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Characterization of Gamma Irradiated Ethylene-Norbornene Copolymer using FTIR, UV-Vis and DSC Techniques

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Summary

Due to their new combination of properties and shortage of the experimental data, the radiolysis of a new class of materials, cyclo-olefin copolymers (COC), which are polymerized from norbornene and ethylene using metallocene catalysts, is of great interest to the study of radiation chemistry and physics of polymeric systems. Ethylene-norbornene copolymer, bare and containing 0.45 wt % of the hindered phenolic type of an antioxidant (IRGANOX 1010) was subjected to gamma irradiation (100, 200 and 500 kGy) in the presence of air and in water. The irradiated copolymer was studied using FTIR, UV-vis spectrophotometric and gel content analysis. The insoluble fraction was formed in copolymer irradiated in water with 500 kGy, in bare 36% and in copolymer with an antioxidant 23%. The radiation induced changes in the molecular structure were correlated to the specific heat capacity and the glass transition temperature measured by DSC method.

Introduction

The polymeric materials used for medical applications represent an important topic in macromolecular chemistry [1]. Through their applications, "intelligent" drug delivery systems like insulin injection pens, powder inhalers for asthmatics, needleless syringes and instruments for minimally invasive surgery can be included. Biocompatible polymers are used in components for diagnostic systems, such as those for blood sugar and blood pressure measurement and in large clinical equipment. Nowadays, the basic as well as applied research in polymers for medical application deals with development of new superior materials which could replace some parts of human tissue [2]. Any particular application of such a material requires proper combination of its end-use properties. It means that material must be tolerated by the organism, must show acceptable combination of physical and mechanical characteristics for reasonable lifetime, and it should be easily processed. Polyolefins belong to synthetic polymers which satisfy basic requirements for some human tissue replacements.

These polymers are mostly biotolerant, resistant to aggressive body liquids and cover broad range of mechanical properties. So e.g. ultrahigh molecular weight polyethylenes (UHMWPE) are used for orthopaedic implants (hip, knee and shoulder joints) [3]. But it is necessary to modify them to achieve material acceptable for particular application. Well known case is a modification of UHMWPE by ionizing radiation under higher temperature in order to achieve network structure more resistant to wear [3, 4]. Radiation modification of semicrystalline polyolefins creates problems with the control of crystallinity fraction [5-11] as well as with great sensitivity of crystal-amorphous boundary layers to post-radiation oxidative degradation induced by the oxygen present in human liquids [12- 14]. This problem could be solved by using an amorphous polymer which can also be modified by ionizing irradiation.

Amorphous ethylene-norbornene copolymer is new polymer with remarkable combination of properties [2, 15, 16]. This copolymer is interesting for application in medicine as well as in optics and microelectronic applications. The copolymerization of olefins with a cyclic monomer leads to predominantly amorphous material with relatively high glass transition temperature, heat resistance, chemical resistance to acids, low moisture uptake, high optical transparency and above all with relatively balanced mechanical properties. Like in case of other polyolefins their structure imparts to this material good resistance against ageing. Moreover, the structure of polymer with homogenous matrix (without varying crystalline fraction) should be more easily controlled. In addition ethylene-norbornene copolymer showed in vitro the highest biotoleration by synovial fibroblasts (in synovial cell cultures) [2].

Due to their useful combination of properties and shortage of the experimental data, the radiolysis of this new class of materials known as cyclo-olefin copolymers (COC), is of great interest to the study of radiation chemistry and physics of polymeric systems. The aim of the work was to provide the first information of some structural alternations of gamma irradiated ethylene-norbornene copolymer. Due to profound influence of environment in which the polymers are irradiated on consequent chemical reactions [12, 17], gamma irradiation was undertaken in both ambient air and distilled water. This investigation is the part of systematic study of modification of ethylene-norbornene copolymer by the ionizing irradiation [18].

Experimental

Materials

The polymer used for this study was ethylene-norbornene copolymer TICONA TOPAS 6015 S-04 (T_g = 160 ^{o}C, M_w = 90000 g mol^{-1}, ρ = 1.02 g cm^{-2}, bulk density 510 kGy m^{-2}), kindly provided by CELANESE, Ticona Engineering Polymers, Germany. This copolymer is consisting of 55 % of bicyclo(2.2.1)hept-2-ene (norbornene) and 45% of ethylene comonomer. In order to investigate the influence of the stabilizer on the radiation effects in copolymer, the hindered phenolic antioxidant IRGANOX 1010 (purchased from Ciba) was used. This type of antioxidant has –OH functional groups. They act as terminators of the chain reaction in the process of oxidation trough transfer of hydrogen to free radical, mainly peroxy radical [17, 19]. The chemical structure of IRGANOX 1010 is tetra [3-methylene 93,5-di-*tert*-butil-4-hydroxypenthyl0-propionate]. The copolymer was dissolved in boiling cyclohexane (saturated with Ar) with antioxidant (0.5 wt %). The pure copolymer was treated

under the same conditions as formulation. The samples in form of sheets of 0.3 mm thickness were obtained after film casting at room temperature.

The content of the antioxidant in the sheets was determined by the BS 2782 method [20], using UV-Vis Perkin-Elmer Lambda 5 spectrophotometer. Comparing the absorption at the λ_{max} =273 nm of samples dissolved in toluene/ethyl alcohol with the calibrating curves of various concentrations of antioxidant, the decrease in the antioxidant content during the sample preparation was about 5 % of the initial concentration (0.45 wt %).

Irradiation

The samples, 40 x 15 mm pieces, were fixed inside the Pyrex glass tubes (φ = 15 mm); for each material one half of samples were immersed in distilled water during irradiation while the second half were kept in air.

The samples of each kind (fixed in the tubes) were simultaneously irradiated by gamma rays on the Co^{60} source at the dose rate of 6 kGy/h. The exposure dose was determined by Fricke dosimeter at room temperature. In order to prevent post-radiation oxidation of the samples and to allow the decay of various free radicals in the samples, the irradiated samples were annealed at 60°C for 2 hours in vacuum, before exposing them to the air. This procedure is performed as general procedure in order to have an equivalent thermal history of the samples.

Characterization

Oxidative degradation was investigated through the oxygen containing group formation by following the increase of the carbonyl groups formation (CO) bands in the IR spectra of the irradiated samples, recorded by IR Perkin-Elmer 983 G spectrophotometer.

Optical properties of irradiated copolymer were investigated by the UV-Vis Lambda 5 Perkin-Elmer spectrophotometer.

Determination of the gel content was performed by extraction of the samples covered with nickel-mesh in a Soxhlet apparatus with boiling cyclohexane (MERCK) for 18 h. Then samples were dried to a constant weight in vacuum at 80°C after washing with alcohol. The weight fraction of gel, W_g in %, was calculated as:

$$W_g (\%) = W_g / W_0 \text{ x } 100$$

where W_g is the weight of dry gel after extraction and W_0 is the initial weight of the dry gel.

Characterization of the heat properties was performed by DSC-2 Perkin-Elmer differential scanning calorimeter at a heating rate of 10°C min^{-1} in nitrogen atmosphere.

Results and discussion

The analysis of IR spectra indicates significant changes in the absorption at about 1700 cm^{-1} assigned to oxidation products, Fig. 1. (a, b and c). Oxidation product which is readily observable with irradiated polymers is the carbonyl group [21, 22]. It can be seen that different carbonyl containing species are formed under the action of irradiation in the presence of oxygen. Carbonyl containing groups in irradiated
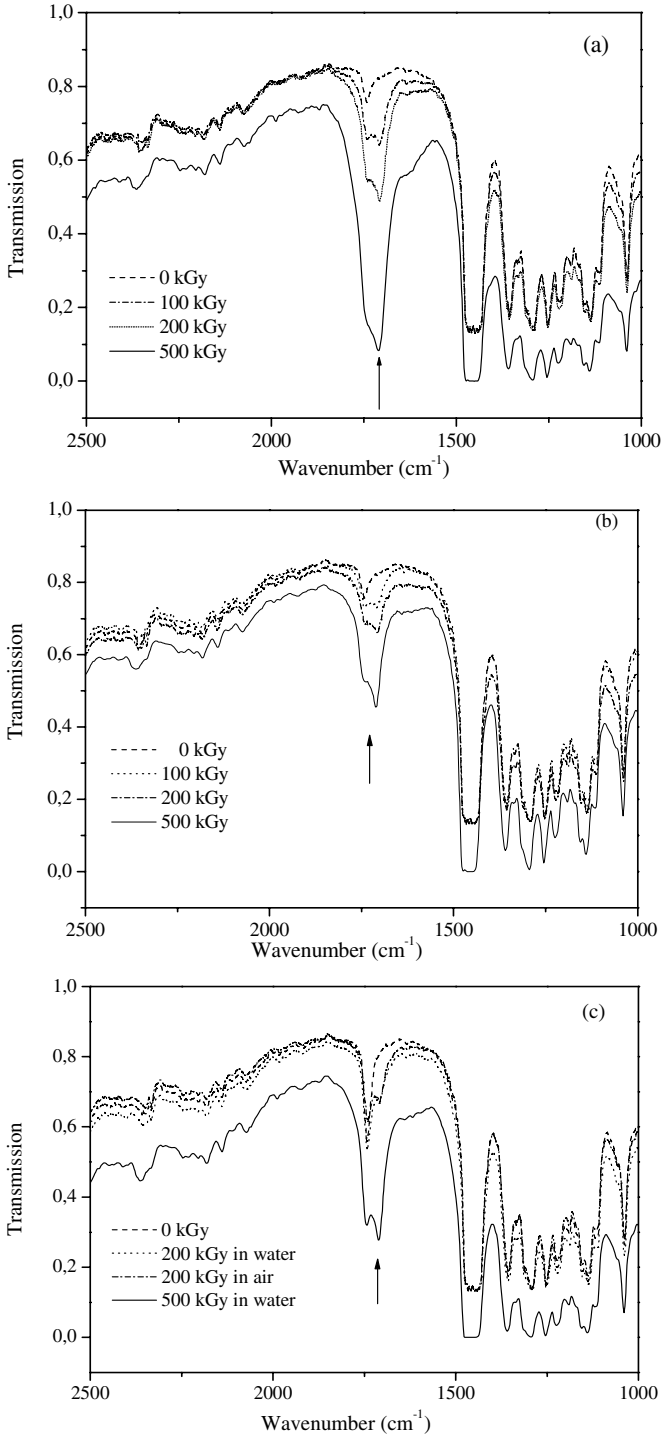
Figure 1. IR spectra of the pristine ethylene-norbornene copolymer irradiated by gamma rays, in the air (a), in the water (b) and with antioxidant irradiated in the air and in the water (c)

ethylene-norbornene copolymer are mainly ketone groups around 1710 cm^{-1} and aldehyde groups around 1740 cm^{-1}. Aldehyde-end groups are formed by the decomposition of peroxides and hydroperoxides formed in the polymer, or by a rearrangement of the peroxy radical intermediate, causing chain scission [23]. The relative contribution of aldehydes and ketones depends on the competition between chain scission reactions and decomposition of hydroperoxides in which water is produced. It has to be noted that in the case of polyethylene, scission processes take place during free-radical mediated chain reaction in irradiated and annealed polyethylene, even significantly under in vacuum conditions [24, 25]. Another carbonyl containing groups formed in the small amount are acid groups at 1705 cm^{-1}, ester groups at 1743 cm^{-1}, α,β unsaturated ketones at 1685 cm^{-1} and peracid at 1785 cm^{-1} [26]. Acid groups are formed in one reaction sequence [27]. Ester formation in heterogeneously oxidizing systems in the solid state is probably caused by condensation reactions between carboxylic acids and alcohol groups [28]. From Fig.1 (a, b and c) it is evident that the evolution of oxidized products is lower in samples irradiated in water, as it was expected. Although the concentration of oxygen in water is much lower than in air, the chemical action of gamma irradiation on distilled water induce generation of oxidizing species the hydroxyl radical and hydrogen peroxide [29, 30], the consequence of which is evolution in oxygen containing groups under the irradiation in water too. In the case of the samples containing an antioxidant, the oxygen containing group observed in the IR spectra originates additionally from the antioxidant itself.

In Figures 2. and 3. the changes in the UV-visible absorption spectra of investigated systems are shown. It can be seen that the increase in the optical absorption occurred both in samples irradiated in air and in water. These changes are assigned to the carbonization and double bond formation which occurred due to the hydrogen evolution. From Fig. 2. it can be seen that double bond formation is not much affected under the irradiation conditions of processing for the lower absorbed doses. The differences are more pronounced for the higher absorbed doses.

On the other hand, the absorption profile is slightly different for the systems containing an antioxidant for irradiation performed in air and in water. This type of primary antioxidant acts as a terminator for the chain reaction in the process of oxidation by the transfer of hydrogen to the peroxy radical [17].

The changes in specific heat capacity and glass transition temperature with the absorbed doses and irradiation conditions for pristine samples and samples containing an antioxidant are shown in Fig. 4. In general, specific heat capacity as well as the onset of various types of molecular motions, e.g. the vibrational and re-orientational motion at the glass-to-rubber transition, the "crankshaft" motion of much shorter segments, depends on the mobility of chain segments. [31,32 and 33]. Mobility and relaxation time of chain segments near T_g depends mainly on free volume [34].

In the glassy state, below T_g, the free volume will be frozen and will remain at a constant value. At T_g, in addition to the normal expansion process, there will be an expansion of free volume itself, which will result in a large expansion of the polymer. Radiation induced crosslinks are fixing the macromolecular segments, resulting in a increase of the glass transition temperature [35]. On the other hand, it is well known that for linear polymers T_g is an increasing function of the molecular weight. T_g varies linearly with the reciprocal of the number-average molecular weight (M_n) of polymers [36]. This dependence is a result of the contribution of chain-end segments to molecular motion. This motion increases the free volume. As the number of chains
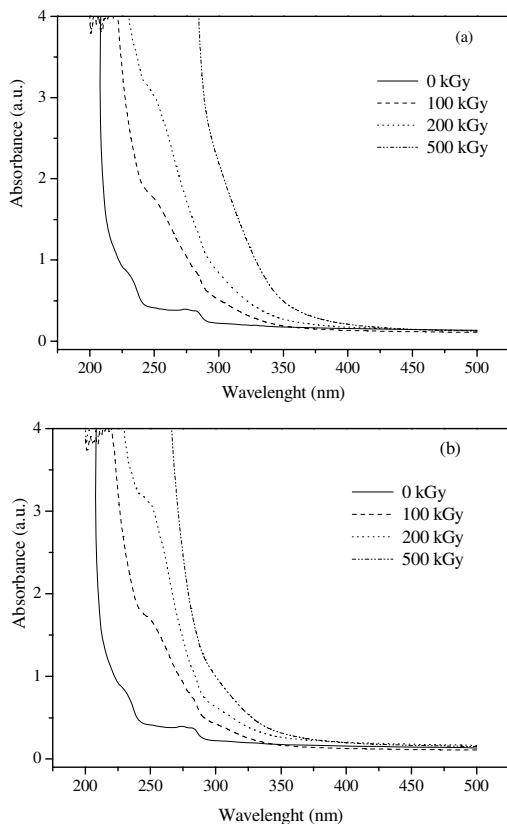
Figure 2. UV-Vis spectra of the pristine ethylene-norbornene copolymer irradiated by gamma rays, in the air (a) and in the water (b)

increases (M_n decreases), the free volume as a whole increases faster with temperature, and the glass transition occurs at lower temperature. Therefore the decrease in the glass transition temperature for the pristine samples irradiated in the air indicates that the oxidative degradation occurred for the absorbed dose of 200 kGy, as shown in Fig. 4(b). It is in accordance with the increase in the carbonyl groups absorption as measured by the IR spectroscopy (Fig. 1). On the other hand, overall decrease in specific heat capacity, especially for absorbed dose of 500 kGy (Figs 4 (a) and (b)) indicates that apart from scission, radiation induced crosslinking occurred. Indeed, according to extraction measurements (as shown in Fig. 5.), the insoluble fraction in samples with antioxidant irradiated with 500 kGy in water was around 23% and in pristine samples irradiated with the same absorbed dose, in water, was around 36%. In general polymers containing at least one hydrogen atom per C atom of the beckbone belong to the gel forming type, but the presence of norbornene in the molecular chains of copolymer causes a higher scission rate compared to polyethylene as well as ethylene-propylene elastomers[37,38]. The greater crosslinking efficiency obtained for samples without antioxidant, irradiated in water, is in accordance with the earlier investigations according to which antioxidants such as hindered phenols suppress crosslinking as well as chain scission reactions [37, 38]. The glass transition temperature remained almost unchanged for the absorbed dose of 500 kGy.
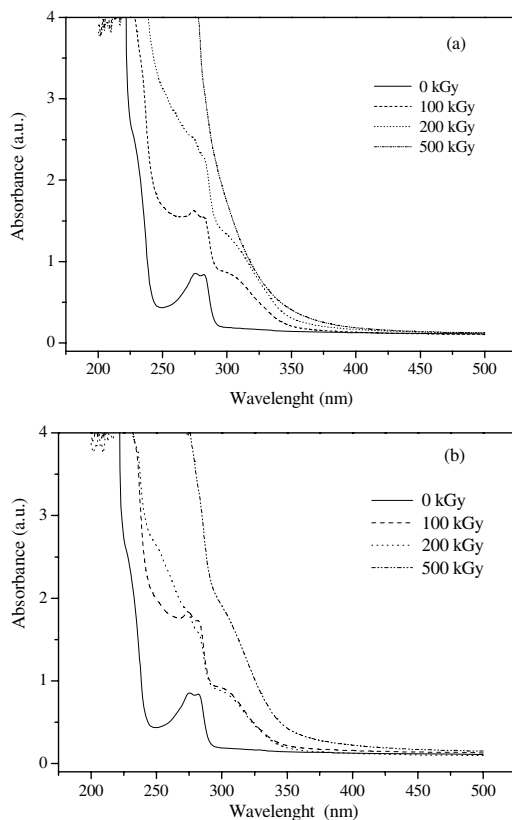
Figure 3. UV-Vis spectra of the ethylene-norbornene copolymer containing an antioxidant irradiated by gamma rays, in the air (a) and in the water (b)
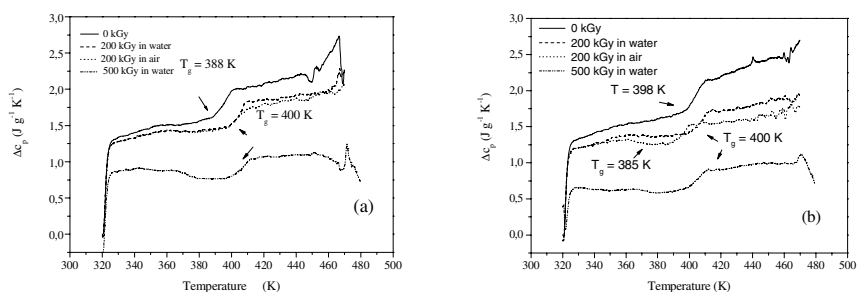

Figure 4. DSC thermograms of the ethylene-norbornene copolymer containing an antioxidant (a), and pristine (b), irradiated by gamma rays in the air and in the water

Appart from the contribution of constrained skeletal vibration, due to crosslinking, to the owerall decrease in specific heat capacity (c_p), changes in the number and the type of group vibrations affect specific heat capacity, even more at the higher temperatures [39]. Namely, contribution of group vibrations to the heat capacity is the result of c_p additivity. In general, for the irradiation of polymer with a moderate amount of energy
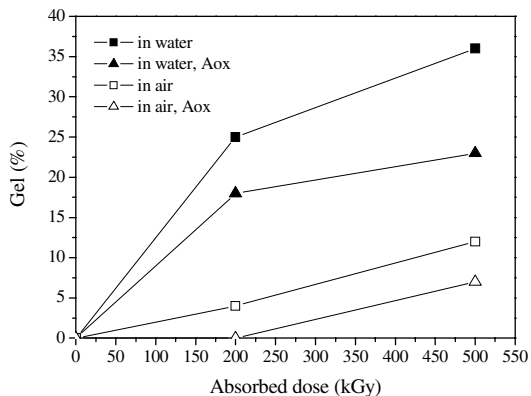
Figure 5. Gel content of the ethylene-norbornene copolymer irradiated by gamma rays in different environments

[40], the accumulation of peroxy radicals produces oxygen containing functions, whose c_p is higher ($c_p = 50.3$ J mol^{-1} K^{-1}) than the value for methylene unit ($c_p = 25.5$ J mol^{-1} K^{-1}). This process occures simultaneously with a branching reactions. Specific heat capacity increases because of the contribution of CH$_3$ unit ($c_p = 29.9$ J mol^{-1} K^{-1}). A longer exposure of polymer samples provides greater amount of free radicals. They are involved in various reactions depending on the availability of oxigen. In the absence of oxigen, recombination, disproportionation and hydrogen abstraction are the main processes that create branches and double bonds on the hydrocarbon chain. Their c_p are 30.9 J mol^{-1} K^{-1} and 22.6 J mol^{-1} K^{-1} respectively. The symilar absorbed dose received by air-irradiated polymer samples generate free radicals which react with molecular oxiden and the peroxy intermediates produce hydroperoxy, hydroxy and ketonic functions. The rate of these processes influences the changing magnitude of the specific heat capacity for irradiated polymer. The c_p values for C-OH and C=O are 16.8 J mol^{-1} K^{-1} and 23 J mol^{-1} K^{-1}, respectively. The contribution of these atom groups to the owerall specific heat capacity value depends on the relative concentration of the constituents.

The differences in the initial glass transition temperatures between unirradiated samples with and without antioxidant are probably the consequence of the presence of the additive. Namely, the antioxidant probably affected mobility, arrangement and packaging of the chains during solvent evaporation and film casting process.

Conclusion

Irradiation of ethylene-norbornene copolymer in different environments caused alternations to the chemical structure of a polymer through different mechanisms of oxidation and change in the amount of double bonds. The difference in the extent of these effects found after irradiation in water and those irradiated in air is caused by the lower concentration of oxygen in water. Insoluble fraction in ethylene-norbornene copolymer was possible to obtain by gamma irradiation with higher absorbed dose for the samples irradiated in water. Changes in the glass transition temperatures and specific heat capacity are observed for the higher absorbed dose.

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