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Radiation and industrial polymers

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Abstract

With the advancement of industrialisation, pollution is a crucial problem for mankind. In the Green drive, i.e to make the world pollution-free, radiation technology takes an important position. Nuclear radiation has made its entry into many chemical processes. ‘Polymerisation’, ‘grafting’ and ‘curing’, all-important chemical processes in the polymer field, can proceed through radiation techniques. The radiation technology is preferred over the other conventional energy resources due to some reasons, e.g. large reactions as well as product quality can be controlled, saving energy as well as resources, clean processes, automation and saving of human resources etc. Apart from this, radiation is also a good sterilising technique over other conventional sterilising techniques. The irradiation of polymers can be applied in various sectors. In this review, the attention has focussed primarily to four sectors, i.e. biomedical, textile, electrical and membrane technology. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Radiation; Crosslinking; Grafting; Hydrogels; Vulcanisation

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1. Introduction

From the age of stone and metals, we have come to the age of nuclear energy and polymers. Indeed, we live in the world of polymers. That is why scientists and technologists have termed this era as the ‘polymeric age’. In every step of our daily lives, we come across things, which are the fruits of polymer research. The ever widening application of polymers in everyday life over the last several decades has generally been acknowledged as a mixed blessing by scientists and technologists. Though started in the middle of the last century, work in this field of chemistry has been so rapid and the application so useful and versatile, that the number of polymer systems are enormous.

The last three decades have also witnessed the emergence of nuclear radiation as a powerful source of energy for chemical processing applications. Thus, it can be applied in different industrial areas. The fact that radiation can initiate chemical reactions or destroy micro-organisms has led to the large-scale use of radiation for various industrial processes. Nuclear radiation is ionising, which on passage through matter, gives positive ions, free electrons, free radicals and excited molecules. The capture of electrons by molecules can also give rise to anions. Thus, a whole range of reactive species becomes available for the chemist to play with.

Radiation-based processes have many advantages over other conventional methods. For initiation processes, radiation differs from chemical initiation. In radiation processing, no catalyst or additives are required to initiate the reaction. Generally with the radiation technique, absorption of energy by the backbone polymer initiates a free radical process. With chemical initiation, free radicals are brought forth by the decomposition of the initiator into fragments which then attack the base polymer leading to free radicals. Sakurada [1] compared the efficiency of the two processes and estimated that the same number of initiating radicals are produced in unit time with a radiation dose of 1 rad/s or a chemical initiator, e.g. benzoyl peroxide, at a concentration of.01 M is used. Chemical initiation is however limited by the concentration and purity of the initiators. However, in the case of radiation processing, the dose rate of the radiation can be varied widely and thus the reaction can be better controlled. Unlike the chemical initiation method, the radiation-induced process is also free from contamination. Chemical initiation often brings about problems arising from local overheating of the initiator. But in the radiation-induced process, the formation of free radical sites on the polymer is not dependent on temperature but is only dependent on the absorption of the penetrating high-energy radiation by the polymer matrix, Therefore, radiation processing is temperature independent or, in other words, we may say it is a zero activation energy process for initiation.

As no catalyst or additives are required, the purity of the processed products can be maintained. With radiation processing, the molecular weights of the products can be better regulated. Radiation techniques also have the capability of initiation in solid substrates. The finished products can also be modifying by the radiation technique.

Nuclear radiation energy, however, is expensive though very efficient in bringing about chemical reactions. The unit cost of installed radiation energy is much higher than that of conventional heat or electrical energy. Despite this fact, the application of nuclear radiation energy has proved its superiority and its cost effectiveness in a number of chemical processes over that of other forms of energy such as heat or electrical energy. Radiation techniques have good efficiencies with regard to power and needs only a small space to be set up.

The application of radiation on polymers can be employed in various industrial sectors, i.e. bio-medical, textile, electrical, membrane, cement, coatings, rubber goods, tires and wheels, foam, footwear, printing rolls, aerospace and pharmaceutical industries. In this review, attention is focused primarily on four sectors: biomedical, textile, electrical and membrane technologies.

2. Types of reactions involved

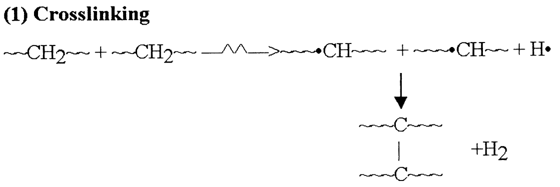
Radiation-initiated reactions can be categorically classified as two types: (1) crosslinking and scission and (2) grafting and curing. Crosslinking is the intermolecular bond formation of polymer chains. The degree of crosslinking is proportional to the radiation dose. It does not require unsaturated or other more reactive groupings. With some exceptions (as in polymers containing aromatics), it does not vary greatly with chemical structure. It does not vary greatly with temperature. Although the mechanism of crosslinking by radiation has been studied since its initial discovery, there is still no widespread agreement on its exact nature. The mechanism of crosslinking generally varies with the polymers concerned. The universally accepted mechanism involves the cleavage of a C–H bond on one polymer chain to form a hydrogen atom, followed by abstraction of a second hydrogen atom from a neighbouring chain to produce molecular hydrogen. Then the two adjacent polymeric radicals combine to form a crosslink. The overall effect of crosslinking is that the molecular mass of the polymer steadily increases with radiation dose, leading to branched chains until, ultimately a three-dimensional polymer network is formed when each polymer chain is linked to another chain.

In contrast, scission is the opposite process of crosslinking in which the rupturing of C–C bonds occurs. Crosslinking increases the average molecular weight whereas the latter process reduces it. If the energy of the radiation is high, chain breaking occurs through the cleavage of C–C bond. In aerated solution medium, however, the mechanistic way of scission proceeds through indirect manner. The polymeric free radicals are generated by solvent-free radicals, which are already formed by radiation. The addition of oxygen with the polymeric free radicals forms the peroxy species, which on decomposition forms smaller molecules. The oxidative degradation of the polymers depends upon the solvent used in the system. Actually, the polymer degradation competes with the oxidation of the solvent.

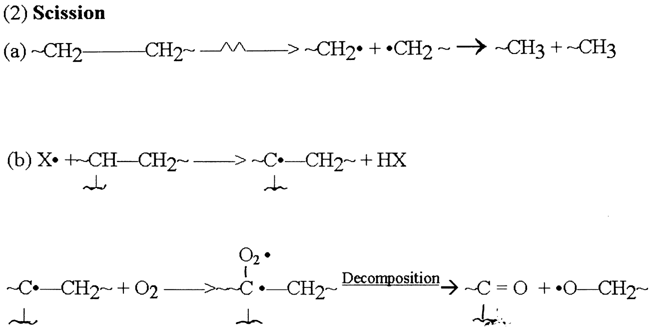
Grafting is a method where monomers are introduced laterally on to the polymer chain where as curing is the rapid polymerisation of an oligomer monomer mixture to form a coating, which is essentially bonded by physical forces to the substrate [2]. In the simplest form, such methods involve heterogeneous systems, the substrate being a film, fibre or even a powder, with the monomer as a neat liquid, vapour or solution. There is a close relationship between grafting and curing although there are certain differences. Actually, there is no time limit for the process of grafting. It can take minutes, hours or even days, whereas curing is a usually very rapid process occurring in a fraction of second. In grafting, covalent C–C bonds are formed whereas in curing, bonding usually involves weaker van der Waals or London dispersion forces. van der Waals bonding operate at distances where there is little or no overlap or exchange and it is generally associated with smaller energies. However, covalent bonding, is effective at small internuclear distances and is associated with electron overlap, exchange, and consequently higher energies. Another important aspect of curing reactions is the possibility that concurrent grafting with curing occurs leading to improved properties of the finished product, particularly in adhesion and flexibility.

Grafting proceeds in three different ways: (a) pre-irradiation; (b) peroxidation and (c) mutual irradiation technique. In the pre-irradiation technique, the first polymer backbone is irradiated in vacuum or in the presence of an inert gas to form free radicals. The irradiated polymer substrate is then treated with the monomer, which is either liquid or vapour or as a solution in a suitable solvent. However, in the peroxidation grafting method, the trunk polymer is subjected to high-energy radiation in the presence of air or oxygen. The result is the formation of hydroperoxides or diperoxides depending on the nature of the polymeric backbone and the irradiation conditions. The peroxy products, which are stable, are then treated with the monomer at higher temperature, whence the peroxides undergo decomposition to radicals, which then initiate grafting. The advantage of this technique is that the intermediate peroxy products can be stored for long periods before performing the grafting step. On the other hand, with the mutual irradiation technique the polymer and the monomers are irradiated simultaneously to form the free radicals and thus addition takes place. Since the monomers are not exposed to radiation in the pre-irradiation technique, the obvious advantage of that method is that it is relatively free from the problem of homopolymer formation which occurs with the simultaneous technique. However, the decided disadvantage of the pre-irradiation technique is the scission of the base polymer due to its direct irradiation, which brings forth predominantly the formation of block copolymers rather than graft copolymers. The different processes are represented through simple mechanisms provided below:

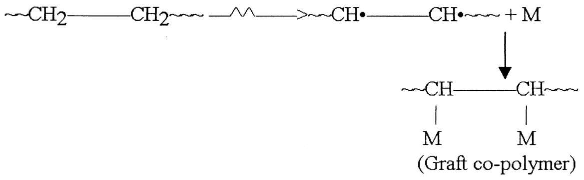
(1) *Crosslinking*:



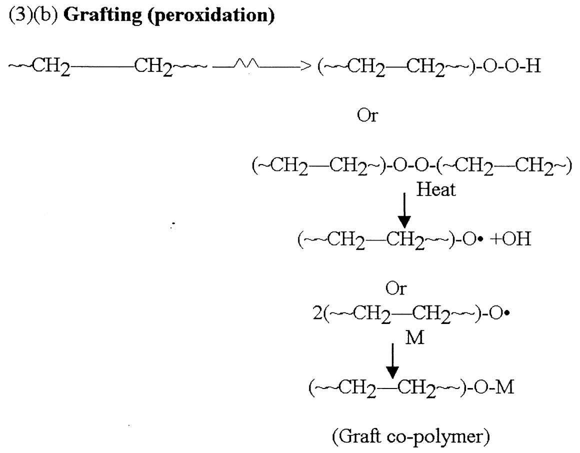
(2) *Scission*:



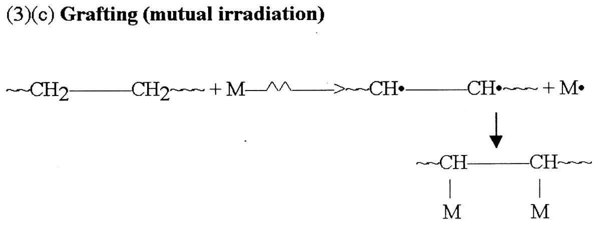
(3)(a) *Grafting* (*pre-irradiation*):



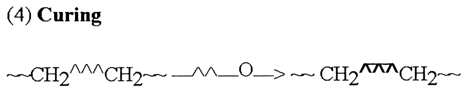
(3)(b) *Grafting* (*peroxidation*):



(3)(c) *Grafting* (*mutual irradiation*):



(4) *Curing*:



(O = oligomer curing gives a smooth finish by filling in the valleys in the surface of the polymers)

3. Bio-medical applications

Medical technologies are often regarded as the greatest intellectual enterprise of human kind. These are interdisciplinary fields and have close interactions with polymer research and technology. Polymers, which are widely used in every sphere of life, have come a long way from being looked upon with suspicion to being accepted as favourable and useful tools in the field of medical science. The history of using polymers in the biomedical field actually begins with celluloid (a hard plastic formed from nitrocellulose) and bakelite (phenol–formaldehyde resin) during the Second World War. Celluloid and bakelite were used for cranial defect repair and arthoplasty of the hip, respectively. The first users of the materials did not aim for the purity as well as bio-stability of the materials. Thus, the materials produced a strong tissue reaction as they interact with the organism in the post-operative cases. That is why they became unacceptable. Afterwards different polymers like poly(methyl methacrylate) (PMMA), poly(vinyl alcohol) (PVA), poly(hydroxy methacrylate) [poly(HEMA)], poly(vinyl pyrrolodine) (PVP) etc. gained importance in biological field as they overcame the said limitations.

Radiation synthesis and fabrication techniques gear up the research on bio-medical applications in early 1960s and at present are in full swing. Charlesby and Chapiro [3,4] are the pioneers for developing this interdisciplinary field. In this field, ‘bio-compatibility’ is the most essential aspect to be considered. It is the most important property of bio-medical materials since these are used in contact with the living organisms such as blood and tissues. Thus, ‘bio-compatibility’ expresses the relationship between a foreign material and the physiological environment. Interactions of the foreign materials with blood proteins and tissue constituents cause biological disorder, e.g. the change in the colloidal stability and viscosity of the blood. Thus, these affect the platelet distributions, blood clotting and circulation of the blood. Radiation processing techniques are employed to modify the properties of the polymeric materials to make them bio-compatible. The process is simple, reliable and the processed materials are non-toxic. In the radiation processing techniques, additive is not required and for this reason, the product quality can be maintained. Moreover, another advantage of these radiation techniques is that the processed materials are also simultaneously sterilised. Research in this field can be classified in two parts according to the purposes of the application: (1) the synthesis of polymers having a special biological function and (2) the preparation of polymeric composites which have special biological component by radiation ‘immobilisation’.

The polymers, which are used in this biomedical field, can be divided in two categories—one is for in vitro class of materials and the other is for in vivo class. The in vitro class of materials meets drugs in the solid state or in the form of solutions, syrups, suspensions, blood products etc. On the other hand, the in vivo class materials are used temporarily and they are mainly the assisting materials such as sutures, surgical adhesives, artificial parts of a more permanent nature (such as vascular grafts, heart valves and catheters, tubings and films as extracorporal circuits and dialysis machines).

In the bio-medical application, polymers especially those which are based on hydrogel biomaterials are in the frontline area due to their bio-compatibility. The hydrogels are polymeric materials which exhibit the ability to swell in water, i.e. they retain a significant fraction of water within themselves but do not dissolve in water. The soft non-abrasive quality, their wettability and permeability to biologically active substances of low molecular weight make them possible to prepare materials which can serve the bio-medical purposes excellently.

The hydrogels can be prepared by ionising radiation. On ionising radiation of macromolecules, at first macroradicals are formed, which when recombined form hydrogels. If the macroradicals are favourably positioned, new covalent bonds between the polymer chains are formed and thus the hydrogel turns into an insoluble fraction depending upon the amount of these new bonds. On further irradiation, the amount of gel increases, although a part of macromolecules (or their fragments) may still be unbound (sol). However the mechanism is rather complicated in presence of water as a solvent and it has been studied by Davies et al. [5].

In the case of hydrogel formation, three-dimensional network is developed and it exhibits higher molecular weight that tends to infinity [6]. The network is represented in Fig. 1. The circle represented in the figure is accessible for diffusion of solutes. In swollen state, this space contains water or the solvent molecules. The dimension of this region and the mesh size depend on the degree of crosslinking of the polymer chains or the density of junction points. The amount of water absorption also depends on the

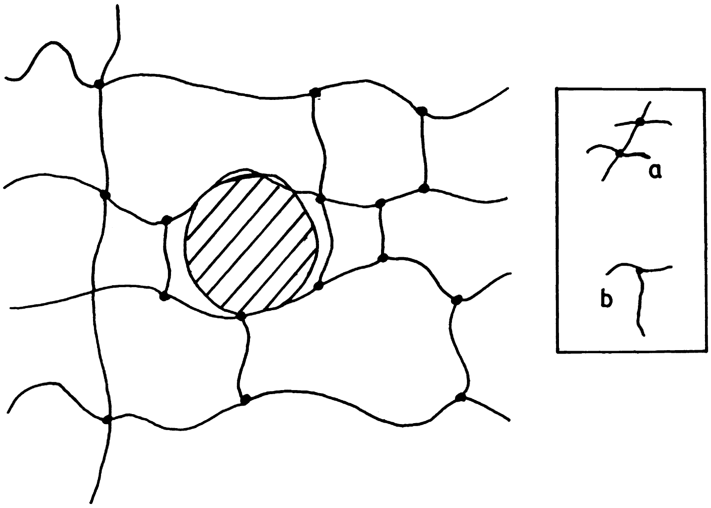


Fig. 1. Scheme of hydrogel network. Circle denotes available space for diffusion. In the insert, four functional (a) and trifunctional (b) points of chain junctions are shown. Reprinted from Radiat Phys Chem 1988;32:691–4, © 2000, with permission from Elsevier Science [6].

degree of crosslinking of polymer chains. The higher the degree of crosslinking is, the smaller is the amount of water–solvent absorbed in this space. Such a schematic representation of a hydrogel network is treated as a network of 'phantom type'. Since in radiation polymerisation no catalyst or heat is required, there is no possibility to bring toxicity in the system and decomposition of the drugs. Thus, it is a very convenient method to prepare drug delivery system. Moreover, by using radiation technique, the hydrophilicity as well as porosity can be controlled at a low temperature [7–9]. Based on the properties of hydrogel, it can be used as carriers for the immobilisation of bioactive compounds and can be used in the controlled release of drugs [10].

'Immobilisation' is the technique by which mobility of the biological species has been lowered. It is the technique to fix the biological component in the surface of the polymer or to entrap it into the polymer matrix. This polymer-based technique has some advantages, i.e. (1) it can be used repeatedly because of fixation, insolubilisation, solidification of the system, (2) it can be shaped into desirable form, the size and structure of which is convenient to reaction and protection (3) the releasing of the biological components from the polymer matrix can be controlled accordingly. The degree of fixation depends on the size of the bio-component. As the size of the biofunctional component increases, the fixation capacity decreases. A small molecule like a drug is leakaged by different rates according to the porosity of the polymer and the nature of the drug [11]. To control the rates of leakage, drug delivery system is needed. Slow controlled release of drug, low or no secondary reaction and better targetting the affected cells, are the basis of the drug delivery system. The polymer-based drug delivery devices have the ability

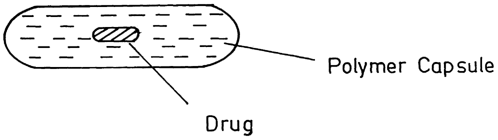


Fig. 2. Schematic presentation of drug–polymer composite.

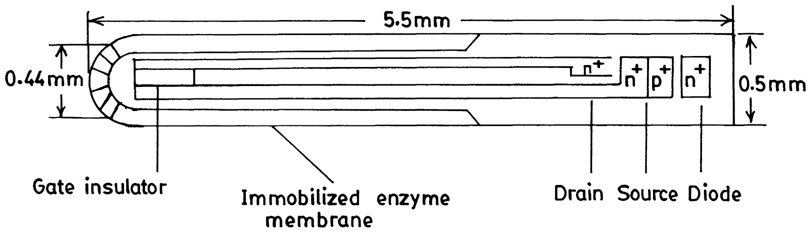


Fig. 3. ISFET bio-chip sensor. Reprinted from Radiat Phys Chem 1995;46:1025–30, © 2000, with permission from Elsevier Science [12].

to control the drug release function at a desired rate and for a necessary period. The polymer acts as a vehicle to the drug molecule. A simple diagram is depicted in Fig. 2 in which the drug is encapsulated in the 'polymer capsule'. The drug releasing process is a continuous automatic and spontaneous process. The rate and period of this process depend on the nature of the polymer and the drug molecule.

The modern chemical delivery device is a composite one and it consists of a sensor and a delivery part. In the sensor part, the actuator transduces an electrical signal to a mechanical energy for an initiation of drug release from the reservoir. The sensor is used as a monitor to control the drug release for a specific time. A biochip is the most suitable to construct the sensor part. The electrically responsive hydrogel has the property of reversible volume change between shrinkage and expansion. An on–off switching electrical field, regulates the releasing of the drug from the gel applying the electrophoresis technique. For this reason, it is useful to act as the actuator and reservoir. The immobilisation is necessary for an enzyme and a drug to construct both the biochip sensor and the actuator–reservoir gel.

In this aspect, Kaetsu [12] developed an immobilised glucose–oxidase sensor. In that sensor, glucose oxidase was immobilised in a thin PMMA membrane on the surface of gate of ISFET (ion-sensitive field effect transistor). It is represented in Fig. 3. The addition of glucose makes this biochip sensitive. The function of on–off switching release of insulin from an electroresponsive hydrogel with the on–off switching of electrical field is shown in Fig. 4. The signal responsive chemical delivery system can be obtained by a combination of such a sensor and electroresponsive substance delivery system immobilising a biofunctional compound to be released with an environmental signal.

The hydrogel-based materials can be useful in the field of wound dressings, especially in burns, ulcers,

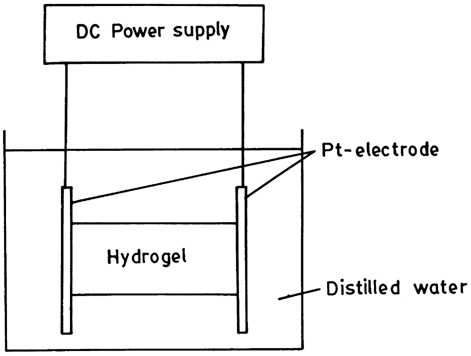


Fig. 4. On–off switching system. Reprinted from Radiat Phys Chem 1995;46:1025–30, © 2000, with permission from Elsevier Science [12].

bedsores and skin grafts. These materials have some advantages such as: (i) slow drug releasing recovers the pain effectively for prolonged period of application; (ii) good barrier of bacteria from outside; (iii) permeable for gases, drugs and water vapour and also (iv) acts as good adhesion to wound and normal skin without sticking. Apart from these, the dressings can reduce the oozing of liquids from the wound to heal faster and thus simultaneously the numbers of dressing changes are greatly reduced. PVP, poly(acrylamide) and their monomers, polyethylene glycol, agar and PVP–PVA-based hydrogels are used for wound dressings [13,14]. PVA–PVP-based hydrogel (drug carrying concentrated aqueous solution of chloramphenicol) is superior to usual gauze bandage especially for curing of large area wound [15]. It is able to perform the function of relieving pain, hemotosis (blood formation) and is able to stop the loss of body fluids. It works as good adhesive to both wound and normal skin.

In therapeutical system for induction of labour, PVP-based hydrogel can be used. Therapeutic induction of labour is necessary to accelarate the beginning of labour in the case of serious prolongation of pregnancy over natural time limit when the lives of women and infants are in emergency. However, the known methods of introducing prostaglandin to accelarate the ripening of the uterine cervix often cause negetive side effects. Therapeutic system for local release of prostaglandin based on hydrogel devices has been developed by irradiation of *N*-vinyl pyrrolidone (VP) [16,17]. A silk surgical thread is fixed in a 35 mm long rod shaped device of 8 mm diameter and equipped with round head on one side and surgical thread on the other. The device has been prepared by the incorporation of prostaglandin (which is carried out by placing the rod in appropriate solution of hormone) after radiation polymerisation of vinyl pyrrolidone. The dried swelled rod is also sterilised by the radiation technique. Preparation of testicular prosthesis with the controlled release of testosterone by radiation polymerisation of HEMA and polyethylene glycol dimethacrylate is reported by Yoshida et al. [18]. It is implanted in the scrotum or in the lower abdomen of patients. The serum testosterone level has been maintained in good level. This technique definitely has a good advantage with the treatment by injection.

The radiation immobilisation technique employing polymerisation in supercooled state is unique. Kaetsu et al. [19–21] found that many acrylates and methacrylates, monomers could be supercooled and could remain stable. The most remarkable characteristic of these types of polymers is the sharp and sudden increase of viscosity as the temperature decreases. The supercooled state has two main advantages for the immobilisation. It can prevent the radiation damage of the biofunctional components owing to the freezing of water. It reduces the attack of radicals from water against biofunctional molecules and increases the porosity in the polymeric matrix due to the freezing of water to form a porous structure after melting. Therefore, the activity of the immobilised composite is increased remarkably in the supercooled temperature region. In this polymerisation, the biofunctional components (enzyme) can be concentrated in an interfacial area between the frozen ice crystal and the supercooled monomer phase. It is immobilised by molecular entanglement between the enzyme and polymer molecules. Thus, it is a different procedure of fixation from the usual entrapping method with a crosslinked structure in a gel. It is some sort of adhesion method. Kubo et al. [22] developed anticancer drug–polymer composites by combining and mutually dispersing anticancer reagents with glass forming monomers, followed by γ-irradiation at a low temperature (-78°C). The controlled slow release of drug is very useful for the treatment of malignant brain tumour. It has certain advantages than the local chemotherapy, which has certain major problems such as quick elimination of drug from the tumour site, damage to normal tissues, poor intratumoural infiltration of the anticancer drug to the blood–brain barrier. For diagnosis of liver cancer, anti-α-fetoprotein immobilising on the polymer film has been carried out [23]. Anticancer drugs, proteins, peptides are also incorporated in to the drug delivery system of poly(2-HEMA), poly(HEMA) which were prepared by radiation technique [24–27]. The potential anticancer drug Narcisclasien, which is known for its remarkable antimitotic activity has not yet been used owing to its toxicity. For this reason, a drug delivery system, (for its controlled release is based on radiation-induced polymerisation at a low temperature) of methacrylic monomers has been prepared.

Apart from the supercooled polymerisation, the room temperature polymerisation can also be effective in this type of polymerisation. In this case, hydrophobic polymers (including methyl methacrylate, ethyl methacrylate and butyl methacrylate) are used for the immobilisation technique. Huaijiang et al. [28] reports the results in which the anticancer drug Cytarabini Hydrochloridium pro-injection (Ara-C) with controlled slow release were made by radiation-induced polymerisation of monomers such as methacrylates at room temperature. In the room temperature, the activity and structure of drugs have not changed. The rate of drug release was controlled by the many factors such as content of drugs, the monomer material, the crosslinking agent, the irradiation dose and the water content etc.

Apart from these activities, the crosslinked hydrogels can be used in different areas such as opthalmic, dental, transdermal and various implantation techniques. The contact lenses are prepared from hydrogel materials itself and their copolymers, e.g. poly(hydroxy ethyl methacrylate), PVP, PVA, poly(methyl acrylic acid) etc. [29,30]. The hydrogels prepared using radiation technique is preferred because the network can be controlled desirably as well as the prepared materials can be sterilised. Most of the products are based on poly(HEMA) hydrogel. Copolymerisation is mainly used to improve poly(HEMA)'s mechanical properties and increase its oxygen permeability. The efficient casting of block materials or manufacturing of lenses by radiation process produce no optical strain when used, as there are no other defects such as cracking and voids. In this case, much reduced quantity of the monomer residue is needed and catalysts are not essential. It can be also used as corneal implants, as well as for the treatment of glaucoma patients. For glaucoma patients, hydrogel strips containing pilocarpine are placed in the formix of the eye-lid [31]. In the case of treatment of cataracts, PMMA has been used in the form of intraocular lens. Radiation polymerisation technique is very advantageous in dental operations also compared to other conventional methods. Polymerisation of HEMA or other hydrophilic monomers/polymers by UV light can be an advantageous process to fill the cavity. First the cavity is filled up by monomer or pre-polymer and then it has been polymerised by radiation technique. Dybek et al. [32] reported the preparation of hydrogel-based material made of PVA and gelatin, which is applicable in dentistry. Collagen-based materials are particularly very effective to plastic surgeons for repairing the cosmetic defects [33].

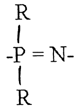
The other interesting types of hydrogels, which have gained considerable attention of the scientists, are thermoresponsive gels [(such as *N*-isopropyl acrylamide, poly(vinyl methyl ether)] [34–37]. They reversibly swell and shrink with variation in the temperature but do not bend. They are used as thermoresponsive soft actuators, thermoreversible separator, artificial muscle/finger, and automatic gel valve etc. In this type of hydrogels, the drug permeation and release are thermally controlled by using modified networks. The activity of the enzyme immobilised in thermoresponsive hydrogel is controlled by temperature cycling. Maolin et al. [38] reported about the immobilisation of bovine serum albumin (BSA), horse radish peroxidase by poly(*N*-isopropyl acrylamide-*co*-*N*-acryloxy succinimide) copolymer. The hydrogels have also been used as postnucleation balls, breast implants, artificial muscles [39,40] etc.

Radiation crosslinked poly(ethylene oxide) is another useful material in the biomedical field. It is used to produce a bio-compatible heat shrinkable sleeve with a low melting temperature ($<60°C$) for a sutureless vascular anastomosis system [41]. This new material, when crosslinked by radiation is both hydrophobic and non-toxic. By this crosslinked polymer, rejoining of several blood vessels (end-to-end anastomosis) without using sutures can be made possible. One of the essential elements of the material is a bio-compatible sleeve that is initially large enough to fit over the two ends of the vessels and contracts on heating both radially and axially to secure them. Grafting of hydrophobic monomers (styrene, ethylene and butadiene) by radiation technique modified the materials in this regard.

Apart from the entrapping technique and adhesion method, there is the another technique of immobilisation, i.e. radiation graft copolymerisation [42–44]. It has been studied by many researchers. In this case, the monomers are grafted on the polymeric backbone by radiation technique and thus it is activated for entrapping the enzymes, proteins or peptides. The technique has more advantages over the other techniques as in this technique the drug molecule can be entrapped on the surface of the polymer backbone. Radiation-induced graft polymerisation has been used as an immobilisation method of biologically active substances (ferments, medicines etc.) on the surface of the polymers to be used in biotechnology and medicine. Hongfei [45] developed acrylic acid and acrylamide-grafted segmented polyether urethane film (SPEU) on which horse radish peroxidase (HRP) was immobilised through chemical binding. By this method, peroxide content in irradiated wine can be analysed. Radiation-induced grafting is also applied for trypsin immobilisation [46]. The nitro groups of *p*-nitrostyrene onto various polymers [47] are transformed in isothiocyanate ones and then trypsin is attached. The immobilised trypsin is used for the milk treatment procedure. The advantage of the grafted polymer is that it can be used as films also. Temporary artificial skin can also be prepared by radiation-induced grafting of acrylamide, hydroxymethylmethacrylate onto a polyurethane film [48]. Advantages of using the grafted polymer are that bacterial invasion can be avoided, permeability of water becomes better and thus fluid accumulation does not occur. It is transparent, adhere well to the wound and can be removed without pain. Excellent plasma separation capability and haemocompatibility [49,50] behaviour are observed in case of polypropylene-*g*-(*N*,*N*-dimethylacrylamide) and polypropylene-*g*-polymethylethylacrylate membrane. Microporus polypropylene is a hydrophobic material, which has excellent dimensional stability upon swelling. However, it is non-wetttable by water and thus plasma does not permeate the membrane in a dry state. In order to hydrophilise it, the polymeric backbone is grafted by hydrophilic monomers. As the plasma collected from blood does not contain various viruses when this material is used as a separator, the limitations of conventional centrifugation system can be overcome. In cardiovascular surgery (artificial heart valves and artificial prosthesis and haemodialysis) [51], *N*-vinyl pyrrolidone grafted silicon rubber material is very useful. DMAA and *N*,*N*-dimethyl amino ethylacrylate grafted natural rubber tubes are better bio-compatible than silicon rubber tube [52,53]. Blood compatibility of the material is improved with the increasing degree of grafting of the monomers. Polystyrene materials frequently used for ELISA (enzyme-linked immuno sorbent assay) microtiter plates are modified by γ-radiation in order to enhance the passive absorption binding capacity of immunoglobuline E [54]. Radiation grafting made it possible to fix the hydrazide functional group onto the polystyrene. It offers the possibility of binding the proteins via covalent linkage with the carbonyl group formed by the oxidation of carbohydrates included in the protein molecule. The binding capacity increases on irradiation dose and conditions (atmosphere, presence of water). In the treatment of acute lymphocytic leukemia [55], the grafted fibre can be used as blood plasma exchange device. In this case, asparginase enzyme is immobilised on methyl acrylic acid and then they are grafted on porous hollow polypropylene fibre and the carboxyl groups are activated with *N*-hydroxy succinimide (NHS) using carbodiimide method.

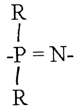
‘Superabsorbing polymers’, which may be termed as polymers which are capable of absorbing and holding large amount of water, has gained considerable attention of the scientists and can be very useful in the bio-medical field. These materials have extensive commercial applications such as ‘infant diapers’, ‘feminine hygiene products and incontinency products. These materials can be fruitfully prepared by radiation grafting technique, e.g. cassava starch-*g*-(polyacrylonitrile), starch-*g*-(acrylamide and acrylamide-2-methyl propane sulphonic acid) [56,57]. These materials are starch-based, biodegradable, and lasts for only about one year.

Apart from these, inorganic polymeric systems have also attracted scientists because of their better flexibility than other organic polymeric systems. Conventional organic polymers provide materials with a broad range of properties but the presence of carbon atom and the short length of the carbon–carbon bond generate a chain stiffness restricting its use in broad temperature range for elasticity and even flexibility. The inorganic polymers can be used as flame-resistant, oxidation-resistant, oil- or solvent-resistant materials and it can be used in high or low temperatures. However the class of inorganic polymers that has received the most extensive development in recent years is the phosphonitrilic polymers or the poly (organophosphazene) system. They are a class of semi-inorganic polymeric systems based on



$$-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{\mathrm{P}}}=\mathrm{N}-$$

backbone or



$$-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{\mathrm{P}}}=\mathrm{N}-$$

containing rings. Depending upon the type of substituents on phosphorus, a wide range of polymers (like organic polymers) can be prepared. Radiation-induced graft copolymerisation of suitable monomers such as *N*-vinyl pyrrolidone, *N*,*N*-dimethyl aminomethyl methacrylate (DMAEM), acrylamide, *N*,*N*-dimethyl acrylamide onto two semi-crystalline elastomers, i.e. [poly(bis(triflouroethoxy)phosphazene)] (PTFP), poly[bis(phenoxy)phosphazene] (PPP) enhances the bio-compatibility of the system [58–60]. Thus, it can be used as better bio-medical devices. Heparinisation (heparin (HEP)) is ionically bonded with a high yield via quarternisation with methyl iodide) induced a noticable anticoagulating action to the polymer surfaces [61,62].

Besides the above applications such as preparation of drug delivery devices, artificial muscles, contact lenses, breast implantations, diapers, catheters etc, the application of radiation for sterilisation of medical devices is now quite common [63–66]. The advantages of this method make it the preferred technique amongst the other conventional methods such as autoclaving, dry heat and use of ethylene oxide gas. The conventional sterilisation process is rather time-consuming process whereas the radiation sterilisation can be done while processing the biomedical materials simultaneously. Use of ethylene oxide is disfavoured not only on cost grounds but also because in this case exposure to the chemicals is more difficult and more expensive to control than exposure to ionising radiation. Ethylene oxide gas which is used widely as steriliser is known to be very dangerous, toxic and may be carcinogenic too, as it suffers from the problem of retention of considerable amount of gas after sterilisation. The efficiency of radiation sterilisation process depends on three parameters viz. the initial microbiological contamination, resistance of micro-organism and sterility assurance level [66].

The reasons for the success of radiation sterilisation are: (a) it is simple and reliable; (b) it is a continuous sterilisation process; (c) it can be carried out in room temperature; (d) its applicability to the sterilisation of single use medical products; (e) freedom of choice of materials and (f) high degree of sterility assurance. The radiation sterilisation process control is simple. It only needs an isotopic radiation source and the conveyor. The conveyor speed is the only factor, which controls the process. The ease of control of the radiation output and the use of well-proven mechanical conveyors assure reliability greater than that experienced with most mechanical process equipments. In this case, the reliabilities are well above 90%. The continuous nature of the radiation sterilisation process outdated the conventional sterilisation process, which is rather in a stepwise manner. The radiation technique is a room temperature process. It allows ideal production flow through manufacturing operations and minimum handling by humans. Thus, it does not need human resources compared to the other techniques. Therefore, there is a low labour cost. In addition, the simple mechanical systems and low speeds of operations assure very low maintenance costs. Radiation sterilisation is the unique one at the time of preparation of health care products. Single-use sterile medical products replaced the conventional resterilisable items. It was found that by using inexpensive plastics and mass production technology, single-use items could be produced less expensively than the cost of labour required to clean and resterilise the products of multiple use. The sterilising ability of ionising radiation is independent of the chemical nature of the materials because of its penetrating nature. The reproducibility and simple control of radiation sterilisation resulted in a very reliable process, almost independent of human error. In addition, the radiation sterilisation process in industry is operated by well-trained and experienced people whose primary responsibility is to assure good process performance. The biggest advantage of radiation over the other methods is that the bio-medical products can be sterilised in room temperature after packaging, avoiding recontamination and thus it is completely safe.

Thus, it may be said in short, the polymers and radiation have taken a vital position to the modern medical science and technology. Polymer science is a branch, which has made tremendous impact on medicine. Based on the properties of the polymer, drug delivery devices can be constructed. The drug delivery devices are based on the slow release of ‘enzymes’, ‘proteins’ and ‘peptides’ that are bounded or entrapped on to the polymer matrix. The radiation-processed polymeric materials, i.e. in vitro class can be useful in opthalmic, dental and transdermal field. The in vivo class of materials such as sutures, surgical adhesive, catheters, heart valves etc are also processed by radiation technique. Apart from the processing of materials, the radiation technique can be used as a sterlising method, which is very important in the bio-medical science. It has definitely some advantages other than the conventional sterilising technique.

4. Textile applications

With the advancement of the world of science and technology, the textile research has also journeyed very far. Textile products have always fulfilled the aesthetic requirements unlike any other consumer products. This is especially the case with clothing textiles. The progress of textile research is based on essential as well as aesthetic requirements of the mankind. To meet these requirements, the textile research is not totally bound to parent cotton fibres, as the manufacturing of fabrics from cotton fibres is a complicated as well as laborious process and it has certain limitations.

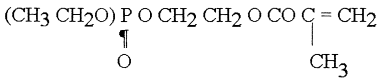
In this aspect, two processes have been developed, one is the modification of cotton fibres and other is the production as well as the modification of man-made (synthetic) fibres. Man-made fibres are those, which are produced in industrial conditions and mainly, consist of organic carbon chain compounds. In the modern era, the production of man-made fibres has been rapidly developed as well as their assortment has also been increased. Thus man-made fibres occupy one of the leading places in the total volume of textile fibres produced. Precisely, the rapid rise in human population and their consequent increasing demands directs the technologists to the production of synthetic fibres. The man-made fibres have more regular properties than natural ones and some of the properties, i.e. length, linear density (mass of a fibre of a certain length) and strength may be adjusted. Moreover, there exist other factors which promote the increase of the production of man-made fibres. The main advantage is that the synthetic fibre production is free from geographical conditions unlike the natural ones, the production of which depends largely on the climate. The natural fibre production is also dependent upon the sowing areas. As the percentage of sowing area decreases day-by-day, the production of natural fibres is affected. Thus, it has become complicated and lengthy process than the synthetic fibre production. The ready accessibility of raw material resources in the manufacture of certain kinds of fibres favours the man-made fibre. Moreover, the production of synthetic fibres can be controlled, as it is dependent on the manpower and chemicals.

It is well known that the cotton and other cellulosic materials possess a very high value of comfort specially when used for garments and apparels, as against the the normal synthetic fibres, which give uneasy and uncomfortable feeling on wearing the clothes made out of them. Cotton fibre contains 97% cellulose, 1.5% pectin substances and pentodes, 0.3% nitrogen and protein substances, 1.0% fats and wax and 0.2% ash. The molecule of cellulose, which is the main substance of the cotton fibre, together Apart from the textile formation, textile finishing is another important step. It involves the processes like dyeing, bleaching etc. The textile fibres are modified and the new properties of the fibres can be achieved through the treatment with different chemical substances. The increase in dye uptake of fibres could be accounted for by the increase in moisture content of the fibres, which may probably be responsible for more fibres swelling at dyeing temperature in the fibre. Since the level of moisture regain and other absorption characteristics of these materials are extremely low giving a dry and harsh handle, i.e. they are very difficult to dye, get soiled easily, accumulate static charges. Therefore, to overcome these limitations, the modification of the fibres is necessary. One way of overcoming these defects is to modify the structure of the fibres. These attempts have not been successful as it alters the fibre-forming characteristics. The other approach is to modify the surface of the fibres by grafting suitable molecules to it. On grafting of various monomers, the fibres are brought at par with cotton and such a grafted synthetic fibre imparts high comfort characteristics to the clothes made out of them. Radiation technology may be employed to modify the structure of the fibres as it has many advantages than the other usual techniques that are already described before.

Potential useful applications of high-energy radiation in textile processing lie in: (1) utilisation of this energy in developing new textile products through chemical modification and (2) the sterilisation of the textile products. In the development of new products, the initiation of chemical reactions at the lowest possible radiation dosages would be advantageous. Thus, any chemical treatment or chemical modification of textile fibre, which would make the molecules more radiosensitive, would be advantageous. On the other hand, in the development and extension of radiation sterilisation processes for the textile products, any increase in radiation resistance of these products would be advantageous, for there will be minimum effects of high-energy radiation on the physical and chemical properties of such products. In the field of textile finishing radiation, this technique plays an important role. Radiation technique for grafting and crosslinking is advantageous compared to chemical procedure as no special treatment of textile polymer with chemicals is involved. The process can be so varied as to change the location of grafted part on the polymeric fibres. In addition, cotton fabrics, crosslinked by radiation technique, have better retention strength.

Hydrophilicity property of the fibres can be imparted by grafting hydrophilic monomers/polymers to serve as soil releasing agents or wicking promoters to increase comfort. Greatly increased hydrophilicity and ion-exchange capacity of fibres can be brought about by grafting of basic/acidic vinyl groups [67–79]. Both of these applications rely primarily on altering the surface properties of the fibres to make them more hydrophilic. Williams and Stannett, however, achieved tremendous increases in fibre swelling by grafting acrylic acid to rayon and afterwards decrystallising the cellulose with concentrated $ZnCl_2$ solution [80,81]. The presence of the grafted polyacrylic acid inhibited recrystallisation and the resulting fibres could swell up to 3000% water. Irradiation gave rise to distribution of monomers over the bulk of the fibres. The grafted chains produced by chemical initiation were located primarily in the surface layer. The authors [82] observed that upon decrystallisation, the fibres obtained by radiation grafting and containing about 100% poly(ethyl acrylate) (PEA) manifested pronounced hyper-elastic properties while no such effect was established in the case of chemically initiated grafting. The hyper-elastic property has been developed due to the uniform distribution of the grafted monomers on cellulose macromolecules (grafting is closer to the molecular level) in the radiation technique. Bashar et al. [67] grafted methylmethacrylate onto cotton, rayon and silk. Grafting depends on the chemical structure of the fibres. The order of grafting of methylmethacrylate on the polymeric backbone is: silk $>$ rayon $>$ cotton. Due to the presence of protein moiety (–NHCO– group), the grafting percentage is maximum in case of silk fibre, whereas amount of –OH group plays the role [83] of grafting in case of rayon and cotton. Additives/coadditives are added during irradiation (such as *N*-vinyl pyrrolidone (NVP), tripropylene glycol diacrylate (TPGDA), trimethylol propane triacylate (TMPTA) and sulphuric acid (H^+), lithium nitrate (Li^+), urea etc) to introduce the requisite properties onto the fibres. The sorption of methyl alcohol is developed by acrylic acid grafted polypropylene and rayon fibre [84]. The sorption depends on the degree of grafting.

The use of radiation to polymerise vinyl functional flame retardants is a useful technique for attaching these to textile chemicals. The mechanism of attachment may be covalent grafting, internal polymer deposition with unextractibility due to intimate entanglement or deposition of crosslinked polymer, either internally or as a fibre coating. Triallyl phosphate and *N*-methylol acrylamide were first ever used as flame retardants to the cotton fabric [85]. Liepens and co-workers used grafting technique with vinyl bromide [86] and a number of vinyl phosphonates [87] to achieve flame retardancy in polyethylene terephthalate fabrics and blends with cotton [88] 2,3-dibromopropyl acrylate was used to impart the flame retardancy to the polyester, cotton fibres as well as polyester–cotton blends by Zaharan et al. [89]. Another unique monomer to impart this property to cotton is diethyl phosphatoethyl methacrylate [90]. This monomer possesses 11.64% phosphorus content and has the formula stated below:



$$(CH_3\,CH_2O)\,\underset{\underset{O}{\P}}{P}\,O\,CH_2\,CH_2\,O\,CO\,\underset{\underset{CH_3}{|}}{C}=CH_2$$

Di-ethyl phosphatoethyl methacrylate

Crease resistance is another basic property for the textile fibres. This is the ability of the fabric to resist crushing and to restore the initial condition after the removal of the fabric bending effort. Most synthetic fibres have excellent wash-wear properties but do not have the comfort like cotton. The wash-wear properties of cotton resins and other compounds are dependent on the nature of the fabric and conditions. Under drastic laundering or repeated cleaning, these are hydrolysed and the fabric loses its crease proofing. Crease recovery of the fabric can be influenced by grafting/crosslinking. In this process intermolecular branching occurs and thus improved the properties. Actually if one of these long-chain cellulose molecules is pulled to one side by forces, the crosslinked polymer is also pulled to one side by forces, the crosslinked polymer within the fibre itself in the amorphous region acts as a spring [91]. In this way, the fabric becomes crease resistant. *N*-methylol acrylamide treated wool fabrics are the best example in this regard. In this case, dry crease recovery angle (DCRA) is remarkably increased because of the formation of additional crosslinks between the polypeptide wool keratins [92]. The additional crosslinks could be ascribed by the dyeing affinity towards s-triazinyl reactive dyestuffs. Wet crease recovery compared to dry crease recovery is better because the grafting/crosslinking process has been generally carried out in swollen condition. Zaharan et al. [73] have shown this behaviour in case of styrene-grafted cotton fabric.

Abrasion resistance is another important criterion for selecting materials in textile technology. This is determined by the resistance at fabric sliding upon some surface. Grafting of various monomers on the surface of the fibres have been used to form a preventive sheath against abrasive forces. Thus, methyl methacrylate, acrylonitrile, ethylacrylate etc. [93,94] have been used effectively for increasing the abrasion resistance of cotton. The properties of the copolymer depend upon the location of the grafting, whether the grafting is in ‘bulk phase’ or in ‘surface phase’. In principle, ‘bulk grafting’ disturbs the other desirable properties where as properties like ‘abrasion resistance’ could be improved by ‘surface grafting’. Walsh et al. [95] grafted ethyl acrylate to cotton fabric to impart abrasion resistance. It was also founded that the ‘surface grafting’ resulted in a four-fold improvement in abrasion resistance whereas the bulk grafting actually decreased the abrasion resistance by 50%. Liepen et al. [88] has conducted somewhat similar studies on the grafting of flame retardant monomers to polyester fibres. He found that, in contrast to the abrasion resistance, bulk grafting is clearly superior to surface grafting as far as flame retardancy is concerned.

The most interesting concept is using radiation to fix dyes having polymerisable vinyl groups in the dye molecule. The aim of the dyeing process is to impart a certain colour to the fabric by applying dyes and their fixing. For dyeing fabrics, most different dyes are used, but the essence of the dyeing process remains unchanged, i.e. the dye molecule penetrates from the solution into the pores of swollen fibres and are retained in them by chemical and physical way. The technology of the dyeing process may be different depending on the dyes used. Dyeing fulfils the aesthatic requirements of the textile fibre. Water absorbancy is the preliminary criterion to fulfil the dyeing condition. Based on this property, designing is developed. It is quite possible to introduce different monomers on a fibre that is sensitive to different dyes and thus different designing is possible. Cellulose fibres can be dyed directly. Nevertheless, as their wash fastness is rapid, the modification of the fibre is necessary. ‘Grafting’ is the most suitable method in this regard. Hydrophilic monomers (e.g. acrylamide, acrylic acid and methylacrylic acid) grafted to the fibre (i.e. natural and synthetic) imparts this property [96–98]. The dyes form covalent bonds with the monomers that are already grafted to the fibres. In this way, radiation grafting improves their dyeing affinity [99–102]. Cotton fabric has no affinity to disperse dyes, however, by grafting styrene to it, they gained the ability to be dyed with disperse dyes. The dyeability of styrene-grafted cotton copolymer may find an application in cotton–polyester blends, which has good crease resistance of polyester and comfort of cotton. The grafting of polystyrene onto cotton also improves its dyeing capacity. Walsh et al. [103,104] have been developed radiation-curable textile printing inks. The inks consist of 80–90% solvent, which contains pigment, latex binder, polymeric thickener, surfactants, dispersing agents, crosslinkers and other auxiliaries. The solvent is an emulsion of mineral spirits in water, which gives the printing rheology. The main advantages of switching to radiation curing from this system are energy savings and higher line speed due to the elimination of the drying and heating necessary to cure the adhesive binder.

Due to certain limitations, in the production of cotton fibres, the aim is shifted to the production and modification of synthetic fibres. Radiation technique is one of the techniques to impart certain physical and chemical properties, i.e. soil releasing properties, hydrophilicity, flame retardancy etc. into the fibres. Apart from the improvement of the properties, the beautification dyeing is essential to the fibres for the aesthetic requirement. Radiation is also promising technique in this regard.

5. Electrical applications

In the electrical field, one of the essential things for electrical wires and cables is insulating and jacketing materials. For many years, the pre-eminent insulation material for power cables was oil-impregnated paper due to its excellent electrical properties. It has also the capacity to withstand a high degree of thermal overload without excessive deterioration. However, due to its hygroscopic nature, the metal sheath is moisture corroded. There was, therefore, a long-felt need for a power cable insulation material, which had a combination of the non-hygroscopic nature of thermoplastic materials.

The continuous research for such a dream material ultimately resulted in the discovery of the cross-linked polyethylene. The crosslinking of polymers refers to the modification of polymer properties by inducing chemical links between individual macromolecules. By crosslinking the polymers such as polyethylene, a three-dimensional network of bonds is formed between polymer chains which increases the molecular weight [105]. This is analogous to the mechanism of ‘vulcanising rubber’.

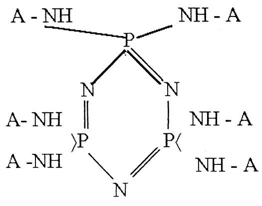
The conventional process of ‘vulcanisation’ entails heating and adding sulphur or other chemicals to form crosslinks between the characteristic long chains of elastomer molecules. This process started long ago and is still being used. The property of the polymer depends on the amount of sulphur used. The more the sulphur used is, the harder is the product, which withstands higher temperature, pressures and mechanical challenges to its integrity. But sulphur vulcanisation has severe drawbacks with respect to human health and environment and has some economic drawbacks. Moreover, it needs high temperature to start the chemical reaction and emits odourous and toxic gases as well as producing numerous unwanted chemical residues that have to be removed from the final product.

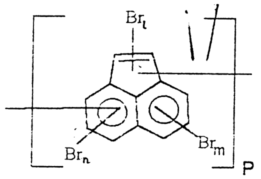
‘Radiation crosslinking’ is the well-proven method that bypasses all these negative effects of the vulcanisation process. It is a room temperature method having in itself an important cost advantage. It is easily controlled and the desired properties of the polymer are obtained simply by changing the dose (irradiation time). The transformed materials are in no way inferior to those produced by sulphur vulcanisation.

The primary object of crosslinking is to upgrade the thermal resistivity. Generally, the maximum allowable temperature in a short circuit is 140°C for non-crosslinked polyethylene cable can be upgraded to 250°C by the radiation crosslinking process [106]. The second most common objective is the memory effect such as displayed by shrink tubing. This is the unusual and valuable property of irradiated polyethylene and it is retained indefinitely within the polymer irrespective of time and of any subsequent number of deformations. Thus, if polyethylene is irradiated in a partly crystalline form (i.e. below its melting point) and then heated to remove the crystals, it can be considerably deformed (e.g. by stretching) and then cooled again to crystals to reform in its new shape. If the material is heated again above melting, these crystals disappear and the rubber-like polyethylene will tend to return to the shape if it is held during irradiation possibly months or years before. Shrink tubing is manufactured by extruding a specially formulated polymer into a tube and subsequently crosslinking this tube. After crosslinking, the tube is heated, expanded and cooled in the expanded form. This expanded tube, once reheated will shrink back to its original shape, which is due to memory effect of crosslinking. Since the polymer molecules are chemically linked to each other and no longer able to move at random, different properties like heat resistance, abrasion resistance, dimensional stability, adhesion property etc. are improved. Thus, crosslinking may impart the desirable properties to the polymer, i.e. toughness, flexibility, impact resistance, chemical resistance etc. Irradiated polyethylene is very widely used for heat shrinkable films for packaging, encapsulation and for electrical connections, which can be readily heat shrunk onto other components. For flexibility, the crosslinked wire/cable installation is easier and it is free from height limitation. Moreover, no metallic sheath is required for maintenance. In addition, the tensile properties are intermediate between a thermoplastic and an elastomer.

The preparation of crosslinked polymers can be done by two different methods. One is the chemical method and the other is the ionising method. Though the realisation of this effect of crosslinking is over 150 years old, the crosslinking effect of ionising radiation was conclusively demonstrated for the first time by Charlesby. The radiation crosslinking method is the most productive for small-sized and thin wall wires [107] and therefore the wires used for electric and electronic equipment have been produced by the radiation crosslinking method. The method is advantageous because of low energy consumption and needs small space. The radiation process is easily controlled and has the potential for energy savings as well as pollution controlled. The specific features of radiation crosslinking are summarised as follows: (1) The production line speed can be controlled. High speed covering (extrusion) is possible, as there is no requirement of crosslinking agent. By the use of an accelerator with high power and low energy, rapid curing can be achieved. (2) Crosslinking uniformity is excellent. The uniform crosslinking by selecting an appropriate machine and adopting optimum design for wire feeding can be carried out. (3) Various kinds of polymers can be prepared, depending upon the degree of crosslinking by radiation crosslinking process. Moreover, the radiation curing process is more preferable than the steam curing process. In the steam curing process, water permeating into the polymer layer under a high steam pressure creates a number of ‘microvoids’, which could induce tree-shaped partial discharge breakdown when the cable is in service. Although the phenomenon is much complicated, the trees can grow and cause a decrease in the dielectric strength of the cables. Apart from these, the steam curing process has some drawbacks from the standpoint of energy consumption: (a) high steam pressure is needed to obtain a high temperature; (b) the efficiency of thermal conduction from outside the cable is low and (c) large amount of energy is consumed by the cable conductor, which results in a lower thermal efficiency and also a longer time for crosslinking reaction. Radiation curing is a candidate for the dry processes. However, it has the problem that the build up of electrons stopped and/or formed in the insulation layer by irradiation can also induce tree-shaped partial breakdown during and after irradiation. It is completely different from the ‘water-free process’. As the polymer cable contains high moisture and large voids, the curing process is necessary. Apart from the above advantages, semiconductor materials may be introduced easily in the radiation curing process which is not easy in case of steam curing process as most of the materials could not withstand the high temperature and pressure.

Since the crosslinking is formed in the amorphous regions between the ends of macromolecules, network develops [108,109]. Thus it gains the ability to bear load, i.e. improves the strength characteristics. Radiation crosslinking of polymers is the basis for a series of radiation-chemical technologies [110]. Crosslinking efficiency can be increased by the addition of suitable monomers. The promotion of crosslinking is needed to decrease the processing costs for the radiation crosslinking of polymers and increase the crosslinking yield as well as decrease the modification dose to reduce the contribution of adverse processes, e.g. radiation dehydrochlorination in PVC. The use of radiation, however, has some drawbacks. In particular, there is some controversy regarding thermal stability of the product, since radiation induces dehydrochlorination which results in the formation of additional initiation sites for thermal degradation. Optimisation of dose is required to avoid the problems of foaming and discharge breakdown. These have been overcome by choosing of proper crosslinking agent with the radiation dose. For this reason, the crosslinking agent plays a far more important role in lowering the irradiation doses required to achieve the crosslinking to a reasonably high degree. In case of polymers (e.g. polyisobutylene, PMMA) which has a chance to degrade in radiation, this is very important. It is possible to satisfy these needs by the use of polyfunctional monomers as promoters of the radiation crosslinking [111]. The most effective compounds until now have been shown to be polyfunctional acrylates and methacrylates especially tri-functional monomers such as trimethylol propane trimethacrylate [112–114]. Apart from that polyfunctional monomers [triallyl cyanourate (TAC)], [triallyl isocyanourate (TAIR)], diallyl sebacate (DAS) were used in the formation of network of PVC [115]. Another important crosslinking agent (i.e. hexafunctional) is HAAP [116]. Monomers usually contain two, three or four unsaturation sites (viz. ethylene glycol dimethacrylate, trimethylol propane trimethacrylate, and pentaerythritol tetramethacrylate) and have different molecular weights, and are very effective to increase crosslinking efficiency in optimum dose and thus increase productivity [117]. It is also seen that methacrylate and acrylate containing monomers have higher crosslinking efficiency than allyl or hydroxyl monomers. Monomers containing acrylate groups confer higher tensile strengths than the corresponding methacrylate monomers:





Apart from the addition of crosslinking agent radiation, grafting also improved the thermal stability of PVC. Yamakawa and Stannett [118] published a detailed study of the thermal stability of radiation-grafted PVC. They observed that grafting of methyl methacrylate and/or styrene and the blending of the corresponding homopoplymer yielded products of improved thermal stability as compared to the unmodified PVC. The radiation grafting was found more efficient for PVC stabilisation than blending. Omichi et al. [119] also carried out radiation-induced graft polymerisation of butadiene gas on to PVC to improve the grafting yield. In this case, mechanical property of PVC is also increased (about 8%).

Radiation grafting technique does also impart the conductivity to the matrix. This is the unique method of combining of conducting matrix on to the insulating one. This technique involves deactivation of backbone polymer with a suitable monomer by grafting and subsequent deposition of the conducting polymer over the active surface of the backbone. Apart from the insulating behaviour, in this case polymer can behave as conducting one. Though it has not yet established, it can exhibit several potential applications such as EMI shielding, conducting coatings and antistatic agents. Bhattacharya et al. [120,121] have prepared the composites TEFLON–FEP-*g*-(AA)–PPY and TEFLON–FEP-*g*-(sty)–PPY. At first, TEFLON–FEP was irradiated form Co-60 source and the film was then dipped in different percentage of monomers. PPy was then deposited over the grafted surface by oxidative polymerisation of pyrrole using ferric chloride as oxidant. The surface resistance is decreased and are of the order of 10^4–10^5 ohm/cm^2. The surface resistance depends on the percentage of grafting of monomers. Using this technique, surface conductivity rather than bulk conductivity can be increased. Photoconducting behaviour of the film can also be imparted by grafting technique. Cellulose acetate-*g*-(*N*-vinyl carbazole) [122] and cellulose acetate-*g*-(*N*-vinyl carbazole–methyl methacylate) [123] are the examples of the photoconducting film.

In the electrical cable industry, mainly polyethylene, polyvinyl chloride (PVC), EPDM rubbers are used. Polyethylene is used because of its excellent electrical properties and its longer duration. Low-density polyethylene is preferred over the high-density polyethylene due to several reasons. The reasons are as follows: (a) more flexibility; (b) higher dielectric strength than high-density polyethylene; (c) longer life than HDPE; (d) less difficult to process than HDPE and (e) less risk of inclusion of voids in the insulation of LDPE, which causes ionisation. Despite all such advantages, LDPE has its own limitations as a cable insulation material. Being a thermoplastic polymer, it has a softening temperature at around 105–115°C and has the tendency for stress cracking to occur when it is in contact with certain surface-active agents. Crosslinking of polyethylene molecules improves the thermal as well as physical properties while its electrical properties largely remain unchanged. Crosslinked polyethylene is, therefore, no longer a thermoplastic polymer. It softens at the crystalline melting point of polyethylene and assumes an elastic, rubber-like consistency, a property which it retains during further rises of temperature, until it becomes carbonised without melting at 300°C. The tendency to stress-cracking disappears entirely and very good resistance to ageing in hot air is acquired. Crosslinked polyethylene cables are widely preferred because of its excellent electrical and physical properties. It is capable of carrying large currents, withstands small radius bending and is light in weight, allowing for easy and reliable installation, i.e. it is free from height limitations since it is not comprised of any oil and thus is free from the failures due to oil migration in oil field cable. It also does not generally require a metallic sheath. Thus, it is free from the failures peculiar to metallic sheathed cables, corrosion and fatigue. Now-a-days, radiation crosslinking is industrially applied to not only polyethylene but also other polymers also such as polyvinyl chloride, polyisobutylene etc. On its own PVC is extremely unstable polymer. It started gaining commercial significance only after the development of effective means of stabilisation. With the help of modifying agents (stabilisers, plasticisers, fillers and other additives), PVC can be made to exhibit a wide spectrum of properties, ranging from extremely rigid to very flexible. The diversity of its application and its low cost are responsible for its importance in the world market.

To increase the crosslinking efficiency, polymers are very seldom used in their pure form. Plasticisers, antioxidants, fillers have their role in their respective way to impart the requisite properties. The addition is better during the crosslinking process. Plasticisers are added to polymers to reduce the brittleness of the polymer product. They affect the crosslinking whenever they take part in the generation of free radicals or enter the propagating reactions. Dibutyl phthalate, tritolyl phosphate and diallyl phosphate

[124,125] are the common examples of the plasticiser to PVC. Flexibility and elasticity, which is very important in electrical insulation, are improved by adding the plasticisers to PVC. Actually in case of PVC, which is polar due to unbalanced structure, gives rise to strong intermolecular bonds, which join the macromolecular chains rigidly, together make it inflexible. Antioxidants are another group of additives, which are necessary for any crosslinked mixture designed for the practical purpose of comparing higher thermooxidative stability on a polymer production. Usually they affect the crosslinking by scavenging radicals, which may form crosslinks. RC (4,4-thio-bis(6-*tert*-butyl-3-methyl phenol), MB (Mercapto benzoimidazole) are the examples of antioxidants which are used by Ueno et al. [126]. In addition to plasticisers and antioxidants, colourants are required, as the wire insulation materials have used especially for appliances. Colourants for plastics include a variety of inorganic and organic materials. The discoloured additives are not preferred in this field. Fillers are generally added to improve their physico-mechanical properties and processability. A positive effect of fillers may be observed during irradiation crosslinking. It is found that the yield of radicals in polyethylene was increased by 50%, when a small amount (0.05%) of aerosil is added [127]. It has been assumed that a higher production of radicals takes place at the interphase aerosil–polyethylene, where macromolecules can be in the non-equilibrium state of uncompensated strains. With a higher content of filler, a transfer of energy from the filler to the polymer phase may occur and thus contribute to a higher yield of free radicals. Moreover, combination of irradiation with reactive admixture may affect the localisation of crosslinks along the polymer chains.

Halogen-containing flame retardants have serious limitations. At high temperature, hydrogen halide forms during radiolysis in the crosslinking process or pyrolysis. This is corrosive to metals as well as generates large amount of smoke in the case of fire at high temperature. That is why scientists' choice lies with halogen-free flame retardants, which are compatible with the polymers. Flame retardancy property can be brought into the polymer by introduction of certain compounds. Metal hydroxides having the crystal water such as $Al(OH)_3$, $Mg(OH)_2$ [128] and phosphorus compounds (viz. red phosphorus, phosphoric esters), deca-bromodiphenyl oxide and tetrabromobisphenol-A are used [126] for this purpose. In order to avoid surface corrosion using phosphorous compounds, it is better to use phosphorous compound with metal hydroxides to obtain higher fire-proofing properties. Flame retardancy as well as super radiation resistant property can be brought by grafting condensed bromoacenaphthylene (Con-BACN) to EPDM rubber [129]. Con BACN retards the radiation degradation of EPDM by suppressing both oxidations on the surface and crosslinking in the interior when the sheet is irradiated in air. In this processing, volume resistance and dielectric breakdown voltage, have also been improved. Uneo et al. [128] also developed the electron beam irradiated halogen-free, heat-resistant, low-voltage electrical wire which does not contain any halogen-based polymer or flame retardants, i.e. AEX (electrical wire insulated with crosslinked polyolefin). It is environmentally friendly in nature.

Blending is another popular method of modifying properties of the polymers. It is the physical mixture of two materials and thus it is termed as 'macromolecular alloy'. Blend of EVA/PE modifies the flexibility of crosslinked PE effectively [130]. The process property of EVA/PE is also good. However, the form of blend of crosslinked PE/PE was sticky, soft, tensile strength is low and it is difficult to process. The radiation-crosslinked blend of EVA/PE possesses good elasticity and flexibility. Its brittle temperature is lowered than that of crosslinked polyethylene. Semi-crystal character and heat shrinking property are also developed.

Apart from the insulating behaviour of polymeric materials, they can be semiconducting also. In this case, conducting particles (positive temperature co-efficient material like carbon black, carbon fibre, metal powder) are doped into the polymer matrix [131]. In the step of radiation crosslinking of polymers, the addition is quite effective as the conducting materials act as stabilisers. The main feature of the positive temperature coefficient material is that its electrical resistivity increases with the rise in temperature [132]. Carbon-black contributes to crosslinking also [133]. Based on these functions, it can be used as self-regulating heaters, current limiters and overcurrent protectors. The carbon-black particle in the system made an interconnected array of channels and thus imparts the conductivity [134]. As the temperature of such a composition increases, the polymer matrix expands at a rate greater than carbon-black particles; the microscopic core expansion disrupts the electrical path between the carbon-black particles. Therefore, it causes a steep increase in resistivity. Upon cooling, it is returned microscopically to original configuration and electrical continuity between the carbon-black particles will be restored. This process can be repeated indefinitely. This self-regulating feature may be put to work in heat tracing pipes in oil fields, chemical plants for freeze protection maintaining flow characteristics of viscous syrups etc.

In short, radiation plays the important role in the polymer processing that is used in electrical field. ‘Radiation crosslinking’ is the phenomena by which the properties of the polymers can be improved. It is the most advanced method such as ‘vulcanisation’ bears some limitations. The crosslinking efficiency can be improved by choice of suitable monomers. In radiation crosslinking process, the plasticisers, fillers and flame retardant addition is quite effective in radiation crosslinking process. The radiation crosslinking method is also very useful in preparation of semiconductor materials. Apart from these, radiation grafting technique can also be employed to prepare the conducting composite film and films with photoconducting behaviour.

6. Membrane technology

In the present age, the effective use of biomass has been developed because of the crisis of fossil resources such as coal and petroleum. In other words, the intention of scientists and technologists has become to develop the techniques in which energy may be saved. Separation carried out by membranes is one of the most promising achievements in this regard as separation by means of distillation or recrystallisation technique consume much heat or electrical energy. Membrane separation techniques have already been used in such industrial applications as desalination of brine; salt manufacturing from seawater and oxygen-enriched air etc. The techniques may also be possible to attain separations of azeotropic mixtures, which have nearly the same boiling points, or of structural isomers. Many potential applications are just entering in the commercialisation phase and look attractive both technically and economically.

The membrane is a heterogeneous phase, which acts as a barrier to the flow of molecular and ionic species present in the liquid and/or vapour contacting the surface. It also provides selective transfer of one species over another or regulates the transport of a material to its environment at a controlled rate. The suitability of a membrane for any particular process is determined by two prime factors viz. chemical and environmental stability. The chemical stability of the membrane means that it remains intact in solution of various pHs, organic solvents, oxidising agents whereas the environmental stability requires avoiding fouling by bacteria. Apart from these, the membrane properties, e.g. permeability (the property by which a membrane under identical conditions, transports the different molecular species at different rates), hyperfiltration (the process of separation of inorganic substance dissolved

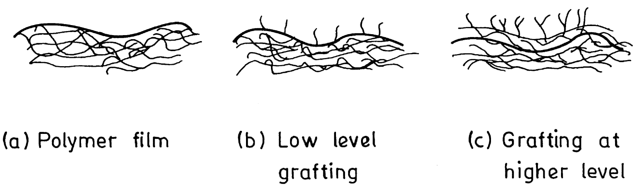


Fig. 5. Schematic representation of physical structure of the grafted surface region (reproduced from Ref. [135]).

in aqueous/non-aqueous solution, under pressure) and pervaporation (the process of separation by varying pressure in different sides of the membrane and thus maintaining different concentration gradient) would develop for acting in different practical fields. The membranes must retain these properties for a longer period.

In order to search membranes that have good applicability as well as chemical/environmental stability, scientists have chosen the polymeric substances. Though the polymeric membranes possess the functional property, they do not exhibit good mechanical properties. That is why the development of the polymeric membrane has begun. ‘Grafting’ is the most popular method to modify the polymeric membranes. It is a very simple method to obtain a ‘tailor-made’ membrane with specific properties by introducing specific monomers. The nature of the monomers in this context plays an important role. The use of radiation-grafted copolymers, as membranes are just an attempt to get a compromise between good mechanical and chemical properties as well as membrane properties. Grafting process can take place in two different ways, i.e. ‘surface grafting’ and ‘bulk grafting’. The ‘surface grafting’ occurs on to the surface of the polymeric membrane whereas ‘bulk grafting’ occurs deep rooted in to the polymer matrix. In case of membrane modification, surface grafting is more suitable than the ‘bulk grafting’. The surface graft polymerisation of monomers can be initiated by trapped free radicals or polymeric peroxides generated in the surface region of the substrate polymer (Fig. 5) [135]. If these initiating active species are present not only in the surface region but also deeply in the bulk phase, the monomer penetration into the bulk phase is prevented. Otherwise, the polymer would suffer from deterioration of the bulk properties by the graft polymerisation. Radiation technique is very useful in this regard as it has the capacity to withdraw electrons from the surface and it can also be applied to a thin membrane. Moreover, the radiation technique has many advantages that have already been described before.

Thus radiation-induced grafting is a versatile technique to modify the surface of the polymeric membranes. However, these membranes play a very important role in various separation processes such as desalting of brackish and sea water, separation of gases, separation of water from organic and inorganic mixture, waste water treatment, battery technology etc.

Radiation-induced grafting of some hydrophilic/hydrophobic monomers onto different polymeric membranes makes them suitable for application in different fields. Grafting of hydrophilic monomers onto the membranes have been found to lead to an increase in wettability, adhesion, dyeing and rate of release of oil stains by detergent solution. On the other hand, if the monomer is hydrophobic, the result will be decreased wetting by all liquids including oil stains [136]. Grafting by suitable monomers produce two types of membranes, i.e. cation exchange and anion exchange membranes. In case of cation exchange membranes, specific cation exchange groups that interact with specific cations are introduced whereas in anionic exchange membrane, the anionic polyelectrolyte layers/groups are introduced. The ion exchange phenomena constitute an important technique in the study of separation chemistry and use of graft copolymers in this domain has been found very fruitful. Various grafted

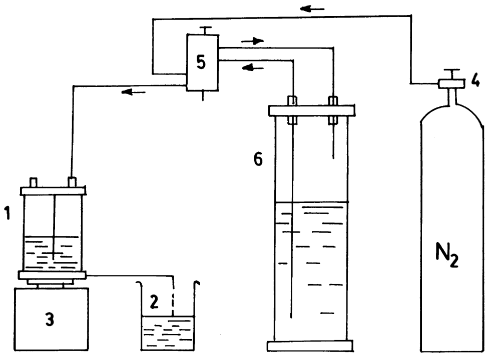


Fig. 6. Membrane filtration unit (system Amicon): (1) filtration cell; (2) membrane filtrate; (3) magnetic stirrer; (4) pressure trap; (5) selector; (6) reservoir with solution of metal salt (reproduced from Ref. [143]).

acrylic monomers in their acid form can be used as cation exchange resins [137]. If however, like vinyl pyridine, monomer is grafted, the resulting graft copolymers may be converted to a form, which can be used as anion exchange resins [97].

Water is an essential commodity of daily life. Although it is a nature's abundant gift, water has attracted considerable attention during the last two decades owing to the serious shortage felt in certain parts of the world. With the advent of rapid industrialisation and growing population, this common as well as abundant commodity is insufficient although attempts have been made for optimum utilisation of the available natural water resources. Thus, it has become necessary to adopt different desalination techniques to convert saline water resource including seawater into usable one. Water absorbancy attendant with salt rejection is very important in this regard. The desalination property is controlled by the membrane materials and high water flux. Various natural and synthetic polymeric membranes can be upgraded by graft copolymerisation of suitable monomers onto it to achieve the diffusion permeability of several solutes. Monomers like acrylic acid, methyl acrylic acid, vinyl acetate, acrylamide and their derivatives, etc. have suitably been used for increasing water absorbancy of the respective graft copolymers [138–142]. Super sorbing property which has considerable importance in industry can be developed by grafting of acrylic acid onto cellulose followed by decrystallisation with 70% $ZnCl_2$ solution [97]. The set up membrane filtration is presented in Fig. 6 [143]. The membrane filtration unit consists of the membrane filtration cell with a magnetic stirrer, the coupled reservoir, the dialysate reservoir, the selector and the pressure source. Water absorbancy attendent with salt rejection property can be developed for polyacrylamide-grafted cellulose acetate system through reverse osmosis process [144]. Styrene-grafted cellulose acetate membrane has also the capability of salt rejection [145]. In this case, the salt rejection of the grafted membrane was 90.5%. In case of multicomponent (i.e. styrene and acrylamide) monomeric grafting on cellulose acetate, Maldas et al. [146] have obtained good result. This activity can also be obtained with the synthetic polymers consisting single component, i.e. polyethylene-*g*-(PAAM), LDPE-*g*-(vinyl acetate), polyethylene-*g*-(acrylic acid), PTFE-*g*-(methyl acrylic acid) [147–149].

Moreover, in some cases further modification of the graft copolymer is required to introduce electrolytic groups so that the swelling behaviour and the electrochemical properties can be improved as well. Thus, ionic character can also be introduced to the vinyl pyridine grafted chains by quarternisation with different quaternising agents such as methyl iodide, allyl bromide and HCl [138,150,151]. The quaternising agent has an influence on the electrical properties of the grafted materials. The size and electronic structure of the quarternising agents affect the electrical behaviour of the grafted films. The quarternised grafted copolymer of plasticised PVC films show electrical conductivity higher than 10^{-9} ohm^{-1} cm^{-1}, which may lead them to being considered as semiconductors.

Diffusion permeability of several solutes can be imparted by grafting of monomers like acrylamide, acrylic acid, styrene and *N*-vinyl pyridine on cellophane. Thus in case of absorption of gases and vapours is very interesting. Membrane for pervaporation of EtOH–water mixtures can also be prepared by grafting of acrylamide and acrylic acid onto porus film [152]. The pervaporation performance for the ionised membranes is somewhat superior to that of acrylamide grafted and the performance of the ionised membranes decreased with increasing acrylamide content. The PP-*g*-(HEMA) membrane showed improved permeability towards urea and uric acid solutes in comparison with polypropylene membrane [153]. Based on this property, the membrane is very promising in the bio-medical technology, which has already been described before.

Hydrophilic and functional groups of complexing ability are very useful in separation technology. The development of technical process of metal uptake from solutions looked to be very promising in case of graft copolymers. In polymer–metal complex, central metal ions are surrounded by an enormous polymer chain/ligand [154]. Due to the presence of polymeric ligand, the polymer metal complex shows interesting behaviour, e.g. especially catalytic activities. The polymer bound metal complex show different behaviour from the corresponding metal complex of low molecular weight. The permeability of solutes into or through the membrane network is an important characteristic, which governs the possible assignment of the membranes to possess and products such as battery separators, desalination membrane, dialysis and catalytic support [155–157]. The poly(AA) grafted onto poly(tetrafluroethylene–perflurovinyl ether) (PFA) and poly(tetrafluroethylene–ethylene) copolymers [158] act as a chelating site for the selected transition metal ions [159]. The structure of complex of each metal ion formed by inter- and/or intramolecular crosslinking in the polymer matrix. This formation is made through the complexation of polymeric ligand with metal ion, i.e. the reaction of a polymer containing a donation group such as –COOH with metal ions. Such prepared copolymer metal complexes can be applied in the field of semiconductor apart from their activities as a cation exchange membrane may be of great interest [160].

The irradiation method was utilised to synthesise ion-exchange membranes, which are useful for battery separators. Acrylic acid graft polyethylene film is one of the examples in this regard. Ion-containing polymers (ICP) can be replaced by radiation-grafted polymers. Ion-containing polymers (e.g. Nafion) have poor mechanical and dynamic properties. Thus, in order to overcome the limitations of ion conducting polymers, scientists have chosen grafted polymers in this regard. The grafted polymers have been modified by chemical treatments such as sulphonation of styrene-*g*-(polyethylene)/polytetrafluroethylene and quarternisation by triethylamine to the vinyl benzoyl chloride grafted (polyethylene)/polytetrafluroethylene [161]. The new generation battery separator polyethylene-*g*-(acrylic acid) [162,163] looks promising compared to cellophane, which was used before in case of the batteries with alkaline electrolyte (such as silver oxide primary cell). Because of its poor durability as it suffers significant degradation because of reaction of constituents, the cellophane-based battery separator is backdated. The acrylic acid grafted polyethylene with respect to the microporus separator, permits the migration of $Ag(OH)_2$ by convection in a silver oxide zinc cell. However, Hsine et al. [164] reported the better performance of PE-*g*-(MAA) than PE-*g*-(AA) as the separator.

In the field of humidity sensors in different consumer products, air-conditioning systems, medical and

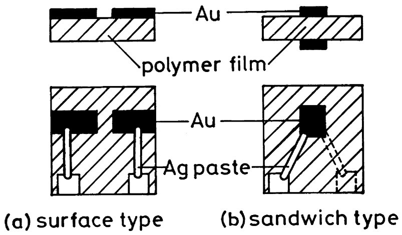


Fig. 7. Schematic representation of humidity sensor (a) surface type and (b) sandwich type (reproduced from Ref. [170]).

industrial equipments, the polymers can be used. In general, polyelectrolytes can be used as humidity sensors since their electrical conductivity increases with the water absorption. Because of the water solubility nature, conventional humidity sensors based on polyelectrolytes have disadvantages against water and dewdrops. However, water-resistant humidity sensor has been developed by scientists using radiation-grafting technique [165–170] on polymer-based membrane. Generally, poly(tetrafluroethylene) and microporous polyethylene films are used as trunk polymers for graft polymerisation. Hydrophilic monomers (such as polystyrene sulphonate, poly(2-acrylamido-2-methyl)propane sulphonic acid, poly(2-hydroxyl-3-methacryloxy propyl trimethyl) ammonium chloride and quaternised poly(4-vinyl pyridine)) are suitable as they show high sensitivity to humidity. Generally, two types of sensors have been reported. In case of thick film (0.5 mm) surface type and for thinner film, surface type as well as sandwich types have been developed. Poly(tetrafluroethylene)-based humidity sensor has been reported by Sakai et al. [170]. Gold electrodes have been vacuum deposited on the resulting graft copolymers. The sketch is represented in Fig. 7.

Fluorine containing polymers have been extensively used for membrane preparation because of their excellent thermal, chemical and mechanical stability. In the field of ion exchange, the fluorine containing membrane based graft polymers are the best. These membranes have been applied to the electrolysis of brine and pure water. They are durable when in contact with chlorine, oxygen and alkaline solution at high temperature. Perfluropolymer membranes are made by the radiation grafting of a fluorine containing monomer (viz. methyl trifluroacrylate (MTFA)) onto a fluorine containing trunk polymer such as polytetrafluroethylene (PTFE), tetrafluroethylene–hexafluropropylene (TEFLON–FEP) and tetrafluroethylene–perflurovinylether (PFA) by Omichi et al. [171–173]. To avoid the limitations in amalgam process, i.e. large amount of mercury and problem of recycling in case of the membrane process seems to be a highly interesting compromise. α,β,β-trifluoroethylene sulphonyl fluoride (TFESF)-*g*-PE and α,β,β-trifluorostyrene-*g*-PTFE are best in NaOH production as they are chemical and heat-resistant ion-exchange membranes [174,175].

The surface grafting can be employed as efficient photostabilisation method as in this case UV-stabilised monomer is covalently bound to the polymer surface. 2-Hydroxy-4-(3-methacryloxy-2-hydroxy-propoxy) benzophenone grafted LDPE and PP films is prepared by Ranogajec et al. [176]. In this way, the problem of evaporation of blended stabilisers during the prolonged use of polymeric material has been overcome.

Oil repellency is also an important factor in industry. Hydrophobic monomers such as 2-methylvinylpyridine when grafted to cellulose have been found impressive in this area. Fluropolymers containing *N*-methylol groups when grafted to cellulose achieve the oil and water resistance properties [177]. Acid resistance property can also be developed in case of hydrophobic monomers (e.g. styrene, methyl acrylate, ethyl acrylate, acrylonitrile or methyl methacrylate) grafted on cellulose.

Thus in this study, the development of cation and anion exchange membranes have been discussed mainly based on monomers using radiation technique. Many of the chemical systems studied do not appear to be of commercial significance at first sight but later they have captured big market. Nevertheless, enough scope exists in designing novel synthesis and modification based on such systems to render them more useful and economically viable.

7. Conclusion

The world's drive toward safer and cleaner development through the radiation technology overcame some big hurdles during the past 30 years. In view of this fact, nuclear radiation has made their entry into various chemical processes. The radiation techniques in polymeric field have occupied the attention of numerous scientists for many years because of certain advantages. Radiation processing typically holds important edges over the alternative industrial processes, which is dependent on the use of chemicals and heat. In almost every type of application using radiation techniques, energy savings are reported to be significant in comparison with competing technologies. The reliability as well as simple process control, reduction or complete elimination of industrial pollutant and superior or even unique quality of products are the other advantages. In the radiation processing, most of the changes have been introduced in the polymer matrix at the manufacturing or processing stage itself. Further improvement by grafting, crosslinking or further polymerisation of the commercially processed films with other reactive compounds can also be possible by the use of nuclear radiation. However, the specific change can also be introduced after the processing stage in the polymer materials without unduly affecting the main matrix. Apart from the advantages mentioned above the radiation polymer, research takes step towards 'bio-degradability' and 'bio-mass conversion'. It may solve some of the problems of environmental pollution caused by undegradable components. In this regard, two approaches have been made so far. One approach is the incorporation of radiation-sensitive groups that can initiate chain scission by radiation and the other is the modification of the polymer such that solubility will improve [178,179]. In the field of biomass conversion, radiation technology has an important role. Man has depended substantially on ruminant animals as convertors of biomass into high value products such as meat, milk, leather, wool, etc. Ruminants are nature's 'prime model' for biomass convertors. These unique animals exist in symbiotic relationship with microbes that inhabit the pre-gastric 'stomach' (rumen) and pre-digest (ferment) whatever these animals ingest. They convert fibrous cellulosic substrates into simplified products. The radiation technology has been used for upgradation of poorly fermented lignocellulosic substrates such as straws, hulls, cobs and wood by-products into readily fermentable and nutritious feedstuffs for ruminents. These can be done by 'grafting' and 'crosslinking' reactions.

Though radiation processing has the potential of preparing the new materials, successful large-scale applications have been disappointing. Perhaps the main reasons for the limited applications are the length of irradiation time and the initial cost for setting up. To accelerate the reaction, radiation-processing field is now expanding rapidly through electron beam processing techniques. The electron beam processing field involves big volume processes operating at relatively fast line speeds. However, further research is required in many smaller scale applications of radiation grafting utilising predominantly Co-60 sources. In all such areas, there is need to reduce radiation doses to a minimum. This aspect is particularly important for thermal- and radiation-sensitive macromolecules such as cellulose and relatively inert polymers like poly(tetrafluroethylene) for which doses for grafting certain monomers are still relatively high. Future research to discover new additives, which will reduce grafting doses to levels even lower than those currently, used, is thus required. In both basic and applied research on radiation chemistry, significant advancements have been made during last three decades. However, with respect to basic research, the contribution made by applied research is quite small. Lastly, it must be mentioned, through the gambling of basic research, the future of the radiation polymeric research is highly prosperous.

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