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A preliminary study on the new thermoplastic vulcanizates

Summary — Thermoplastic elastomers (TPEs) are new type of elastomer materials with comparable and sometimes better mechanical properties than conventional elastomers, while having processing characteristics of thermoplastic materials. Thermoplastic vulcanizates (TPE-V) are elastomer/thermoplastic polymer microheterogenic blends in which elastomer phase is crosslinked and dispersed in a continuous thermoplastic matrix. The subject of this study was evaluation of the phase structure and mechanical properties of the TPE-Vs obtained by reactive processing in the molten state of PP and ethylene-octene elastomer (EOE) blend using silane/moisture as crosslinking system. Morphology was studied by scanning electron microscopy (SEM) and thermal behavior of the blends was studied by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and differential thermal analysis (DTA). It was observed that both thermal behavior and mechanical properties of the compositions were very dependent on blend composition when specimens are subjected to heat or mechanical loads. Glass transition temperature (T_g) decreases with increase in concentration of elastomer in TPE-V.

Key words: ethylene-octene copolymer, silane-moisture crosslinking system, thermoplastic vulcanizates, glass transition temperature, morphology, mechanical properties.

NOWE TERMOPLASTYCZNE WULKANIZATY — BADANIA WSTĘPNE

Streszczenie — Termoplastyczne elastomery (TPE) stanowią nową grupę materiałów elastomerowych o właściwościach mechanicznych porównywalnych, a często korzystniejszych niż w przypadku konwencjonalnych materiałów termoplastycznych. Termoplastyczne wulkanizaty (TPE-V) są mikroheterogenicznymi mieszaninami, w których plastomer tworzy fazę ciągłą, a fazą zdyspergowaną są cząstki selektywnie usieciowanego elastomeru. Przedmiotem badań była struktura i właściwości mechaniczne TPE-V wytworzonych w procesie reaktywnego przetwórstwa w stanie stopionym mieszaniny PP i elastomeru etylenowo-oktenowego z zastosowaniem układu sieciującego silan/wilgoć. Morfologię TPE-V (rys. 2) badano metodą skaningowej mikroskopii elektronowej (SEM), a właściwości termiczne (rys. 4—6, tabela 2) metodami dynamiczno-mechanicznej analizy termicznej (DMTA), skaningowej kalorymetrii różnicowej (DSC) oraz różnicowej analizy termicznej (DTA). Stwierdzono, że zarówno właściwości mechaniczne (rys. 1, tabela 3), jak i termiczne kompozycji zależą od składu próbek poddanych działaniu mechanicznych naprężeń i temperatury. Temperatura zeszklenia (T_g) próbek obniża się ze wzrostem udziału elastomeru w TPE-V.

Słowa kluczowe: kopolimer etylen/okten, układ sieciujący silan/wilgoć, termoplastyczne wulkanizaty, temperatura zeszklenia, morfologia, właściwości mechaniczne.

Thermoplastic elastomers (TPEs) are known as materials showing the processing characteristics of thermoplastics and mechanical properties of vulcanized rubbers [1—9]. They achieve such properties by a physical process — mixing of the thermoplastic polymer and the elastomer together using high shear compounding equipment. The properties of these materials depend on the elastomer and thermoplastic polymer used, as well as on their ratio and miscibility.

Thermoplastic vulcanizates (TPE-V) are the special class of TPEs [10—11]. These materials are elastomer/thermoplastic polymer blends in which elastomer phase is crosslinked and dispersed in the continuous thermoplastic matrix. They are manufactured by mixing of the elastomer with the thermoplastic polymer performed under high shear and above the melting point of the thermoplastic. During this process the elastomer phase is selectively crosslinked and dispersed in a continuous thermoplastic matrix. Rheological and physical properties of the materials manufactured in such way are very dependent on both the ratio of thermoplastic polymer and elastomer, and the morphologies of both phases, including the size of crosslinked rubbery particles dispersed in the thermoplastic phase. Among the factors which affect the crosslinking degree of the dispersed phase are properties of both the thermoplastic polymer and elastomer used, temperature conditions and technology of dynamic vulcanization. The critical parameter in optimization of the properties of TPE-V is also the choice of the curing system.

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A number of studies on TPE-Vs those based on thermoplastic polyolefins such as low density polyethylene (PE-LD) or linear low density polyethylene (PE-LLD) or polypropylene (PP) and different types of elastomers have been performed. Their mechanical properties and processing characteristics have been reviewed by several authors [12—19]. The TPE-Vs based on semicrystalline isotactic PP and ethylene-propylene-diene elastomer (EPDM), having the double bonds needed for most of the curing systems, are commercially important. Usually, in above-mentioned blends, sulfur-based systems or substituted phenol-formaldehyde resins as well as peroxides are used as curing agents. Due to processing characteristics, improved impact properties and capability for recycling, the application of TPE-Vs in the automotive applications is extended, what is a reason to looking for new such materials made of new type of elastomers.

The use of ethylene-octene copolymers due to their low glass transition temperature (T_g < -45 °C) are desirable for many applications. They belong to a new family of ethylene higher α-olefin copolymers in the density range of 0.865—0.905 g/cm^3. These products made with use of a single-site metallocene catalyst, show a uniform compositional distribution, where every polymer chain has about the same composition, and narrow molecular weight distribution ($M_w/M_n \approx 2.0$) compared to the products synthesized with use of conventional multi-site catalysts. They can be readily crosslinked by irradiation, peroxides or silane/moisture system [20—22].

Crosslinking with silane has been known for some time. This technology is today the most economical process for producing moisture crosslinkable grafted polyolefins and does not require specific equipment [23]. Silane molecule has to contain a central silicon atom bounded to two types of groups: alkoxy and functional ones, which exhibit different reactivity. Crosslinking mechanism of polyolefins by silane involves two steps. First is the grafting of polymer backbone by silane, in a free-radical reaction. Second is the linking of chain *via* condensation of silanols in the presence of moisture. In this process, polyolefins are linked mostly through Si-O-Si bridges, which are more flexible than C-C bond formed *via* peroxide or radiation cure. However, a little has been published on the effect of silane/moisture crosslinking system on the final properties of PP and ethylene-octene copolymer composition produced by dynamic vulcanization process.

The subject of this study is evaluation of the phase structure and mechanical properties of TPE-Vs obtained by reactive processing in the molten state of PP and ethylene-octene elastomer blend using silane/moisture as crosslinking system [24, 25]. Morphology of the blends was studied using scanning electron microscopy (SEM) and thermal behavior by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and differential thermal analysis (DTA).

EXPERIMENTAL

Materials

Polypropylene (PP, trade name Malen P F-401) with melt flow rate (MFR) — 2.4 g/10 min at 190 °C and crystallinity degree of 95 % was supplied by Orlen S.A.

Polyolefin elastomer (trade name Engage 8180) — ethylene-octene copolymer (EOE), with comonomer content 42 wt. % measured by ^{13}C NMR/FTIR, density 0.863 g/cm^3, Mooney Viscosity ML(1+4)121 °C equal 35 °M was the product of Dow Elastomers.

The other additives of compounds were:

— vinyl-tris(2-metoxyetoxy)silane (trade name Silquest A-172 Silane) and 3-methacryloxypropyltrimethoxysilane (trade name Silquest A-174 Silane) both Witco's products,

— dicumyl peroxide, 99 %, a Perwalt Chemie product (used as initiator),

— dibutyl-tin dilaurate, an Aldrich Chemie product (used as catalyst),

— tetrakis[methylene-(3,5-di-tertbutyl-4-hydrocinnamate) methane], a Ciba-Geigy product (used as antioxidant).

Preparation of TPE-Vs

Periodic process

Dynamic vulcanizates were prepared at laboratory scale by melt-mixing of polypropylene, ethylene-octene copolymer and antioxidant in a Brabender W 50 H Plasticorder mixer, at 190 °C and rotors speed of 40 rpm. After about 2—3 min, when the melt was formed the silane and peroxide were added. The mixing process was continued for about 10—15 min at 190 °C until the mixing torque had been stabilized.

Specimens for mechanical properties determinations were obtained by compression molding technique, under the following conditions: temperature 190 °C, heating time — 4 min, pressing time under 10 MPa — 4 min. Then the plates were incubated in the high humidity chamber for 96 h at 60 °C and humidity of 70 % to reach, in the presence of moisture, the networks of siloxane linkages.

Continuous reactive extrusion process

The Brabender double-screw extruder, DSK 42/6D was used to prepare dynamic vulcanizates of PP/ethylene-octene copolymer in the pilot scale. Extrusion was carried out at temp. 180/185/190 °C and the screws speed of 40 rpm.

One or two step process was applied to prepare the blends of PP/silane-grafted ethylene-octene copolymer.

The one-step process. Polypropylene and elastomer were mixed in a laboratory mixer with the solution of peroxide in silane and antioxidant at 50 °C and this mixture was then melt-processed in a double-screw extruder. The final material was pelletized and cooled in the water bath.

Two-step process. In the first step polypropylene, elastomer and antioxidant mixed at room temperature were melt-processed in double-screw extruder and pelletized. Next, the extrudate was premixed with silane/peroxide solutions and such the mixture was melt-processed, pelletized and cooled in the water bath.

In the final step, the grafted product and masterbach containing dibutyl-tin-dilaurate as catalyst were mixed together. The extrudate was cooled in water bath and next incubated in the low-pressure steam autoclave.

Specimens for mechanical properties determinations were obtained by injection molding performed in the injection molding machine (Arburg). Condition of injection molding:

— cylinder temperature 195/200/210/210 °C,
— injection pressure 900—1000 bars,
— injection flow rate 10 cm^3/sec,
— cycle time up to 45 sec.

Extent of crosslinking of the elastomer

The compositions were extracted with cyclohexane during 72 h at room temperature (to remove uncrosslinked elastomer) and with boiling xylene during 8 h (to remove uncrosslinked elastomer and polypropylene phase).

Testing procedures

The melt flow rate (MFR) was examined in plastometer type II RT according to Standard PN-93/C-89069 (PN ISO 1133/1991) at 190 °C.

Dynamic Mechanical Thermal Analysis (DMTA) was performed using Polymer Laboratories DMTA MKK II viscoelastometer within the temperature range from -10 to +100 °C, at the heating rate of 3 °C/min. The oscillating frequency was 1 Hz. The viscoelastic properties, such as the storage modulus (E'), loss modulus (E''), and loss factor (tan δ) were recorded as functions of temperature.

The morphology of the fracture surface of specimens was analyzed by scanning electron microscope (SEM), model Joel JSM 6100. Specimens were freeze fractured in liquid nitrogen and sputtered with gold before examination.

Differential scanning calorimetry (DSC) measurements were performed using Perkin-Elmer DSC-7 apparatus. The specimens were heated at a rate of 10 °C/min up to temp. 210 °C, then cooled at 10 °C/min down to -50 °C, and heated again at the same rate for a second time. The glass transition temperature (T_g) was determined from the thermograms as temperature corresponding to the upper inflection point or maximum on the curve. The melting point (T_m) was determined as corresponding to the maximum on the endothermic curve.

Differential thermal analysis (DTA) measurements were carried out using thermal analytic system TGA/DTA/STAR R 51. Specimens were heated from 25 °C up to 550 °C, at a rate of 10 °C/min under nitrogen atmosphere.

Tensile tests were carried out at room temperature using universal tensile testing machine — Instron model 4505, at a crosshead speed of 50 mm/min according to PN-EN ISO 527. The flexural tests, according to PN-EN ISO 178, were performed using Zwick apparatus, at room temperature. Izod impact notched test was carried out according to ISO 180. Hardness (H) was performed according to PN-80/C-04238 using Shore D apparatus and (HK — ball hardness) according to PN-ISO 868. Vicat softening temperature was measured according to PN-93-C/89024. Heat distortion temperature was measured according to ISO 75-1.

RESULTS AND DISCUSSION

A series of blends based on ethylene-octene elastomer (EOE) and polypropylene (PP) was prepared at laboratory scale with different PP/EOE ratios. In all the blends the same crosslinking system: silane A-172/dicumyl peroxide was used with the silane and peroxide content kept constant 3.0/0.03 wt. % based on the total weight of elastomer, respectively. The grafting process was carried out in the presence of 0.2 wt. % of antioxidant.

When mixing, for the same process conditions, the addition of the silane/peroxide system causes an increase in the final mixing torque. The magnitude of torque remained constant till the end of melt blending. Simultaneously, with increase in the elastomer content the increase in mixing torque was observed (Table 1). It indicates both grafting process and lack of the degradation of polymers during melt processing.

Table 1. Selected properties of the dynamically crosslinked blends in relation to PP/EOE weight ratio

Properties	PP/EOE weight ratio				
	100/0	85/15	70/30	55/45	40/60
Mixing (rotor) torque, Nm	—	15.0	15.5	16.0	16.5
Hardness, °ShD	80	63	57	50	36
MFR (190 °C, 2.16 kg), g/10 min	2.4	1.63	1.29	1.28	1.15
MFR (190 °C, 5 kg), g/10 min	—	5.06	5.89	5.80	4.90
T_{A120}, °C[a]	152	143	130	106	~60
Hardness HK, MPa[b]	24.7	16.1	12.2	11.8	8.7
Part of elastomer soluble in cyclohexane, wt. %	—	—	13.9	12.03	14.2
Part of elastomer soluble in boiling xylene, wt. %	—	—	24.0	33.0	42.0

[a] T_{A120} — Vicat's softening temperature.
[b] HK — ball hardness.

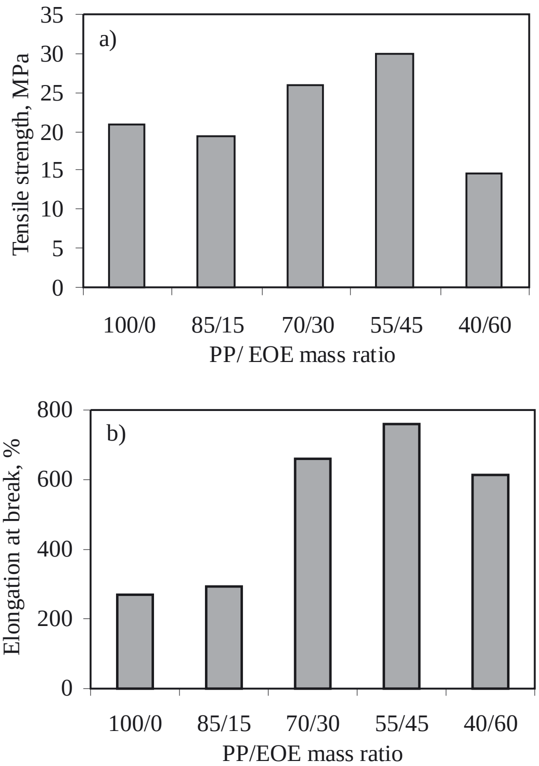

Fig. 1. Mechanical properties of dynamically crosslinked blends versus PP/EOE weight ratio: a) tensile strength, b) elongation at break

The temperature and rate of mixing as well as the amount of an antioxidant used were sufficient to melt the hard thermoplastics and to cause the grafting/crosslinking processes. Polymers used were thermally stable under these conditions. The thermooxidative degradation of polypropylene was not observed.

The effect of polypropylene/elastomer ratio on the mechanical properties such as tensile strength and elongation at break of TPE-V is shown in Fig. 1. As it can be seen (Fig. 1a) the tensile strength increases from 18 to 30 MPa when a content of elastomer increases from 15 to 45 wt. %. The same relation has been observed for elongation at break (Fig. 1b). In given above range of elastomer content, the elongation at break increases from 300 to 770 %. For higher content of EOE (above 50 %) the decrease in tensile strength and elongation at break are observed. The values of these parameters were 15 MPa and 600 %, respectively.

On the other hand the other properties (listed in Table 1), such as hardness (HK) and Vicat softening point, steadily decrease when content of elastomer increases from 15 to 60 wt. %.

The presented above properties of the blends containing small amounts of elastomer (15—30 %) are similar to those of PP. Increase in the elastomer content over 50 % improves the rubber-like properties of the blends.

The best properties, *e.g.*, tensile strength, elongation at break and rheological properties were achieved for the grafted/crosslinked PP/EOE blend at weight ratio of 55/45. Moreover, the results of extraction test suggest that the application of silane/peroxide grafting/crosslinking system let achieve a good modification of elastomer (Table 1).

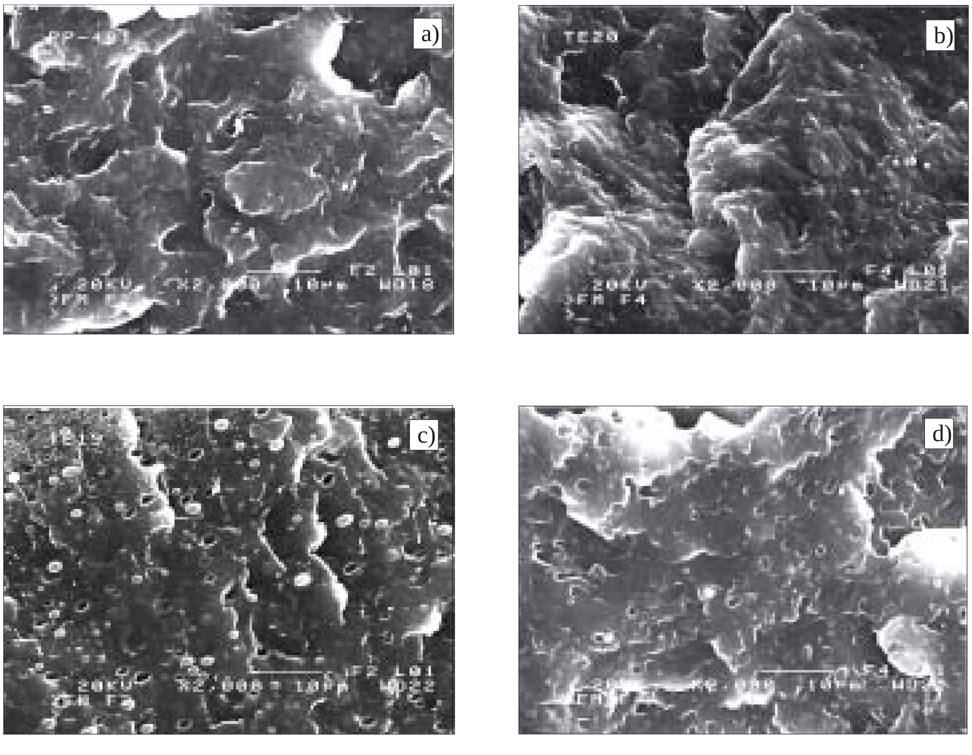

Fig. 2. SEM images of neat PP (a) and dynamically crosslinked PP/EOE blends with weight ratios: 85/15 (b), 70/30 (c), 55/45 (d); magnification 2000 times

The amount of uncrosslinked elastomer soluble in cyclohexane at room temperature and in boiling xylene, based on the total weight of elastomer present in the blends, was about 12—14 % and 24—42 wt. %, respectively.

The images of fractured surface (SEM) of PP and selected crosslinked blends with different PP/EOE ratios (listed in Table 1) are shown in Fig. 2. The different type of morphology was clearly observed. The fracture surface of PP has shown the cracks typical for semi-crystalline polymer. They appeared on the boundary line between the crystalline and amorphous areas or across the amorphous areas only. The blends of PP/EOE different in their ratios are heterogeneous; the continuous phase of semi-crystalline PP matrix and dispersed phase of elastomer are observed.

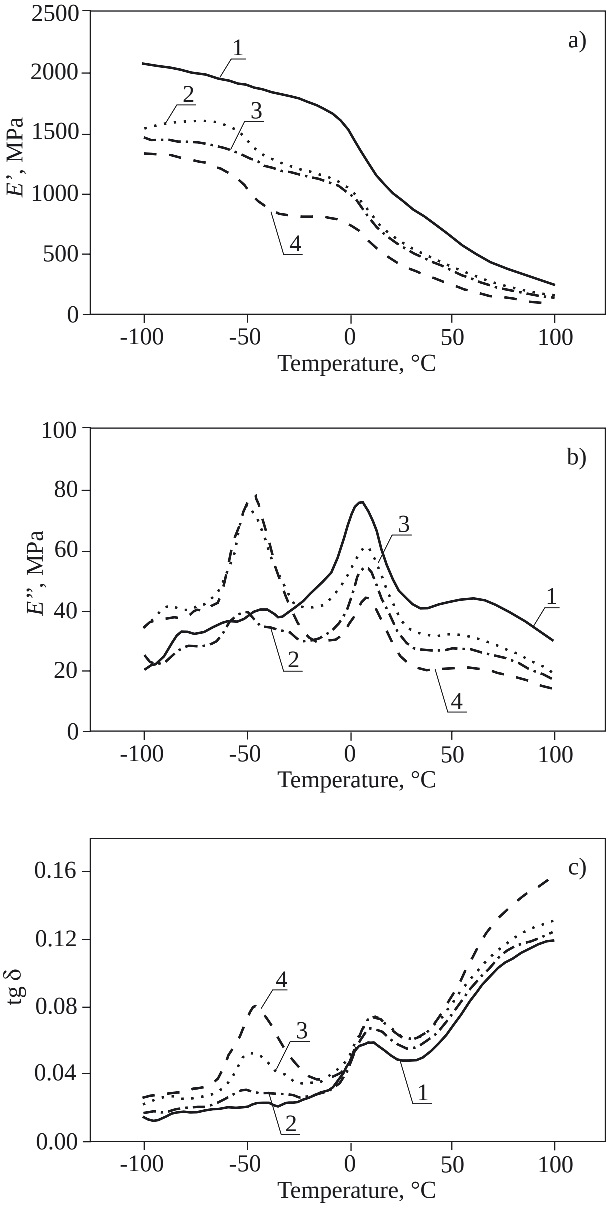

Fig. 3. The dynamic mechanical properties of neat PP and dynamically crosslinked PP/EOE blends versus temperature: a) storage modulus (E'), b) loss modulus (E"), c) loss tangent (tan δ); denotations of curves for blends with PP/EOE weight ratio: 1 — 100/0, 2 — 85/15, 3 — 70/30, 4 — 55/45

The size of dispersed phase domains in the blend containing 15 wt. % of elastomer is smaller than that in a case of higher concentration of elastomer. Some of elastomer particles are visible under the surface of the semi-crystalline PP matrix what can be due to a change of intermolecular interactions. From this it could be supposed that the grafting process during preparation of the crosslinked PP/EOE blends stabilizes the morphology of the polymeric systems.

Results of DMTA are presented in Fig. 3. The shapes of the dynamic mechanical properties curves of the dynamically grafted/crosslinked PP/EOE blends are similar to those of PP. However, the value of storage modulus (*E'*) of PP is higher as compared to the blends of PP/EOE containing 15, 30 or 45 wt. % of elastomer, respectively (Fig. 3a). The fast decrease in the storage modulus is related to the glass transition of the blends, and it is distinctly visible for higher concentration of elastomer. It can be due to the formation of higher amount of grafted copolymer.

Two well-shaped maxima of the dependence $E'' = f(T)$ are observed. The peak at lower temperature corresponds to T_g of the elastomer whereas the peak at higher temperature is T_g of PP. The fast decrease in *E"* above the glass transition is due to the subsequent degradation of the physical junctions differing in energy and related to the beginning of melting process.

The temperatures of relaxation transitions of PP and crosslinked PP/EOE blends are shown in Table 2. This type of blends, based on semi-crystalline polymer such as PP and low-crystalline EOE copolymer, shows two relaxation transitions, which correspond to those of the neat homopolymers, demonstrating the low miscibility of both components in these systems.

Table 2. Values of T_g and E'' obtained from DMTA tests for PP/EOE blends dynamically vulcanized

PP/EOE weight ratio	I maximum		II maximum	
	E'', MPa	T_g, °C	E'', MPa	T_g, °C
100/0	—	—	76.0	5.93
85/15	40.43	-50.45	56.20	7.89
70/30	74.29	-50.01	62.43	8.39
55/45	78.83	-47.02	55.71	8.82

DSC measurements confirmed the two-phase structure of the blends as well (Fig. 4). On the DSC diagram of PP/EOE (55/45) blend the temperature -46.39 °C is connected with T_g of EOE whereas the peak at 162.8 °C is the melting point of PP for the thermoplastic matrix of the blend. Decrease in melting point of PP phase of PP/EOE grafted/crosslinked blends as compare with neat PP

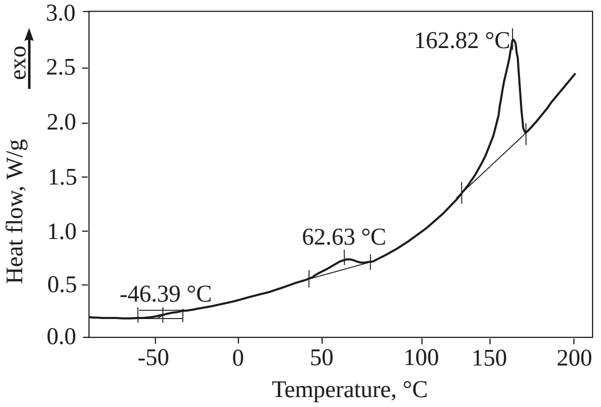

Fig. 4. DSC curve of dynamically crosslinked PP/EOE blends with weight ratio 55/45

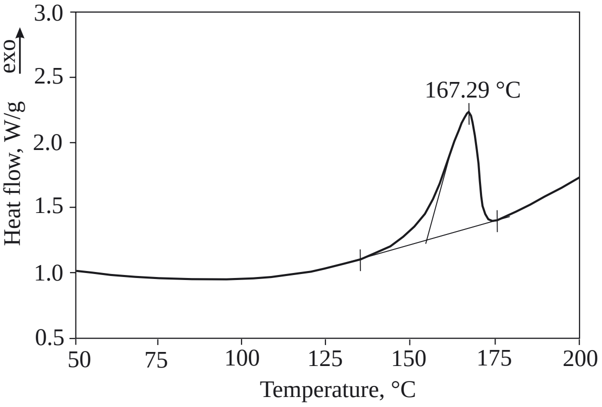

Fig. 5. DSC curve of neat PP

suggests the changes in the thermoplastic matrix and/or degradation of PP by β-scission caused by the peroxide used (Fig. 5).

To compare the properties of the grafted/crosslinked blends manufactured using periodic and continuous mixing method the series of TPE-Vs were prepared in one — step or two-step reactive extrusion processes. Two PP/EOE blends with weight ratio of 55/45 and Silane A-174/peroxide (Specimen TE-1) and Silane A-172/peroxide (Specimen TE-2) as grafting/crosslinking system were selected to our study. Concentration of the silane/peroxide system was the same as in the first series of blends.

The results of investigations of mechanical properties of the crosslinked blends differed in type of Silane used are listed in Table 3.

They are similar and characterized by high both elongation at yield point and at break as well as high impact strength if compared with those of PP. Dispersed and crosslinked particles of EOE in the PP matrix act as special modifier and improve properties of low impact resistant PP. Simultaneously, the reduction in the tensile and flexural moduli can be observed.

The DTA measurements of crosslinked PP/EOE blends from both processes of one-stage and two-stage extrusion confirmed the decreasing in melting point of PP phase related with the changes in the polymer matrix due to high temperature processing (Fig. 6). This may be attributed to disordering of semi-crystalline structure of PP, or it may suggest that matrix is not formed by neat PP, but it is PP-rich phase containing a small amount of EOE.

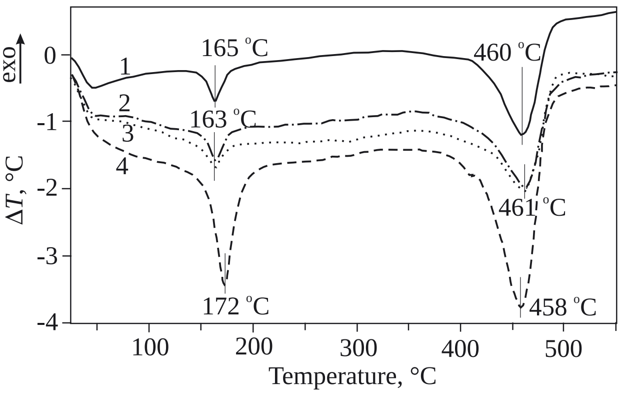

Fig. 6. DTA curves of neat and dynamically crosslinked blends with PP/EOE weight ratio of 55/45 (according to Table 3); denotations of curves: 1 — specimen TE-2 (first extrusion), 2 — TE-2 (second extrusion), 3 — specimen TE-1, 4 — neat PP

Table 3. Selected properties of neat PP and dynamically crosslinked blends with 55/45 PP/EOE weight ratio, using different type of silane in crosslinking system

Properties	PP	Specimens	
		TE-1	TE-2
		Silane A-174	Silane A-172
Yield point, MPa	31.4	12.1	12.5
Elongation at yield point, %	9.4	25.1	33.0
Breaking stress, MPa	15.1	15.5	18.3
Elongation at break, %	196	443	440
Tensile modulus, MPa	1455	476	430
Flexural stress, MPa	39.6	13.0	10.4
Flexural modulus, MPa	1499	504	415
Heat distortion temperature under load 1.8 MPa, °C	50.5	38	38
Impact notched Izod, kJ/m^2	3.16	46.7	43.0

The optimization of the crosslinking process in the presence of moisture and catalyst should allow achieving better properties of dynamically crosslinked blends.

CONCLUSIONS

Preliminary results obtained in this study suggest that reactive blending of polypropylene and ethylene/octane elastomer in the presence of silane/peroxide crosslinking system is the useful technique to manufacture two kinds of polymeric materials:

— high impact resistant polymeric materials — the blends of PP/silane grafted Engage 8180,

— thermoplastic elastomer with dynamically crosslinked Engage 8180 in PP matrix after diffusion of moisture in the presence of catalyst.

On the basis of SEM, DMTA, DTA and DSC data we can conclude that both types of polymeric materials are disperse system: the continuous phase of semi-crystalline PP matrix and dispersed small particles of crosslinked ethylene-octene elastomer, which acts as a modifier of properties and stabilizer of the two-phase structure of polymeric material.

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