Some properties and applications of radiation modified polymeric materials

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Recently, there has been considerable interest in methods of radiation modification of polymeric materials. This has arisen because of the industrial importance of these methods and also because of the rapid progress that has been made recently in design and construction of low-energy accelerators. This progress consists primarily in the reduction of power consumption and improvement in the safety of use of accelerators, enabling them to be used in processing lines (refs. 1 – 4). Apart from modification by means of electron radiation, isotope methods are also used, where the source of gamma irradiation is usually cobalt 60. The qualitative changes occurring in the irradiated polymer material are similar in both cases, though the time of irradiation and the quantitative changes are different (refs. 5 and 6).

The polymeric materials subjected to radiation modification are generally those that have a much greater crosslinking capacity than their degradation capacity. These are principally materials and products made from low-density polyethylene (PE-LD), in which the mechanisms of radiation changes are the best known (refs. 7 – 9). The main object of radiation modification is crosslinking of the polymeric material, resulting in materials with better service properties (refs. 11 and 12). An important application area of radiation techniques is the curing of protective coatings, lacquers and adhesives (refs. 13 and 14). A separate group consists of polymeric materials and products employed in medical applications, which are subjected to ionising radiation (mainly gamma radiation) for sterilisation purposes (refs. 15 and 16). Also promising are the trials involving ionising radiation aimed at obtaining new polymeric materials (ref. 17) and also in processes for conversion of polymer waste (ref. 18).

The effects of radiation crosslinking of a polymeric material depend mainly on the type of material and on the dose and conditions of radiation. Crosslinking has a beneficial effect on the mechanical properties of the material, particularly the tensile strength and flexural strength, longitudinal and transverse elastic moduli, hardness and abrasion resistance. There are similar changes in the thermal properties, the most important of which are an increase in the stability of dimensions and shape of the irradiated products during temperature changes, a rise in the melting point, increased resistance to changes in the structure of the material under the action of heat and an increase in ageing resistance at elevated temperatures. Additionally crosslinking reduces the solubility of the polymeric material in various solvents and increases their resistance to swelling and degradation that occur under the action of various media (refs. 5 and 6).

Radiation crosslinked polymeric materials and products have found many different industrial applications. These cover areas such as:
- insulation of electric and telecommunication cables;
- installations for heating of premises (including under-floor heating), hot and cold water supplies and gas supply, using crosslinked polyolefin pipes;
- packaging and heat-shrinking pipes;
- plastic construction components for various types of equipment, fabricated mainly by injection moulding;
- protective coatings, paints, lacquers and adhesives;
- implants and medical materials;
- novel polymeric materials with new properties.

The aim of the present article is to report on some properties and applications of radiation modified polymeric materials.
CROSSLINKING OF INSULATION FOR CABLES AND CONDUITS

Crosslinking of polymeric insulation for electrical cables and conduits using a high-energy beam of electrons was used in the cable industry already in the 1960s. This technology straight away became an attractive alternative to chemical methods of crosslinking polymers. Its particular advantages are the much lower energy consumption, the smaller area required for the processing equipment, easier control of the process and the possibility of crosslinking a large group of plastics (ref. 19).

The classical method of chemical crosslinking using peroxides, primarily dicumyl peroxide with a decomposition temperature of about 120°C, involves subjecting the plastic to the action of water vapour at a temperature of > 200°C and high pressure; the crosslinking process takes place via a radical mechanism. A two-stage process of chemical curing with silane compounds is regularly employed for crosslinking low-pressure insulation made from PE-LD. The long time of crosslinking in association with a relatively short pot life of such compounds restricts the usefulness of this method. Only PE-LD and some types of rubbers can be crosslinked in this way, whereas a much larger group of plastics can be crosslinked by electron radiation, including the various types of polyethylene, polyamide (PA) and polyvinyl chloride (PVC) and also fluorine-containing plastics and rubbers (refs. 20 – 22).

Apart from the good mechanical, thermal and chemical properties resulting from radiation crosslinking, also very important are the dielectric properties of insulating material, i.e. dielectric strength, volume resistivity, dielectric permittivity and dielectric loss coefficient (refs. 23 and 24).

The dielectric strength is defined as the quotient of the voltage causing electrical breakdown of the insulating material and its thickness. Breakdown occurs when a high energy is reached by the free electric charges located in the material, the energy being sufficient for ionisation of its atoms or molecules. The source of this energy is an external electric field. The dielectric strength of most polymers is high and may theoretically exceed a value of 1000 MV/m. It is found from tests during use, however, that the actual dielectric strength is considerably lower. This is due to impurities in the material (including additives and auxiliary agents), structural defects and moisture. The changes that occur during radiation treatment do not appreciably alter the dielectric strength of polymeric materials.

The volume resistivity depends largely on the additives and auxiliary materials, and primarily on the type and content of fillers, flame retardants, plasticisers and antioxidants. It is also greatly affected by the type of plastic; for example in the case of PE-LD it is about 10^18 ohm.m, whereas in the case of plasticised PVC it from 10^11 to 10^14 ohm.m. Structural defects of an insulating material such as those formed during irradiation cause a reduction in the volume resistivity.

The relative dielectric permittivity of polymeric materials is reduced under the action of electron irradiation by an average of 10 – 20% in comparison with the permittivity in the non-crosslinked state. The permittivity values of PE-LD and plasticised PVC are respectively: in the non-crosslinked state 2.3 and 3.8, and when crosslinked 2.0 and 3.2. The dielectric loss coefficient decreases only very slightly as a result of this irradiation.

The slight deterioration in dielectric properties that can occur when polymeric materials are irradiated is fully compensated by a considerable improvement in the mechanical and thermal properties. This is important in the case of prolonged thermal loading, and also in the case of short-term rise in temperature such as occurs in cables during short-circuiting. The long-term permissible service temperature of crosslinked PE-LD increases from about 70°C to about 140°C. Similar effects are achieved with plasticised PVC. Another important property of insulating material is non-flammability, which is increased by the addition of flame retardants to the polymer (refs. 25 and 26).

Typical cable insulation materials which are modified by radiation are PE and PVC. With PE the electron irradiation doses are in the range from 250 to 300 kGy. The use of crosslinking catalysts can reduce these doses by about 40%. Standard PVC is not suitable for radiation crosslinking since it readily degrades. It can be crosslinked only with the addition of special additives. The radiation doses used are considerably lower than those employed for crosslinking of PE and are generally 50 – 80 kGy.

The thickness range of radiation-crosslinked insulation for cables and conduits carrying a voltage of 3 kV is usually 0.5 – 4 mm. Radiation modification of these insulating materials requires an electron beam with an energy of up to 2 MeV. High-voltage cables with an insulation thickness of up to 1.5 mm can also be radiation-crosslinked, but this requires the use of accelerators with a power in excess of 100 kW and an electron energy of about 5 MeV. These requirements restrict the range of crosslinking, especially in view of the high investment costs.

Figure 1 shows a diagram of a cable with radiation-crosslinked insulation. In accordance with the indications given in this Figure during one-sided irradiation of insulation made from PE we can determine the necessary depth of penetration of the electrons (HPE) using the dependence given in ref. 26: \( H_{PE} = 2(g + d)^{0.5} \) (for the meaning of the symbols see Figure 1).

As is seen from Figure 1, one-sided irradiation of the insulation of wires and cables is ineffective because of the non-homogeneous crosslinking of the material (screening effect) and the need to use high energy electrons. To avoid this irradiation of the cables and wires from different sides

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is used. This can be achieved with the use of several appropriately positioned accelerators, but this method requires several investment costs. For this reason frequent use is made of special systems of rolls conducting the wire so that it is twisted and passed several times through the radiation zone. A diagram of the system is shown in Figure 2. The maximum homogeneity of crosslinking is obtained when the wire is twisted continuously during passage through the radiation zone. This variant is suitable mainly for wires with insulation more than 2 mm thick. Here the linear rate of movement of the wire, its angular rate of twist and the frequency of the scanner carrying the electron beam have to be accurately synchronised. For this purpose servo mechanisms are used, which increases the cost of the entire system. However, the benefits of this are considerably greater, since in this system we can restrict the penetration by the electrons to a depth equal to the thickness of the insulation and thus reduce the costs of the accelerator.

During crosslinking of insulating material there arise unwanted phenomena, namely the formation of volatile substances (mainly hydrogen) and excessive electric charges. The volatile substances give rise to the formation of free spaces in the insulating material, which can be a source of partial discharges causing damage to the material. The excessive electric charges are caused by electrons emitted from the accelerator and deposited in the insulating material. These electrons move under the effect of the external electric field, leading to an increase in the leakage current.

Electrical cables and wires with radiation-crosslinked insulation are employed in many areas of engineering and technology. The most important of these are TV equipment and domestic appliances, telephones, computers and automobiles (where the insulation is required to show high resistance to heat and to be of low thickness) and also wires for control systems in industrial installations. A separate group of applications consists of insulation for cables and wires used in atomic power stations, where the quality requirements are very stringent.

CROSSLINKING OF HEAT-SHRINKING PIPES AND FILMS

Crosslinked plastics, especially PE, are characterised by post-deformation reversion. This occurs as a result of the mutual penetration of the crystalline and amorphous phases in the polymer. It is also linked to the three-dimensionally crosslinked structure of the polymeric material. To bring this about it is necessary to heat a previously crosslinked plastic to a temperature higher than the softening point of the crystalline phase. Then the heated material has to be appropriately stretched, causing the formation of mechanical stresses. Cooling of such a plastic, which is continuously in a stretched state, leads to the formation in it of crystallites preventing changes of the shape obtained. Renewed heating causes the disappearance of these crystallites and thus the material reverts to its original form.

The phenomenon of post-deformation reversion is widely used for the manufacture of heat-shrinking films and pipes. Films have also found wide use as a packaging material for collections of items and as packaging for individual food items and consumer goods. In the first case the articles are arranged in blocks and covered with heat-shrinking film, which is then heated with hot air or infrared waves. The heat causes the film to shrink and tighten against the material enclosed. Individual packaging with heat-shrinking film is often used to make bags for packaging of food products. An undesirable feature

Figure 1. Range of penetration of electron beam in cable insulation: 1 – scanning horn of accelerator, 2 – electron beam, 3 – wire insulation, 4 – metal core of wire, 5 – shielded part of insulation, d – diameter of metal wire, g – thickness of wire insulation, H – required range of electrons.

Figure 2. Diagram of four-sided system of irradiation of cable insulation: 1 – scanning horn of accelerator, 2 – cable, 3 – rotating rolls.
Another application of radiation treatment is crosslinking of PE pipes intended for heat-shrinking screening. These are used as a rule for insulating junction points of electric cables and wires. In such cases a segment of crosslinked pipe is placed on the site where two fragments of wire or cable are joined and then heated, usually with a gas jet. After the pipe has cooled it forms a tight seal to the junction point, protecting it effectively from external agents. In this way there is a reduction in time and costs of laying cable networks and also a reduction in damage. Similar seals are made for connections in heating systems.

The first and so far the only industrial installation for radiation crosslinking of pipes from PE-LD was brought into operation in Poland in 1982. It is equipped with an ILU-6 accelerator (power 20 kW, electron energy 2 MeV) and is used for crosslinking pipes of diameter from 1 to 250 mm and wall thickness up to 7 mm. The manufacture of crosslinked pipes consists of several processing operations. In the case of thin-walled pipes or conduits these operations consist of extrusion of the pipe, crosslinking of the pipe in the accelerator chamber under a continuous dose of 120 kGy, heating the pipe with ultraviolet irradiators, stretching of the pipe using compressed air (mainly in a radial direction – as a result of stretching the diameter of the pipe increases to 300% of the original value), cooling while stretched and finally winding the pipe on a spool. Pipes with thicker walls, which cannot be wound, are cut up into segments after extrusion, installed on a special carriage and taken to the accelerator chamber, where they undergo batch crosslinking. During crosslinking the sections of these pipes are rotated using a drive installed in the carriage around their axis of symmetry. On conclusion of the crosslinking process the pipe segments are placed on a special mechanism used for stretching them (Figure 3) and carried into the heating chamber. After heating and mechanical stretching they are cooled, and retain a hexagonal moulded cross-section. The stretched pipe segments can be coated with adhesive on the inside, which later provides an additional sealing of the joint. The crosslinking doses and degree of stretching of the pipe segments are similar to those used for wires.

An important area of application of the radiation technology is crosslinking of polyolefin pipes employed in installations for heating building, supplying hot and cold water and in gas supply installations (ref. 22). In these cases the main purpose is to increase the mechanical strength and long-term operating temperature of the pipes. As a result of crosslinking the latter increases to 130°C. The methods or irradiating these pipes are chosen individually according to various criteria (refs. 28 and 29). Increasing use is also being made of radiation in processes for manufacturing three-layer thick- and thin-walled pipes from PE-LD with an intermediate layer of aluminium sheet (ref. 30).

RADIATION MODIFICATION OF POLYMER BLENDS

A polymeric material is in general chemically and physically non-homogeneous. A polymer together with added components (fillers and auxiliary agents) or different polymers forming a material are called polymer blends. Most polymers are thermodynamically non-miscible, and hence do not form stable single-phase systems for any ratio of the mixed components. This means that there is no possibility of their uniform mixing at the molecular level (ref. 31). The miscibility of polymers is also restricted by the difference in viscosity of the components being mixed and the difference in their rate of crosslinking, which during radiation modification can lead in extreme cases to crosslinking of only one of the components of the blend. An important role is played here by the phenomena occurring at the interface and the surface properties of the components, such as their polarity, free surface energy, free inter-phase energy and solubility. On the basis of the difference in values of these characteristics two groups of polymers are distinguished: polymers which are mutually or partially miscible and polymers which are mutually non-miscible (ref. 32).

When polymer blends are subjected to irradiation changes take place in their individual components and at the interfaces between them. These changes cover both crosslinking and degradation of the polymer. Processes occurring at the interface may lead to the formation of graft copolymers, which increases the mechanical strength and long-term operating temperature of the polymeric material. Such processes are accompanied by changes in the free surface energy, the free inter-phase energy and the formation of polar groups, which can improve the miscibility of the components of the material being irradiated.
Various mixtures of polyolefins and elastomers are modified by radiation, including for example ethylene/propylene/diene terpolymer (EPDM), ethylene/vinyl acetate copolymer (EVA), three-block styrene/butadiene/styrene copolymer (SBS), two-block styrene/butadiene copolymer (SB) and ethylene/propylene copolymer (EP). The efficiency of crosslinking under ionising radiation of the blends PE-LD/EP and PE-LD/EPDM can be increased by adding trimethylpropane trimethacrylate. The resulting materials have a fairly homogeneous structure, increased dielectric strength and high elasticity. The tensile strength of material irradiated with 100 kGy is similar to that of the non-irradiated material. Irradiating a blend of PP with EPDM causes degradation of the PP, crosslinking of the EPDM and mutual crosslinking between the PP and EPDM. With equal fractions of these components and using a dose of 50 kGy the gel fraction content, which is a measure of crosslinking, is greater than 80%, and the elasticity and dynamic strength of the material are considerably improved (ref. 12).

The elongation at break of a blend of PP/SBS (1:1 mass ratio) irradiated with 60 kGy increases by almost 80% compared with that of the uncrosslinked material. Irradiation also brings about a drastic reduction in the melt flow index, from 1.9 to 0.1 g/10 min. It is observed from studies that the mechanical loading in this material is borne mainly by the SBS. Irradiation does not cause any changes in the content of crystalline structure, but reduces the initial melting point of the crystallites. This may indicate changes in the structure of the material at the interface (refs. 11 and 33).

Significant changes are observed in the mechanical and thermal properties and in the gel fraction content in an irradiated blend of PE-LD/EVA. In EVA, even under the effect of scarcely half the radiation doses the same degree of crosslinking can be achieved as in PE-LD. Therefore the addition of EVA to the PE-LD facilitates crosslinking of a blend of these two. The gel fraction content, tensile strength, relative elongation, hardness and heat resistance of the PE-LD/EVA blend are located between the values found in the case of PE-LD and EVA. These values depend on the mass fraction of each of these components in the blend (refs. 34 and 35).

In order to obtain the most homogeneous blend of PA and PE chemical or radiation modification of the PE is used. Under ionising radiation the PE undergoes oxidation and polar groups are formed (peroxide, hydrogen peroxide, carbonyl and hydroxyl), which interact at intermolecular level with the polar groups of the PA. This leads to an increase in homogeneity of the PA/PE blends. This improvement in miscibility occurs independently of the type of PE, which may be PE-LD, PE-HD or PE-LLD. Radiation modification of PE-HD produces a less marked improvement in the miscibility of this polymer with PA than that found with the other types of PE. The mechanical properties of materials made from blends containing radiation modified PE are considerably better than those of blends containing non-modified PE. The rate of irradiation also has an effect on the properties of materials made from blends of PA and PE. When PE-LD is irradiated with gamma radiation using low dose rates (≤ 0.1 kGy/h) there is an increase in tensile strength and impact strength, whereas when a dose rate higher than 3.5 kGy/h is used this causes a deterioration of these properties. The increase in mechanical strength with low dose rates is due to an increase in the intermolecular forces associated with the formation of polar groups in the irradiated PE-LD, which also improves its miscibility with PA. The reduction in mechanical strength arising from a low dose rate is caused by a greater degree of crosslinking of the PE-LD macromolecules, leading to the occurrence of microstresses at the interface between the crosslinked fragments of PE-LD and the PA macromolecules (ref. 12).

Marked differences in the values of tensile strength and also the varying effect of the radiation dose of gamma radiation on these properties were observed in the course of studies carried out on specimens made from four different types of blends of polyimides. In these studies doses of up to 400 kGy were used, and the specimens were studied at temperatures of 230 - 315°C (ref. 36).

Increasing use is being made of blends of various waste plastics, also with fillers to act as modifiers. This applies mainly to six types of plastics: PE-LD, PE-HD, PVC, PP, PET and PS. The service properties of these plastics are improved by introducing crosslinking catalysts, and ionising radiation is employed. When a blend of PE-HD (50%), PP (30%) and PS (20%) is irradiated with a dose of up to 600 kGy there is an increase of more than 10% in the flexural strength as compared with the non-irradiated material. Also, irradiation of a blend of waste PP with PA fibre and of PE-HD used as an additive to waste PET promotes an improvement in the mechanical properties of these materials (refs. 18 and 37 – 40).

In blends of PA with high impact PS irradiated with high doses (up to about 1 MGy) of gamma rays the radiation effects are different in the two polymers. Whereas in the PA crosslinking is dominant, in the PS degradation occurs. At the same time, with low doses the content of crystalline phase increases in these blends, whereas with under high doses breakdown of the crystalline structures takes place. It has been found from studies that the relation between the insol fraction and the radiation dose is better described by the modified equation of Zhang-Sun-Qian than the classical Charlesby-Pinner equation (ref. 41).

Irradiation with a beam of electrons or gamma rays allows us to obtain new properties of blends of non-miscible polymers and to stabilise their internal structure, which is not possible using conventional mixing. Importantly, this means that we can accurately control the
processes of crosslinking and degradation and the phenomena occurring at the interface between the different components of these blends. This is very important in the processing of blends whether virgin or recycled.

CURING OF PROTECTIVE COATINGS, LACQUERS AND ADHESIVES

Radiation curing of coatings, lacquers and adhesives is an attractive alternative to conventional methods, i.e. UV radiation curing and thermal curing. The basic radiation reactions occurring in this process are crosslinking (also via crosslinking of vinyl groups) and graft copolymerisation. Since these reactions are very quick, high yields of the modified material can be obtained. In the case of radiation curing of coatings of films and tapes their rate of movement through the irradiation zone can exceed 1000 m/min. This technology can be used during the manufacture of coatings of polymeric materials, wood, paper, metals and ceramics (ref. 13).

An important advantage of radiation curing of coatings (including lacquers, paints and adhesives) using low-energy electrons is the fact that such electrons are deposited mainly in the coating and only interact to a slight extent with the material underneath the coating. For this reason the energy of the electrons is chosen individually in each case depending on the thickness of the coating, according to the criteria shown in Figure 4 (ref. 42). It is assumed here that the dose coming out of the coating being cured should be 80% of the maximum dose, and the sum of the losses in the accelerator window (made of titanium foil) and the losses in the air correspond to the grid value 120 g/m². Here the gram content of coating cured by an electron energy of 180 keV is 120 g/m², and under an energy of 250 keV this value is higher than 240 g/m².

Hence it is seen that the electron energy can be selected in the curing process not only according to the thickness of the coating but also according to the density of the material in this layer (ref. 42).

The main advantages of curing using a stream of electrons are:
- total cure of the coating and no monomer residue;
- the possibility of uninterrupted curing at the end of the process, without the necessity of carrying out this process at individual stages of coating, printing, decorating or laminating;
- possibility of easy cure of internal layers of adhesive during lamination of multi-layer sheets;
- absence of thermal stresses either in the coating being cured or in the substrate, since in most materials the doses are not higher than 20 kGy;
- very high homogeneity of the coatings of a quality unachievable by conventional methods.

The main obstacle to the wide use of radiation curing was initially the high cost of accelerator installations. Progress in this area has however resulted in a reduction of costs size and mass of accelerators and the accompanying equipment. These accelerators can be installed directly in processing lines without the need to build special screens to absorb radiation. Hence radiation curing of coatings has also become competitive economically with classical methods (refs. 43 – 45).

The radiation processes occurring during cure by a stream of electrons and by UV radiation are similar. However, the former method has several important advantages. These include:
- the possibility of curing coatings containing large amounts of pigment, which is not possible with the use of UV radiation, since this has a significantly lower capacity for penetration of modified material;
- the possibility of curing a lacquer or adhesive located below a thin metallic layer, e.g. in a multi-layer laminate containing paper, plastic sheet and a layer of sprayed aluminium;
- high efficiency of cure determined by the degree of reaction of the coating material, which is in excess of 99%, whereas with the UV method it is about 95%;
- curing without the participation of aromatic photoinitiators (which are necessary with the UV method), thus eliminating a source of an unpleasant aroma, which is important in food packaging;
- approximately 90% less energy used in the cure process;
- better quality of the cured coatings.

Compared with heat curing an advantage of the method using a stream of electrons is the possibility of its use for materials not containing solvents. With this method we can therefore cure materials containing more than 90%...
radiation for the sterilisation of polymeric medical equipment. The use of ionising radiation produces packages of the equipment to ensure optimum sterilisation, and the need for special planning and this gas in the sterilised equipment, the lack of complete quality requirements it has been found that this method has many drawbacks, such as the presence of toxic residues of many years has been manufactured from polymeric materials. One of the basic requirements for apparatus of this type is complete sterility, i.e. the absence of any kind of micro-organisms or their spores. This condition is provided by subjecting the material to a sterilisation process. The oldest and most widely-used industrial method involves the use of ethylene oxide. A beneficial effect of using radiation curing is the lack of readily flammable solvent fumes, which eliminates a potential fire hazard. Other important advantages are the considerably lower energy consumption, the smaller area required for installing the accelerator, the short duration of the curing process and the lack of mechanical stresses caused by large and rapid changes in temperature in the material being treated (refs. 14 and 46).

Because of its advantages, curing with a stream of electrons is finding an increasingly wider use in industry. It is also employed for manufacturing decorative materials from paper and plastics, since it makes possible accurate curing of a thin layer of lacquer and gives a high gloss and high mechanical strength to this layer. Also in the case of lacquered films used for packaging of food products these advantages are highly important. Another application area of this method is the curing of a layer of lacquer applied to products made from wood, plywood or other wood type products (ref. 47). It can also be used processes for making polymeric melt adhesives.

Rapid developments are taking place in the technology of radiation curing in processes for making laminates. They are particularly effective during curing of adhesives and lacquers in multi-layer laminates. They result in high mechanical strength of adhesive bonds in such different materials as polymer sheet, paper, wood and metal. They are also increasingly used for curing protective coatings applied to metal sheets. These coatings may be copolymers of acrylic compounds with polyfunctional vinyl monomers acting as crosslinking components.

Electron irradiation of coatings consisting of aliphatic urethane compounds using doses up to 20 kGy gives them higher mechanical strength than that achieved with an equivalent dose of UV radiation (ref. 48).

RADIATION STERILISATION OF POLYMERIC MATERIALS

Medical equipment coming into direct contact with patients has for many years been manufactured from polymeric materials. One of the basic requirements for apparatus of this type is complete sterility, i.e. the absence of any kind of micro-organisms or their spores. This condition is provided by subjecting the material to a sterilisation process. The oldest and most widely-used industrial method involves the use of ethylene oxide. However, with increasingly stringent quality requirements it has been found that this method has many drawbacks, such as the presence of toxic residues of this gas in the sterilised equipment, the lack of complete sterilisation, and the need for special planning and production of packages of the equipment to ensure optimum penetration by the ethylene oxide. The use of ionising radiation for the sterilisation of polymeric medical equipment permits these drawbacks to be avoided. Hence increasing importance is being attached to the methods using gamma and electron radiation (ref. 15).

Radiation sterilisation is employed for example in the sterilisation of dressings for scald and burns (hydrogel and collagen), single-use syringes, various containers, tubes and pipettes, sheets and operating gowns, and also surgical masks and gloves. The most important advantages of radiation sterilisation are:

- very high effectiveness in destroying micro-organisms not only on the surface of the apparatus but also in its walls;
- the possibility of accurately choosing the required dose on the basis of individual microbiological tests, allowing complete sterilisation of the medical equipment;
- sterilisation of equipment in packs, thus eliminating the possibility of its infection with micro-organisms during packing or with micro-organisms originating from the packaging material;
- possibility of sterilising equipment and packages which are not resistant to heat;
- absence of contamination of objects being sterilised with foreign bodies or contamination of the medium with toxic substances;
- possibility of carrying out sterilisation at ambient temperature (refs. 49 and 50).

As a result of many years of study, and following international meetings and negotiations it has been accepted in most countries that the minimum dose for sterilisation should be 25 kGy (ref. 16). However, even such a small dose can cause degradation in polymeric materials, leading to a decrease in mechanical strength, mainly the dynamic strength and colour change. For this reason certain polymers employed in the construction of equipment subjected to radiation sterilisation, mainly PP (which very rapidly loses its tear strength under ionising radiation (ref. 51)) and PVC, have to be appropriately modified.

PP is widely used for single-use syringes which are radiation sterilised. A considerable defect of PP is its poor radiation resistance, resulting from its chemical structure. Degradation is observed under doses above 10 kGy, which are significantly lower than the minimum sterilising dose. Post-radiation processes can occur in PP even after several months following irradiation, leading to colour change and increase in fragility of the plastic, and these are also stimulated by diffusion of atmospheric oxygen (refs. 52 and 53).

PP can be modified using various additives that cause a so-called external protective effect, and this limits the occurrence of these undesirable phenomena (ref. 54). Radical collectors and antioxidants and photostabilisers are used for this purpose, including octadecyl ester of propionic acid (“Irganox 1076”) (ref. 55). Such substances
are usually derivatives of phenols and amines with a branched structure and are added in amounts of less than 1% by mass.

Aromatic compounds also have a protective effect during irradiation of PP. Because of their low mass fraction and the statistical nature of the effect of ionising radiation on the individual molecules of the irradiated material, there is little probability of direct take-up of this radiation energy by the molecules of the protective agent. Therefore the protective effects are possibly due to the mechanism of charge and energy transfer and transmission of this energy from the excited polymer molecules to the molecules of the protective agent (ref. 54).

The resistance of PP to ionising radiation can be increased also during synthesis of the polymer by trying to obtain the narrowest molecular weight distribution, so that the post-radiation processes increase the fragility of the material to a lesser extent. Increase in the isotacticity of PP facilitates its crosslinking and restricts the formation of hydrogen and methane during irradiation (ref. 56). A beneficial effect on the mechanical and thermal resistance of the irradiated PP can be obtained by using trimethylolpropane trimethacrylate as a stabiliser (ref. 57).

Plasticised PVC is used in single-use products, mainly those such as containers for blood and infusion liquids, drains, probes and tubes. Its advantages in these applications are ease of processing, transparency, avoidance of precipitation of stored or transported liquids on the walls of apparatus and low cost. However, radiation sterilisation causes the PVC to degrade, leading e.g. to change of colour and the release of toxic low-molecular compounds.

Studies have been continuing for many years into methods of preventing radiation degradation of PVC. So far the methods developed rely mainly on the use of the following substances:

- known heat stabilisers and antioxidants, including salts of metals and fatty acids, mercaptoesters, compounds containing amine groups and cyclic esters. These prevent the formation of HCl by bonding chlorine and also de-activate free radicals and double bonds.
- special stabilisers employed mainly to absorb the energy of radiation with its subsequent dispersion in the form of heat, which limits the radiation changes in the PVC. Stabilisers of this kind include compounds with condensed aromatic rings, salts of metals (e.g. barium sulphate), oxides of zinc, magnesium and calcium, alkylated aromatic compounds, aluminium silicates and organotin stabilisers. However, he use of any of the stabilisers must be preceded by tests excluding possible harmful effects on the human body.
- plasticisers, lubricants, antioxidants and PVC with increased radiation resistance. Aliphatic plasticisers are more effective than aromatic plasticisers in preventing unwanted radiation changes in PVC, and suspension PVC shows fewer changes during radiation sterilisation than other types of PVC, since it has fewer structural defects.

The conditions of processing of the PVC are also an important factor. The thermal degradation that takes place means that the polymer is much more liable to radiation degradation (refs. 58 and 59).

Ultrahigh molecular weight polyethylene (PE-UHMW), which is produced in powder form is fairly difficult to process. It belongs to the group of linear polymers, has an average molecular weight of the order of $10^6$ and density of about 0.94 g/cm$^3$. Owing to its excellent physical properties, and in particular its very low coefficient of friction, high abrasion resistance, high dynamic strength and biocompatibility with regard to living tissues, it has long been used in manufacturing implants of human organs. The acetabula or shells of hip joints are most frequently made from it. Increasing use is being made of radiation sterilisation of implants, since heat sterilisation causes changes in their dimensions and shapes, and sterilisation with ethylene oxide gives rise to toxic residues. The classical radiation phenomena occur in PE-UHMW during radiation sterilisation, primarily crosslinking, degradation and oxidation of the polymer. They change the structure of the material, e.g. the average molecular weight distribution and crystallinity. This leads to certain changes in the physical properties, depending mainly on the radiation dose, atmosphere in which the sterilisation is carried out and the shape of the implant. These changes are not very marked and hence it is not necessary to use preventive agents. In addition, the post-radiation processes occurring in PE-UHMW do not visibly affect the service properties of this material (refs. 60 and 61).

OTHER APPLICATIONS

New discoveries in the field of the influence of ionising radiation on changes in properties of plastics are extending the possible applications of the radiation technique. Some of them, relating to the production of polymeric materials with previously unattainable parameters and recycling of these materials will be dealt with in the present section.

Polymeric materials or their derivatives can be given completely new properties by irradiating them in an oxygen-free atmosphere at elevated temperatures and using high doses of radiation. An example is ceramic fibres (SiC) made from polycarbosilicon fibres (PCSF) by pyrolysis carried out temperatures above 1200°C. To prevent the PCSF breaking down at such a high temperature it has to be crosslinked beforehand. When this process is carried out in air, atmospheric oxygen combines with the molecules of the PCSF, leading subsequently at high temperature to the breakdown of the silicon fibres.
containing oxygen. To prevent this undesired phenomenon PCSF is crosslinked by radiation in a helium atmosphere, a stream of which passes through the fibres, simultaneously acting as a cooling agent. For adequate crosslinking of the PCS fibre high doses of radiation have to be used, exceeding 10 Mgy. The oxygen content in the fibres crosslinked in this way does not exceed 0.3%, which permits pyrolysis of the fibres in argon and at temperatures up to 1500°C. During the process of pyrolysis oxygen and methane are released, and the PCS fibres are converted into ceramic fibres. They are characterised by a very high tensile strength, with a maximum value of about 2.8 GPa. They can be used at temperatures up to 1700°C, which is about 500°C higher than ceramic fibres made using the traditional method (ref. 62).

Irradiation of polytetrafluoroethylene (PTFE) in a molten state at about 340°C leads to its crosslinking. The crosslink density increases with the dose absorbed, and the value of the dose can reach as high as 2 Mgy. In the molten state the main chains of the PTFE form a straight structure which acts as a steric hindrance to rotational movements. Under the effect of ionising radiation and separation of fluorine atoms from the carbon atoms double bonds and alkyl and allyl groups are formed. The interaction of these groups leads the formation of crosslinks. On reduction of the temperature to the ambient temperature and the resulting change in structure of the PTFE the steric hindrance disappears, but the polymer retains the properties resulting from crosslinking. As a result of crosslinking in the molten state there is an increase in the mechanical strength of the PTFE when solid, plus a decrease in its light transmission which is caused by a reduction of the crystalline phase. PTFE crosslinked in this way also shows an increase in resistance to ionising radiation. The increase in resistance to abrasive wear is particularly marked, since after crosslinking abrasion is reduced by 100 - 1000 times as compared with the abrasion of non-crosslinked PTFE (ref. 63).

The radiation technique is also used for the purposes of degrading PTFE. This polymer, when subjected to a high dose (of the order of 10 Mgy) of electron or gamma radiation in air undergoes degradation to powder form and can then be used for making lubricants or protective coatings. Using considerably lower doses (500 - 1000 kGy) it is possible to modify the surface layer of the PTFE so that the polymer can be used in membranes and also as one of the components of composites (refs. 64 and 65).

Polymeric materials employed for making constructional components and in human organ implants must be characterised by high hardness and resistance to abrasive wear. Such materials include polycarbonate (PC) and polysulphone (PSU). Their hardness can be increased by about 30% by irradiating them with small doses (from 3 to 4 kGy) without air access in a temperature range including the glass transition temperature (Tg). In

the case of PC this range is 144 - 154°C (Tg = 149°C) and in the case of PSU it is 173 - 183°C (Tg = 178°C). The increase in hardness of these materials is accompanied by an increase in resistance to abrasive wear. A characteristic feature of the two polymers is the fact that when the limits of the temperature of irradiation defined as Tg ± 5°C and irradiation doses of 3 - 4 kGy are exceeded their hardness and resistance to abrasive wear decrease. The beneficial range of crosslinking can be explained by the synergistic effect of changes in the physical state of the polymer at a temperature close to Tg and the action of small doses of ionising radiation. This favours a denser packing of the atoms in the surface layer of the PC and PSU and their crosslinking, which increases the hardness and produces an increase in the abrasion resistance. Studies of the density of the surface layer of PC support this hypothesis. It is significant that the thickness of the surface layer of PC hardened under these conditions is greater when gamma radiation is used than when electron radiation is used. This is due to the greater penetration of the polymer material by gamma rays than by electrons (ref. 17).

Ionising radiation can be used for degradation of butyl rubber waste (copolymer of isobutylene with less than 3% by mass of isoprene) used in the production of car tyre covers and tubes. The bonds at the quaternary carbon atoms in the main chain of butyl rubber can be broken under ionising radiation. The rate of scission of chemical bonds in this copolymer is about 4 and is approximately ten times greater than the crosslinking yield. Degradation occurs even with a dose of 50 - 100 kGy. After radiation degradation and the resulting reduction in strength of the butyl rubber waste it is broken down mechanically and added in powder form to virgin material. A fraction of degraded waste in the virgin material not exceeding 10% by mass does not yet cause a deterioration in its service properties. Butyl rubber waste can be used to make roofing materials, seals for water installations and waterproof materials (ref. 66).

CONCLUSIONS

The new possibilities opened up by progress in the construction of electron accelerators, including low-energy (50 - 100 keV) electron accelerators, are a stimulus for the increasingly wider use of radiation technology for modifying polymeric materials. This concerns especially sheet materials, including heat-shrinking films used everywhere as a packaging material, and the curing of protective plastics coatings, lacquers, printing inks and adhesives. Radiation crosslinking of thin-walled insulating materials for electric cables and wires has provided a new impulse for further development. An important sphere is also crosslinking of plastics pipes for supplying gases and liquids, and heat-shrinking thin-walled pipes.
Modification of polymer blends by ionising radiation gives more homogeneous materials than those obtained by traditional mixing. The radical processes occurring under this radiation lead to the formation of crosslinks both in the macromolecules of the individual polymer components and between the macromolecules of the different polymers. This is important not only during the manufacture of new products from virgin polymers but also in processes of conversion of plastics waste. It also makes it possible to obtain valuable properties in blends of thermoplastic polymers and elastomers.

Irradiation of polymers at elevated temperatures and without oxygen access is an effective method for obtaining new materials with original properties. By selecting the right dose, rate of dosing and atmosphere of irradiation we can induce changes in the physical properties and hence in the service properties of various polymeric materials. This is currently an enormous challenge in the sphere of basic studies and in the sphere of new developments and applications.

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