

Influence of e-beam irradiation on the chemical and crystal structure of poly(aliphatic/aromatic-ester) multiblock thermoplastic elastomers

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Poly(aliphatic/aromatic-ester) (PED) multiblock copolymers belong to the class of thermoplastic elastomers (TPEs), characterized by a physical network of semi-crystalline hard segments. The PEDs were modified with e-beam to create an additional network structure. Polymers were evaluated using SEC, WAXS, DSC and quasi-static tensile tests. E-beam irradiation induced a significant increase of molecular weight and tensile strength of the PEDs. This effect, together with the diminished degree of crystallinity can be explained by the formation of chemical crosslinks, which are located in the hard phase segments.

Keywords: biopolymers, thermoplastic elastomers, e-beam irradiation, multiblock polyesters, DSC.

INTRODUCTION

Thermoplastic elastomers (TPEs) are polymeric materials, which combine the mechanical properties of vulcanized rubbers with the processability and recyclability of thermoplastics. Multiblock-type thermoplastic elastomers (TPEs) such as poly(ether-ester)s or poly(ether-amides) contain at least two types of chemically attached incompatible polymeric blocks. While macroscopically homogeneous, these polymers phase separate on a microscopic (nanometer) scale. The discreet plastic phases embedded in the continuous elastomer phase provide “physical crosslinks” and self-assemble to form a stable but thermally reversible structure. They can be tailor-made by using simple step growth polymerization processes with precisely adjusted amount of constituting blocks (segments) on the feed. Their properties are changing with composition, starting from soft “rubber-like” materials to hard and stiff “thermoplastic-like” polymers. TPE can be easily modified by chemical and physical methods in order to change surface characteristics or mechanical performance. If good fatigue properties (low creep) are required, they can be modified with e-beam radiation^{1,2}.

In our work we investigate multiblock poly(aliphatic/aromatic-ester) copolymers (PED) recently developed for medical applications. These PEDs are transparent at < 50 wt.-% hard segment content and they resemble medical-grade silicone rubber. The PED copolymers contain hard domains of an aromatic ester, poly(butylene terephthalate) (PBT), and soft segments composed of hydrogenated and distilled dimerized fatty acid (vegetable derived liquid fatty acid, abbreviated here as (di) linoleic acid, DLA), creating aliphatic ester sequences upon reaction with glycol. Since these poly(aliphatic/aromatic-ester)s show biocompatibility *in vitro* and *in vivo*³⁻⁶, their resistance to potential radiolysis when sterilized or e-beam modified is of great importance⁷. We already demonstrated that PED copolymers showed enhanced stability toward ionizing radiation without sign of stable free radicals formation⁷. In this paper, we focused on the chemical and crystal structure changes upon PED modification with various dosages of e-beam irradiation. The effect of observed changes on thermal and mechanical properties will be discussed.

EXPERIMENTAL

Materials and synthesis

The materials for this study are segmented polyesters containing poly(butylene terephthalate) (PBT) sequences (hard segments) extended with the butylene ester of dimerized fatty acid (DLA), abbreviated here as (di) linoleic acid (soft segments). The semi-crystalline PBT is the hard segment phase while DLA is an amorphous material, which imparts the elastomeric characteristic to the polymer and therefore represents the soft segments phase. The biocompatibility of PBT and DLA has been well established and both can be used as a biomaterial or as blend components. The chemical structure of the segmented PED copolymer is shown in Fig. 1.

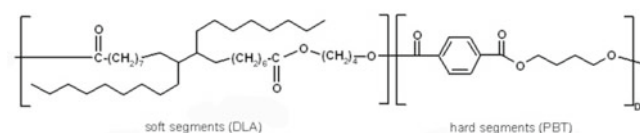


Figure 1. Chemical structure of poly(aliphatic/aromatic-ester) (PED) multiblock copolymers

In this study, two hard/soft segment ratios were investigated (PBT-26 and PBT-30) containing 26 wt.-% PBT and 74 wt.-% DLA, and 30 wt.-% PBT and 70 wt.-% DLA, respectively.

The segmented PED multiblock copolymers were obtained in a two-stage process of transesterification and polycondensation from the melt, which was described in previous publications^{3,6}.

Irradiation

After polymerization, the materials were first compression-moulded and then e-beam irradiated at the Institute of Nuclear Chemistry and Technology (Warsaw). A linear electron accelerator Elektronika 10/10 was used to generate a 10 MeV beam for different dosages, namely 50, 75 and 100 kGy at room temperature.

Size exclusion chromatography (SEC)

The molecular weight (M_n , M_w) and molecular weight distribution (M_w/M_n) of the block copolymers were

determined by Size Exclusion Chromatography (SEC) using a Waters system equipped with six Styragel-HR columns (106, 105, 104, 103, 500, and 100 Å pore sizes), thermostated at 35°C, a Waters 410 DRI detector thermostated at 40°C, a Dawn DSP 18 angle laser light scattering detector (MALLS) (Wyatt Technology), and a Waters 996 UV detector. The mobile phase for the SEC was tetrahydrofuran (THF) at 1 ml/min, continuously distilled off CaH₂ and recirculated. The ASTRA[®] software (version 5.3.2.14) was used to obtain MW data calculate using $dn/dc = 0.183$ given for polystyrene (polystyrene equivalent M_w) and also, assuming 100% mass recovery. This method gave good agreement with M_w data obtained by assuming 100% mass recovery on the columns.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) scans were performed with a TA Instruments (DSC Q100) apparatus. The samples were dried in vacuum at 60°C, and then kept in a desiccator. The process was carried out in a triple cycle: first heating, then cooling, and second heating in the temperature range from -100 C to 50°C higher than the melting point of the hard phases of each copolymer. The rate of heating and cooling was 10°C min⁻¹. In addition, the melting enthalpy ΔH_m (second heating) of PBT and the mass content of PBT crystallites w_c were calculated.

Wide-angle X-ray scattering (WAXS)

WAXS spectra were recorded at room temperature and 2θ values between 10° and 38° were obtained at a rate of 0.5°/min with 0.02° steps. The TUR M62 X-ray Diffractometer set in reflection mode was operated at 40 kV and 30 mA with a Cu-K α radiation wavelength of 1.542 Å. To prepare for the experiment, thin film specimens of both the neat and after e-beam irradiation thermoplastic elastomers were prepared via compression molding.

Tensile testing

The quasi-static tensile data were collected at room temperature with an Instron TM-M tensile tester equipped with a 500 N load cell employing a crosshead speed of 100 mm/min according PN-ISO 527-1:1998. The starting clamp distance was 25 mm. The obtained results were averaged from 6 specimens with cross section of 0.5×4 mm.

Gel fraction

The gel fraction was measured by extraction. Small pieces of polymer films (0.1–0.2 g) were placed in Schott's crucibles (P2 type) and extracted with boiling THF (100cm³) for 3 h. The samples were then dried and weighed in order to calculate the gel fraction using equation (1):

$$X = (m_1/m_0) * 100\% \quad (1)$$

where: m_1 – mass of dried sample after extraction
 m_0 – mass of sample before extraction

RESULTS AND DISCUSSION

Size exclusion chromatography (SEC)

Fig. 2 shows the high resolution SEC traces. In general, polymer of lower hard segments content, PED-26 (Fig 2a) showed a multimodal distribution (especially after radiation modification) with high M_w shoulder in the MALLS curve while material containing higher content of hard segments, PED-30 (Fig 2b) showed multimodal distribution.

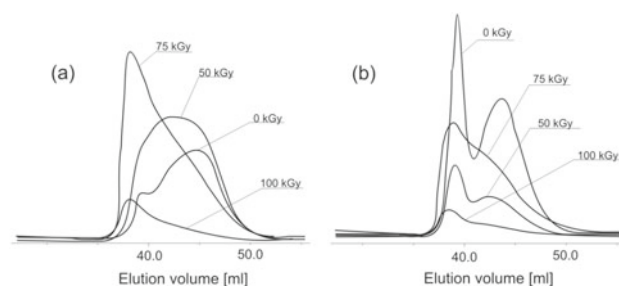


Figure 2. SEC traces of PED-26 (a) and PED-30 (b) copolymers before and after e-beam irradiation

There is a high M_w shoulder (8 800 g/mol) in the SEC trace of the neat PED-26 (0 kGy), with the main peak centering around 45 ml. The main peak shifted to higher molecular weights after irradiation. At 100 kGy the material gelled (the gel fraction determined from Soxhlet extraction was 67%), therefore the small amount of soluble fraction yielded a low intensity signal.

In the case of PED-30, the high M_w peak is more prominent (12 600 g/mol). Similarly to the PED-26, the lower M_w peak shifted towards higher M_w , reaching the peak M_w of the high fraction. Again, at 100 kGy the material gelled (the gel fraction determined from Soxhlet extraction was 75%), and the small amount of soluble fraction yielded a low intensity signal. Comparison of retention volume changes of the lower M_w maximum peak (a) and the higher M_w maximum peak (b) for PED-30 with the increasing radiation dose are presented in Fig.3.

As the effect of e-beam irradiation of PED-26 and PED-30 differing in hard segments content, different character of M_n changes with increasing radiation dose was observed (Fig. 4). PED-26 is a polymer where calculated degree of polycondensation (on the monomers feed) was ≈ 1 . It means that such material should be considered as a homogenous mixture of hard and soft segments rather than multiblock polymer with well defined hard and soft phases. Therefore, increasing radiation dose has no significant effect on M_n changes for PED-26 (Fig. 4), while for PED-30 (degree of polycondensation = 1,3), M_n increases with increasing radiation dose, thus indicating that e-beam radiation is affecting mainly hard domains structure and introduces more cross-links into PED-30 copolymer.

The summary of GPC/SEC numbers for PED-26 and PED-30 is given in Table 1.

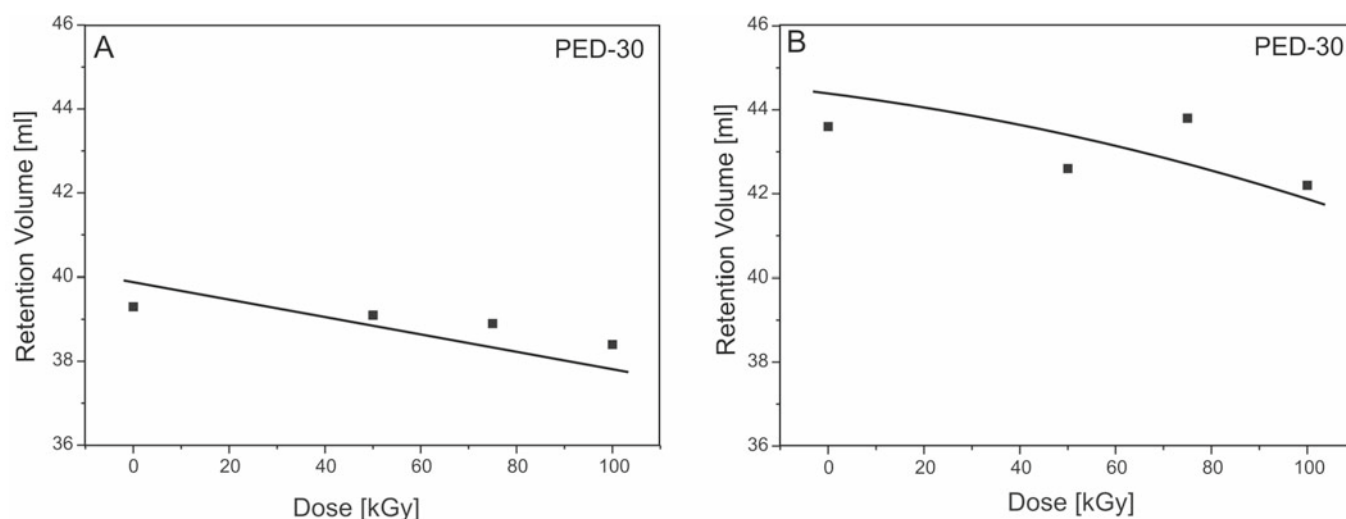
Thermal properties

Formation of a physical (native) and chemical (after modification) double network was also investigated by

Table 1. GPC/SEC characteristics for PED-26 and PED-30 multiblock copolymers

Sample	Concentration [mg/ml]	dn/dc [mL/g]	M_w/M_n	M_n [g/mol]	M_w [g/mol]	M_z [g/mol]	R_n [nm]	R_w [nm]	R_z [nm]	η_n [mL/g]	η_w [mL/g]	η_z [mL/g]
PED-26 0 kGy	1.920	0.879	2.04	4 300	8 800	44 200	19.3	17.1	19.8	416.7	594.3	952.7
PED-26 50 kGy	1.157	0.955	2.40	2 311	5 531	20650	25.1	23.0	25.0	920	1383	2581
PED-26 75 kGy	0.670	0.792	2.97	4 270	12 690	83380	34.1	33.7	39.0	964	1409	2755
PED-26 100 kGy	0.241	0.259	4.01	3 238	12 990	71260	33.2	32.4	46.3	1220	1955	4508
PED-30 0 kGy	0.398	0.828	2.27	5 600	12 600	55 4500	19.6	19.0	22.8	498.6	657.2	963.9
PED-30 50 kGy	0.123	0.298	2.13	3 670	7 819	24610	30.7	30.6	33.2	1413.3	1836.4	3211.1
PED-30 75 kGy	0.113	0.331	2.16	6 028	13 000	49100	42.3	41.8	42.6	1312.4	1725.6	2788.9
PED-30 100 kGy	0.046	0.149	1.70	7 003	11 920	26170	49.1	48.4	48.2	2162.2	2361.4	2527.4

where: M_w/M_n - molecular weight distribution, M_n , M_w , M_z [g/mol] - molecular weight, R_n , R_w , R_z - the intermediate radius of the inertia of the macromolecule (nm), η_n , η_w , η_z - the intermediary radical viscosity (mL/g)

**Figure 3.** Changes of a retention volume of the lower MW maximum peak (a) and the higher MW maximum peak (b) for PED-30

differential scanning calorimetry (DSC). PED materials are thermoplastic elastomers showing low temperature glass transition (T_g) and high temperature melting (T_m) as can be seen from Table 2.

The native „physically crosslinked” polymer structure is modified after exposure to e-beam as reflected by significant shift of T_g toward lower temperatures at 100 kGy dose (from -51 to -58°C for PED-26, and from -50 to -56°C for PED-30, respectively). Along with this change, increase of T_m (ascribed to the hard phase) with increasing radiation dose is also observed (from 83 to 112°C for PED-26, and from 122 to 126°C , respectively).

This clearly indicates that microphase separated structure is significantly changing upon e-beam irradiation, and additional chemical network within the hard segments is formed (Fig. 5).

Good illustration of the additional network formation is presented in Fig. 5. showing degree of crystallinity changes with increasing radiation dose. The content of the crystalline PBT phase in the polymer for lower hard segments content, i.e. PED-26 is gradually decreasing achieving the critical reduction in crystallinity up to 3% at 100 kGy dose. Such value shows that there are only some crystallites capable to crystallization, and that the

Table 2. Phase transitions determined with differential scanning calorimetry for non-irradiated and electron beam-irradiated samples

Sample	Dose [kGy]	ΔC_p [J/gK]	T_g [$^\circ\text{C}$]	T_m [$^\circ\text{C}$]	ΔH_m [J/g]	T_c [$^\circ\text{C}$]	ΔH_c [J/g]	w_c [%]
PED-26	0	0.622	-51.5	83	8.94	11.2	8.5	6.2
	25	0.762	-51	94.3	9.7	13.1	7.9	6.7
	50	0.539	-57.4	98.4	7.2	10.1	8.4	5
	75	0.520	-56.8	113.6	7.6	10.5	7.9	5.3
	100	0.555	-58	112	5.2	9	6.2	3.6
PED-30	0	0.570	-50.7	122	12.5	33.4	11	8.7
	25	0.400	-51	122.5	13	32.3	12.2	9
	50	0.680	-49	121	17	32.3	12.5	11.8
	75	0.580	-48.3	125	17.3	32.4	17.6	12
	100	0.444	-56.7	126.5	12	32.6	11.6	8.3

where: ΔC_p - a change of the capacity heat in T_g , T_g - glass transition temperatures of soft blocks, T_m - melting, temperatures of hard blocks, T_c - crystallisation temperatures of hard blocks, ΔH_m - heat of melting, ΔH_c - heat of crystallization, w_c - degree of crystallinity of PBT in polymer

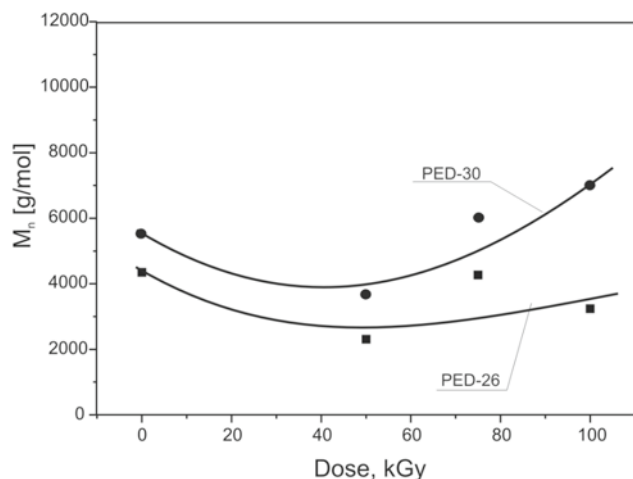


Figure 4. Changes of M_n with increasing radiation dose for PED-26 and PED-30

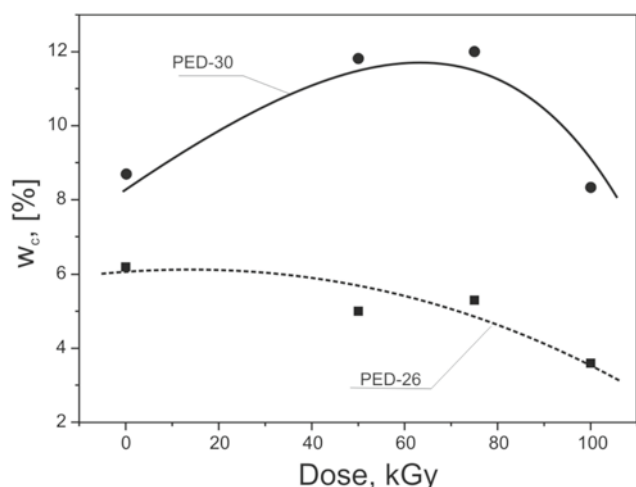


Figure 5. Degree of crystallinity of PBT in polymer (w) versus doses of ionizing radiation: ----- PED-26, – PED-30

e-beam irradiation reconnects hard domains by chemical bonds.

In the case of PED-30 copolymer we can observe increase of the degree of crystallinity at doses of 50 and 75 kGy, while at 100 kGy, the w_c dramatically decreases to the value of non modified material. The observed significant increase of the degree of crystallinity up to 75 kGy for material containing higher hard segments content indicates significant reorganization of the hard phase domains which are randomly reconnected by newly formed chemical bonds. At high radiation dose, i.e. 100 kGy significant drop of the degree of crystallinity indicates that e-beam irradiation significantly changes microstructure due to polymer chain scission and material degradation.

PED structure by wide angle x-ray scattering (WAXS)

WAXS method was used to qualitatively estimate PED's physical structure and to confirm changes in polymer microstructure revealed from differential scanning calorimetry (DSC).

Fig. 6 shows diffractographs of PED 30/70 copolymer before and after modification with 50 and 100 kGy. The qualitative estimation of WAXS patterns confirms the appearance of signals ascribed to crystalline phases of PBT hard segments (see the diffractograph of the PBT homopolymer). These signals, however, are very diffused what indicates on rather low degree of crystallinity, as

already found from DSC (see Table 2). Increasing dose of e-beam radiation broadens and flattens significantly these peaks what indicates on strong disturbances of the crystalline structure, and thereby on difficulties with crystallization process. This can be directly addressed to increasing role of chemical crosslinks formed upon irradiation (formation of network structure).

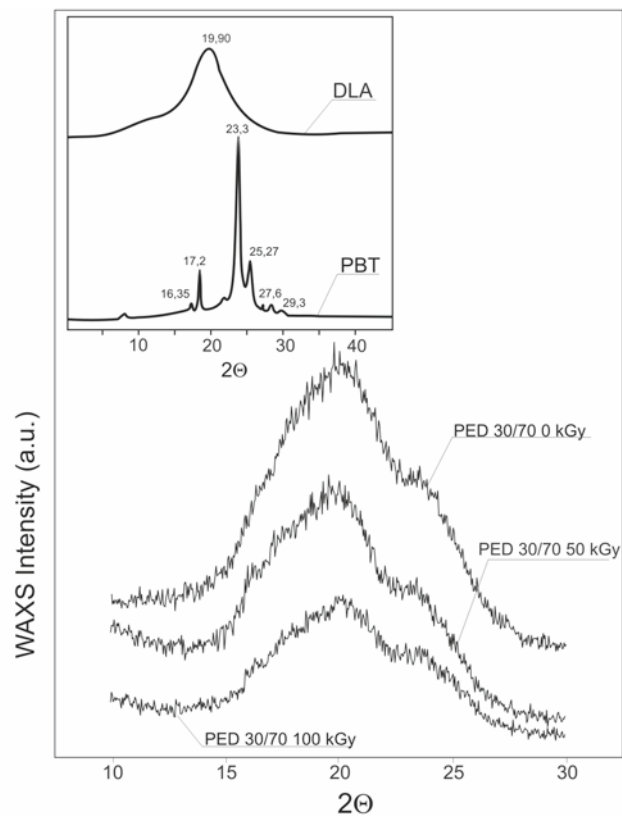


Figure 6. WAXS diffractographs for PED-30 before and after e-beam irradiation

Quasi-static tensile tests

Screening of the material mechanical behaviour was performed in order to evaluate how the e-beam irradiation and the formation of the double-network structure affects the tensile properties. Fig. 7 presents the results for E_{mod} , σ_{max} and ϵ_{max} . The comparison of the neat materials, PED-26 and PED-30, respectively, show that higher hard segments content lead to higher Young's modulus, tensile strength and elongation at break for PED-30.

The increase of mechanical properties can be related to the polymer microphase separated structure, which is better pronounced for PED-30, while at higher soft-phase content, i.e. PED-26, more homogeneous mixture of hard and soft segments is formed rather than the microphase separated structure. Moreover, PED-30 is stiffer than PED-26, therefore the Young's modulus increases from 7.7 MPa to 12.9 MPa. These results reveal the favourable contribution of a higher concentration of the hard phase (PBT) to enhanced mechanical properties in thermoplastic elastomers (the higher hard segments content, the higher stiffness).

Both materials, PED-26 and PED-30 have a relatively high elasticity, what can be related to the long aliphatic DLA chains in the soft phase. Fig. 7 shows that increasing e-beam irradiation dose increases σ_{max} and ϵ_{max} of the materials due to formation of the crosslinked network structure. The e-beam irradiation has no effect on E_{mod}

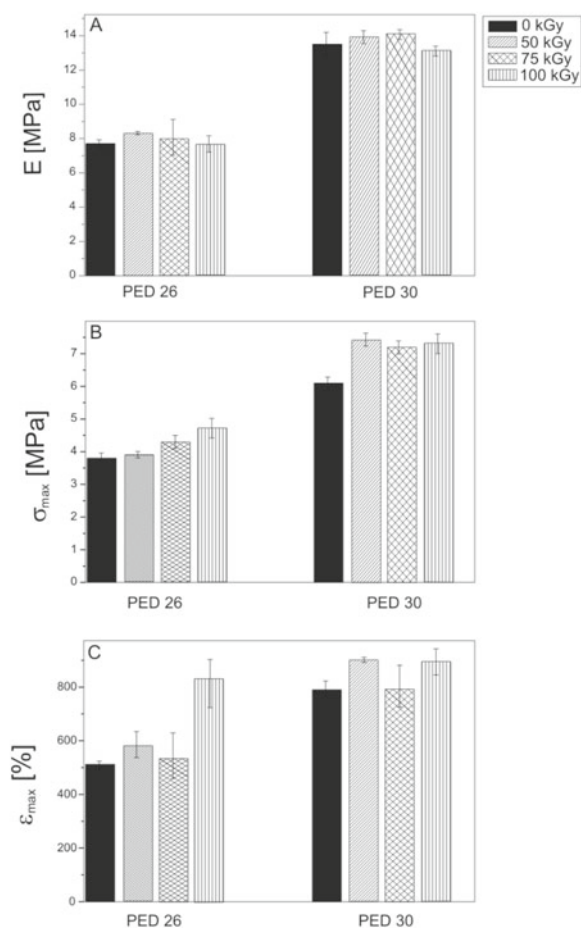


Figure 7. Static tensile properties of PED-26 and PED-30. The measurements were performed on 1 mm thin films with a cross-head speed of 100 mm/min

for both, PED-26 and PED-30 materials.

Gel fraction

The observed changes in mechanical properties were correlated with the gel fraction content and are showed in Fig. 8.

The Young's modulus (E_{mod}) was higher for samples characterized by higher gel content thus indicating that mechanical properties of PED copolymers can be effectively modified with e-beam radiation which is leading to crosslinking of materials (manifested by increased gel fraction content).

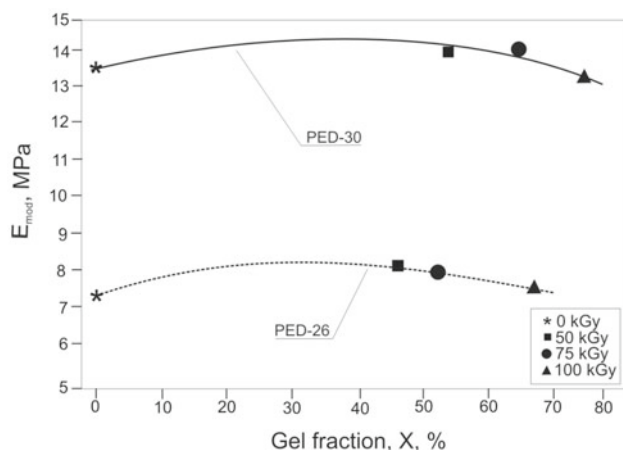


Figure 8. Young's modulus of PED-26 and PED-30 versus gel fraction content – at 0 kGy, – at 50 kGy, – at 75 kGy, – at 100 kGy

CONCLUSIONS

Poly(aliphatic/aromatic-ester) multiblock copolymers (PEDs) modified with various dosages of e-beam irradiation were investigated to evaluate the effect of such modification on the molecular weight and structure. DSC measurements indicated that crosslinking mainly occurs within the PBT hard phase, as demonstrated by the slight increase of T_m and the decrease of the crystallinity. It was found that the introduction of the additional chemical network influences the microstructure as revealed by WAXS diffractograms. The formation of an additional crosslinked network in the polymer is responsible for improving the quasi-static mechanical properties of these PED multiblock copolymers.

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