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MODIFICATION OF ETHYLENE-NORBORNENE COPOLYMER BY GAMMA IRRADIATION

The possibility of modifying polyethylene and many other polymers with high energy radiation has led to many useful applications. Due to their new combination of properties and the shortage of experimental data, the radiolysis of a new class of materials, cyclo-olefin copolymers (COC), polymerised from norbornene and ethylene using metallocene catalysts, is of great interest to the study of radiation chemistry and the physics of polymeric systems. Ethylene-norbornene copolymer, pristine and containing an antioxidant were subjected to gamma irradiation in the presence of air and in water. The irradiated copolymer was studied using IR and UV-vis spectrophotometric analysis. The radiation-induced changes in the molecular structure were correlated to changes in the glass transition temperature measured by the DSC method.

The possibility of crosslinking polyethylene and other polymers with high energy radiation, primarily fast electrons and gamma rays, has led to many useful applications and to the understanding of how radiation interacts with large molecules-polymers and how they can be modified beneficially [1-3]. On the other hand, the performance of polymeric materials used in a broad range of applications from electrical supplies to outer space, can be compromised by their working environments, the most deleterious of which are those where ionising radiation is present [4].

The radiation-induced ionisation of the material gives rise to radicals and the subsequent alternation of the structure of the material via radical chemical action. Ionising radiation can cause alternations to the chemical structure of a polymer through mechanisms such as crosslinking, chain scission, oxidation, change in the number and nature of double bonds [5].

Due to their interesting new combination of properties and the shortage of experimental data, the radiolysis of a new class of materials known as cyclo-olefin copolymers (COC), which are obtained by polymerising norbornene and ethylene using metallocene catalysts, is of great interest to the study of the radiation chemistry and physics of polymeric systems. They rank among new polymer materials with remarkable combination of properties, such as glass transition temperature, heat resistance, chemical resistance to acids, low moisture uptake, transparency and, above all, relatively balanced mechanical properties. Moreover, the structure of a polymer with a homogenous matrix enables its use as a

material acceptable for particular applications such as skeletal implants. The aim of the study was to provide the first information on some structural alternations of gamma-irradiated ethylene-norbornene copolymer, as well as information on changes in the glass transition temperature. The glass transition temperature is a property of the polymer related to molecular movements of the chain segments [6, 7]. The amplitudes and frequencies of these movements are highly affected by radiation-induced changes in the polymer chemical structure (chain scission and crosslinking). Due to the profound influence of the environment in which the polymers are irradiated on the consequent chemical reactions [8], gamma irradiation was undertaken in both ambient air and distilled water.

EXPERIMENTAL

Materials

The polymer used for this study was ethylene-norbornene copolymer TICONA TOPAS 6015 S-04 ($T_g = 160^\circ\text{C}$, $M_w = 90000 \text{ g mol}^{-1}$, $\rho = 1.02 \text{ g cm}^{-2}$, bulk density 510 kGy m^{-2}), kindly provided by CELANESE, Ticona Engineering Polymers, Germany. IRGANOX 1010, a phenolic type of antioxidant (purchased from Ciba-Geigy AG), was used. The copolymer was dissolved in boiling toluene with antioxidant (0.5%). The pure copolymer was treated under the same conditions as the stabilised one. Samples in the form of sheets of 0.3 mm thickness were obtained after film casting at room temperature. The samples, 40 x 15 mm pieces, were fixed inside Pyrex glass tubes ($\varphi = 15 \text{ mm}$); for each material one half of the samples were immersed in distilled water during irradiation, while the second half were kept in air.

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Irradiation

Five samples of each kind (fixed in the tubes) were simultaneously irradiated by γ -rays of a Co^{60} source at a dose rate of 6 kGy/h, determined by Fricke dosimetry, at room temperature. In order to prevent the 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 exposure to air.

Characterisation

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

The optical properties of the irradiated copolymer were investigated using a UV-Vis Lambda 5 Perkin-Elmer spectrophotometer.

The thermal behaviour was characterised by a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of 10°C min⁻¹ in nitrogen atmosphere.

RESULTS AND DISCUSSION

Analysis of the IR spectra indicates significant changes in the absorption at about 1700 cm⁻¹ assigned to the oxidation products. The oxidation product which is readily observable in the case of irradiated polymers is the carbonyl group. It may be seen that different carbonyl-containing species are formed during irradiation in the presence of oxygen. The carbonyl groups are mainly ketone groups at 1718 cm⁻¹ (at 1685 cm⁻¹ α,β unsaturated ketones) and aldehyde groups at 1733 cm⁻¹ and both are formed in the amorphous region of the polymer. Aldehyde-end groups are formed by the decomposition of peroxides and hydroperoxides formed in the polymer, or by the rearrangement of peroxy radical intermediates, causing chain scission [9]. The relative contribution of aldehyde and ketones depends on the competition between chain scission reactions and the decomposition of hydroperoxides in which water is produced. It must be noted that crosslinking and scission processes take place during free-radical mediated chain reactions in irradiated and annealed polyethylene, even significantly under vacuum conditions [10,11]. Acid groups, at 1705 cm⁻¹, are formed in one reaction sequence [12]. Other oxygen containing groups are the 1743 cm⁻¹ ester-carbonyl and 1785 cm⁻¹ peracid [12]. Ester formation in a heterogeneously oxidising system in the solid state is probably caused by condensation reactions between carboxylic acids and alcohol groups [13]. It is evident from Figure 1 that the evolution of oxidised products is lower in samples irradiated in water, as expected. Although the concentration of oxygen in water is

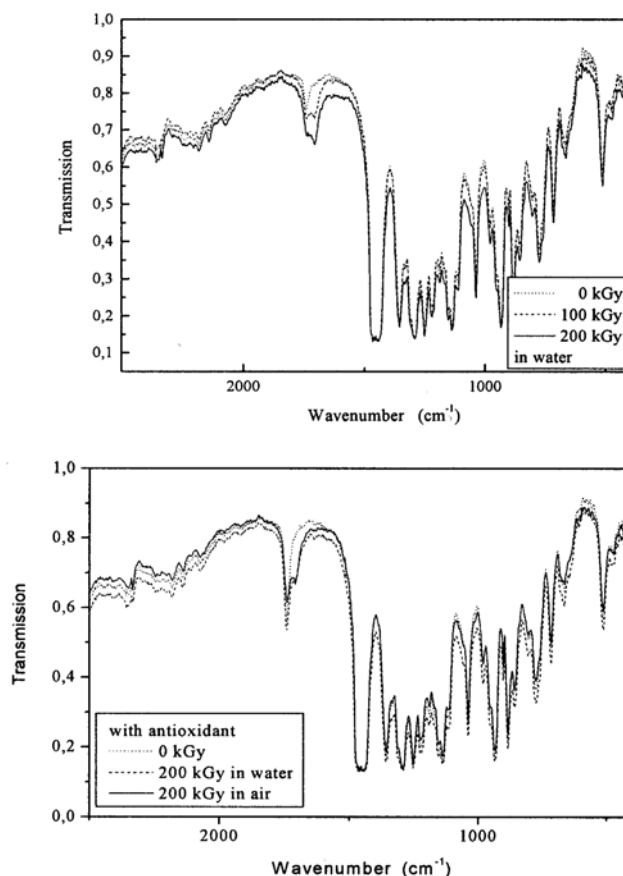


Figure 1. IR spectra of the pristine ethylene-norbornene copolymer and irradiated by gamma rays, in air and in water

Slika 1. IR spektri nemodifikovanog etilen-norbornen kopolimera i ozračenog gama zracima na vazduhu i u vodi

much lower than in air, the chemical action of γ -irradiation on distilled water induces the generation of oxygen [14], as well as oxidising species, the hydroxyl radical and hydrogen peroxide [15], the consequence of which is also the evolution of oxygen-containing groups under the irradiation in water. In the case of samples containing antioxidant, the oxygen-containing group observed in the IR spectra originates from the antioxidant itself.

The changes in the UV-visible absorption spectra of the investigated systems are shown in Figures 2 and 3. Due to its excellent optical properties, ethylene-norbornene copolymer has drawn attention as a candidate for the matrix of polymer-based nanocomposite systems, due to possible applications in optical devices. So the changes in the optical properties under the action of ionising irradiation are important from the practical point of view. It may be seen that the changes in the optical absorption spectra occurred both in samples irradiated in air and in water. These changes were assigned to double bond formation, which occurred after the hydrogen evolution. It may be seen in Fig. 2 that this

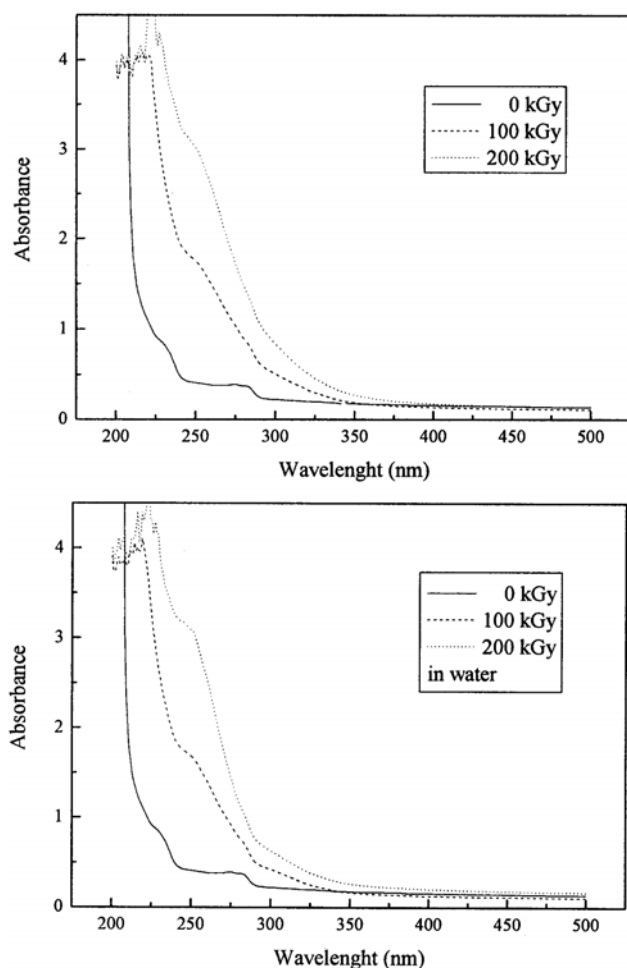


Figure 2. UV-Vis spectra of the pristine ethylene-norbornene copolymer and irradiated by gamma rays, in air and in water
Slika 2. UV-vis spektri nemodifikovanog etilen-norbornen kopolimera i ozračenog gama zracima na vazduhu i u vodi

effect is not affected by the irradiation conditions of the copolymer.

On the other hand, the absorption profile is slightly different for the systems containing the antioxidant for irradiation performed in air and in water. This type of primary antioxidant acts as a terminator for the chain reaction during oxidation by the transfer of hydrogen to the peroxy radical [2].

The changes in glass transition temperature with the irradiation conditions are shown in Figs. 4 and 5. In general, for the irradiated polyolefins, the lower evolution of oxidised products in samples irradiated in water leads to higher crosslinking compared to the effects measured after irradiation in air [2]. The onset of various types of molecular motions, e.g. 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. The manner in which the crosslinking density (gel content) increases with absorbed

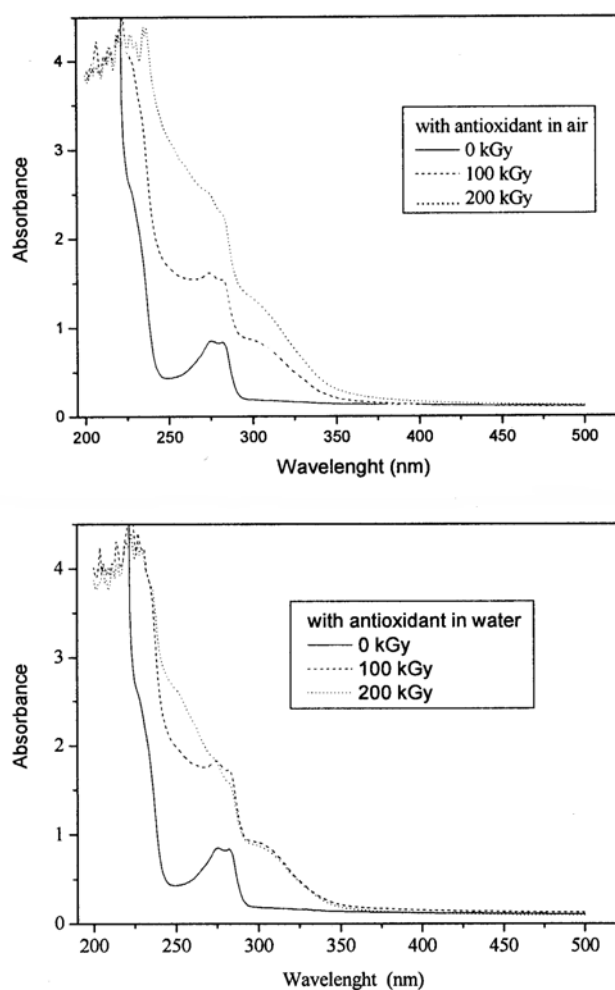


Figure 3. UV-Vis spectra of the ethylene-norbornene copolymer containing an antioxidant irradiated by gamma rays, in air and in water

Slika 3. UV-vis spektri etilen-norbornen kopolimera koji sadži antioksidant, ozračenog gama zracima na vazduhu i u vodi

dose and irradiation conditions indicates the manner in which the restriction in segment mobility due to crosslinking will cause changes in the glass transition temperature [16,17,18]. An increase in the glass transition temperature in the case of antioxidant-containing samples both irradiated in water and in air, as shown in Fig. 4, indicates that crosslinking started at the absorbed dose of 200 kGy.

On the other hand, the decrease in the glass transition temperature for the pristine samples irradiated in air indicates that oxidative degradation occurred at an absorbed dose of 200 kGy, as shown in Fig 5, and is in accordance with the increase in the carbonyl group absorption as measured by IR spectroscopy (Fig. 1). The differences in the initial glass transition temperatures between non-irradiated samples with and without antioxidant are probably the consequence of the presence of the additive.

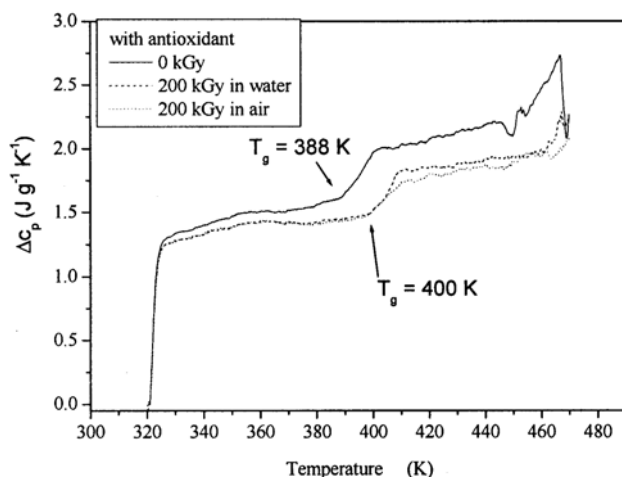


Figure 4. DSC curves of the ethylene-norbornene copolymer containing an antioxidant irradiated by gamma rays, in the air and in the water

Slika 4. DSC krive etilen-norbornen kopolimera koji sadrži antioksidant, ozračenog gama zracima na vazduhu i u vodi

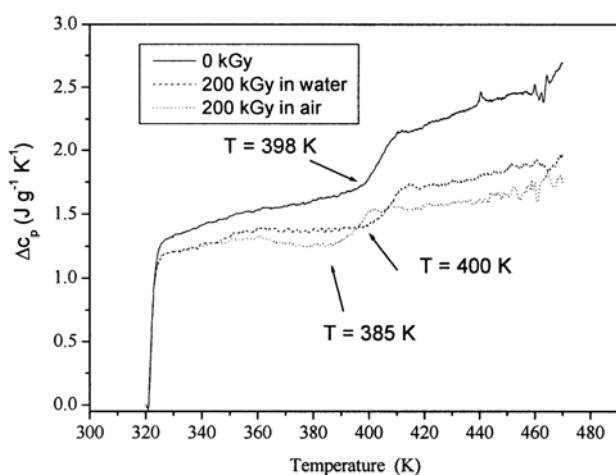


Figure 5. DSC curves of the pristine ethylene-norbornene copolymer and irradiated by gamma rays, in air and in water

Slika 5. DSC krive nemodifikovanog etilen-norbornen kopolimera i ozračenog gama zracima na vazduhu i u vodi

CONCLUSION

The irradiation of ethylene-norbornene copolymer in different environments caused different alternations of the chemical structure of the polymer by different oxidation mechanisms and changes in the nature of double

bonds. The difference in the extent of these effects found after irradiation in water and those irradiated in air was caused by the lower concentration of oxygen in water. Changes in the glass transition temperatures indicated the possibility of crosslinking the investigated copolymer by gamma irradiation in the presence of phenolic type antioxidant.

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IZVOD**MODIFIKOVANJE ETILEN-NORBORNEN KOPOLIMERA GAMA ZRAČENJEM**

(Naučni rad)

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Mogućnost modifikovanja polimera, posebno polietilena, jonizujućim zračenjem omogućila je njihovu mnogobrojnu primenu. Radijaciono modifikovani polimeri se pored ostalog primenjuju i kao skeletni implantati pošto je zračenjem dobijena umrežena struktura otporna na trenje. Usled heterogene distribucije radijacionih efekata u polimerima, kontrola kristalne faze modifikovanih semikristalnih poliolefina je otežana. Amorfni etilen-norbornen kopolimer dobijen pomoću metalocenskih katalizatora je novi polimer sa izvanrednom kombinacijom svojstava pogodnim kako za skeletne implantate, tako i za matricu nanokompozitnih sistema.

U radu su ispitana oksidativna degradacija, optička i toplotna svojstva radijaciono modifikovanog kopolimera do apsorbovanih doza od 200 kGy kao i kopolimera koji sadrži antioksidant fenolnog tipa. Zbog značajnog uticaja sredine u kome je polimer ozračivan, ozračivanje je vršeno na vazduhu i u destilovanoj vodi.

Rezultati IC spektroskopske analize su pokazali da je oksidativna degradacija najzastupljenija u sistemu ozračenom na vazduhu, zbog manje koncentracije kiseonika u vodi. Karbonilne grupe prisutne u uzorcima koji sadrže antioksidant potiču od samog antioksidanta.

Optička svojstva etilen-norbornen kopolimera, dobijena UV-vis spektroskopskom analizom, se menjaju pod dejstvom gama zračenja do apsorbovanih doza od 200 kGy a promene su nezavisne od sredine u kojoj je zračenje izvršeno. Pri ozračivanju u prisustvu antioksidanta optička svojstva sistema ozračenih u vodi, do apsorbovanih doza od 200 kGy se malo razlikuju od onih ozračenih na vazduhu.

Promene temperature ostakljivanja su direktna posledica kako radijaciono indukovane degradacije tako i poprečnog povezivanja. Rezultati merenja specifičnog toplotnog kapaciteta DSC metodom pokazuju nižu temperaturu ostakljivanja za kopolimer ozračen na vazduhu u odnosu na neozračen kao posledicu oksidativne degradacije. Za sisteme koji sadrže antioksidant porast temperature ostakljivanja u odnosu na neozračen kopolimer ukazuju na mogućnost radijacionog umrežavanja etilen-norbornen kopolimera u prisustvu antioksidanta fenolnog tipa.

Ključne reči: Etilen-norbornen kopolimer • Gama zračenje • Antioksidant • Karbonilne grupe • Temperatura ostakljivanja •

Key words: Ethylene-norbornene copolymer • Gamma irradiation • antioxidant • Carbonyl groups • Optical properties • Glass transition •