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Physical effects of radiation processes in poly(aliphatic/aromatic-ester)s modified with e-beam radiation

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ABSTRACT

In this paper, the physical effects of radiation processes in poly(aliphatic/aromatic-ester)s (PED) containing hard segments as in poly(butylene terephthalate)(PBT) and soft segments of dimer of linolic acid (DLA) are reported. PED materials were modified at various doses of ionising radiation (25, 50, 75 and 100 kGy). Radical processes initiated by radiation were investigated by the electron paramagnetic resonance (EPR) and gas chromatography (GC). The results revealed that radiation induced oxidation observed in two different multiblock PBT/DLA copolymers (containing 26 and 30 wt% hard segments, respectively) was strongly inhibited in the presence of α-tocopherol because a significant decrease in consumption of oxygen as well as in production of peroxyl radicals was confirmed.

1. Introduction

The behavior of polymeric materials under the exposure to ionising radiation depend greatly on their chemical and physical structure. From the chemical point of view, a polymer is resistant to radiation if the effect of radiation crosslinking predominates over the degradation process [1,2]. Such a tendency usually results in the improvement of the mechanical properties and is widely applied in radiation processing. The other factor affecting the radiation stability is the ability to efficiently dissipate the energy absorbed during irradiation. It is generally accepted, that aromatic rings, owing to many low lying excited states, are able to dissipate a part of the energy supplied during the radiation treatment and to transform this energy into the heat thus providing protective effect [3].

The oxidative degradation of biomaterials (e.g. in permanent implants as polyethylene components in knee or hip prosthesis) after exposure to radiation is one of main concerns and different antioxidants whose –OH groups acts as a proton donor or acceptor are used to combat this process [4]. Moreover, if polymers are used in drug delivery systems or as scaffolds in tissue engineering, e.g. poly(hydroxybutyrate-hydroxyvalerate) [5,6] and poly(lactide-co-glicolide) [7–9] aliphatic polyesters, they are naturally biodegradable, and their stability/degradability needs to be elucidated in details. The investigation of intermediate species resulting from gamma radiation indicated that the majority of unpaired spins are localized on aliphatic linkages at carbon atoms adjusted to the carbonyl groups [6,7]. EPR spectra of irradiated aliphatic polyesters consist of many lines characteristic for hyperfine splitting of α and β protons. Some of identified radicals proved to be stable even after several weeks [7].

However, when one of the aliphatic ester segments is replaced with aromatic ester sequence, the radiation induced effect in such a copolymer is supposed to change significantly. Among aromatic polyesters, the radiation chemistry of poly(ethylene terephthalate) (PET) is the most widely documented [10,11]. Breakage of the main chain is believed to result predominantly from β-bond scission of alkyl radicals [12]. In order to inhibit such a tendency, Jones et al. [13] successfully applied the impregnation with acethylene, whereas Abdel-Reim et al. [14] used an addition of polyfunctional monomers.

Nevertheless, the physical and mechanical properties of copolymers constructed from components of well known characteristics cannot be predicted on the basis of the monomer features as our earlier studies confirmed that in segmented copolymers the ionising radiation induces other radicals in domains constructed from ε-caprolactone units than that found in poly(ε-caprolactone) homopolymer [15]. Thus, the effect of irradiation has to be investigated for each particular copolymer system.

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In our study we examined multiblock copolymer's behavior upon the exposure to different doses of ionising radiation. These systems contain hard domains of aromatic ester as in poly(butylene terephthalate) (PBT) and soft segments composed from hydrogenated and distilled dimer acid (vegetable derived liquid fatty acid, abbreviated here as dilinoleic acid, DLA), creating aliphatic ester sequences upon the reaction with glycol. Since these poly(aliphatic/aromatic-ester)s (abbreviated in this work as PBT/DLA or PED copolymers) are biocompatible *in vitro* and *in vivo* [16,17], their resistance to potential radiolysis when sterilized or e-beam modified is of great importance. The phenylene groups present in the copolymer structure should partly preserve the material from decomposition initiated by irradiation. DLA monomer is characterized by good hydrolytic and thermo-oxidative stability, but in order to protect PED against possible radiation induced degradation, we used α-tocopherol (TOH) (high efficiency of this agent on radiation stability of different systems was suggested earlier by many authors [18,19]). However, no data existed to show that α-tocopherol (vitamin E) is as an effective antioxidant for PED after irradiation. Therefore, the EPR spectroscopy was used to investigate the nature and relative concentration of radicals formed upon the exposure of PED copolymers to ionising radiation. The physicochemical effects of the radical processes were estimated in this work.

2. Experimental

2.1. Materials

Two different PBT/DLA copolymers containing 26 wt% and 30 wt% PBT hard segments, and 74 wt% and 70 wt% DLA soft segments, with chemical structure presented in Scheme 1, were synthesized by melt polycondensation as reported earlier [20]. Their analogues containing 1 wt% (0.6 wt% by monomers feed) α-tocopherol solution (97%) obtained from Medana Pharma Terpol Group, were synthesized in an identical way. The composition and selected properties are presented in Table 1.

Table 1
Description of synthesized PED multiblock copolymers.

Sample code	Sample abbreviation	PBT content (wt.%)[a,d]	α-tocopherol	DPh	Mn [g/mol][b]	[η] [dL/g][c]
1	PBT/DLA 26/74	26	–	1	220	0.790
2	PBT/DLA 30/70	30	–	1.3	286	0.998
3	PBT/DLA 26/74 + TOH	26	+	1	220	0.866
4	PBT/DLA 30/70 + TOH	30	+	1.3	286	0.870

DPh – Degree of polymerization of the hard segments.

[a] Calculated from the feed at the entrance to the reactor.

[b] Molecular weight of the hard segments calculated from the DPh values.

[c] Limiting viscosity number (inherent viscosity) determined in PhOH/$CHCl_3$ solution at 30 ± 1 °C.

[d] The rest are dimmer fatty acid (here dilinoleic acid) segments.

2.2. Irradiation

Polymers were examined at room temperature and irradiated with a 10 MeV electron beam generated in a linear electron accelerator Elektronika 10/10 to the following doses: 25, 50, 75 and 100 kGy. The total doses were obtained by multipass exposure (ca. 25 kGy per one pass).

Only for EPR measurements samples were irradiated in a ^{60}Co gamma source (Issledovatel, dose rate – 1.28 kGy/h) to a dose of 5 kGy at 77 K (samples were immersed in liquid nitrogen). The cryogenic conditions were necessary in this case since preliminary EPR experiments showed that in studied copolymers, the radicals generated by radiation are unstable at ambient temperature and decay just during irradiation.

2.3. EPR spectroscopy

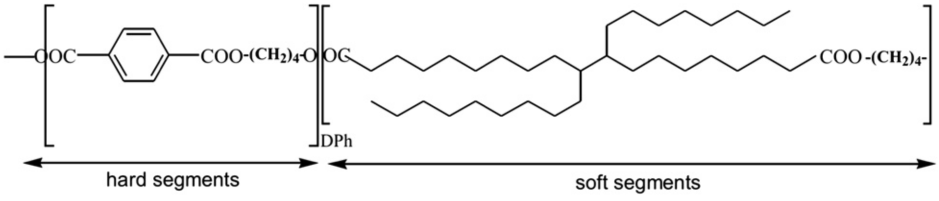
EPR spectra were recorded using a CW Bruker ESP 300 series spectrometer operating at 100 kHz field modulation. The microwave power was set up at 100 μW for all measurements. The spectra were recorded directly upon irradiation of the samples, as well as after their annealing at temperatures indicated in the figures and recooling to 77 K. We assumed that the polymers are in equilibrium with surrounding oxygen since, except temporary settings in liquid nitrogen, the copolymers remained in contact with air. Temperature was controlled with a thermocouple placed in the middle of the samples inserted in quartz finger dewar. The radical concentration was determined by comparison of the spectra areas obtained by double integration of experimental signal.

2.4. Gas chromatography

The radiation yields of hydrogen G(H_2) abstracted from polymers together with consumption of oxygen from the space above samples G($-O_2$) were determined with a gas chromatograph Shimadzu – 14B. A 1 m long column packed with 5A molecular sieves and the thermo-conductivity (TCD) element by Shimadzu was used as detector. The chromatograph was attached by interface ADAM (range 1 V or 0.15 V), with sampling frequency of 10 Hz to the PC computer where the data were acquired by program CHROMNEW and processed by program CHROMAP. The carrier gas was argon (99.99%), calibration gas – hydrogen 99.99%. The measurements were performed using syringes, capacity 25 μL. The system was operated at 220 °C, temperature on the column was kept at 40 °C and on the detector at 120 °C. The flow rate of carrier gas was 10 mL/min.

2.5. Contact angle measurements

Dynamic contact angle *versus* water was measured using Tensiometer K100C (Krüss) supplied with the thermostattable sample vessel at 23 °C. Applying Wilhelmy method, ten measurements for each copolymer were performed (film size: c.a. 2 × 3 cm,



Scheme 1. Structure of poly(aliphatic/aromatic-ester)s (PED). DPh – Degree of polycondensation of hard segments (1 and 1.3 for samples 1, 3 and 2, 4, respectively).

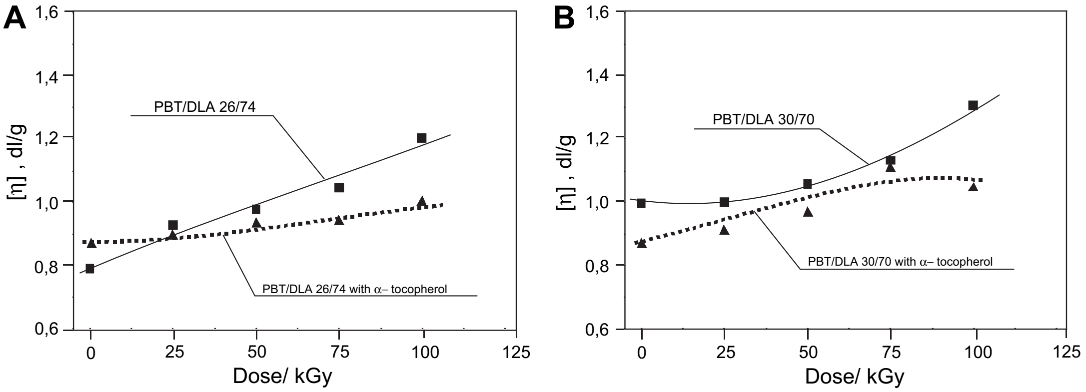


Fig. 1. The limiting viscosity number [η] of PEDs with and without α-tocopherol (A-26 and B-30 wt% of hard segment) *versus* doses of ionising radiation.

thickness 0.2 mm). Reported results correspond to the average value.

2.6. Viscosity

The limiting viscosity number ([η], LVN) of PBT/DLA copolymers in phenol – trichloroethylene (50:50 vol/vol) was determined by an Ubbelohde viscometer IA at 30 °C.

2.7. Gel fraction

The gel fraction [X] of PBT/DLA copolymers in thetrahydofuran was determined by Soxhlet extraction.

3. Results and discussion

The method of e-beam radiation is widely used for the improvement of mechanical properties of polymer and functional features such as shape memory, sterilization or surface grafting. Usually, the changes in polymer properties, including viscosity and crosslink density are increasing with radiation dose if the crosslinking processes prevail over the degradation.

The limiting viscosity number was measured for PED copolymers and the results are presented in Fig. 1. As can be seen from the graph, the intrinsic viscosity gradually increases with increasing radiation dose. This can be ascribed to the formation of crosslinks upon irradiation. The effect is more significant for materials containing a higher percentage of PBT hard segments. Interestingly, the materials containing TOH showed lower values of [η] as compared to un-modified polymers.

It can be postulated, that an increase in the inherent viscosity indicates that radiation crosslinking proceeds and this process exceeds the main chain scission. Measurements of the gel fraction, X, supports this observation indicating an increase of X values with increasing radiation dose, as presented in Fig. 2.

In order to verify this statement and to investigate the nature and relative concentration of radicals formed upon the exposure of PED copolymers to ionising radiation, the EPR measurements were performed. All EPR spectra were recorded at 77 K in order to eliminate the influence of dynamics on the shape of detected signals. Both copolyesters (PBT/DLA 26/74 and PBT/DLA 30/70, Table 1), regardless of differences in proportions between hard and soft segments, show similar EPR spectra upon irradiation. For that reason, a sequence of detected EPR signals is presented only for PBT/DLA 26/74 sample. A singlet of $g = 2{,}0028$ and half-intensity linewidth $H = 0.97$ mT has a dominant contribution at 77 K, Fig. 3A. There are also traces of other components as indicated on wings of the spectrum recorded directly after irradiation. The separation between the extrema of outermost peaks reaches 12.5 mT. Sample annealing at 150 K results in decrease of the central singlet whereas a slope of side-absorptions slightly rises. Above 150 K an asymmetric singlet of parameters characteristic for peroxyl radicals is growing. Just at 180 K this is the only paramagnetic product present in the system that subsequently decays gradually to 210 K.

The main products observed after radiolysis cannot be unambiguously identified due to lack of lines typical for the interaction

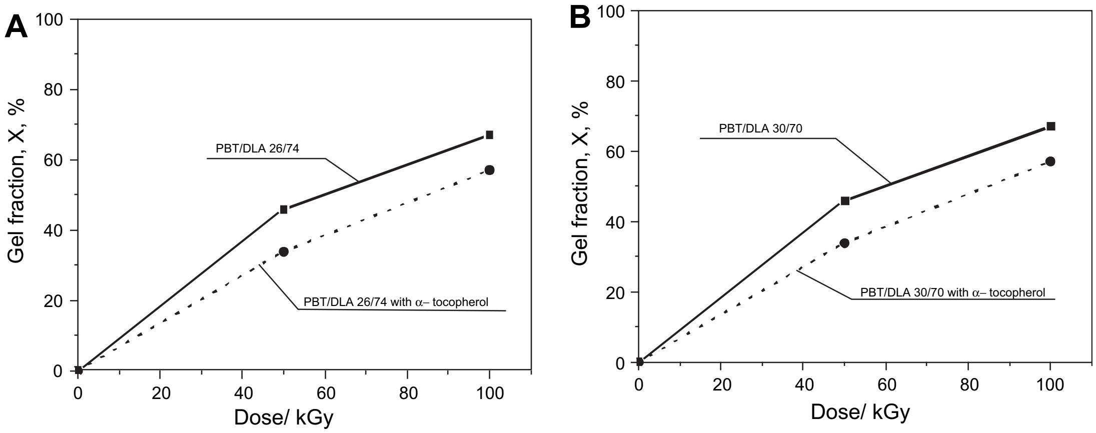


Fig. 2. The gel fraction [X] of PEDs with and without α-tocopherol (A-26 and B-30 wt% of hard segments) *versus* doses of ionising radiation.

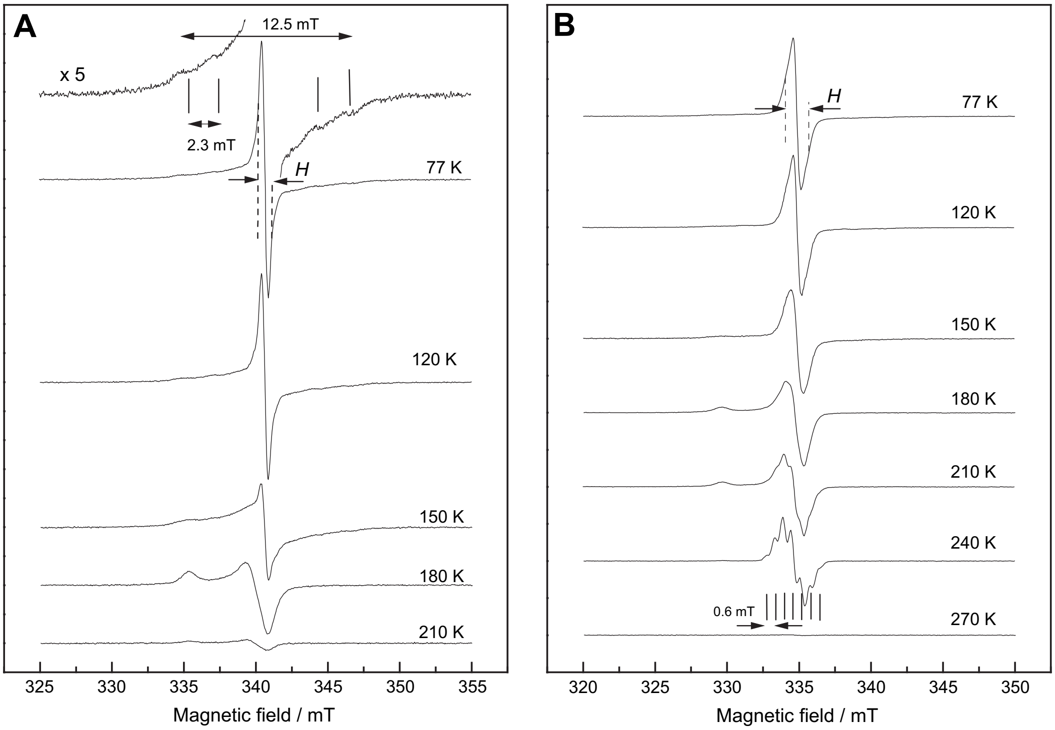


Fig. 3. EPR spectra measured at 77 K and upon annealing to indicated temperatures. A – sample 1, B – sample 3.

between unpaired spin and protons, contrary to the paramagnetic species found previously in aliphatic polyesters. In irradiated poly-(D,L-lactide-*co*-glycolide) several such species were confirmed: $-CH_2^{\bullet}$, $-CH^{\bullet}(CH_3)$, $-C^{\bullet}(CH_3)-$, $-OCH^{\bullet}-$, some of them are stable even at ambient temperature [5,6]. On the other hand, radiolysis of PET containing aromatic rings in the main chain was studied by Jones et al. under cryogenic conditions [13]. According to the authors, the ethylene linkage facilitates the probability of β-bond scission; consequently the extension of alkyl chain, e.g. in PBT, should improve the radiation stability. Such a conclusion was also confirmed by Aliev et al. who estimated that the yield of radiation degradation of PBT and PET is 0.014 and 0.023 µmol/J, respectively [12].

Based on the results presented in Fig. 3A, we suggest that detected singlet is a superposition of several radical products having the active centre located at the position that render hyperfine splitting originating from hydrogen atoms impossible. At 77 K the most probable intermediate is anion radical associated with the aromatic groups of macromolecules. Pierpoint et al. [21] and Cooke et al. [22], suggested that the fragmentation of polyester based polyurethane might result in the formation of first ordered

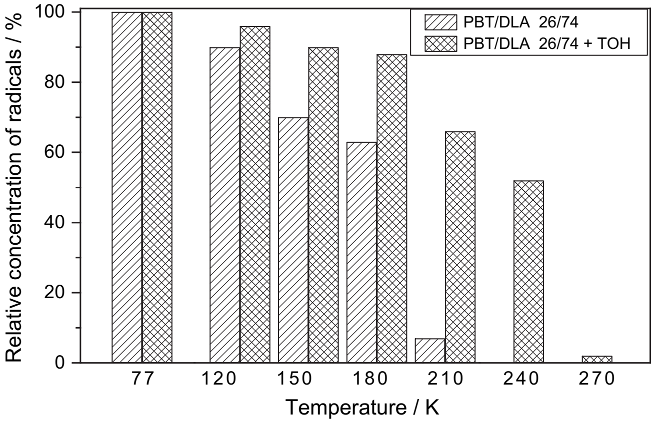


Fig. 4. Relative concentration of radicals in function of temperature for samples 1 and 3.

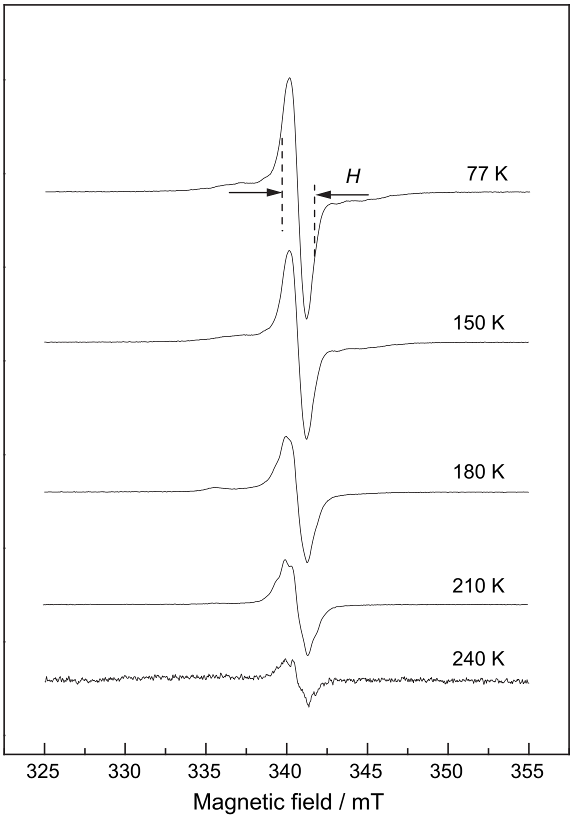
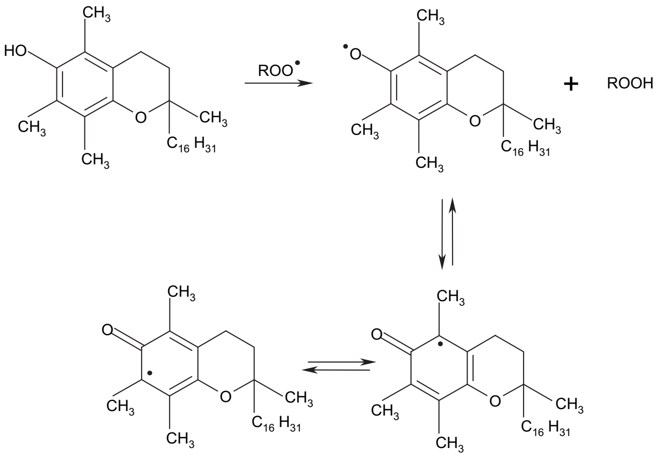


Fig. 5. EPR spectra of α-tocopherol measured at 77 K and upon annealing to indicated temperatures.



Scheme 2. Formation of hydroperoxide.

Table 2
Advanced contact angle of materials before and after irradiation.

Sample	Contact angle before irradiation [°]	Contact angle after irradiation with a dose of 25 kGy [°]	Contact angle after irradiation with a dose of 50 kGy [°]
1.	89 ± 3	86 ± 4	84 ± 2
2.	83 ± 3	84 ± 3	84 ± 2
3.	83 ± 3	87 ± 5	86 ± 5
4.	90 ± 1	84 ± 2	85 ± 2

alkyl radical $–CH_2–CH_2•$. Production of this intermediate has to be associated with formation of five lines separated by a distance typical for this type of radicals. However, the EPR spectra detected for PEDs do not confirm the presence of such a product. The external lines of very weak intensity and a distance of c.a. 2.4 mT represent probably alkyl radical, $–CH_2–CH•–CH_2–$ [23], which was identified also in other esters [24]. On the other hand, the spectrum might be also superposition of several carbon-centered radicals as revealed hyperfine splitting is characteristic for these types of intermediates.

Double integration of EPR spectra enabled to estimate changes in relative concentration of radicals since the obtained value are proportional to a number of unpaired spins in the system. Assuming that at 77 K concentration of all detected radicals constitute 100%, the quantitative analysis allowed to determine the relationship between annealing temperature and fraction of paramagnetic species which avoid decomposition at selected temperature, Fig. 3. At 180 K the only detected paramagnetic intermediate was peroxyl radical of characteristic $gz = 2.035$ and unresolved gx and gy lines [25] (Fig. 4).

It was found that at this temperature almost 60% of all radicals detected at 77 K is still present in the sample, thus we concluded that such a fraction of paramagnetic species undergoes oxidation. It is generally accepted that the process between O_2 and carbon-centred radicals is very efficient. Between 120 and 150 K the formation of additional amounts of carbon-centred radicals results in a gradual increase in absorption on the both sides of diminishing centerfield singlet. In the range of temperatures 150–180 K these intermediates are promptly oxidized to peroxyl radicals, $R• + O_2 \rightarrow ROO•$. It was confirmed that free radicals decay completely just below the glass transition temperature of soft segments, $T_g = 220$ K.

Oxidative degradation might be partly inhibited by antioxidants. The EPR spectra of irradiated copolymers doped with 1% admixture of α-tocopherol are shown in Fig. 3B. At 77 K a half-intensity linewidth of the singlet (marked on the figures with symbol “H”) recorded for PBT/DLA 26/74 + TOH is about twice larger than the linewidth of the material without α-tocopherol, 2.01 and 0.97 mT, respectively. These changes result from contribution of the signal attributed to α-tocopherol radicals which linewidth H at 77 K is near 2.2 mT, Fig. 5. During irradiation, the primary species are generated in a chief constituent, i.e. in the polymeric matrix, thus a considerable increase in the linewidth observed for PBT/DLA 26/74 + TOH signal in comparison with linewidth of the spectrum detected for the sample free from α-tocopherol, has to result from transfer of active sites generated in the copolymer towards doped antioxidant. Eventually, they are trapped forming relatively stable tocopherol radical. Such a phenomenon was earlier observed for sterically hindered phenols in non-polar systems [26]. It was found that radical ions of polyethylene, specially cationic intermediates, react very efficiently with the antioxidant forming phenoxyl radicals.

At elevated temperatures, the paramagnetic species convert to peroxyl radicals. Nevertheless, in the presence of α-tocopherol, hydroperoxide is formed efficiently due to hydrogen transfer shown in the Scheme 2. The stabilising action interrupts the migration of radical centres in macromolecules. The fully methylated ring together with chroman group significantly increase the stability of tocopherol phenoxyl radical [18].

According to the above mechanism, after annealing, the delocalisation of the unpaired electron in π system of aromatic ring is possible enabling its interaction with hydrogen atoms. In liquid phase hyperfine splitting (hfs) of phenoxyl radical is arising from interaction between spin and six hydrogen atoms located in

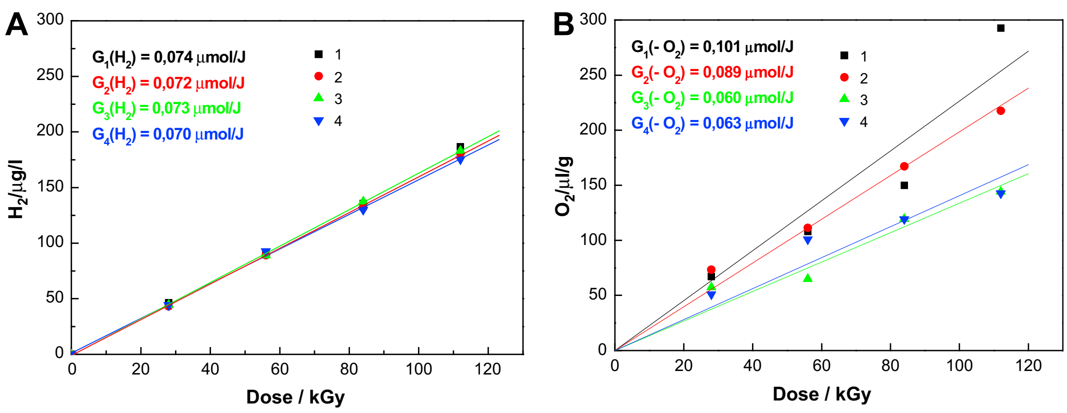


Fig. 6. Radiation yield of A – emission of hydrogen $G(H_2)$ and B – uptake of oxygen $G(–O_2)$.

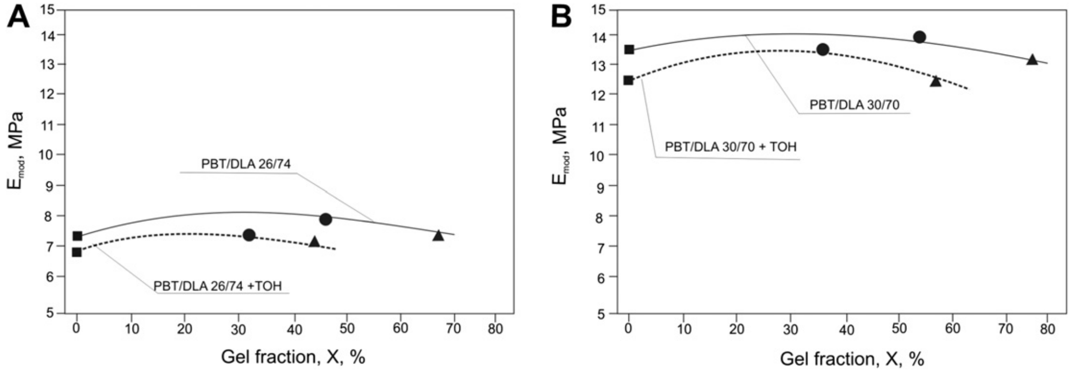


Fig. 7. Modulus at 10% strain of PEDs with and without α-tocopherol (A-26 and B-30 wt% of hard segment) *versus* content of gel fraction, X. ■ – at 0 kGy, ● – at 50 kGy, ▲ – at 100 kGy.

two ortho-methyl groups together with small couplings with some other protons [27]. Nevertheless, in rigid polymeric matrix only hfs originated from two methyl substituents was revealed since a characteristic septet is observed at elevated temperatures, Fig. 3B; a distance between the lines is almost constant (c.a. 0.6 mT) what confirms coupling of unpaired electron and six nearly equivalent hydrogen atoms. Such a spectrum of weakly resolved lines contributes also in the EPR signal detected for α-tocopherol following annealing at 240 K, Fig. 5. At this temperature, an irradiated TOH reveals similar absorption of the same distances among emerging lines what confirms earlier interpretation. The changes observed in the EPR spectra we attributed to the relaxation of phenoxyl radical structure initiated by heating above 200 K [28].

The results indicate that radical centres are transferred to α-tocopherol in early stages of radiolysis as well as upon radical oxidation protecting material against subsequent radical processes. For the sample containing TOH, half of radicals detected at 77 K survive annealing to 240 K whereas in copolymer free from the antioxidant all radicals decay, Fig. 3. Thus quantitative analysis of EPR spectra indicates that α-tocopherol traps at least 50% of the primary intermediates detected directly upon irradiation or their successors and that its activity in studied multiblock poly(aliphatic/aromatic-ester)s is relatively high.

Radiation yields of hydrogen for all studied copolymers, both doped and undoped with TOH, are comprised in the range of 0.070–0.074 μmol/J, as presented in Fig. 6A. Such insignificant changes indicate that the presence of the antioxidant does not influence on the hydrogen abstraction. Thus TOH activity is important for radical processes other than homogeneous dissociation of C–H bonds. Radiation yield of hydrogen G(H2) is considered as a result reflecting extend of the production of alkyl radicals that might contribute in crosslinking. As was found by EPR spectroscopy, the competition process, i.e. oxidation, is effective and concerns both primary and secondary alkyl radicals. The tendency is limited by α-tocopherol since uptake of oxygen for the system containing the antioxidant is almost twice lower than for the material free from protective agent (sample 1 and 3), Fig, 6B. Affinity to oxygen is slightly higher for samples characterized by lower contribution of aromatic hard segments.

PED multiblock copolymers constructed predominantly from soft segments of hydrogenated hydrocarbon chains of 70–74% are hydrophobic and therefore relatively high average dynamic contact angles *versus* water were found for all samples, i.e. about 86° (Table 2). Contact angles are important macroscopic parameters characterizing surface wettability. As was unambiguously confirmed by EPR spectroscopy the radical processes initiated by ionising radiation lead to the formation of peroxyl radicals, precursors of many polar, oxygen containing groups, e.g. hydroperoxide, hydroxyl or carboxyl groups [6]. Taking into account what the content of polar moieties increases, contact angle values for irradiated materials *versus* water ought to be lower than for the untreated materials. Contrary to this expectation upon irradiation with doses of 25 and 50 kGy, variations in the values of advanced contact angle are in the limits of experimental error. Earlier studies carried out by Gorna and Gogolewski [29] confirmed that the contact angle in some cases even arises, in spite of oxidation. They suggested that after irradiation, the contact angle of hydrophilic materials is reduced whereas in hydrophobic, e.g. poly(ester-urethanes), the tendency is opposite due to the reorganization of the domains. Such a process leads to migration of soft segments towards the surface and to the growth of hydrophobic features. It seems that a similar phenomenon is observed for PBT/DLA copolymers. Admixture of α-tocopherol has no influence on the character of surface wettability.

In our earlier work [30,31], we demonstrated that that the use of e-beam irradiation and the amount of irradiation dosage had a significant influence on the mechanical properties increasing tensile strength and elongation at break of the materials due to the formation of the crosslinked network structure. The observed changes in mechanical properties (E modulus vales taken from [30]) were correlated with gel fraction content and showed in Fig. 7. The E modulus is higher for samples characterized by higher gel content thus indicating and confirming that the crosslinking predominantly occurs in the hard segments, what has already been postulated in our earlier work [30,31].

4. Conclusions

Poly(aliphatic/aromatic-ester) PED multiblock copolymers are very interesting group of materials (intensively investigated for medical applications) that might be efficiently modified by ionising radiation. EPR as well as GC results indicate that the formation of radicals proceeds together with their dehydrogenation during the irradiation. Although the phenomena can lead either to radiation crosslinking or radiation decomposition (e.g. by β-scisson), it seems that the first effect prevails over degradation as a gradual increase of gel fraction was observed with increasing dose up to 100 kGy. However, for long term effects of radiation induced oxidation, confirmed by EPR and GC techniques, might play an important role. It was found that α-tocopherol inhibits the formation of peroxyl radicals as well as consumption of oxygen, acting as an efficient antioxidant.

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