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JOINT REUSE OF POST-CONSUMER POLYOLEFINS AND GROUND TIRE RUBBER FOR THERMOPLASTIC ELASTOMERS PRODUCTION. MECHANICAL PERFORMANCE, THERMAL AND RADIATION STABILITY

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Abstract. The effect of the irradiation (γ-rays or electron beam) on structure-property relationships for the high performance thermoplastic elastomers (TPEs) obtained as a result of dynamic vulcanization of the blends of recycled high-density polyethylene (HDPE), ethylene/propylene/ diene monomer (EPDM) rubber, and ground tire rubber (GTR, pre-treated with Bitumen), has been investigated. Bitumen was used as a multifunctional agent providing partial devulcanization of GTR (during GTR pre-treatment) as plasticiser and to improve adhesion between the GTR particles and surrounding thermoplastic matrix. The structure-property relationships of individual components, initial TPEs and TPEs irradiated by various doses of *g*-rays or *e*-beam were studied using Thermogravimetric Analysis (TGA), Transmission Optical Microscopy technique, Size Exclusion Chromatography (SEC), Elementary Analysis methods, mechanical testing, etc. It was established that irradiation treatment of the studied TPEs provided significant increasing in gel fraction content. Nevertheless, a substantial decrease in gel fraction content was achieved by using α-Tocopherol (Vitamin E) as antioxidant in the TPE recipe. It was found that *γ*-irradiation treatment of HDPE/EPDM/GTR based TPEs resulted in improvement of the tensile properties thereof. A positive effect of antioxidant on tensile properties of the *e*-beam irradiated TPEs was observed. All the irradiated TPEs exhibited thermal behaviour similar to basic non-irradiated blends in the temperature range up to ~593 K and some improvement of stability against thermal oxidative degradation was fixed for the irradiated samples of different recipes in the temperature range of 593 to 823 K.

Keywords: gamma-irradiation, electron beam, polymers, composites, mechanical characterization.

1. Introduction

Thermoplastic elastomers (TPEs) are of great importance for the fundamental research and practical application, and blends of elastomeric and thermoplastic polymers obtained through dynamic vulcanization of rubber inside thermoplastic matrix have attracted much attention [1-5]. These TPEs have characteristics of the elastomers and are being melt (re)processable as typical thermoplastics. Replacement of TPEs virgin components (fully or partly) with recycled polymers is very important from economic and ecological standpoints.

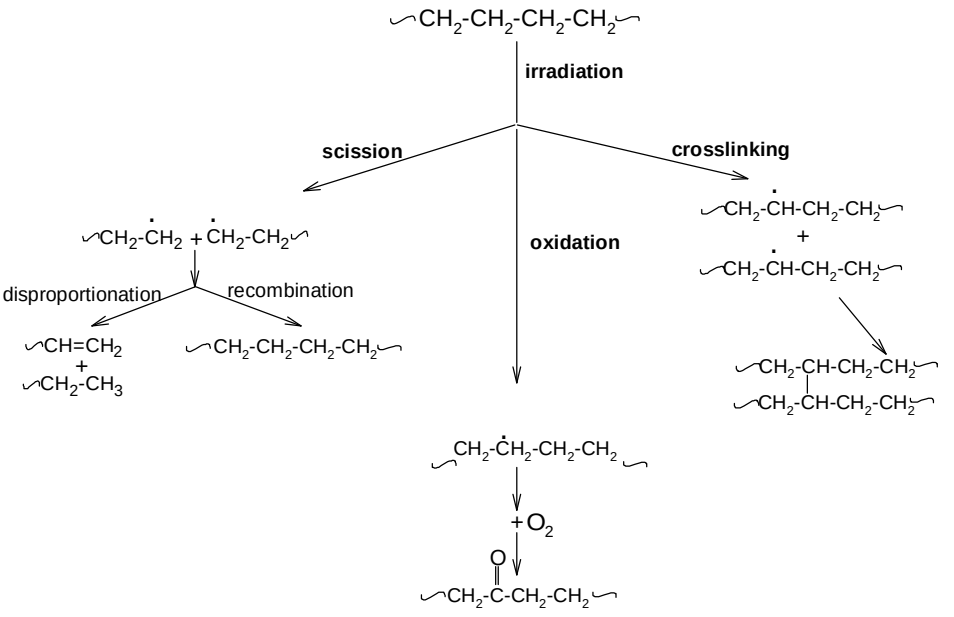

Fig. 1. Scheme of main processes occurred at irradiation treatment of polyethylene

Polymer waste, especially polyolefins and rubbers, including tire rubber, have become a serious environmental problem. Numerous approaches were proposed to recycle large amounts of such polymer waste. A standard approach is replacement of a part of virgin polyolefin (*e.g.* polyethylene) with a certain recycled analogue in the production of some technical articles (films, crates). Similarly, a part of virgin rubber is replaced with ground tire rubber (GTR) in tire formulations [6, 7]. Unfortunately, direct introduction of GTR into recipes of different polyolefin/rubber TPEs results in a significant decrease in their tensile strength and especially ultimate elongation [8-12] caused by poor interface adhesion between the blend components [13, 14]. Various modifiers for compatibilization of components of rubber/polyolefin blends with and without reclaimed GTR are used [15-17]. Preliminary results demonstrated that Bitumen was a suitable reclaiming agent for GTR under the special treatment conditions providing partial devulcanization and surface activation [10] that is important for utilization of the latter in polymer blends. Under special temperature conditions Bitumen components, such as asphaltenes, malthenes, and oils penetrate into the structure of GTR, which swells increasing its size 5–15 times. Finally, partial destruction of elastomeric network through breaking the $-(S)_x-$ bonding occurs (it should be noted here that the energy of S–S bond is 268 kJ/mol, while the energy of C–C bond is 352 kJ/mol) [18] leading to reactivation of at least GTR surface layer. At that decreasing gel-fraction content for GTR reaches 13–18 %. Additionally, during melt processing of HDPE/EPDM/GTR based TPEs, Bitumen plays a dual role: it acts as a curing (vulcanizing) agent for rubber components of TPEs and as an effective compatibilizer for blend components [10, 11].

The elaboration of novel radiation technologies and investigations in the field of the radiation chemistry of polymers and polymer blends is an intensively developing area of research [19-26]. Irradiation of polymers is widely used for grafting polymerization, modification, functionalization, and reactivation of polymers (including the recycled ones) [23, 24]. In Polymer Science Research a significant attention is currently paid to the problem of reducing phase separation between components in heterogeneous polymer systems in order to improve their final physical-chemical properties [25].

During irradiation of such polyolefins as polyethylene, two main competing processes occur: scission of polymer chains and their crosslinking (see Fig. 1). The dominance of one or another process is controlled by structural peculiarities of the polymer and irradiation conditions, *i.e.* type and dose of irradiation, atmosphere (oxygen), presence of anti-oxidants, *etc.* [26].

In this paper, the effect of radiation treatment (the dose of γ-rays or *e*-beam) and the presence of antioxidant (α-Tocopherol) in TPE recipes on physical and mechanical properties of TPEs based on EPDM, post-consumer HDPE, and GTR, pre-treated by Bitumen, was investigated.

2. Experimental

2.1. Materials

Post-consumer high density polyethylene, HDPE, was used as a polyolefin. HDPE granules were prepared from post-consumer bottle transportation crates collected in Kyiv (Roksana Ltd., Kyiv, Ukraine). Waste of the bottle transportation crates were first washed, then dried and cut to pieces with further granulation in an industrial machine. Virgin HDPE (trademark "HDPE 277-73" from KazanOrgSintez, Russia) was used for comparison with post-consumer HDPE used in TPEs recipes.

A GTR fraction with particles size of 0.4 to 0.7 mm was kindly provided by Scanrub AS (Viborg, Danmark). High quality GTR powder with a large surface/diameter ratio was produced by grinding tire rubber at supersonic speeds. As the powder and granulate is made of a large number of different tire types, Genan cannot give any extract values for the elastomeric composition of the powder/Granulate. The following can be used as a guideline: Natural rubber ~ 30 %, SBR (Styrene-butadiene rubber) ~ 40 %, BR (butadiene rubber) ~ 20 %, IIR/XIIR (Butyl- and halogenated butyl rubber) ~ 10 %. Some basic characteristics of GTR used are shown in Table 1.

As fresh rubber, ethylene/propylene/diene monomer (EPDM) containing rubber (trademark Buna® EP G6470 of Bayer, Germany) was used. EPDM rubber with 71 wt % of ethylene and 4.5 wt % of ethylidene norbornene contents, respectively, had a Mooney viscosity, ML equal to 59 at 398 K.

Table 1

Basic characteristics of GTR studied

Characteristic	Standard	Value
Specific gravity, g/cm^3	ISO 2781	1.1–1.20
Ash, %	ASTM E1131-86	0–5
Acetone extract, %	ISO 1407-81	11–17
Carbon black content, %	ASTM E 1131-86	32–36
Rubber hydrocarbon content, %	Calculated	~ 42
Free textile <1.0 mm, wt %	Genan	0–0.8
Free textile > 1.0 mm, wt %	Genan	0–1.2
Tensile Strength, *TS*, MPa	ISO R 37	> 5.0
Elongation at break, *EB*, %	ISO R 37	>90
Hardness, Shore A	ISO R 868	72
Density, g/cm^3	ISO R 868	1.18
Resiliency, %	DIN 53.512	40
Abrasion Loss, mm^3	DIN 53.516	220
Gel fraction content, wt %	ASTM D2765 - 01(2006)	86.5

Table 2

Basic characteristics of Bitumen BN-4 (State Standard SS 6617-76)

Characteristic	Value
Softening temperature, K	351
Penetration, dmm	30
Flash point, K	> 513
Fire point, K	> 623
Density at 293 K, g/ml	0.957
Asphaltenes content [a], wt %	31–32
Gel fraction content, wt %	0
Molar mass distribution [b]: M_w; M_n; M_w/M_n	12 000; 5 600; 2.1
Element content, wt.% [c]:	
C (carbon)	83.8–83.9
H (hydrogen)	10.0–10.3
S (sulfur)	3.5–3.6
N (nitrogen)	1.0–1.2
Other elements	1.1–1.7

Notes: [a] determined according [36]; [b] determined using Size Exclusion Chromatography method; [c] determined using Elementary Analysis method [30]

As a suitable multifunctional agent, BN-4 grade Bitumen (Ukrainian State Standard SS 6617-76) was used. Table 2 shows some characteristics of the Bitumen.

In some recipes of TPE samples *a*-Tocopherol (vitamin E, 97 %, from Aldrich) was used as antioxidant.

2.2. GTR Pre-treatment

In this work, the thermal-chemical-mechanical method of GTR particles partial devulcanization (decrosslinking) was used. GTR was first mixed with Bitumen and the mixture was pre-heated at $T \approx 443$ K for about 5 h followed by rolling for about 40 min using masticating mills.

2.3. Preparation of TPEs

For the manufacture of TPE samples, the twin-rotor mixer PL 2000 Brabender Plasticorder (433 K, rotor speed 80 rpm, time ~ 10–15 min) was used. First, HDPE was melted for about 2 min, then EPDM was added, and the melt was mixed for about 2 min; finally, GTR or GTR/Bitumen mixture (1/1 or 2/1 by weight) was added and masticated with other components for further ~ 10 min [27, 28]. All the samples of TPE HDPE/EPDM/GTR or HDPE/EPDM/(GTR/Bitumen) were blended in the ratio of 40/35/25 wt %. For GTR-free TPEs the ratio for HDPE/EPDM was 53/47 wt %, which exactly corresponds to HDPE/EPDM ratio 40/35 wt % in GTR- or GTR/Bitumen-based TPE recipes.

The TPE sheets with the thickness from 1 to 1.5 mm were produced by compression molding at 453 K and pressure 10 MPa with electrically heated hydraulic press (Carver Inc., USA).

2.4. Irradiation Treatment of TPE Samples

To check the effect of irradiation on the properties of TPEs developed and their radiation stability, two types of irradiation treatment (*e.g.*, γ-rays and accelerated electrons) were applied. Treatment of the TPEs by γ-rays was carried out using ^{60}Co source (energy 1.25 MeV; dose rate 2.27–28 kGy/h; full adsorbed dose 100–500 kGy). The TPE samples treatment with electron beam was performed using accelerator of free electrons (energy of accelerated electrons 3 MeV; full adsorbed dose 100 kGy).

2.5. Characterization Techniques

Thermogravimetric analysis was performed with TA-1000 Q-50 thermal analysis system (TA Instruments, USA). TGA traces were registered within the temperature range from 303 to 973 K with the heating rate 20 K/min in air by evacuating volatile products. The samples weight was 2–4 mg.

Mechanical measurements were performed using Instron 1122 machine at the ambient temperature, elongation rate (speed of upper cross-arm) 100 mm·min^{-1}; average tensile strength at break (*TS*), and average elongation at break (*EB*) were calculated for 6–7 specimens.

In order to estimate the TPEs crosslinking degree, the residual gel fracture content was determined *via* Soxhlet extraction with *o*-xylene. The extraction was carried out for 16 h (~ 10 times circulation of solvent per hour) followed by drying the samples in air oven (323 K for 24 h) and subsequent weighing. *o*-Xylene insoluble fraction was considered corresponding to the residual gel fracture content.

TPEs prepared morphology was studied with Optical Microscope "Carl Zeiss Primo Star" (Germany), resolution 1 μm.

Wide-angle X-ray scattering (WAXS) curves were recorded with X-ray DRON-4-07 diffractometer (Orel-nauchpribor, Orel, Russia), Cu-K_α radiation monochromatized by a Ni-filter. The degree of crystallinity (X_c) was calculated by the Matthews method [29]:

$$X_c = \left[Q_{cr} \Big/ (Q_{cr} + Q_{am}) \right] \times 100, \% \qquad (1)$$

where Q_{cr} – area under the crystalline maxima; Q_{am} – area under the amorphous halo.

Molar mass distribution of the Bitumen used was estimated using Size Exclusion Chromatography technique measured with Du Pont LC System 8800 with ultraviolet detector (wavelength 280 nm) and bimodal exclusion columns AZorbax@. Chloroform containing 5 % of methanol was used as an eluent. The samples weight was from 0.01 to 0.02 g. The calibration of columns was carried out with polystyrene standard of molar weight 30,000 and polydispersity M_w/M_n=1.01.

DSC study was performed with DuPont Thermal Analyzer (Model 910). The scans were performed in the temperature range from 173 to 473 K with the programmed heating rate of 20 K/min. Melting temperature (T_m) corresponding to the maximum in fusion endotherm was determined. Heat of fusion ($\triangle H_f$) was determined from the area under endothermic peak and degree of crystallinity (X_c) was calculated:

$$X_c = \left[\Delta H_f \Big/ \Delta H_{f\,100\%} \right] \times 100, \% \qquad (2)$$

where $\triangle H_{f100\%}$ – melting enthalpy value for 100 % crystalline polyethylene ($\triangle H_{f\,100\%} \approx 283$ J/g).

The Bitumen used element content was determined by the elementary analysis methods [30]: hydrogen and

carbon values – by the Pregl method, nitrogen – by the Dumas method and sulfur – by the Schöniger method.

Rheological measurements were performed with the melt indexer type MV-2 capillary micro viscometer (capillary diameter 1.26; length 8.3 mm) at the temperatures 413, 433, 453, and 473 K. The wall shear stress t_w, wall shear rate g_w, and shear viscosity h were calculated using standard equations.

3. Results and Discussion

3.1. Comparison of Virgin and Post-Consumer HDPE Properties

The comparative analysis of structure and properties of the post-consumer HDPE to be used in TPE recipes and that of virgin HDPE ($HDPE_{vir}$) was performed. FTIR spectroscopy demonstrated that their FTIR spectra (not shown here) are similar, though certain redistribution of intensities of some characteristic absorption bands is observed in HDPE FTIR spectrum compared to that of $HDPE_{vir}$. In the spectrum of HDPE, a band of low intensity with the maximum at 1720 cm^{-1} appears, indicating the presence of some C=O groups, certainly formed due to photo- and thermally induced oxidative processes occurred during operation in environment (atmospheric effects).

The TGA method has shown the similar character of thermo-oxidative destruction of the samples of virgin and recycled polymers, but HDPE is slightly less thermally stable in air. The temperature of maximal rate of mass loss for HDPE is by 19 K lower compared to $HDPE_{vir}$ (732 and 751 K, respectively).

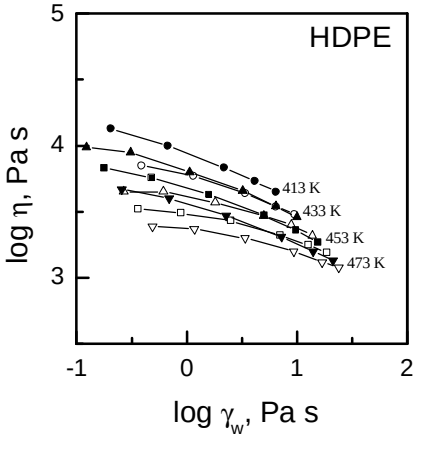

Fig. 2. Dependence of shear viscosity (η) *versus* shear rate (γ_w) for virgin (open symbols) and post-consumer (solid symbols) HDPE at several temperatures

The wide-angle X-ray scattering (WAXS) and DSC methods were used to characterize the structure of HDPE and $HDPE_{vir}$ crystalline phases. As it can be seen from Table 1 the basic parameters of crystalline structure of these polymers, such as average size of crystallites (D), interplanar spacing (d), crystallinity degree (X_c), and melting temperature (T_m) are similar.

It was also found that HDPE та $HDPE_{vir}$ have close flow behavior and viscosities (see Fig. 2), as well as physical-mechanical properties (Table 3).

Thus, we can conclude that structure and properties of the recycled HDPE are very similar to those of the virgin polymer, which enables the utilization of the recycled material instead of the virgin material in TPE recipes.

3.2. Effect of g-Rays Treatment on the GTR Decomposition Degree

GTR powder underwent irradiation by *g*-rays with a dose from 100 to 500 kGy. Fig. 3 shows the effect of γ-rays dose on the GTR decomposition degree. The experimental data clearly demonstrate the irradiation effect caused on the GTR gel-fraction: the higher the *g*-rays dose, the lower the gel-fraction content of GTR. This fact is explained by breaking of GTR network sulfuric bonds and possible partial destruction of its carbon backbone chains.

As one can see from Fig. 3, the gel-fraction content of the irradiated GTR decreases with increasing irradiation dose up to 100 kGy, and then it remains nearly constant after GTR treatment with irradiation doses up to 250 kGy. It is likely that the energy supplied at irradiation doses up to 250 kGy is quite enough to destroy the S–S bridges in the network, but not enough to ensure scission of carbon backbone chains, the latter occurs at doses higher than 250 kGy only (further reduction in gel-fraction content is observed).

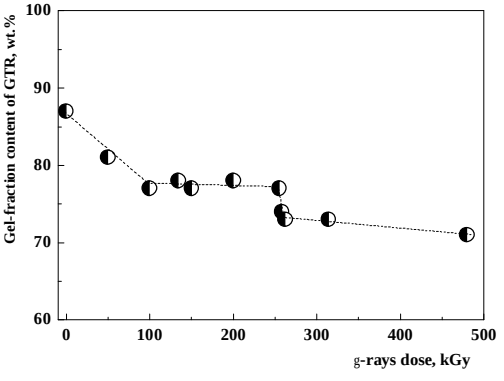

Fig. 3. Effect of *g*-ray irradiation on GTR decomposition degree

3.3. Effect of Radiation Treatment on Cross-linking Degree of Different TPE Recipes

The post-vulcanization is evidenced by the results of sol-gel analysis. TPEs gel-fraction content determination reveals increase of polymer chains crosslink degree in the *g*-irradiated TPEs compared to the untreated samples (see Table 4). One can see that the higher the *g*-irradiation dose, the higher gel-fraction content and, correspondingly, higher crosslink degree for TPE studied.

Data on gel-fraction content determination for TPE samples irradiated by electron beam (see Table 5) evidence increasing crosslink degree for TPEs after irradiation by electron beam as well.

Interestingly, that the values of gel-fraction content for electron beam irradiated TPEs (see Table 5) are higher than those for γ-irradiated TPEs of the same composition (see Table 4). This fact evidences that electron beam irradiation of these TPE samples results in additional intermolecular crosslinking with participation of all the components of the blend.

Table 3

Comparison of properties for post-consumer and typical virgin HDPE

Material	Melting temperature, T_m, K	Degree of crystallinity, X_c, %		Average crystal size, *D*, nm	Interplanar spacing, *d*, nm	Tensile strength, *TS*, MPa	Elongation at break, *EB*, %	Flow activation energy, E_a kJ/mol	Melt flow index, $MFI_{190/2.16}$ g/10 min	Gel fraction content[a], wt %
	DSC	DSC	WAXS							
HDPE	408	70	55.6	12.4	0.419	17.7	8	33.0	2.13	0
$HDPE_{vir}$	408	62	58.6	12.2	0.419	19.0	11	29.3	2.02	0

[a] determined as *o*-xylene insoluble fraction

Table 4

Gel-fraction content for initial TPE samples of different recipes and the same samples irradiated by *g*-rays

TPE sample	Component content, wt %	γ-Irradiation dose, kGy	Gel-fraction content, %
HDPE/EPDM	53/47	0	30.8
		100	64.9
		150	65.2
HDPE/EPDM/GTR	40/35/25	0	42.8
		100	44.3
		150	62.8
HDPE/EPDM/GTR/Bitumen	40/35/17/8	0	21.4
		100	44.6
		150	48.8
HDPE/EPDM/GTR/Bitumen	40/35/12.5/12.5	0	15.2
		100	45.2
		150	50.0

Table 5

Gel-fraction content for TPE samples irradiated by *e*-beam

TPE sample	Component content, wt %	Dose of irradiation by electron beam, kGy	Gel-fraction content, %	
			TPE without antioxidant	TPE with antioxidant
HDPE/EPDM	53/47	0	30.8	29.3
		100	79.4	77.2
HDPE/EPDM/GTR	40/35/25	0	42.8	42.0
		100	80.5	76.4
HDPE/EPDM/GTR/Bitumen	40/35/17/8	0	21.4	20.7
		100	68.3	62.2
HDPE/EPDM/GTR/Bitumen	40/35/12.5/12.5	0	15.2	15.0
		100	71.7	61.3

3.4. Effect of *g*-Rays Treatment on Physico-Mechanical Properties of TPEs Studied

Fig. 4 summarizes tensile properties of various HDPE-based TPEs depending on composition and dose of *g*-irradiation applied.

First of all it should be noted that tensile properties of the TPEs studied strongly depend on TPE recipe (see Fig. 4). One can clearly see that incorporation of cross-linked GTR particles into HDPE/EPDM matrix leads to drastic decrease of *TS* and especially *EB* values. As it was mentioned above, this is a result of poor interphase adhesion between the blend components. TPEs containing GTR pre-treated with Bitumen exhibit improved tensile properties compared to the Bitumen-free TPE. As it was discussed above, Bitumen acts as an effective devulcanizing agent on the stage of GTR pre-treatment; then, in the next steps of TPE production, Bitumen acts simultaneously as curing agent for the rubber components (EPDM/pre-devulcanized GTR) and as compatibilizer for the blend components. It is known [31] that effective compatibilization of the blend components decreases interfacial tension, leading to improved interfacial adhesion, that provides enhanced mechanical characteristics of the polymer blend.

The most significant changes in *TS* and *EB* values are observed for basic HDPE/EPDM (53/47) TPE and for HDPE/EPDM/GTR/Bitumen (40/35/12.5/12.5) TPE. The *TS* values for these TPEs reduce by ~ 20 % and 90 %, respectively, and *EB* values decrease three times at applying irradiation dose of 150 kGy for both of the TPEs (see Figs. 4a and 4c, respectively). It can be explained by partial destruction of the TPE components followed by re-crosslinking of the chain fragments formed at destruction. With high Bitumen content, oxidization of the latter at *g*-irradiation in air can play significant role [32, 33], decreasing interfacial adhesion and finally decreasing mechanical characteristics of the TPEs.

The Bitumen-free HDPE/EPDM/GTR TPE and the TPE of composition HDPE/EPDM/(GTR/Bitumen) = 40/35/(17/8) with low content of Bitumen are stable to γ-irradiation (see Figs. 4b and 4d, respectively). For Bitumen-free GTR-containing TPE, tensile properties are even improved with increasing irradiation dose. *TS* increases by ~8 % and EB by ~69 % (see Fig. 4b) with increasing irradiation dose up to 150 kGy. For the TPE of HDPE/EPDM/(GTR/Bitumen) = 40/35/(17/8) with low Bitumen content (see Fig. 4d), *TS* increases by ~60 % and *EB* slightly decreases (by ~15 %) with increasing irradiation dose up to 150 kGy (see Fig. 4d). This effect is explained by the inter-crosslinking reactions in the blends studied, increasing the total degree of curing accompanied by logical increase of *TS* and decrease of *EB* [34].

Thus, we can conclude that the *g*-irradiation of GTR-containing TPEs is an effective method for post-curing (post-vulcanization), improving their mechanical properties. However, it is worth mentioning that the increase of Bitumen in GTR-containing TPEs has a negative effect. The presence of Bitumen and irradiation of TPEs lead to decreasing vulcanization effect.

3.5. Effect of *e*-Beam Treatment on Tensile Properties of Various TPEs

Fig. 5 shows mechanical properties of TPEs based on HDPE depending on composition and irradiation dose of electron beam. The results obtained evidence that the influence of electron beam irradiation on tensile properties depends on TPE composition. Fig. 5 also demonstrates an effect of the presence of antioxidant in *e*-beam irradiated TPEs. For example, tensile properties, *TS* and *EB*, of the samples of TPE HDPE/EPDM (see Fig. 5a) and HDPE/EPDM/GTR/Bitumen (40/35/12.5/12.5) (see Fig. 5c) are reduced under an action of accelerated electrons, but the presence of antioxidant prevents the material from oxidation at irradiation in air and, consequently, *TS* and *EB* of TPE samples, containing vitamin E (*a*-Tocopherol), are higher. One can see that antioxidant compensates the effect of *e*-beam irradiation on the samples irradiated by the dose of 100 kGy (see Figs. 5a-5c).

A different behavior is observed for the samples with higher content of GTR: HDPE/EPDM/GTR (40/35/25, see Fig. 5b) and HDPE/EPDM/GTR/Bitumen (40/35/17/8, see Fig. 5d). For these TPEs *TS* increases by 17–51 %, and *EB* by ~50 % (see Fig. 4 for data on corresponding non-irradiated samples). This effect can be explained by radiation induced chemical grafting of matrix components onto the GTR surface, providing improvement of compatibility between the filler (GTR) and the surrounding polymer matrix and subsequent enhancement of mechanical properties of these compositions. The co-crosslinking phenomenon improves interfacial adhesion between polyethylene and rubber. According to Sonnier *et al.* [35] the presence of free radicals, appearing at the interface during irradiation, promotes compatibilization of the TPE components, and improves mechanical properties. They found that the effect of the compatibilization prevents debonding and breaking of the material.

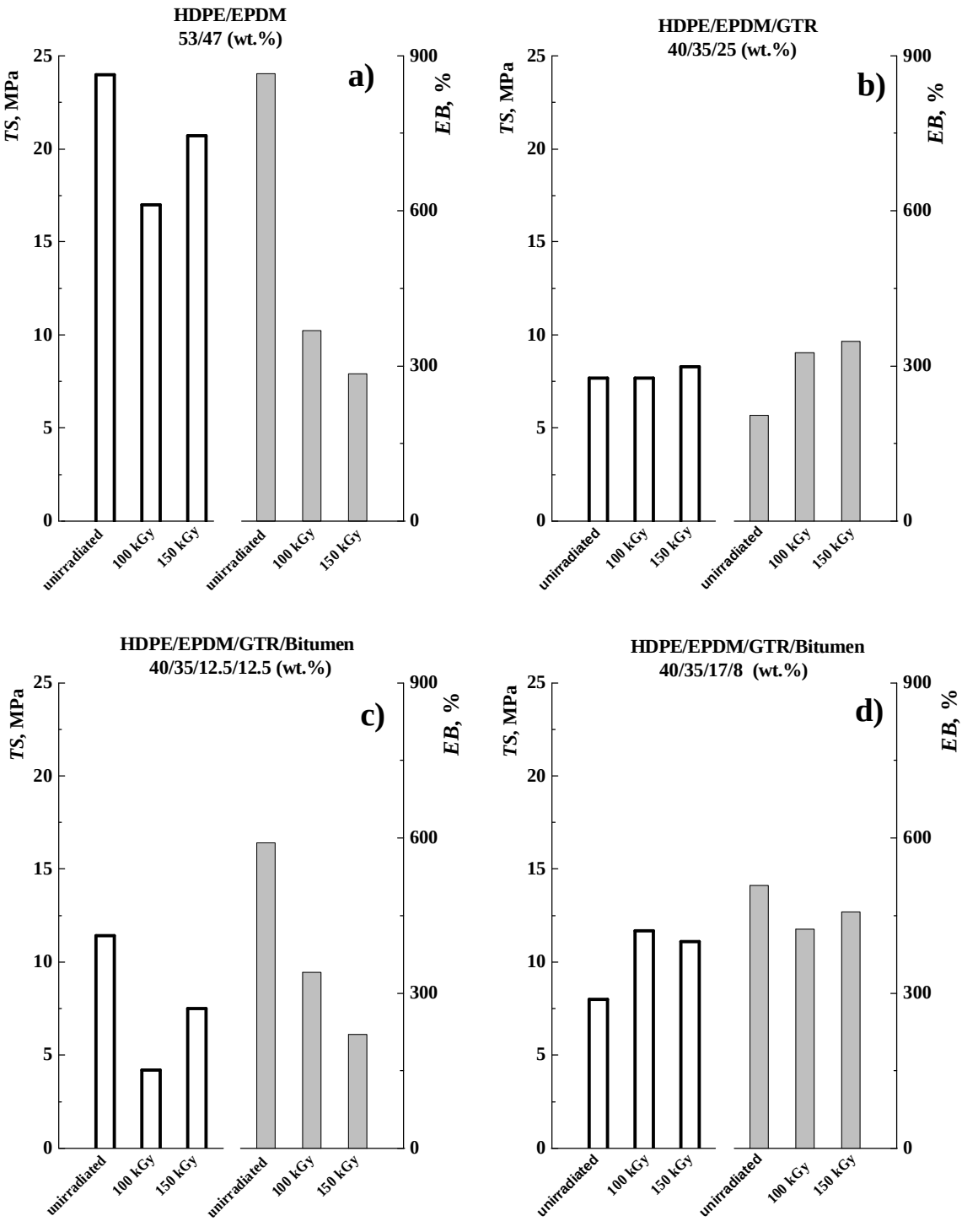

Fig. 4. Effect of γ-ray irradiation on tensile properties of TPEs of different recipes (indicated in the plot)

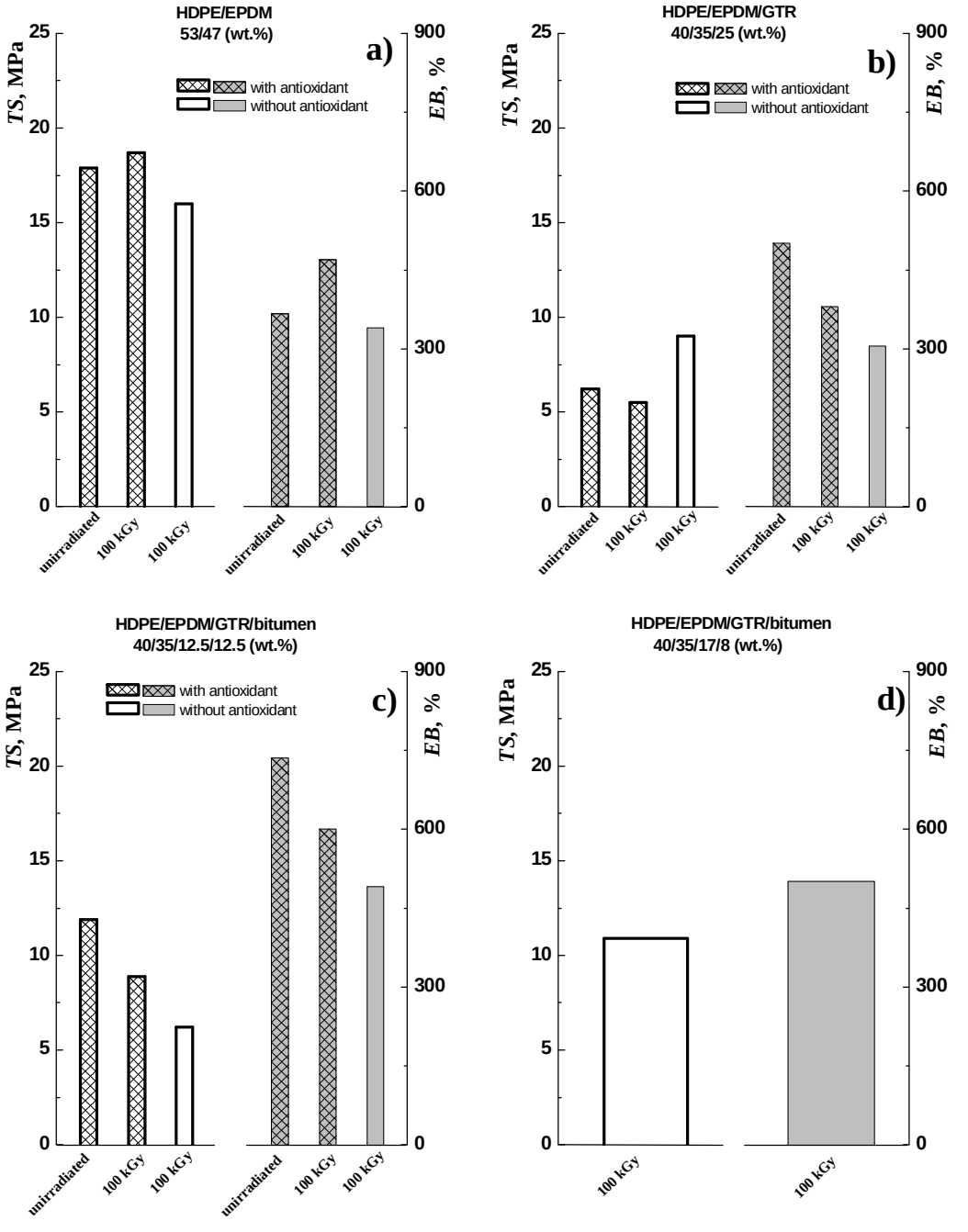

Fig. 5. Effect of *e*-beam treatment and antioxidant content on tensile properties of TPEs of different recipes (indicated in the plot)

3.6. Effect of Radiation Treatment on Thermal Properties of Various Recipes TPEs

Fig. 6 depicts the TGA thermograms of non-irradiated and irradiated samples of TPEs. Table 6 summarizes temperature conditions of weight loss for these composites. It is clearly seen that all non-irradiated and irradiated TPEs are thermally stable with no difference in weight loss up to ~ 533 K. Fig. 6 shows that irradiation of TPEs is not accompanied by significant changes in thermal stability. However, increasing temperature of the maximal rate of decomposition in the region from 533 to 783 K by 10–35 K is observed for the irradiated TPEs compared to that for the non-irradiated

ones, except for the sample HDPE/EPDM/(GTR/Bitumen) = 40/35/(12.5/12.5) γ-irradiated with the dose of 100 kGy. Obviously, in this case, scission of the polymer chains predominates over their crosslinking and it is in a good agreement with the tensile data for this sample (see Fig. 5). In the temperature region above 783 K, thermal behavior of all the TPEs studied is quite similar. Generally, we can conclude that the irradiated TPEs have rather higher thermal stability than the non-irradiated ones. This behavior may be attributed to increasing interface linking and crosslink density leading to higher thermal stability [36]. The comparison of the TGA and DTA curves for the same TPE recipes treated by γ-rays or *e*-beam evidences that *e*-beam has a higher effect on thermal degradation behavior of the irradiated TPEs. For example, the temperature of the beginning of intensive degradation (see Fig. 7a) and the temperature of maximal rate of thermal degradation (see Fig. 7b) for the TPE sample HDPE/EPDM/GTR/Bitumen (40/35/12.5/12.5) irradiated by *e*-beam of the dose of 100 kGy shift to the higher temperature region by 19 and 27 K, respectively, compared to that for the same sample irradiated by γ-rays of the same dose. Table 6 shows the similar dependence for other TPE compositions.

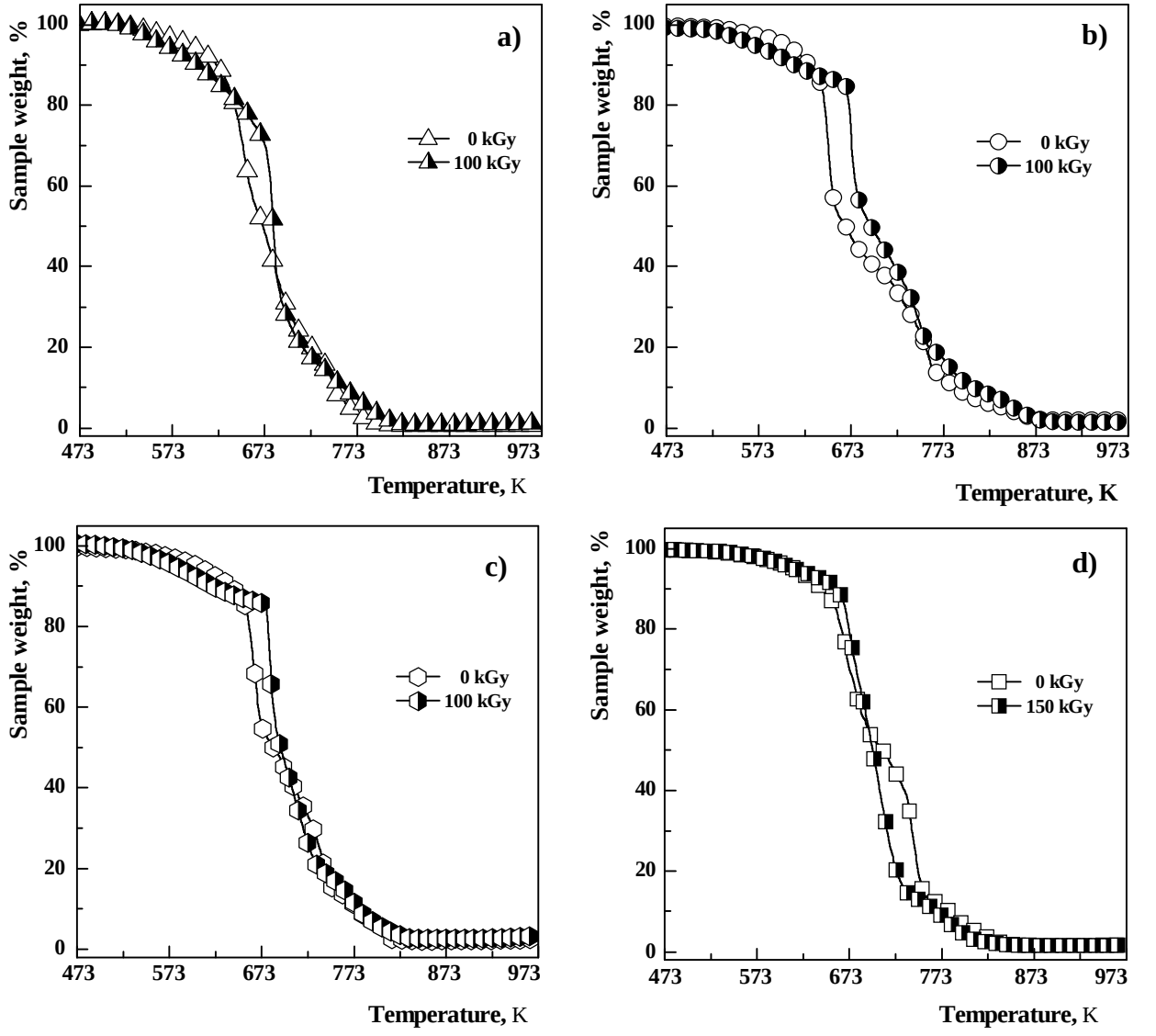

Fig. 6. Effect of γ-ray irradiation on stability to thermal oxidation destruction (TGA data) of different TPEs studied (wt %): HDPE/EPDM (53/47) (a); HDPE/EPDM/GTR (40/35/25) (b); HDPE/EPDM/GTR/Bitumen (40/35/17/8) (c) and HDPE/EPDM/GTR/Bitumen (40/35/12.5/12.5) (d)

Table 6

Thermal properties (TGA data) of TPE samples studied

HDPE/EPDM/GTR/Bitumen, wt %	Irradiation (type/dose), kGy	Decomposition temperature, T_{di}, at sample weight loss, K				T_{dmax}, K
		10 %	20 %	40 %	50 %	
53 / 47 / 0/0	-	618	642	649	651	649
53 / 47 / 0 / 0	γ-ray/100	600	647	680	681	681
40 / 35 / 25 / 0	-	627	645	652	668	646
40 / 35 / 25 / 0	γ-ray/100	612	671	678	695	672
40 / 35 / 17 / 8	-	639	660	669	685	665
40 / 35 / 17 / 8	γ-ray/100	597	679	685	690	682
40 / 35 / 12.5 / 12.5	-	643	664	685	708	670
40 / 35 / 12.5 / 12.5	γ-ray/100	625	654	669	683	661
40 / 35 / 12.5/12.5	γ-ray/150	660	673	690	698	705
40 / 35 / 12.5 / 12.5	*e*-beam/100	652	675	684	690	680

3.7. Effect of Radiation Treatment on Morphology of TPEs Studied

Figs. 8 and 9 present the optical images taken from the surfaces of the sheets of an initial TPE samples and TPEs irradiated by the dose of 100 kGy using γ- or *e*-beam irradiation. One can clearly see (Fig. 8a) that GTR particles directly dispersed in HDPE/EPDM blend (*i.e.* without Bitumen) are very poorly bonded to the matrix, some GTR particles are observed outside the matrix indicating a lack of interaction between them. We consider that no interfacial layer between cross-linked GTR particles and surrounding matrix (HDPE/EPDM) is formed in this TPE sample. As a result tensile properties of this TPE are drastically lower (see Fig. 4b) compared to the basic HDPE/EPDM blend (see Fig. 4a).

It can be seen that the surface of the HDPE/EPDM/GTR (40/35/25) TPE irradiated by the dose of 100 kGy using γ-rays or *e*-beam (see Figs. 8b and 8c, respectively) looks more homogeneous and phase boundaries are more diffused and less visible. It can be concluded that in such a case bonding between GTR particles and surrounding matrix is improved, which results in some increasing of elongation at break (see Figs. 4b and 5b). However, the compatibilization effect achieved was not enough to reach high level of tensile properties for the samples studied.

It can be seen (Fig. 9a) that the surface of initial (non-irradiated) TPE samples based on HDPE/EPDM/GTR/Bitumen (40/35/17/8) looks much more homogeneous compared to Bitumen-free TPE (see Fig. 8a). This indicates increasing interaction between GTR particles pre-treated with Bitumen and surrounding HDPE/EPDM matrix. As a result these TPEs exhibit improved tensile properties compared to TPE based on non-pretreated GTR (see Figs. 4b and 4d).

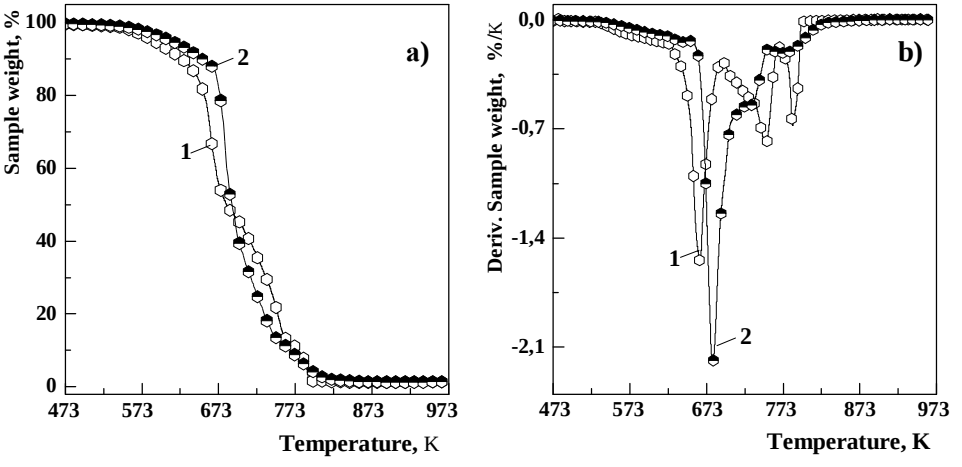

Fig. 7. The TGA (a) and DTG (b) data for TPE based on HDPE/EPDM/GTR/Bitumen (40/35/12.5/12.5) irradiated by γ-rays (1) and *e*-beam with the dose of 100 kGy (2)

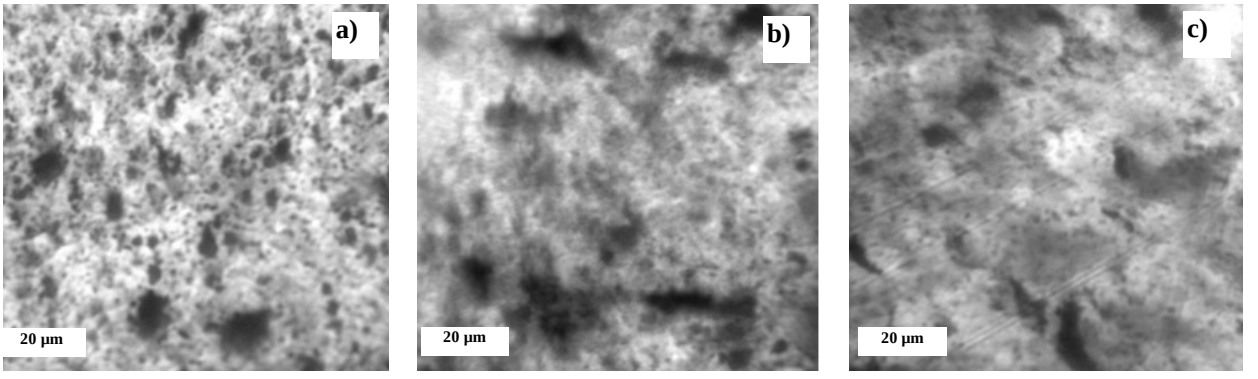

Fig. 8. Optical images for HDPE/EPDM/GTR (40/35/25) TPEs studied: initial samples (a); samples irradiated by dose of 100 kGy using γ-rays (b) and samples irradiated by dose of 100 kGy using *e*-beam (c)

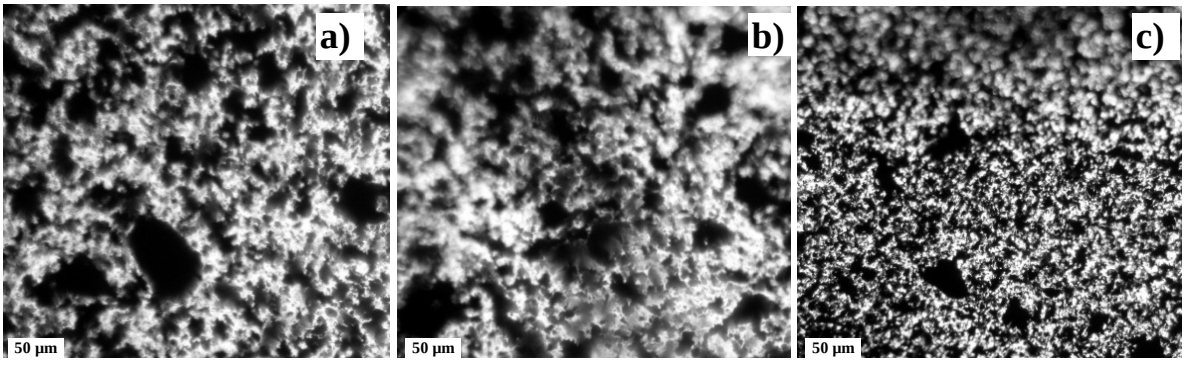

Fig. 9. Optical images for HDPE/EPDM/GTR/Bitumen (40/35/17/8) TPEs studied: initial samples (a); samples irradiated by dose of 100 kGy using γ-rays (b) and samples irradiated by dose of 100 kGy using *e*-beam (c)

For the irradiated TPE of the composition of HDPE/EPDM/GTR/Bitumen = 40/35/17/8 a better bonding between GTR particles pre-treated with Bitumen and the matrix is clearly observed (see Figs. 9b and 9c): the surface of the sample is characterized by higher level of homogeneity compared to the corresponding non-irradiated TPE sample, the apparent size of the GTR particles is reduced, and the small GTR particles are well incorporated into the matrix. It can be considered that the improved interfacial layer between partially devulcanized GTR, pre-treated by Bitumen, and other components of the TPE is formed due to irradiation treatment. This conclusion is confirmed by increasing tensile strength and elongation at break for the TPE recipes studied (see Figs. 4d and 5d). Finally, it can be concluded that irradiation treatment (*γ*-rays or *e*-beam) of the TPEs studied leads to improvement of their morphology.

4. Conclusions

The influence of *g*-rays and electron beam irradiation on the structural characteristics and mechanical and thermal properties of high value thermoplastic elastomers (TPEs) based on recycled high-density polyethylene (HDPE) and ethylene/propylene/diene monomer (EPDM) rubber, as well as with additions of ground tire rubber (GTR, industrial and renovated by pre-treatment with Bitumen) prepared by using dynamic vulcanization technology has been investigated. It was established that irradiation of HDPE/EPDM composition resulted in reduction of mechanical characteristics thereof, which allows to make a conclusion about the low radiation stability of this material. Replacement of some part of the EPDM rubber in the composition above with GTR provides some improvement of stability of the TPEs against both γ-rays and electron beam. Pre-treatment of GTR with Bitumen has a positive effect on the mechanical and thermal properties of TPEs studied however high amount of Bitumen decreases radiation stability of the compositions. By composition optimization TPEs with high performance characteristics and high radiation stability can be obtained. A negative effect of Bitumen on the radiation stability of TPEs can be compensated by the use of antioxidants, such as *a*-Tocopherol (Vitamin E). The behavior of TPEs under the influence of irradiation is

discussed in terms of competition of scission and recombination (destruction and post-curing) processes of polymer chains in TPE components, as well as of inter-crosslinking of the chains of polymers of different nature.

Abbreviations

EB - elongation at break
EPDM - ethylene/propylene/diene monomer
FTIR - Fourier transform infra-red
GTR - ground tire rubber
HDPE - high density polyethylene
kGy - kilo gray
SEC - size exclusion chromatography
TGA - thermogravimetric analysis
TPE - thermoplastic elastomers
TS - tensile strength
WAXS - wide-angle x-ray scattering

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СПІЛЬНЕ ВИКОРИСТАННЯ ВТОРИННИХ ПОЛІОЛЕФІНІВ І ПОДРІБНЕНОЇ ШИННОЇ ГУМИ ДЛЯ ВИРОБНИЦТВА ТЕРМОЕЛАСТОПЛАСТІВ. МЕХАНІЧНІ ВЛАСТИВОСТІ, ТЕРМІЧНА ТА РАДІАЦІЙНА СТАБІЛЬНІСТЬ

Анотація. *Досліджено вплив опромінення (g-променів або прискорених електронів) на взаємозв'язок структура-властивості для термоеластопластів (ТЕП), отриманих динамічною вулканізацією сумішей вторинного поліетилену низького тиску (ПЕНТ), потрійного кополімеру етилен/пропілен/дієновий мономер (ЕПДМ) та подрібненої шинної гуми (ПШГ), модифікованої бітумом. Бітум використовували як мультифункціональний агент, який забезпечує, одночасно,*

часткову девулканізацію ПШГ, діє як пластифікатор та підсилювач адгезії між частинками ПШГ і термопластичною матрицею. Структуру та властивості індивідуальних компонентів, а також вихідних ТЕП та ТЕП, опромінених різними дозами g-променів або прискореними електронами, досліджували методами термогравіметричного аналізу, оптичної мікроскопії, гель-проникною хроматографією, елементним аналізом. Проведені фізико-механічні випробування сумішей. Встановлено, що радіаційне оброблення досліджуваних ТЕП призводить до суттєвого підвищення вмісту гель-фракції. Водночас, використання в рецептурі ТЕП антиоксиданту Вітаміну Е сприяє зниженню вмісту гель фракції в зразках. Визначено, що оброблення g-променями ТЕП складу ПЕНТ/ЕПДМ/ПШГ призводить до підвищення міцності на розривання. Зафіксовано позитивний вплив антиоксиданту на показники міцності на розрив ТЕП, опромінених прискореними електронами. Усі опромінені ТЕП демонструють термостійкість, аналогічну базовим неопроміненим ТЕП в температурному діапазоні до ~593 K. Встановлено деяке підвищення термоокиснювальної стабільності опромінених зразків ТЕП різних рецептур в температурному діапазоні від 593 до 823 K.

Ключові слова: *g-опромінення, прискорені електрони, полімери, композити, механічна характеристика.*