

IONIZING RADIATION-INDUCED CROSSLINKING AND DEGRADATION OF POLYMERS

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1. INTRODUCTION

The interaction of ionizing radiation with matter results in the formation of very reactive species (free neutral radicals, cationic and anionic ions, excited molecules). These can significantly modify the molecular structure of the irradiated material. In particular, irradiation of organic polymers induces molecular chain branching, crosslinking and molecular degradation or scissioning. Chain branching and crosslinking increase the molecular weight of the polymer. Crosslinking forms an insoluble three-dimensional polymer network; while degradation or scissioning causes a reduction of the initial molecular weight [1, 2].

During irradiation, all these phenomena coexist and their prevalence depends on several factors, such as the initial molecular structure and morphology of the polymer and the irradiation environment. If the polymer is irradiated in presence of air, the molecular modifications are different with respect to the effects of irradiation in vacuum or in presence of an inert gas. During irradiation in air, the free radicals, produced by interaction of ionizing radiation and polymers, can also react with oxygen, giving rise to oxidative degradation, which competes with other reactions that occur in absence of oxygen. All these molecular modifications can modify the properties of the material.

Studies have been devoted to understanding the mechanisms of the modification of the molecular structures and of the properties of polymers resulting from exposure to ionizing radiation.

Such studies are of importance for using polymeric materials in radiative environments, such as in nuclear power plants, in space or in the sterilization of polymeric medical disposables or of food plastic packaging [3-8].

The irradiation of polymers is a very useful industrial process, an alternative to the more traditional chemical processes, which induce or modify some

material properties. Some industrial applications are the crosslinking of wire and cable insulation, the formation of heat recoverable films and tubings, foams, and the degradation of some polymers to help produce powders used in non-stick or release applications [9-11].

Regardless of the different kinds of molecular modifications induced by irradiation, it is possible to divide the polymers in three categories, related to their resistance to ionizing radiation.

Highly radiation-resistant polymers are characterized by an almost unmodified molecular structure up to the absorbance of doses in the range of 250-1000 kGy in air. These polymers contain aromatic groups in their molecular structure, such as polyimides, polyphenyl ethers, polyphenyl ketones, aromatic polyamides, polysulphones, polyetherimides, epoxy resins, polyphenylene sulphide, polyethylene terephthalate, polyethersulphones, polyphenylene oxides.

Aliphatic polyethers, aliphatic polysulphones and polymers containing C-Cl bonds in the macromolecular structure are highly sensitive to irradiation; their molecular structures undergo dramatic changes after the absorption of only a few tenths of a kGy in air.

Polymers such as polyolefines, polyamides and aliphatic polyesters present an intermediate resistance.

2. MOLECULAR MODIFICATIONS OF IRRADIATED POLYMERS

2.1. IRRADIATION UNDER VACUUM

When polymers are irradiated under vacuum or in presence of an inert gas, their molecular modifications depend only on their initial molecular structure and morphology. Ionizing radiation of polymers causes chain branching, crosslinking or scissioning (degradation).

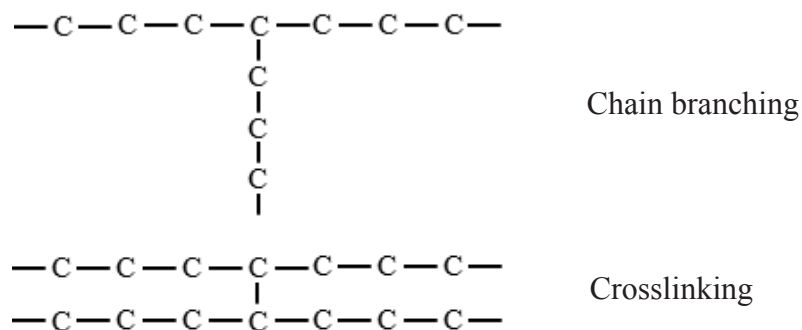


Fig.1. Scheme of chain branching and crosslinking.

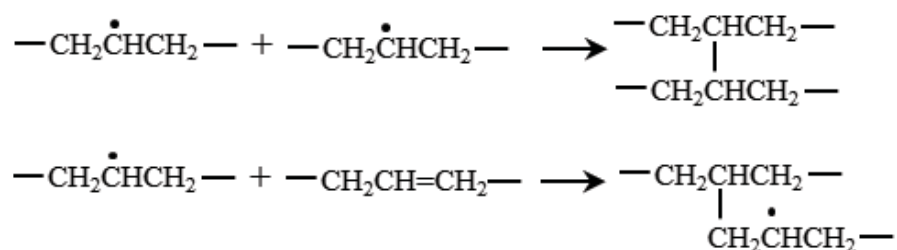
Chain branching and crosslinking are the predominant effects for polymers having relatively unhindered main chains, according to the scheme shown in Fig. 1.

When the polymers have highly substituted quaternary atoms, molecular degradation or scissioning is the main effect.

The molecular modifications are essentially due to the reactions of free radicals, produced by both the direct action of ionizing radiation on the macromolecular structure and the further evolution of ionic and excited species initially produced by irradiation.

Several mechanisms dealing with the molecular modifications induced by irradiation have been reported in the literature [1, 2, 12].

For example, in the case of polyethylene (PE), the free radicals formed by dissociation of C–H and C–C bonds (alkyl, allyl, polyenyl) and the double bonds formed with H₂ evolution give rise to either crosslinking or chain branching reactions:



When degradation occurs, the stable free radicals formed by the dissociation of quaternary carbon bonds do not migrate along the polymer chains and the steric hindrance favours their further evolution toward disproportionation and chain scission reactions, according to the scheme reported for poly(methyl methacrylate) (Fig. 2).

The quantitative determination of molecular modifications induced by ionizing radiation has been made through the measurement of the G-value, which represents the number of molecules formed or changed for 100 eV of absorbed energy. G(X) is the number of crosslinks formed per 100 eV of absorbed energy,

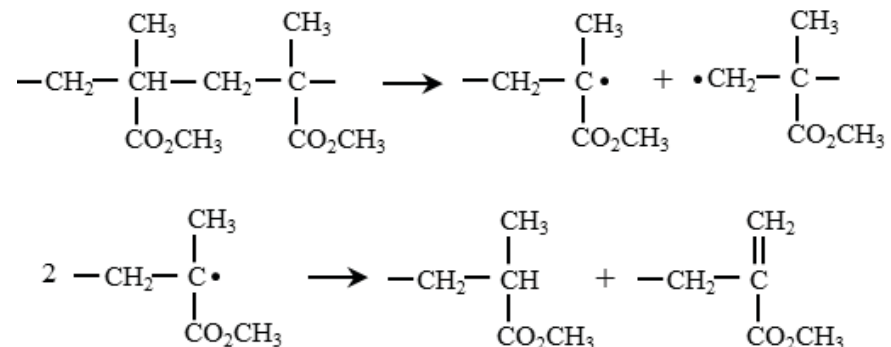


Fig. 2. Example of chain scission reaction in the case of poly(methyl methacrylate).

while $G(S)$ is the number of chain scissions formed by 100 eV of absorbed energy.

As two polymer chains are joined when a crosslink is formed, $G(\text{chains linked}) = 2 G(X)$.

The most common methods used to measure $G(X)$ and $G(S)$ are based on solubility tests. Crosslinking causes the formation of three-dimensional insoluble networks (gel). The “gel fraction” is the ratio of the weight of the insoluble part divided by the initial weight of the polymer, while the remaining part is the “soluble fraction”.

Solubility data are used in the Charlesby-Pinner equation:

$$s + s^{0.5} = \frac{p}{q} + \frac{1}{q P_n D} \quad (1)$$

where: s – the soluble fraction, p – the chain scission probability per unit dose per monomer unit, q – the crosslinking probability per unit dose per monomer unit, P_n – the number average degree of polymerization for the polymer of the most probable distribution of molecular weight, D – the absorbed dose.

The Eq. (1) can be expressed in terms of $G(S)$ and $G(X)$:

$$s + s^{0.5} = \frac{G(S)}{2G(X)} + \frac{4.82 \times 10^6}{G(X) M_n D} \quad (2)$$

where M_n is the number average molecular weight.

Plotting Eq. (2) as function of $1/D$ allows one to determine $G(S)$ and $G(X)$. The extrapolation of the curve until $1/D = 0$ gives the ratio $G(S)/2G(X)$, while $G(X)$ is calculated from Eq. (2) the slope of the curve.

In Ref. [9], the values of $G(X)$ and $G(S)$ for the most common polymers are reported.

Many authors have found deviations in their experimental results from the Charlesby-Pinner equation which have been attributed to the non-random distribution of the initial molecular weight.

Other experimental techniques, such as elastic modulus, swelling values or light scattering and ^{13}C NMR measurements can be also used to calculate $G(X)$.

The extent of chain branching and crosslinking depends on the amorphous phase content of a polymer, which occurs along molecular chains in the solid state, where there are amorphous and crystalline regions. Polymers with similar molecular structure but different degrees of crystallinity give different values of $G(X)$ and $G(S)$ for the same irradiation conditions. For example, in Ref. [9], isotactic polypropylene $G(X)$ varies in the range 0.3-0.5, while for atactic polypropylene $G(X)$ is higher, 0.4-1.1. Similar results are shown in Ref. [9] for polyethylenes with different degrees of crystallinity.

2.2. IRRADIATION IN AIR

When polymers are irradiated in air, the free radicals produced by ionizing radiation can yield oxidized functional groups (carbonyl, peroxides, hydroperoxides, hydroxyl, carboxyl). Oxidized macromolecules can undergo chain scission with molecular weight decrease.

The oxidative degradation induced by irradiation in air can be studied by different techniques.

The most common is infrared analysis, which allows one to monitor the formation of the oxidized groups and other molecular modifications (double bonds,

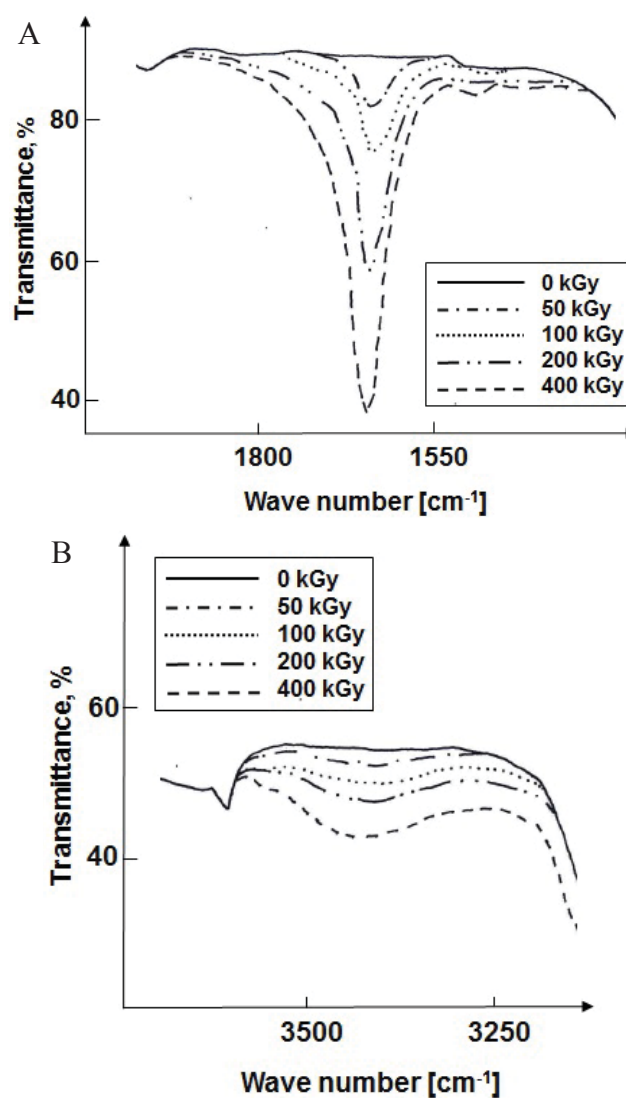


Fig.3. IR analysis of LDPE, irradiated at various doses and at constant dose rate: (A) wavenumber range of 1720 cm⁻¹, (B) wavenumber range of 3500 cm⁻¹.

terminal methyl group formation, *etc.*) resulting from molecular degradation. The decrease of molecular weight can also be determined by gel permeation chromatography (GPC) and by the measurement of intrinsic viscosity.

Figure 3 shows the infrared analyses of a low density polyethylene (LDPE) irradiated in air at different doses, in the wavenumber range of 1720 cm^{-1} (A), the typical absorption range of carbonyl groups, and in the wavenumber range of 3500 cm^{-1} (B), the typical absorption range of hydroxyl groups.

Irradiation in air causes the formation of both carbonyl and hydroxyl groups, and their amounts increase with increasing dose. A useful relative quantitative determination of the extent of oxidation reactions can be done by measuring the height of the peaks corresponding to the oxidation functional groups. If the thickness of the analysed sample is constant, this value can be related to the oxidized functional group concentration in the irradiated sample and to the extent of oxidative degradation reactions. The peak generally used for the evaluation of the oxidation reactions is the carbonyl one at 1720 cm^{-1} wavenumber.

Other indirect techniques can measure the modifications of the physicochemical (glass and other molecular transitions), mechanical and electrical properties due to irradiation.

The formation of oxidized physicochemical groups and the molecular modifications due to irradiation of a solid polymer in air are not uniform within the material. The extent of the oxidative degradation phenomena is higher in the external layers of the polymers and a concentration gradient of oxidized groups, moving from the external surfaces toward the bulk, has been observed. A similar trend can be also observed for the molecular weight modifications. This non-uniformity can be more or less marked, depending on the molecular structure and morphology of the polymer and on the irradiation conditions.

During irradiation in air, a polymer undergoes different reactions depending on its molecular structure and morphology (chain branching, crosslinking and degradation or scissioning). These also occur during irradiation under vacuum or in presence of inert gases. The oxidative reactions due to interaction of free radicals with atmospheric oxygen dissolved in the solid polymer. For a given polymer, the prevalence of one or the other depends on the reaction kinetics.

The reactions of free radicals with oxygen are very fast and the free radicals produced by irradiation react immediately with oxygen dissolved in the solid polymer. The kinetics of the further oxidative reactions is controlled by the oxygen diffusion rate through the polymer. Those molecular structures, morphologies and irradiation conditions which favour the oxygen diffusion in the polymer cause a more uniform oxidation within the material, while a marked gradient of these phenomena is observed when oxygen diffusion is hindered. In the first case the material mainly undergoes oxidative degradation, while, in the second case, a prevalence of the reactions usually occurring during the irradiation under vacuum or under inert atmosphere occurs.

The study of non-uniform oxidation of polymers during their irradiation in air can be carried out by microtome cutting very thin polymer sheets moving from the external surfaces toward the interior bulk. These sheets can be then analysed by experimental techniques apt to measure the molecular modifications due to irradiation, and in particular by IR analysis. Also other techniques such as GPC, solubility, density measurements, calorimetric analysis and mechanical property determinations can be used.

In Fig.4, the IR analysis and solubility tests results for a linear low density polyethylene (LLDPE) irradiated in air are shown. Sheets of the same thickness were cut by a microtome and the extent of the oxidation reactions was measured through the carbonyl group absorption peak, while the corresponding molecular weight modifications were measured by gel extraction tests. The carbonyl concentration and the gel fraction profiles, *i.e.* measured as a function of the distance from the external surface of the irradiated polymer, are shown.

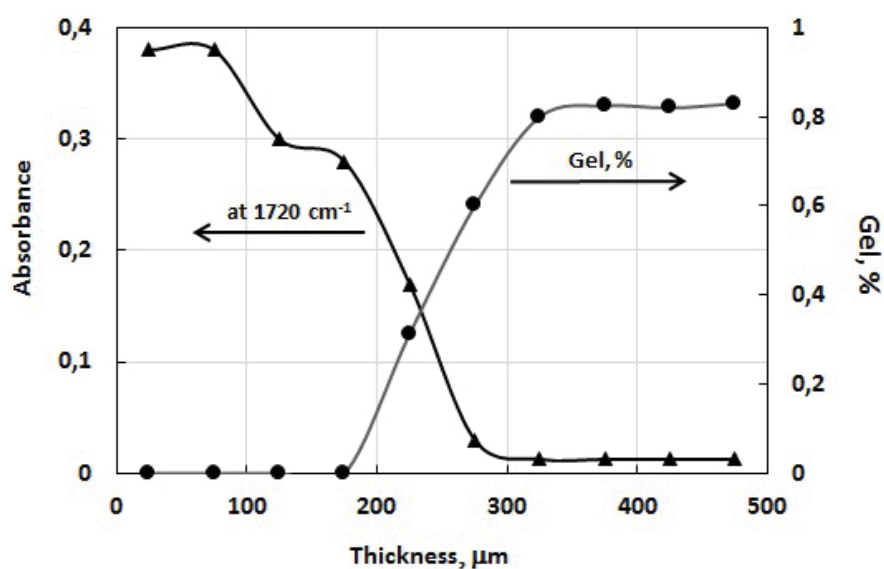


Fig.4. Carbonyl concentration and gel fractions profiles for a LLDPE sample irradiated in air at the dose of 170 kGy and the dose rate of 1 kGy/h.

In the outer layers the oxygen penetration favours oxidative degradation while crosslinking occurs in the bulk, as evidenced by the decrease of carbonyl group concentration, accompanied by the increase of gel fraction.

In Fig.5, the IR analysis results for two linear low density polyethylenes, irradiated in air at the same total dose and dose rate, are shown. The carbonyl concentration profiles are noted.

Before irradiation the two polymers have different crosslinked densities, as determined by gel extraction tests performed in xylene (a typical solvent for polyethylene), which indicate a total solubility of the uncrosslinked sample and

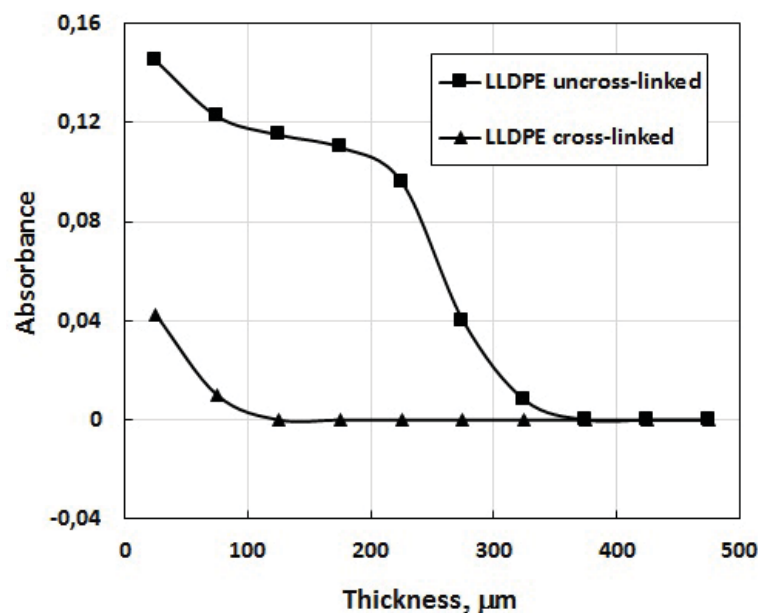


Fig.5. Carbonyl concentration profiles for two LLDPE. Irradiation conditions: dose rate – 1 kGy/h, dose – 100 kGy.

a gel fraction of about 80% for crosslinked one. A marked and deeper oxidation is observed for the first one with respect the crosslinked polyethylene. This can be attributed to the higher diffusivity of oxygen in the uncrosslinked polymer.

In Fig.6 the effects of irradiation in air on three different types of polyethylene, low density polyethylene, linear low density polyethylene, and high

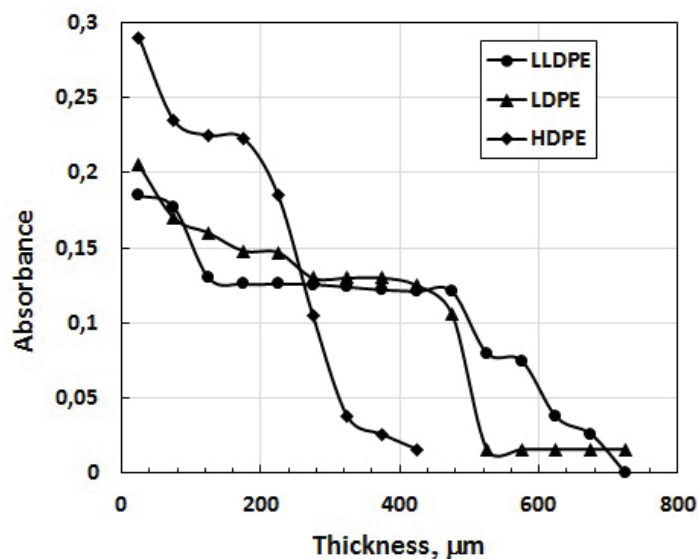


Fig.6. Carbonyl concentration profiles for LLDPE, LDPE and HDPE. Irradiation conditions: dose rate – 0.1 kGy/h, dose – 10 kGy.

density polyethylene (HDPE), irradiated at the same total absorbed dose and dose rate, are shown. The difference in the carbonyl concentration profiles can be attributed to the different oxygen diffusivity in the three polymers. LDPE and LLDPE have almost the same crystallinity degree and almost the same oxygen diffusivity, while HDPE has higher crystallinity and a lower oxygen diffusivity. The thickness of the oxidized layers is almost the same for LLDPE and LDPE while less interior oxidation is observed for the more crystalline HDPE.

Processing parameters, the dose rate and the total absorbed dose, play an important role in determining the extent of crosslinking and oxidative degradation phenomena.

In Fig.7, the carbonyl concentration profiles for LLDPE samples irradiated in air at the same total dose but at different dose rates are reported.

At high dose rates, the instant concentration of free radicals in the polymer is so high that the oxygen, diffusing in the polymer from ambient conditions, is immediately consumed close to the surfaces. At lower dose rate the lower instant concentration of free radicals allows for diffusion of the oxygen into the bulk of the irradiated sample with an increase of the thickness of the oxidized layer.

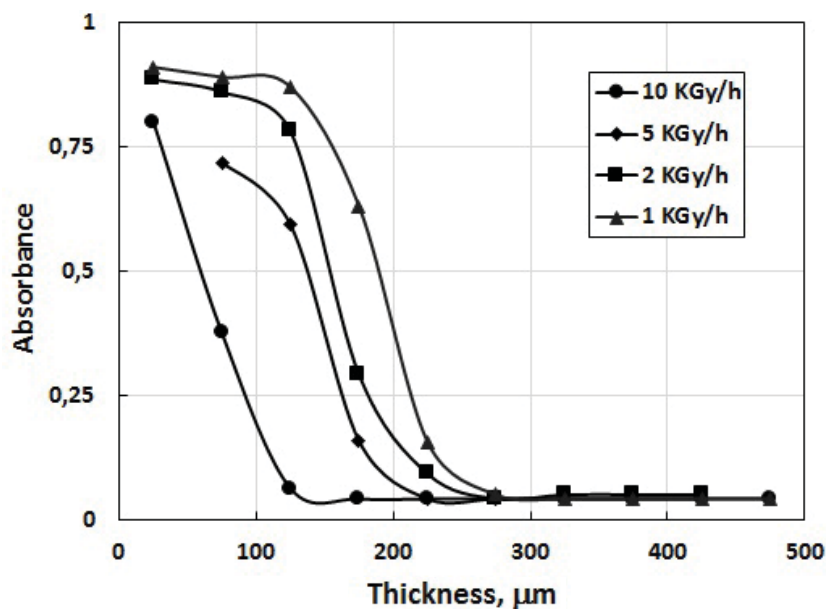


Fig.7. Carbonyl concentration profiles for samples of LLDPE irradiated in air at the total absorbed dose of 675 kGy and different dose rates.

Consequently, the whole effect of irradiation on the same polymer and at the same dose is different because of changing the dose rate.

At high dose rates the oxidative degradation phenomena are essentially concentrated in the external layers. As already described, the bulk of the material undergoes the same reactions occurring during irradiation under vacuum

or under inert atmosphere and in particular for polyethylene the main effect is crosslinking.

At low dose rates the degradation phenomena involve larger parts of the irradiated material.

These considerations are confirmed by the results shown in Fig.8, where the carbonyl concentration profiles for samples of LLDPE irradiated in air at the same dose rate and different total doses are reported.

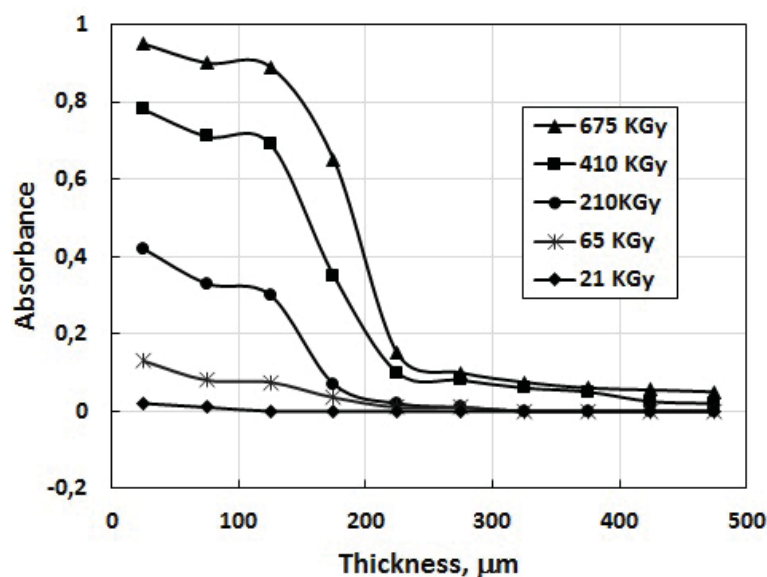


Fig.8. Carbonyl concentration profiles for samples of LLDPE irradiated in air at the constant dose rate of 1 kGy/h and different total absorbed doses.

Since the polymer is always irradiated at the same dose rate, the thickness of the oxidized layer is always the same, while the concentration of carbonyl groups increases with the absorbed dose.

Other examples based on the measurement of other properties can be found in the literature.

In Ref. [13], the density profiles for a non-irradiated LDPE and for LDPE irradiated in air at different doses and different dose rates are shown. The increase in density is related to oxidation reactions. It is possible to observe, by decreasing the irradiation dose rate, a generalized increase of density with respect to the non-irradiated starting material. The density profiles show that this effect is confined to external surfaces at high dose rates and involves deeper penetration at low dose rates.

In Ref. [14], the molecular weight of nylon-6 wire jacketing irradiated in air at different dose rates and to different total doses had been measured. Decreasing the dose rate, increased the extent of the oxidative degradation and decreased the average molecular weight of the irradiated polymer.

All these results have very important practical consequences.

For instance, polymer samples with different thicknesses, irradiated in air with the same dose and dose rate conditions, present a different ratio between oxidative degradation and crosslinking extent. This effect will affect the properties of the polymeric material, as it will be discussed in the following sections.

For the polymeric materials used in radiative environments for long periods of time at very low dose rates, as in nuclear power plants or in space, the influence of the dose rate in the study of the reliability of a material has to be taken into account. Careful consideration of the dose rate effects is needed for the extrapolation to the effective working conditions from laboratory results obtained both in short timeframes and at high dose rates [13].

The molecular modifications induced by the action of ionizing radiation can also occur after irradiation. This is very significant for semi-crystalline polymers, such as polyethylene and polypropylene. The macroradicals formed in the amorphous regions rapidly react with each other or with the oxygen diffused into the polymer, while those formed in the crystalline regions in order to react, need to diffuse to the surface of the crystallites or to the amorphous phases. The radical diffusion rate can be very low and the irradiated materials can undergo chemical modifications for long periods of time after irradiation (up to several days). In Ref. [14], the post-irradiation oxidation of polypropylene was studied by IR analysis. The results showed that the carbonyl group concentration increases during storage in air.

2.3. IONIZING RADIATION EFFECTS ON POLYMER PROPERTIES

The molecular modifications induced by irradiation modify polymer properties, such as the thermal behaviour and the mechanical and electrical characteristics.

2.3.1. Thermal behaviour

The most common technique used to study the thermal behaviour of polymers is the differential thermal calorimetry (DSC) which determines the melting temperature and the melting enthalpy for semi-crystalline polymers, and for all polymers, the glass and other secondary transitions occurring in the amorphous phases. Other experimental methods are dynamic mechanical thermal analysis (DMTA) and dielectric tests, performed at different temperatures and frequencies.

The melting behaviour depends on the crystalline properties of the polymer. The melting enthalpy indicates the amount of the crystalline phase with respect to the total mass of the polymer (crystallinity degree), while the melting temperature can be affected by the crystallite regularity.

Since molecular modifications induced by ionizing radiation occur mostly in the amorphous regions, at low doses irradiation does not appreciably

modify the crystallinity of the polymer. A modification can occur at higher irradiation doses with introduction of irregularities in the crystallites due to both crosslinking and degradation which is enhanced by oxidation. In these cases, the DSC curves show a decrease of both in the melting temperature and in the enthalpy with the formation of additional small melting peaks at low temperatures, due to the presence of low molecular weight molecules [15, 16].

The glass transition is related to the free movement of the main chains of the polymers, while the other secondary transitions are related to similar phenomena involving smaller molecular segments. Chain scission and degradation favour molecular mobility and a decrease of the temperatures of all the transitions, while an opposite effect is caused by chain branching and crosslinking [17, 18].

2.3.2. Mechanical properties

The mechanical properties of polymers can be studied through different tests: tensile, compression, flexural, *etc.* Among all, tensile tests are the most sensitive to the molecular modifications induced by irradiation. Here tensile mechanical tests are considered, even if similar consideration can be made on other experimental techniques.

The most significant tensile parameters are the Young's elastic modulus, the elongation at break and the breaking strength.

The mechanical behaviour essentially depends on the molecular weight and on the degree of crystallinity. The increase of the crystallinity and of the molecular weight due to crosslinking causes an increase in the mechanical strength, with an increase of the Young's elastic modulus. For the elongation at break, which is related to the ductile or brittle behaviour of the material, two effects can be observed: an increase in the molecular weight increase and a reduction, up to the start of brittleness, caused by crosslinking and crystallinity. The chemical bonding of polymer chains, in the case of crosslinking, and the crystallinity act as links which hinder their free movement. All these properties affect the breaking or ultimate strength, *i.e.* the stress corresponding to the breaking of the polymer chains. High elastic modulus values correspond to a high stress levels and tend to increase the ultimate strength, which decreases the elongation at break and starting brittleness.

Ionizing radiation mainly affects the molecular behaviour of polymers and does not modify appreciably the crystallinity, at least up to the absorption of moderate doses. The mechanical behaviour of irradiated polymers essentially depends on the relative extent of chain scission, chain branching and crosslinking [13, 19].

As for degradation or scissioning phenomena, a great interest has been devoted to the worsening of the mechanical properties, which can become dramatic in the case of oxidative degradation. Defects induced in the molecular structure can strongly reduce the elongation at break, changing the poly-

meric properties from ductile to brittle. This is very important when the materials are used in the presence of ionizing radiation and good mechanical performance is required.

It has been shown above how the different molecular, morphological and processing parameters involved in ionizing radiation effect the molecular structure of the materials. In Ref. [14], the effect of the dose rate on the elastic modulus of a Viton rubber irradiated in air had been studied. Sheets of the same thickness were cut, starting from the surface and going toward the bulk, and the tensile elastic modulus was determined. The non-irradiated sample had a uniform modulus value for all of the tested sheets. For the irradiated samples a non-uniform profile was observed. Compared to the non-irradiated material, modulus decreases in the outside layers, while it increases in the bulk. This is explained by non-uniform molecular modifications induced by irradiation in air: oxidative degradation in the external layers and chain branching and crosslinking in the bulk. Decreasing the dose rate, the modulus profile along the thickness becomes more uniform, with lower modulus values.

According to what has already observed for the ratio between external oxidized and internal non-oxidized layers of polymer irradiated in air, the mechanical strength also depends on the thickness. Under irradiation, thicker samples present a higher mechanical strength.

Since the elongation at break is very sensitive to degradation phenomena, its reduction has been used as a reliable parameter for polymers used in radiation environment. For example, in Ref. [14], data corresponding to the reduction of 50% of the elongation at break of the non-irradiated material was reported for the most common polymers.

In evaluating the effect of ionizing radiation on the mechanical properties of polymers, also post-irradiation effects have to be considered, which can cause further worsening of the properties [14].

The improvement of mechanical properties by irradiation has been important in applications of radiation processing of polymers, such as the irradiation of ultra-high molecular weight polyethylene for medical prosthesis devices.

2.3.3. Electrical properties

The modifications induced by ionizing radiation effect both the conductivity and the dielectric properties of polymers.

The most common polymers are insulating materials characterized by the presence of a completely full valence band and of a conductive band separated by a prohibited energy interval. In general, their conductivity is strongly affected by the presence of impurities which cause the formation of additional bands, which decrease the insulating properties.

The electrical conductivity is increased by irradiation. This is due to the formation of mobile charge carriers: electrons, holes, ions, which create additional energy intervals [9-20].

There are two different kinds of irradiation-induced conductivity: pulse and stationary conductivity.

The pulse conductivity is induced by pulse irradiation and is proportional to the dose rate. It is subdivided into the instant and the delayed conductivity.

The instant conductivity is characterized by a very short lifetime of about 10^{-10} s.

The delayed conductivity continues also after irradiation. It relaxes down to a dark value which, for doses causing significant structural modifications of a polymer, can be appreciably different from the initial value before irradiation.

The stationary conductivity is induced by continuous irradiation and depends on dose rate according to the Eq. (3):

$$\sigma = k D^\alpha \quad (3)$$

where $0 < \alpha < 1$, until a saturation value.

The dielectric properties of polymers can be described by a model based on a set of capacitors and resistance elements.

If an alternating field is applied, the material is crossed by a current out of phase, in advance, with respect to the applied voltage, of an angle ϕ .

The dielectric behaviour of a polymer is described by two properties: ϵ' and ϵ'' ; ϵ' is the permittivity (or dielectric constant) and it is related to the capacity and to the stored energy, while ϵ'' is the loss factor and it is related to the resistance and to the dissipated energy. The ratio $\epsilon''/\epsilon' = \tan \delta$ is the tangent of the loss angle, complementary of the phase angle ϕ , which is also related to the dissipative phenomena. All of these properties are essentially due to the presence and mobility of charges and polar groups in the polymer backbone and depend on polarization phenomena of different types, occurring in different times: 10^{-15} s for electronic polarization, 10^{-14} - 10^{-12} s for atomic polarization, from 10^{-10} s to seconds or minutes for dipolar polarization due to the presence of polar groups, and longer times for interfacial polarization effects.

Irradiation mainly affects the dipolar polarization and the effects can be both transitory and permanent. The transitory effects derive from the short-lived irradiation products (trapped electrons, peroxide and hydroperoxide groups during irradiation in air), while the permanent effects derive from the permanent induced changes in the molecular structure.

Molecular degradation causes an increase in the molecular mobility and consequently in the permittivity. This effect is enhanced by oxidative degradation phenomena, which also causes an increase in the oxidized groups.

An opposite effect is observed in the case of crosslinking which reduces the molecular mobility.

$\tan \delta$ and ϵ'' are increased by degradation and decreased by crosslinking.

Related to these phenomena is the dielectric strength, *i.e.* the maximum applied electrical field before the occurrence of dielectric breakdown. The dielectric strength can be dramatically decreased by both localized defects due

to molecular degradation and localized heating due to the increase of conductivity and of polarization.

As with the mechanical effects, the knowledge of radiation effects on the electrical properties of polymers is very important for several applications.

This is the case of polymers used as insulating materials in radiative environments, where the preservation of their electrical properties is required.

On the other hand, the positive effect of crosslinking on both the dielectric properties and dielectric strength values is the basis of the electron beam irradiation-induced crosslinking of polymer insulating materials, which is one of the most successful industrial applications of radiation processing.

3. CONCLUSIONS

This chapter dealt with the modifications induced by ionizing radiation on the molecular structure and on the properties of polymers.

Under ionizing radiation polymers undergo chain scission, chain branching and crosslinking reactions and their relative extent depends on the initial molecular structure and morphology of the polymer and on the irradiation conditions.

In particular the effect of irradiation in air has been illustrated with particular emphasis on the conditions which cause more or less uniform distribution of oxidation effects on irradiated samples.

The molecular modifications effect the polymer properties, such as the physicochemical, the mechanical and the electrical behaviour.

These results are very important for both the knowledge of the reliability of polymers used in radiative environments and the improvement of the applicative properties of polymeric materials by radiation processing.

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