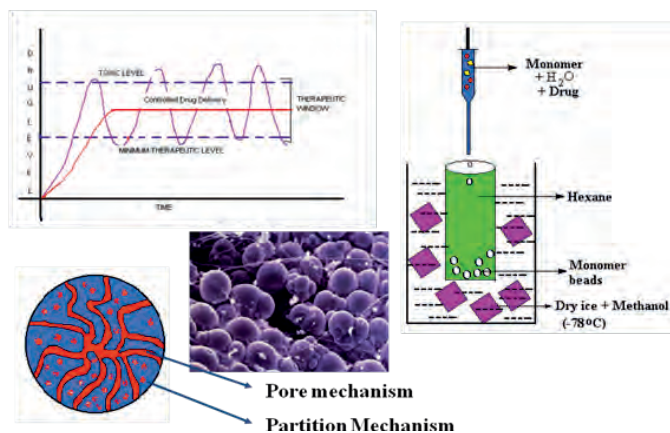


Figure 1: Porous bead synthesized at -78°C through radiation polymerization

An initial burst of drug release followed by slow release was observed. The initial burst was attributed to release due to pore mechanism while latter slow release was due to partition mechanism. The drug trapped in pores (formed due to frozen water) is washed out fast due to ingress of saline solution into the pores while the drug trapped in polymer matrix slowly diffuses out due to swelling of the polymer matrix with time [1]. Figure 1 shows experimental set-up and concept of CDD & porous beads formed due to radiation induced polymerization of 2-HEMA at sub room temperature.

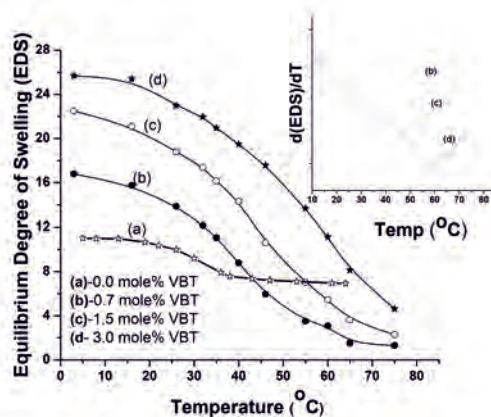


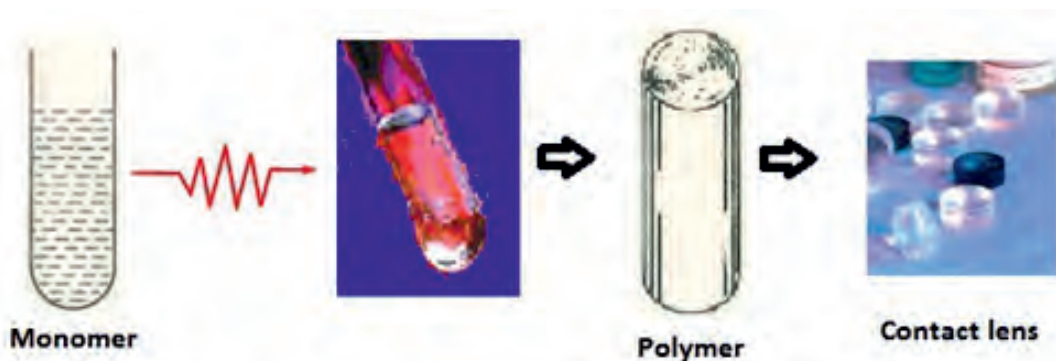
Figure 2: Thermo-sensitivity of PNIPA-co-VBT hydrogel synthesized by gamma irradiation. Inset: Derivative of EDS vs Temperature

2.2 Radiation induced polymerization of thermo-sensitive monomer *N*-Isopropylacrylamide (NIPAm)

NIPAm has a critical solution temperature (LCST) of 34°C i.e. on heating beyond this temperature it precipitate outs from the medium. Polymerization and simultaneous cross-linking of NIPAm using high energy radiation was studied [2]. It was observed that use of gamma and electron beam (EB) result in different swelling kinetics. The gels so obtained can undergo several cycles of swelling-deswelling without any compromise in other properties. NIPAm can even be radiation co-polymerized with other monomers to synthesize pH-co-thermo-sensitive gels. Figure 2 shows the affect of introduction of VBT (vinylbenzyltrimethylammmonium chloride) on swelling of NIPAm [3]. The figure clearly shows the copolymerizing affects the LCST and swelling extent significantly.

2.3 Radiation induced polymerization for synthesis of ultra-pure polymers for contact-lenses

Contact lens, are ocular prosthetic devices worn to correct vision (therapeutic reasons) or for cosmetic reasons. As the contact lens remains in contact with eye, a very sensitive body part, the material of contact lens has to be light weight, biocompatible along with fulfilling its functional requirement. Vinyl polymer based transparent polymers, polymerized/cross-linked by conventional methods have been used for this application for last several decades. In view of the possibility of additive free polymerization as well simultaneous sterilization the synthesis of contact lenses using radiation has graduated to industrial scale. Hard, soft, semi-soft contact lenses have been prepared by radiation induced polymerization & cross-linking of monomers like methyl methacrylate (MMA), 2-Hydroxyethyl methacrylate (HEMA) and N-Vinyl Pyrrolidone (NVP). A dose of ~10 kGy is sufficient for polymerization of these monomers [4]. Synthesis through radiation polymerization is easy and reliable and economic, as only one parameter, the absorbed dose has to be monitored which does not require high skilled labour. The polymer obtained can be machined to desired optical requirement and shape. Schematic 2 shows scheme for synthesis of acrylic base lenses through radiation polymerization



Schematic 2: Radiation induced synthesis of contact lenses

The radiation induced polymerisation is now quite well understood and documented [5].

3. Radiation processing of polymers

Polymers being long chain molecules, final outcome of interaction of radiation with polymers may be their degradation (fragmentation) or cross-linking (entanglement). A special variation to these two processes is using irradiated polymer as radical bank and growing another polymer on it to form grafted co-polymer as shown in Figure 3. Though all polymers undergo degradation and cross-linking simultaneously the predominant effect depends on the chemical structure of constituent monomer, crystallinity and physical state of polymer during radiation processing. The extent of effect (cross-linking/degradation) is a strong function of molecular weight and crystallinity of the polymer. However as cross-linking and degradation are not intrinsic properties of polymers a degrading type polymer may act as cross-linking type and vice versa depending on the conditions [6].

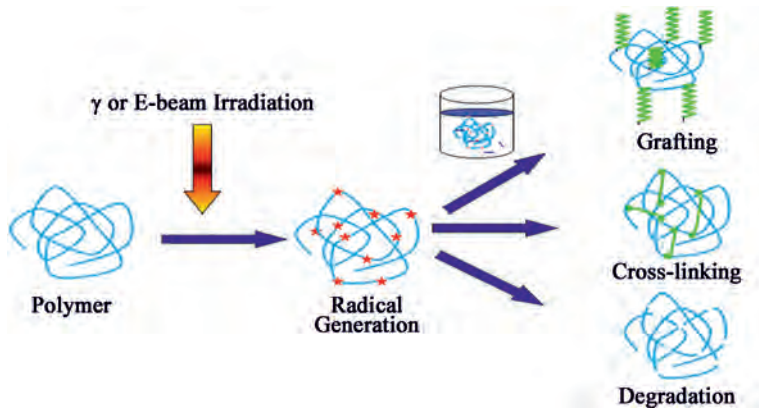


Figure 3: Radiation effect on polymers

3.1 Radiation processing of polymers: Cross-linking applications

Radiation vulcanization of natural rubber latex: Natural rubber latex (NRL) is a milky fluid obtained from rubber tree that consists of extremely small particles of rubber (*cis*-poly isoprene) dispersed in an aqueous medium. The coagulated rubber has poor mechanical properties, thus

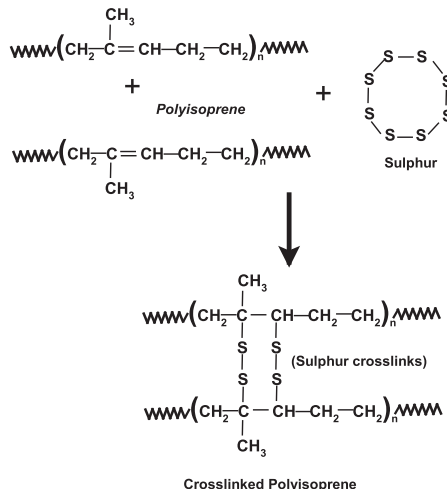
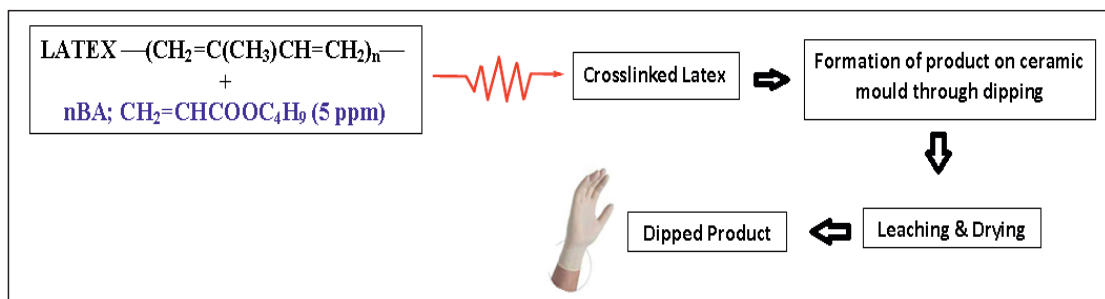


Figure 4: Conventional rubber vulcanization process

vulcanization of NRL is carried out to improve upon its tensile strength, resistance to swelling, abrasion strength and its elastic properties over wide range of temperature. In its simplest form, vulcanization is brought about by heating rubber with sulfur. Sulphur forms bridges between individual polymer molecules when heated with rubber (Figure 4). Often catalyst, initiator and anti-oxidants (nitrosoamines, dithiocarbamate) are added to accelerate the vulcanization process and to increase shelf-life. These chemicals are known carcinogens and released to environment during vulcanization. Residual chemicals may cause earlier failure of the finished dipped products like balloons, gloves due to pinhole formation.

Radiation vulcanization of natural rubber latex (RVNRL) is an additive free process particularly useful for dipped products where *cis*-polyisoprene of NRL is vulcanized in latex itself. Ceramic molds of desired product (shape) are dipped in vulcanized latex to get vulcanized product shape on moulds. The dipped product then undergoes usual leaching-drying process to produce final products (glove, balloon etc.) (Schematic 3). The radiation dose requirement for vulcanization has been brought down to 15 kGy from 40-50 kGy for commercialization of radiation vulcanization by using emulsified acrylates like n-butyl acrylate (nBA) at ppm concentration during vulcanization. nBA forms soft rubbery polymer on irradiation. When irradiated in latex it forms soft-rubbery extended chains covalently linked to *cis*-polyisoprene. It has been postulated these poly(nBA) cause extensive bundling of *cis*-polyisoprene through random entanglement contributing to enhanced mechanical properties for NR vulcanized in presence of nBA [7]. A RVNRL pilot plant is operating at Rubber Board, Kottayam since early nineties [8].

Among advantages of RVNRL, it is an environmental friendly process since no additives are added and incineration of such products does not release SO₂ to atmosphere.

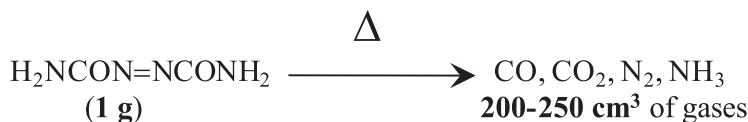


Schematic 3: Rubber vulcanization process

3.2 Radiation processed polymer foams

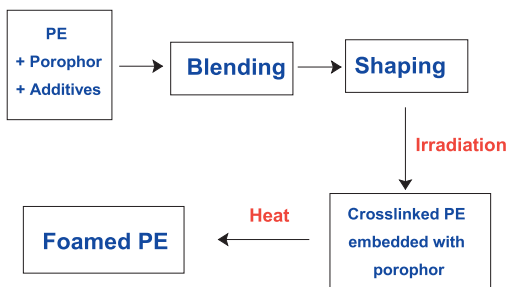
Polymer foams are prepared by forming gas bubbles in polymers using a blowing agent. Their cellular structure with entrapped gas allows high volume/mass ratio. Poly ethylene (PE) foams are prepared either through conventional peroxide cross-linking or through cross-linking induced by high energy irradiation. Distinct advantage of radiation cross-linking is excellent surface appearance of the product formed due to closed cells. Radiation cross-linking leaves scope of controlling extent of cross-linking and thus foaming extent through dose delivered in the processed polymer-foam blend before causing foaming. Schematic 4 shows the process of PE foam synthesis through radiation cross-linking.

Azodicarbonamide ($\text{H}_2\text{NCONNCONH}_2$) (ADCA) an exothermic blowing agent is commonly used as poro-former for foaming. Post irradiation, cross-linked PE plates are thermal expanded to produce foams in an oven at $\sim 200^\circ\text{C}$ using forced air stream for appropriate time during which ADCA decomposes to form gaseous products.



$$\text{Foaming Coefficient} = (\text{Final volume} - \text{Initial volume}) / \text{Initial volume}$$

The amount of ADCA to be incorporated depends on the foaming coefficient desired. ADCA to an extent of 10-15% (w/w) can be easily loaded into PE matrix. Irradiation leads to the cross-linking of PE. When heated beyond its melting point it turns to non-flowing viscous mass which hinders release of generated gases resulting in volume expansion and formation of foam. Radiation dose of ~ 50 kGy is sufficient to crosslink PE for formation of foams.



Schematic 4: PE foam synthesis through radiation processing

Radiation processed heat shrinkable: Heat-shrinkables are the materials that recover their original length on heating. Their major applications include harnessing multiple wires together, color coding of cables, sealing of cable joints. The heat induced shrinking is a result of cross-links introduced into heat shrinkables. The cross-links i.e. inter chain covalent bonding causes plastic memory effect in matrix as a result of which cross-linked polymer stretched into an expanded shape shrinks back to its original dimensions when heated above certain temperature (Figure 5).

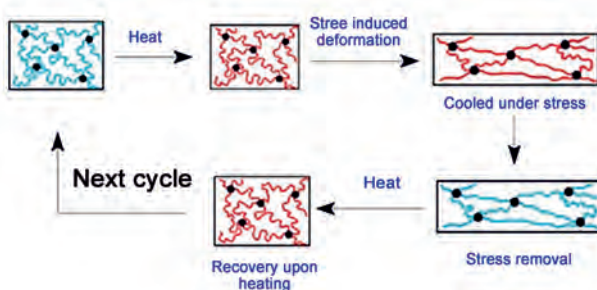
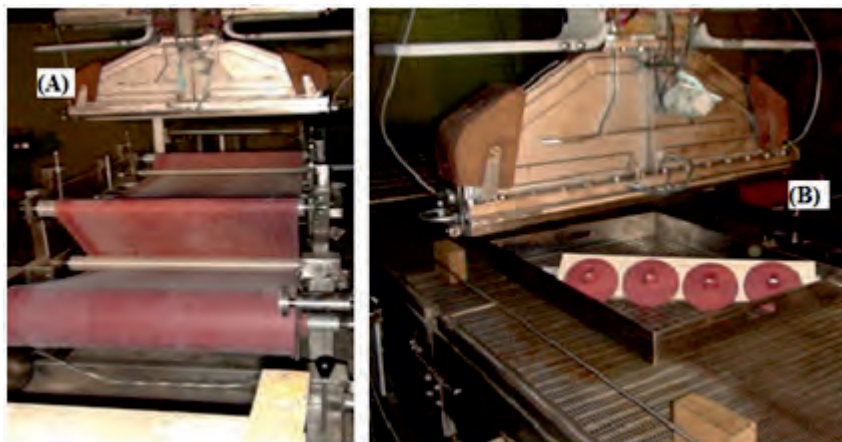


Figure 5: Heat-shrinkable synthesis through radiation processing

Radiation cross-linked heat shrinkables display comparatively uniform shrinkage as the cross-linking of the matrices using radiation is uniform. Heat shrinkables are labeled with a shrink ratio, e.g. a heat shrinkable tubing marked with 4:1 shrink ratio has expanded diameter four times that of its shrunken diameter. Radiation dose of ~ 100 kGy is generally recommended for polyolefin based heat shrinkables.



**Figure 6: EB processing of (A) Vacuum moldable polymer sheets
(B) Components for high temperature vacuum shaping**

BARC in collaboration with M/s RayChem RPG has developed EVA-LDPE blend formulation and irradiation protocol for EB cross-linking of these blends. The EB cross-linked sheets find application as heat shrinkable for sealing of high voltage cable joints as well as vacuum moldable insulation sheets [9]. Figure 6 shows EB cross-linking of some industrial products.

Cross-linking of wires and cables: Wires and cables are conductor strands, sheathed in a jacket of insulation to prevent the conductors from making unwanted contacts. The insulator jacket also avoids electrical shock to user. Polymers are widely used for this application because of their high breakdown voltage, easy availability with wide range of properties, low cost, ease of processing and resistance to wear and solvent attack. However linear polymers creep under load and are not mechanically strong. Cross-linking of polymers ties C-atoms from different polymer chains through covalent bonding as a result of which chains can no longer slide past each other, and flow as it requires rupture of covalent bonds. Direct consequence of cross-linking is higher tensile strength and stiffness (especially at high temperatures), improved impact resistance and environmental stress-cracking resistance, higher long-term service temperatures. Higher service temperatures disallows immediate melting of insulation hence less short circuits and also no dripping, less smoke, less flame spreading and less pollution in case of fire e.g. PE which melts at $\sim 100^\circ\text{C}$ can easily withstand temperatures up to 200°C for several hours without melting after cross-linking.

The conventional chemical monosil and sioplas cross-linking techniques include use of silane coupling agents followed by moisture curing. Chemically cross-linked wires and cables suffer from electrical and water treeing defects which ultimately cause early failure of wire and cable insulation during their life-time. Prominent advantages of electron beam (EB) cross-linking are

- i) The wire & cable are processed in finished state thus there still exists a window for varying the cross-linking extent.
- ii) The product is more uniformly cross-linked.
- iii) Only one parameter, the dose to be delivered to be controlled.

Electron beam irradiation of cables: Depending on the a priori knowledge of insulation material & thickness and extent of desired cross-linking the dose to be delivered and under beam geometry are decided. Under beam geometry during irradiation has to be carefully decided for uniform dose delivery. Energy of electron beam (EB) indicates the penetration capability while current determines the dose delivery capacity and power determines overall throughput capacity of the EB accelerator. Radiation doses of ~300 kGy are sufficient for wire and cable cross-linking. In BARC extensive work has been done in collaboration with Indian industry which has led to establishment of EB machines dedicated to wire and cable cross-linking in private sector. BARC under a MoU, collaborated with M/s NICCO, Calcutta to develop EB cross-linkable cables as well as to formulate technical specification and evaluate conceptual design of EB accelerator for this application. Under the MoU more than 100 km of cables of different diameters were irradiated using indigenously developed conveyor system. The irradiated cables were found to meet the specifications desired by the end-users. Based on this collaborative work a trial development order from Chittaranjan Locomotive Works Ltd., Indian Railways, to NICCO cables for supply of EB cross-linked cables was successfully executed [10]. Figure 7 shows pictures related to wire and cable cross-linking.

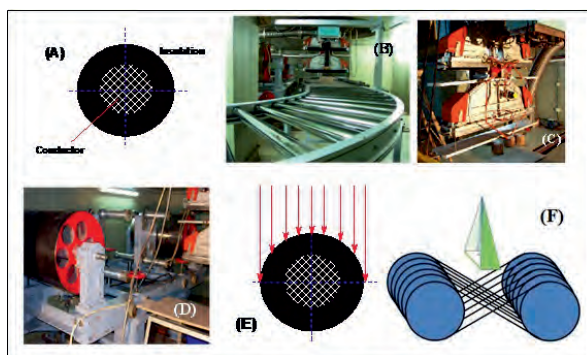


Figure 7: EB crosslinking of cables at BARC (A) Cable cross section (B) 5 MeV EB accelerator (C) 4-channel EB horn (D) Drum conveyor (E) Cable cross section one side irradiation (F) Continuous 8-shape conveyor for both side crosslinking of cable

Radiation crosslinked O-rings: O-rings are used as gaskets to avoid leakage from filled containers. Low density polyethylene (LDPE) has a melting temperature of 110°C and softening temperature of about 60°C. However, cross-linked LDPE can retain its dimensional stability at higher temperatures. Process optimization studies were carried out for radiation cross-linking of polyethylene “O” rings to impart dimensional stability at temperatures as high as 200°C. In collaboration with Indian industry BARC has developed protocol for uniform cross-linking of O-rings on commercial scale. A rotating 16-spindle conveyor system has been designed for the purpose which can irradiate 1,00,000 O-rings/day [11]. Radiation cross-linking being chemical free process, the O-rings processed through EB have inherent advantage for application in food related applications with appropriate FDA clearances. Figure 8 shows the spindle geometry for EB cross-linking.

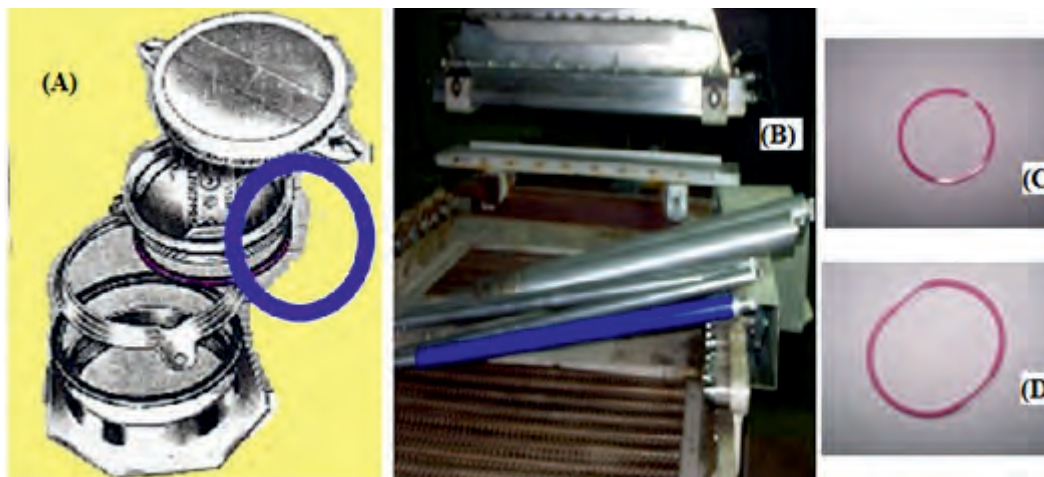


Figure 8: EB crosslinking of O-rings (A) O-ring use (B) Multi-spindle under-beam irradiation (C) Un-crosslinked O-rings (D) Crosslinked O-rings

Radiation processed hydrogels: Hydrogels are the class of polymeric materials that can absorb significant amount ($>20\%$ w/w) of water while maintaining a distinct three dimensional (3-D) structure.

Healing of wounds and burns is a difficult medical problem as they are to be covered to avoid infections as well as require optimum moisture and air for fast healing. Hydrogels because of their hydrophilic character and permeability to air are suitable candidates for this application. BARC has developed gamma radiation processed hydrogels for burn and wound dressing [12]. These dressings have also been observed to heal difficult wounds like leprosy and diabetic ulcers, bed sores and post surgical wounds. The technology has been transferred to four private agencies. Figure 9 shows pictures of hydrogels developed at BARC.



Figure 9: Radiation processed hydrogels (A) Commercial product (B) Non-iodinated & iodinated hydrogels

3.3 Radiation processing of polymers: Degradation application

Radiolytic degradation of Poly(tetrafluoroethylene) (PTFE): In spite of high chemical inertness and temperature stability PTFE (trade name Teflon) in solid state, is highly prone to radiation induced degradation, unlike PE which undergoes cross-linking predominantly. The powdered Teflon has several applications in water-proof inks and paints, as solid lubricant etc. Cryogenic powdering is energy and time intensive and does not lead to decrease in molecular weight of PTFE. This results in agglomeration of PTFE powder when in use. Low molecular weight Teflon powder on the other hand does not agglomerate. On irradiation Teflon undergoes decrease in molecular weight and turns into a brittle, friable matrix is well established [13]. At BARC EB irradiation has been used to degrade PTFE scrap to powder of different particle size [14]. Figure 10 shows EB degradation of PTFE scrap.

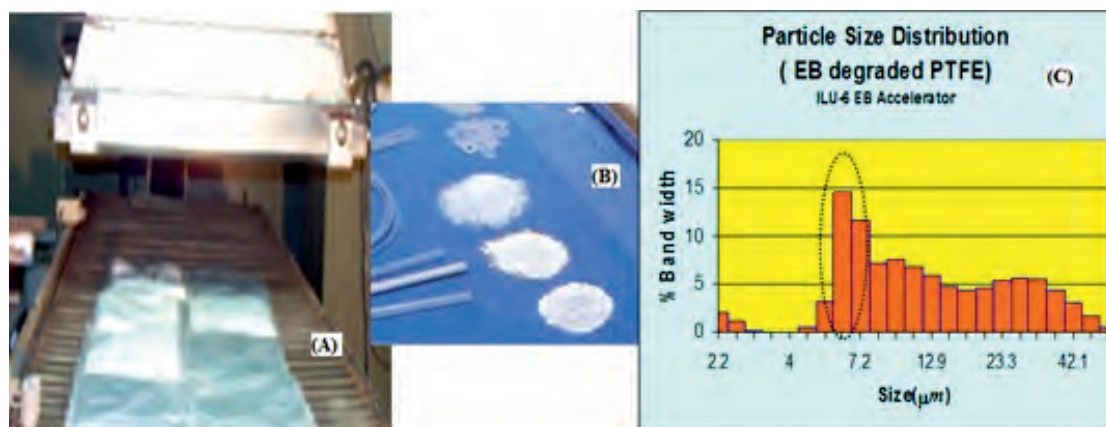


Figure 10: Radiation degradation of Teflon (A) EB processing of Teflon scrap (B) Degraded Teflon powder (C) Particle size distribution of degraded Teflon

Radiolytic degradation of cellulose for viscose–rayon industry: The viscose–rayon industry is highly polluting industry as it uses huge volumes of CS_2 and other chemicals for aging of pulp to enhance its solvation. Therefore, suitable modifications in the processes have been tried to decrease the consumption of these chemicals. Irradiation of cellulose results in decrease in degree of polymerization (DP) as well as altering the crystallinity of cellulose. Both these effects are of immense benefit to viscose–industry as it eliminates the aging process and considerably enhances the salvation thereby reducing the consumption of CS_2 . Dose of 5–10 kGy is sufficient to reduce the DP of paper pulp from 650–800 to about 400–450 that is generally achieved by the conventional aging process. The concentration of CS_2 required to dissolve the irradiated paper pulp reduces to 18% as compared to the 34% for the conventional process on using irradiated pulp [15].

3.4 Radiation processing of polymers: Radiation induced grafting

Grafting essentially involves covalently attaching a polymer/group of interest to the existing polymer backbone for the desired application. Intention here is to get a product which has properties of both the input materials economically. Figure 11 gives an established procedure for carrying out mutual radiation grafting of polymers.

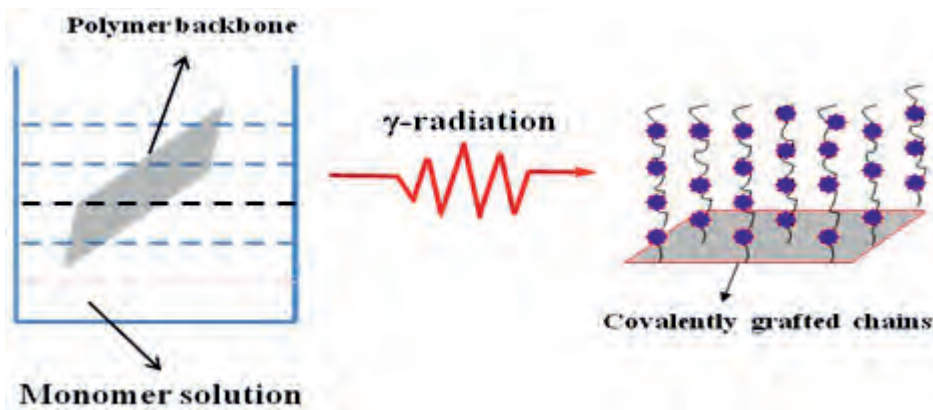


Figure 11: Mutual radiation grafting

Extensive work has been carried out at BARC for radiation grafting of several monomers of interest on existing polymer backbones. Radiation grafting has been used to impart antibacterial property to cellulose by grafting of tralkyl ammonium chlorides [16], designing efficient adsorbent for removal of heavy metal ions and dyes from aqueous medium [17], hydrophilization of Teflon surface [18], converting low cost polypropylene (PP) for selective adsorption of species of interest from sea water [19]. The work on radiation grafting has led to technology transfer for arsenic removal from drinking water to three private entrepreneurs [20] and also other is under-going field trials for adsorption of dyes from dye industry effluent in collaboration with dye industry.

3.5 Radiation processed blends and composites

Polymer blends are mixtures of at least two polymers or copolymers with/without any chemical bonding between them. The objective of polymer blending is to end up with mix of polymers which has properties of both parent polymers. However, mixing polymers is tricky

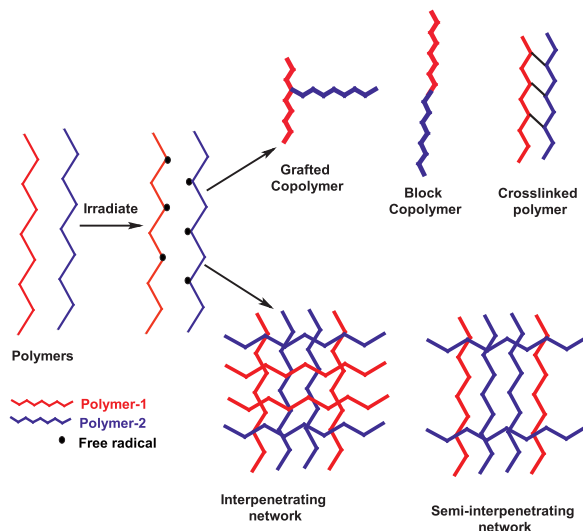


Figure 12: Probable copolymer structure generated on irradiation of two polymers

due to several reasons as a result of which the expected increase in properties is rarely observed. High energy radiation generates radicals on polymers. The combination of radicals generated on two polymers can lead to formation of grafted copolymer, random block copolymer, cross-linked polymer interpenetrating networks or semi-interpenetrating networks as shown in Figure 12. Formation of any of these co-polymer structures in any of the morphologies allows decrease in interfacial tension and enhanced compatibility between the blend components which contributes to enhanced mechanical and other properties. Several radiation processed polymer blends for different applications have been studied at BARC [21].

Radiation processed composites : Composites are defined as materials that consist of two or more chemically and physically distinct materials which when combined have improved properties over the individual materials. Polymer composites consist of a continuous phase (polymer) and a dispersed embedded discontinuous phase (filler). Polymer is usually soft and ductile while dispersed phase is stronger (therefore also termed as reinforcing phase). Polymer acts as binder of the filler and shares load with it when under stress. Radiation has been utilized for (i) Modifying polymer or filler surface for enhancing the compatibility between the polymer and filler (ii) Uniform cross-linking of the finished composites as a result of which a well distributed and well dispersed filler remains permanently embedded in the composite. Radiation processing of polymer composites has been extensively explored at BARC for synthesis of chemi-resistive sensors [22], tenso-resistive sensors [23], designing X-ray shielding material [24], for synthesis of ESR dosimeters [25] and for imaging purpose [26]. Figure 13 shows protocol for preparing polymer composite based chemi-resistive sensor.

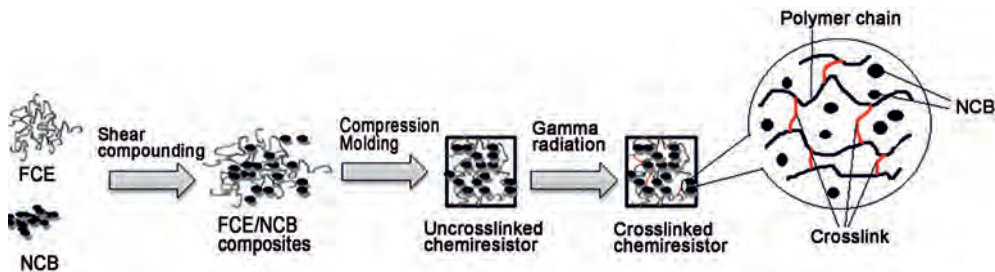


Figure 13: Protocol for synthesis of radiation processed chemi-resistive sensor

On exposure to chemical analyte the polymer of the composite matrix interact with the analyte as result of which the continuous conducting network of the filler is broken leading to increase in resistance (Figure 14). On desorption of the analyte the polymer regains its original shape due to cross-links induced by irradiation. Thus the composite matrix can be cyclically used analyte sensing.

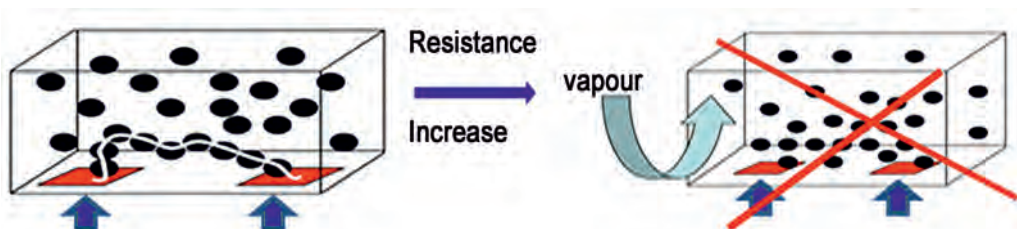


Figure 14: Disturbance in conductive network of composite due to interaction of organic analyte with polymer phase

4. Conclusion

Radiation processing of polymers is a clean, reliable, reproducible, easy and upscale technology which enriches the quality of our life in many ways. Radiation processed polymers find applications in industry, healthcare, agriculture and environment. The longer life of radiation processed polymer based products would contribute to less generation of polymer waste. With recent developments in the area of radiation processed advanced nanomaterials, the applications of radiation technology is expected to grow further.

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