

RADIATION-INDUCED OXIDATION OF POLYMERS

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1. INTRODUCTION

A polymer is a macromolecule formed by the combination of simple molecules, monomers, of low molecular weight. A polymer molecule usually has at least 2000 atoms linked by covalent bonds.

In general, polymers can be divided into inorganic and organic, and also into naturally occurring and synthetically produced. Polymers may contain additives such as dyes, fillers, antioxidants, flame retardant materials and other components needed to carry out their use in many application areas. The properties of polymers largely depend on both their microstructure and macrostructure.

Ionizing radiation excites active species, like radicals. In the radiation processing of polymers, usually two kinds of radiation are used: (i) high energy electrons from accelerators, which give continuous and homogeneous radiation, but have limited penetration depth, and are a source of high doses of radiation per unit of time, and (ii) gamma rays from radionuclides of cobalt-60 and cesium-137, which more deeply penetrate materials and give relatively small doses of radiation per unit of time.

2. THE INFLUENCE OF IONIZING RADIATION ON THE MOLECULAR STRUCTURE OF POLYMERS

For macromolecules, degradation indicates changes in physical properties caused by chemical reactions resulting in the breaking of macromolecular chains. As a result, polymers have shorter chain molecules and a reduced molar mass.

Polymer degradation can be induced by thermal, mechanical, photochemical, biological, or chemical treatments or by ionizing radiation:

- Thermal degradation is caused by exposure to elevated temperatures and takes place without chemical agents.
- Mechanical degradation is caused by the application of external factors, *e.g.* external stress on moisture diffusion, oxygen, temperature.
- Photochemical degradation is caused upon the absorption of light wherein triplet oxygen converts to singlet oxygen, a highly reactive form of the gas, which effects spin-allowed oxidations. In the atmosphere, the organic compounds are degraded by hydroxyl radicals, which are produced from water and ozone.
- Biological degradation is caused by the action of enzymes on polymers. Microorganisms produce a variety of enzymes capable of reacting with both natural and synthetic polymers.
- Chemical degradation is caused by solvolysis and mainly by hydrolysis to give lower molecular weight molecules. Hydrolysis takes place in the presence of water containing an acid or a base. Polymers are susceptible to attack by atmospheric oxygen, especially at elevated temperatures encountered during processing.
- Ionizing radiation causes some chemical degradation in polymers such as the breaking of the main chains of the macromolecule, changes in the number and nature of double bonds, and the emission of low molecular weight gaseous products, as well as oxidation of the polymer.

The interaction between the incident radiation and the irradiated material is characterized by linear energy transfer (LET). Electrons or gamma rays have a relatively small value in contrast to the alpha particles [1]. Ionizing radiation

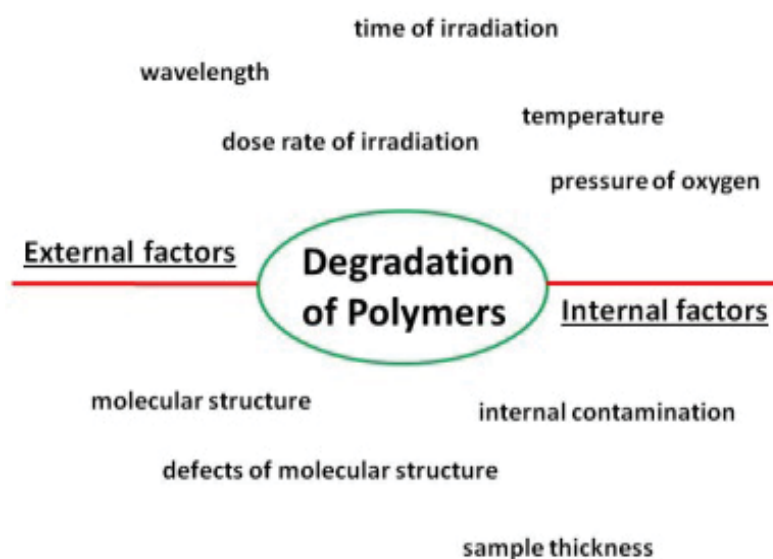


Fig.1. Scheme of the impacts of the main factors leading to polymer degradation.

transfers a large quantity of energy towards the irradiated material. The transfer of the energy is not selective and represents a principal difference with the photochemical processes. Degradation of polymers is a consequence of radical processes which are generated in a material upon irradiation. The extent of free radical degradation increases as the dose increases.

There are strong connections between different types of degradation [2]. Usually there is simultaneous and overlapping of several types of degradation. A typical example of this is the simultaneous action of light, oxygen and other atmospheric agents, or the simultaneous influence of heat, mechanical stresses and oxygen. Figure 1 is a diagram of the impact of the most important factors leading to polymer degradation.

The molecular modifications induced by ionizing radiation are shown in Fig.2:

- crosslinking reaction forming new C–C covalent bonds between adjacent molecular chains, increasing the polymer molecular weight up to the formation of a three-dimensional network;
- chain scission of a backbone resulting in a decrease of the molecular weight of the polymer;
- changes in the nature and number of double bonds;
- oxidation degradation of the polymer during irradiation in the presence of oxygen.

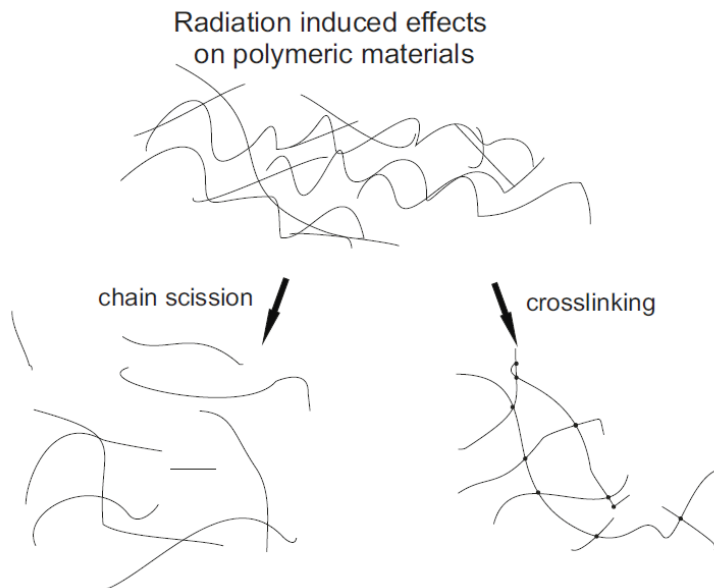


Fig.2. Ionizing radiation-induced crosslinking and chain scissioning of polymeric materials.

Polymers in which ionizing radiation causes crosslinking often have better mechanical properties. If chain scissioning dominates, *e.g.* polypropylene, then

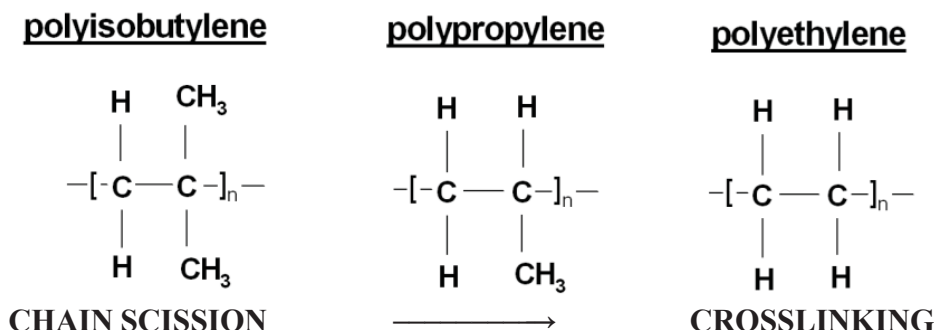


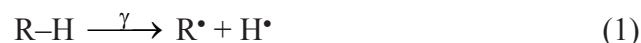
Fig.3. The pathway of the influence of ionizing radiation on different chain structure polymers.

low molecular weight fragments, gas evolution (odor) and unsaturated bonds (color) may appear.

Free radicals determine the initiating centers for scissioning and/or crosslinking, hence for the induced modifications within the macromolecular chain (Fig.3). In polymers containing mainly $-\text{CH}_2-\text{CH}_2-$ units, crosslinking predominates; if a polymers has a tetra-substituted carbon, as of the type $-\text{CH}_2-\text{CR}_1\text{R}_2-$, chain scissioning (degradation) predominates [3].

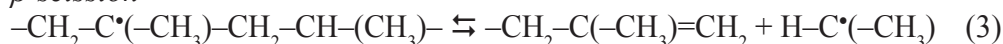
The mechanism occurring during irradiation has three distinct stages: initiation, propagation and termination. The chemical reactions induced by ionizing radiation on polypropylene are as follows:

- Initiation

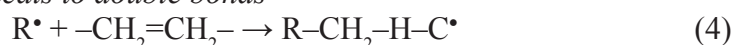


- Propagation

β-scission



Addition of free radicals to double bonds



- Termination



3. RADIATION-INDUCED OXIDATION OF POLYMERS

By definition, the term “oxidation” occurs when a polymer molecule reacts with oxygen *via* peroxide radicals. The irradiation of polymers in the presence of oxygen gives different results with respect to irradiation under vacuum. The presence of oxygen affects the quantitative and qualitative degradation processes, and increases the rate of degradation and possibly the crosslinking of

a polymer. The oxidation of aliphatic and aromatic polymers leads to the emergence of alcohols, ketones, carboxylic acids as stable by-products of radiolysis [4]. The gamma oxidative degradation of a polymer in air, for example, is described by the following chain reaction scheme:

- Initiation



- Propagation



- Termination



It should be noted that the free radicals R^\bullet react with molecular oxygen and/or hydroperoxides thus initiating new chain reaction.

If two carbon-centered radicals recombine with each other, the polymer can form a three-dimensional network, crosslinking. Crosslinking is effective in the amorphous phase of polymers since their chains are highly mobile; whereas radicals in crystalline regions are localized in the ordered crystalline lamellae and their transfer is very limited.

During irradiation in the presence of oxygen (reaction (7)), radicals react with oxygen to form highly active peroxy radicals. The resulting peroxides are thermally stable. Oxidation initiates chain reactions predominantly in the amorphous regions, because oxygen is unable to penetrate into the ordered crystalline regions. Therefore, in presence of oxygen, with some polymers, chain scissioning predominates over crosslinking. The rate at which peroxy radicals of alkyls are produced is very high. Hydroperoxide is a precursor of many oxygen containing groups, but is not stable and over time leads to oxidation degradation products which are mainly ketones, esters, and carboxylic acids. The formation of oxidation by-products is accompanied by chain scissioning and a deterioration of mechanical properties. The reactions leading to the formation of stable by-products, such as carboxylic acid groups or carbonyl structures, are slow.

Sometimes, the effect of oxidation is preferred, and even desirable, as in the process of grafting polymers through peroxide groups to modify surfaces and some chemical and physical properties. Active superoxide radicals bind other functional groups of polymers when used for grafting [5].

The study of the oxidative degradation of polymers is frequently conducted through the use of complementary analytical techniques, such as EPR

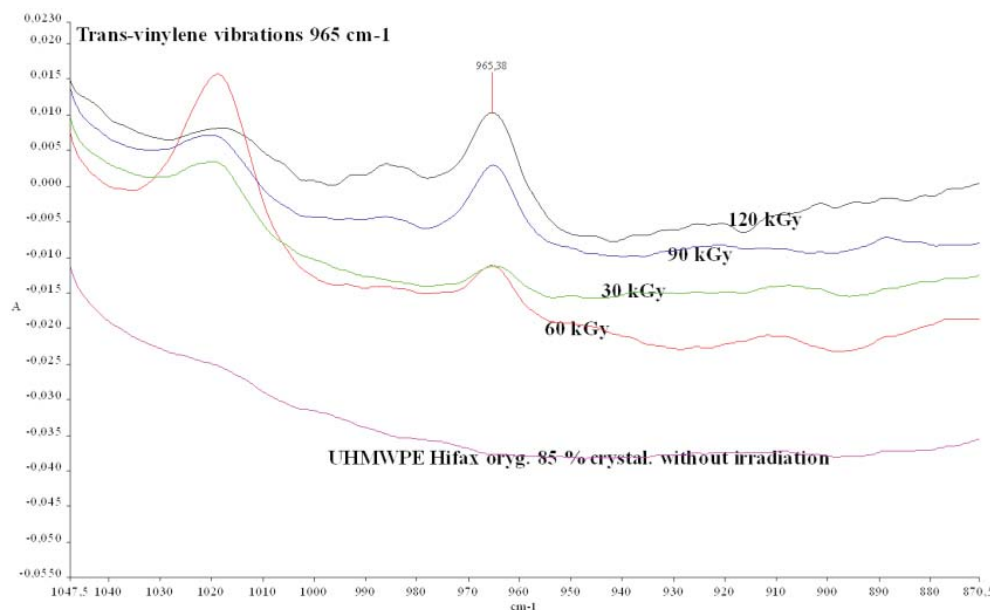


Fig.4. FTIR spectra of UHMWPE irradiated to 0 (—), 30 (—), 60 (—), 90 (—) and 120 (—) kGy.

(electron paramagnetic resonance) and FTIR (Fourier transform infrared) spectroscopy. EPR spectroscopy explores the radicals produced in polymers upon irradiation and assesses their decay as a function of time. FTIR spectroscopy estimates the presence and the amount of double bonds and of oxidation products in a polymer.

For example, the use of ionizing radiation with ultra-high molecular weight polyethylene (UHMWPE) shows both the formation of radicals and of stable products. The primary effect is the random scissioning of C–C and C–H bonds. The scissioning of a C–H bond gives vinylene double bonds, trans-vinylene double bonds, H• radicals, and secondary alkyl macroradicals in both the crystalline and in the amorphous phase of the polymer.

The trans-vinylene yield can be quantified using infrared spectroscopy by monitoring the absorbance band at 965 cm^{-1} . Figure 4 shows the absorbance spectra of the trans-vinylene unsaturation bond after the irradiation of UHMWPE at different doses. The increase of the irradiation dose results in an increased concentration of trans-vinylene groups, which shows that the radicals were incorporated into the polymer chain. The increase in trans-vinylene groups is used as an internal dosimeter for crosslinked UHMWPE, when radiation is used for improving UHMWPE's wear resistance or sterilizing medical device made thereof [6]. The content of carbonyl and carboxyl groups and of unsaturated compounds also increases.

In the presence of oxygen, radicals are oxidized. Such radical processes compete with crosslinking. Figure 5 shows the mutual quantitative relationship

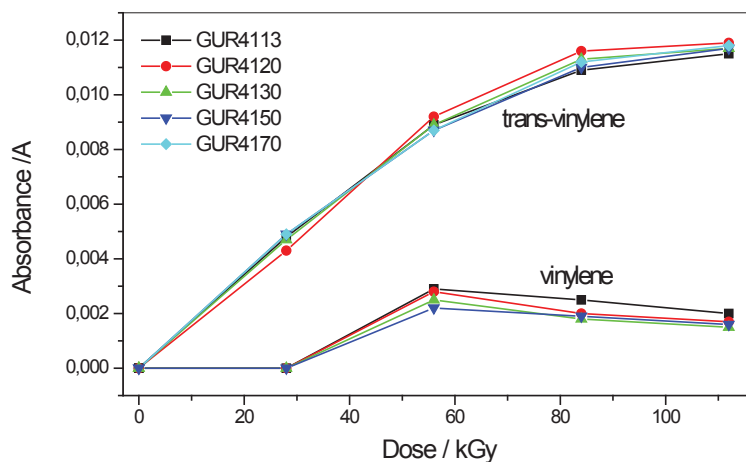


Fig.5. FTIR spectra of UHMWPE irradiated to 0 (—), 30 (—), 60 (—), 90 (—) and 120 (—) kGy.

of both types of unsaturated bonds present in UHMWPE after irradiation at different doses. These are precursors which are attacked by oxygen radicals.

The formation of double bonds in the polymer shown in the FTIR tests is compatible with EPR results when there are alkyl radicals produced by allyl radicals resulting converted from alkyl ones [7]. Both of these radicals oxidize and convert to the radicals as indicated in Fig.6.

The FTIR spectra, reported in Fig.7, contain important information on the reaction of the peroxy radical population. One of stable products of this process are ketons which spectra are detected at 1718 cm^{-1} , as shown in Fig.7. The dominant ketonic species probably result from β -scissioning reaction of alkoxy radicals.

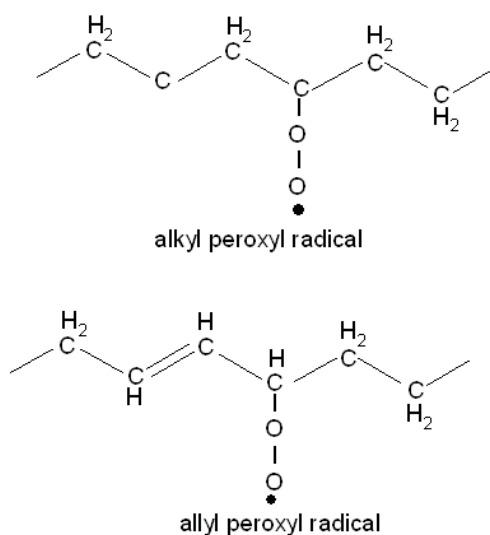


Fig.6. Structure of the alkyl peroxy radical and allyl peroxy radical.

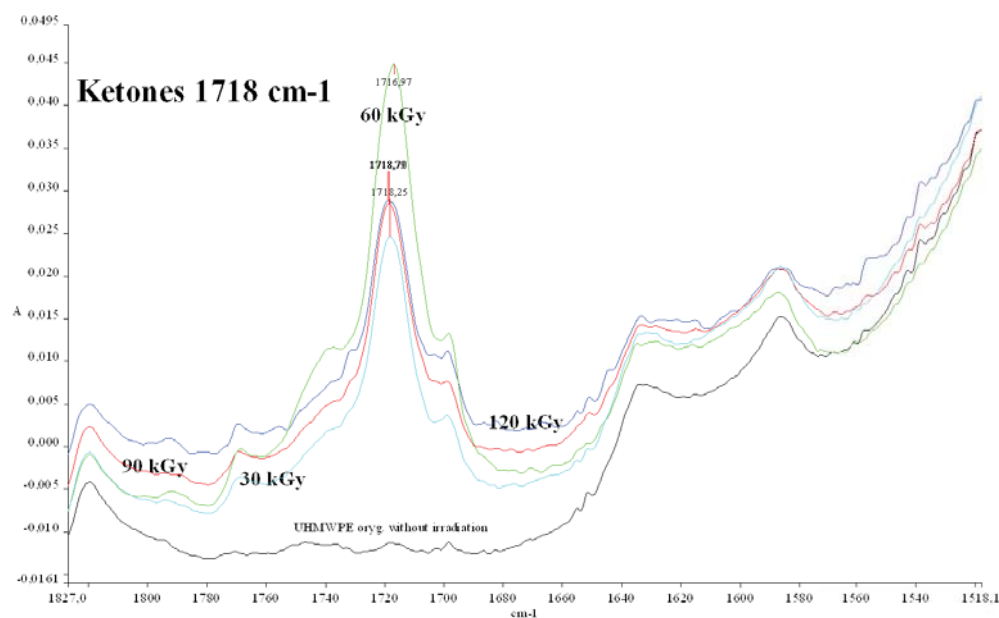


Fig.7. FTIR spectra of UHMWPE irradiated to 0 (—), 30 (—), 60 (—), 90 (—) and 120 (—) kGy.

4. POST-IRRADIATION OXIDATION

The effect of radiation on polymers can be seen in two ways. First is the direct action and the second is a delayed action as in the post-irradiation effects observed during storage. The degradation of polymers due to post-irradiation effects results from the reactions of residual radicals with oxygen in the air [8]. Free radicals trapped in the crystalline regions move toward the boundary regions and to the amorphous phases where they undergo oxidative degradation reactions with oxygen dissolved in the polymer. In order to avoid this, free radicals can be removed by thermal annealing. Oxidation can also be inhibited by suitable additives which act as radical scavengers.

Removing impurities is also a response to the benefits of the oxidation of polymers. This method, which has been used in environmental protection, reduces the molecular weight allowing for biodegradation. Oxygen-biodegradation is a two-step process:

- oxidized polymers are converted into water wettable fragments,
- biooxidative degradation produces CO_2 , H_2O and biomass.

5. ANTIOXIDANTS

The post-irradiation oxidation of polymers can also be avoided by using antioxidants, such as hindered-amine light stabilizers (HALS) resins. The electronic structure of piperidyl type molecules acts as radical traps. The effect of substituents on the antiradical activity is important and determines their properties. Differences in radioprotection effects are attributed to a variety of reactivity of nitroxides with radiation-induced secondary free radicals. Amine stabilizers can efficiently scavenge radicals responsible for the oxidative chain [9]. This efficiency results from the cyclical regeneration of the scavenging piperidyl species.

For example, the protection of polymers by HALS is as follows:

- Amines are oxidized by superoxide
 $>\text{NH} + \text{ROO}^\bullet \rightarrow >\text{NO}^\bullet + \text{ROH}$
- Aminoethers nitroxyl radicals are formed by reaction of alkyl radicals
 $>\text{NO}^\bullet + \text{R}^\bullet \rightarrow >\text{NOR}$
- Regeneration of nitroxyl radicals
 $>\text{NOR} + \text{ROO}^\bullet \rightarrow >\text{NO}^\bullet + \text{ROOR}$

The addition of antioxidant additives not only causes the faster decay of radicals in the amorphous phase, with inhibition of radiation damage, but also can increase the apparent viscosity in the molten state by increasing crystallization temperatures due to influence of the stabilizers on nucleation, which can be followed by degradation and exhaustion of the additives.

Another way to achieve resistance to ionizing radiation in polymers could be to mix them with elastomers. Some elastomers may be more radiation tolerant than polyolefins. Elastomers with phenyl rings can increase the stability to radiation since the ring structure dissipates the energy. A styrene-butadiene-styrene (SBS) triblock copolymer in a blend with polypropylene should have such an effect. Protective role of the elastomer towards polypropylene needs insight into radiation chemistry of the materials.

Compounds playing the role antioxidants often occur in nature. The use of natural antioxidants in polymers is encouraging because of their stabilization effects as well as their non-toxic character. The bioactive form of vitamin E, α -tocopherol, is a compound with very low toxicity and extremely effective antioxidant properties for plastics and rubbers, *e.g.* as used in the melt processing of polyolefins [10]. The recommended concentration of α -tocopherol in UHMWPE at 0.3 mass% gives comparable results to the addition of synthetic antioxidants (as BHT and Irganox 1076) used at higher concentrations [11]. Such small additions of vitamin E are effective to protect polymers from exposure to environmental factors after the irradiation treatment.

The use of antioxidants makes possible the radiation sterilization of polymers.

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