

Thermoplastic Elastomers Based on Recycled High-Density Polyethylene, Ethylene–Propylene–Diene Monomer Rubber, and Ground Tire Rubber

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ABSTRACT: High-performance thermoplastic elastomers (TPEs), based on recycled high-density polyethylene (HDPE^R), olefinic type ethylene–propylene–diene monomer rubber (EPDM), and ground tire rubber (GTR) treated with bitumen, were prepared by using dynamic vulcanization technology, and their structure–property relationships were investigated. It was established that special pretreatment of GTR by bitumen confers outstanding mechanical properties on the resulting TPEs. TPEs, containing GTR pretreated by bitumen, exhibit thermal behavior similar to that of the HDPE^R/EPDM basic blend in the temperature region up to about 340°C. Rheological measurements showed that bitumen acts as an effective plasticizer for the GTR-containing TPEs. SEM, DSC, and DMTA results revealed improved adhesion between the particles of GTR treated by bitumen

and the surrounding thermoplastic matrix, compared to that of the untreated GTR particles. It was concluded that bitumen acts as an effective devulcanizing agent in the GTR treatment stage. In the following steps of TPE production, bitumen acts simultaneously as a curing agent for the rubber components (EPDM/GTR) and as a compatibilizer for the blend components. GTR-containing TPEs, prepared by extrusion technology, were reprocessed (by passing through the extruder six times) without any observable changes in their tensile properties, thermal stability, and melt viscosity. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 659–671, 2005

Key words: thermoplastics; recycling; ground tire rubber (GTR); bitumen; compatibilization

INTRODUCTION

Thermoplastic elastomers (TPEs), especially blends of elastomer and thermoplastic obtained by dynamic vulcanization of rubber in thermoplastic, and having characteristics of elastomers while retaining thermoplasticity, have been of serious interest to scientists and manufacturers in the last decade.^{1–5} For both economical and ecological reasons the replacement of virgin components of TPEs (fully or partly) by recycled polymers is very important. The problem is to obtain materials having beneficial properties (preferably not inferior to those of traditional TPEs, with respect to primary properties). Waste plastics, especially polyolefins, and rubbers, including tire rubber, have caused a series of environmental problems. Many approaches have been proposed to use the large amount of waste polymers. The standard use is a replacement of a part of

virgin polyolefin (e.g., polyethylene) by some recycled grades. Similarly, part of the virgin rubber can be replaced by ground tire rubber (GTR) in less-demanding, and even in tire, formulations.^{6,7}

In recent years, a potential way to use GTR in thermoplastic elastomers has been developed. Numerous investigations,^{8–17} including our own, have shown that introducing GTR directly into recipes of different polyolefin/rubber TPEs results in a substantial decrease in their tensile strength and, especially, ultimate elongation. This is the result of poor interphase adhesion between the blend components.^{18,19} Various modifiers have been used to compatibilize rubber/polyolefin blends with and without reclaimed GTR. Short reviews concerning advantages of functionalization and compatibilization of TPEs including GTR were recently published by Li et al.^{20,21} For reactive compatibilization (which seems to be the most effective method), the components of TPEs including GTR should be functionalized or at least their surface must be activated, which can be done by chemical grafting of reactive monomers onto the polymer surface or, in the case of GTR, by thermal, thermomechanical, thermochemical, and ultrasonic devulcanization techniques, for example.^{6,7,11,20}

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TABLE I
Characteristics of Bitumen Used

Characteristic ^a	Value
Softening temperature, °C	78
Penetration, dmm	30
Flash point, °C	>240
Fire point, °C	>360
Ash content, wt %	<0.5
Water content, wt %	Traces
Water-soluble acids or alkali	Absent
Solubility at 25°C (toluene, chloroform), %	>99.5
Density at 20°C, g/mL	0.957
Asphaltenes content, wt %	31.4–32.1
Molar mass distribution ^b : $M_w; M_n; M_z; M_w/M_n$	12,059; 5,647; 26,491; 2.135
Element content (wt %) ^c :	
C (carbon)	83.78–83.90
H (hydrogen)	10.04–10.27
S (sulfur)	3.47–3.57
N (nitrogen)	1.01–1.20
Other elements	1.06–1.7

^a According to the USSR State Standard SS 6617–76.

^b Determined by size-exclusion chromatography method.

^c Determined by elemental analysis method [Mázor, L. Methods of Organic Analysis; Akadémiai Kiadó: Budapest, 1983].

Preliminary results^{14,15} have shown that significant improvement of tensile properties can be achieved if ethylene–propylene–diene monomers (EPDM) with high ethylene content (~ 70%) is used as the rubber component of polyolefin/rubber/GTR compositions. On the other hand, using bitumen as a plasticizer and reclamation agent for GTR allowed us to produce TPEs containing recycled low-density polyethylene (LDPE^R).^{16,17,22} The beneficial properties of LDPE^R/EPDM/GTR/bitumen blends, with and without dynamic curing, were attributed to improved blend compatibility. Note that the major criteria for TPEs are elongation at break > 100% and compression set < 50%.²²

This article reports the investigation and preparation of reactively compatibilized TPEs based on EPDM, recycled high-density polyethylene (HDPE^R), and GTR. Bitumen, contributing to GTR devulcanization and to the compatibilization of the TPE components, was used throughout the investigation. Structure–property relationships were investigated using thermogravimetric analysis (TGA), rheological measurements, differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and scanning electron microscopy (SEM) techniques, as well as mechanical testing.

EXPERIMENTAL

Materials

HDPE^R, from postconsumer bottle transportation crates collected in Kyiv (Roksana Ltd., Kyiv, Ukraine), was

used. Waste, of bottle transportation crates, was washed, dried, and cut into pieces by use of an industrial apparatus. The HDPE^R was characterized by melt flow index (MFI_{190/2.16}), 2.13 g/10 min; tensile strength, 17.7 MPa; and ultimate elongation, 10%.

EPDM rubber (Buna[®] EP G 6470 of Bayer AG, Leverkusen, Germany), with 71 wt % of ethylene and 4.5 wt % of ethylidene norbornene contents, was used. EPDM had a Mooney viscosity [ML₍₁₊₄₎ at 125°C] of 59. For some samples a butadiene–methylstyrene rubber (SBR, SKMS-30ARKM-15; Nizhnekamskneftechim (Nizhnekamsk, Russia), with ML₍₁₊₄₎ (at 130°C) of 47, was used.

GTR fraction with a particle size of 0.4 to 0.7 mm was kindly provided by Scanrub AS (Viborg, Denmark). High-quality, large surface/diameter ratio powder was produced by grinding in an airgap at supersonic speeds. The basic composition of GTR was as follows (in wt %): natural rubber (NR), 30; styrene–butadiene rubber (SBR), 40; butadiene rubber (BR), 20; butyl- and halogenated butyl rubber (IIR/XIIR), 10; carbon black, 32.0–36.0.

Bitumen (BN-4 of UkrTatNafta Ltd., Lisichansk, Ukraine) was used as modifier; some characteristics of the bitumen are shown in Table I.

All materials were used as received.

Preparation of TPE samples

The recipes and processing conditions used for the TPE compositions are given in Tables II and III, re-

TABLE II
Composition Recipes Used

Composition	Component content (wt %)		
	Recipe "a"	Recipe "b"	Recipe "c"
HDPE ^R /rubber ^a	53.3/46.7 ^b	61.5/38.5 ^c	50/50
HDPE ^R /rubber ^a /GTR	40/35/25	40/25/35	50/25/25
HDPE ^R /rubber ^a /(GTR/bitumen)	40/35/25(1/1)	40/25/35(1/1)	50/25/25(1/1)

^a EPDM was used as a rubber in the blends of the recipes "a" and "b"; SBR was used as a rubber in the blends of the recipe "c".

^b Ratio of HDPE^R/rubber = 53.3/46.7 (wt %) is equal to 40/35 (wt %) in other blends of the recipe "a".

^c Ratio of HDPE^R/rubber = 61.5/38.5 (wt %) is equal to 40/25 (wt %) in other blends of the recipe "b".

spectively. In one test series (cf. Table III) mastication of the compositions was carried out in the kneading chamber of a Brabender plasticorder (model PL 2000; C. W. Brabender Instruments, South Hackensack, NJ) at 160°C and 80 rpm. HDPE^R was melted first for 2 min, then EPDM was added and melted for 2 min, and finally the GTR or GTR/bitumen blend (1/1 by weight) was added and masticated with the other components for a further period of about 10 min.

In the other test series (cf. Table III) mastication of the compositions was carried out by using a single-screw extruder (model PLV 150). First, the GTR powder was extruded, together with the bitumen, at a temperature profile of 155/165/175°C and a screw speed of 40 rpm, followed by granulation of the extrudate. Afterward, the granulated GTR/bitumen blend was extruded again, together with other components ($T = 155/165/175^{\circ}\text{C}$, 40 rpm).

Some compositions (cf. Table III) were prepared by rolling. GTR/bitumen blends and the related TPE compositions were produced on mill rolls at $T \sim 60^{\circ}\text{C}$ for 40 min.

Reclamation of GTR

The GTR reclamation procedure was performed under various conditions, listed in Table III. In one test series the reclamation of GTR by bitumen was carried out by preheating the GTR/bitumen blend (1/1 by weight) at $T = 170^{\circ}\text{C}$ for 4 h in an oven. For some samples the additional rolling of reclaimed GTR/bitumen blend was carried out in a mill roll (as described in the previous section).

In the other test series the reclamation of GTR was carried out continuously in a laboratory single-screw extruder (cf. Table III), under conditions described in the previous section.

Tests

Tensile tests were performed on dumbbell-shape specimens at ambient temperature at a crosshead speed of 100 mm/min, using an Instron (Canton, MA) 1122 type universal testing machine. The average data from six to seven parallel tests are given in this work. Pa-

TABLE III
Conditions and Codes of Producing Methods Used

Conditions of producing method	Code
Mastication by using Brabender plasticorder	
1. Mastication of composition (in Brabender plasticorder).	A
1. Heating of GTR/bitumen blend.	B
2. Mastication of HDPE ^R /rubber/(GTR/bitumen) blend followed by its rolling.	
1. Heating of GTR/bitumen blend followed by its rolling.	C
2. Mastication of HDPE ^R /rubber/(GTR/bitumen) blend.	
1. Heating of GTR/bitumen blend followed by its rolling.	D
2. Mastication of HDPE ^R /rubber/(GTR/bitumen) blend followed by its rolling.	
Mastication by using single-screw extruder	
1. Mastication of GTR/bitumen blend followed by its granulation.	E
2. Mastication of HDPE ^R /EPDM/(GTR/bitumen) blend.	
1. Mastication of GTR/bitumen blend followed by its rolling and granulation.	F
2. Mastication of HDPE ^R /EPDM/(GTR/bitumen) blend.	
1. Heating of GTR/bitumen blend followed by its mastication in extruder and granulation.	G
2. Mastication of HDPE ^R /EPDM/(GTR/bitumen) blend.	
1. Heating of GTR/bitumen blend followed by its rolling, mastication in extruder and granulation.	H
2. Mastication of HDPE ^R /EPDM/(GTR/bitumen) blend.	

rameters, such as tensile strength at break and elongation at break, were determined.

The TGA was performed using the Q-1500D Derivatograph system [developed by F. Paulik, J. Paulik, and L. Erdey (Magyar Optikai Művek, Budapest, Hungary)]. TGA traces were registered in the temperature range from 25 to 660°C, at a heating rate 10 K/min in air, by evacuating the volatile products. Weight of the samples was 50 mg.

Rheological measurements were performed using a PIRSP-03 rheometer, developed by SCD of the Institute of Petrochemical Synthesis (Moscow, Russia) with a cone-plate geometry at temperatures of 180, 190, and 200°C, respectively. Before investigation the TPE sample was pressed using a hydraulic press at $T = 180^\circ\text{C}$ and a disk cutoff was used (diameter 3.2 and height 0.7 cm, respectively). The shear stress τ , shear rate $\dot{\gamma}$, and shear viscosity η were calculated using the following equations:

$$\tau = 3M/2\pi R^3 \quad (1)$$

$$\dot{\gamma} = 6.28n/\tan \alpha \quad (2)$$

$$\eta = \tau/\dot{\gamma} \quad (3)$$

where n is cone rotation frequency, α is cone angle ($\alpha = 0.035$ rad), M is torque, and R is cone radius ($R = 20$ cm).

Precut specimens were fractured after immersion in liquid nitrogen and their surfaces were inspected in a scanning electron microscope (SEM; JSM-5400, JEOL, Tokyo, Japan) to investigate the morphology of the various compositions.

DSC study was carried out using a DuPont thermal analyzer (Model 910, DuPont, Boston, MA). The scans were taken in the temperature range from -100 to 200°C with a programmed heating rate of $20^\circ\text{C}/\text{min}$. Melting temperature (T_m), corresponding to the maximum in fusion endotherm, was noted. Heat of fusion (H) was calculated from the area under the endothermic peak and the degree of crystallinity was calculated using a melting enthalpy value, $H_m = 283$ J/g, for the 100% crystalline polyethylene (PE).

The viscoelastic behavior of the resulting TPEs was investigated using a DMTA device (Eplexor 150N of Gabo Qualimeter, Ahlden, Germany). Rectangular sheets (dimensions: $6 \times 1 \times 0.25$ cm³) were subjected to oscillating tensile loading. The testing temperature ranged from -100 to 150°C at a heating rate of $3^\circ\text{C}/\text{min}$.

To estimate the crosslinking degree of samples produced, the residual gel content was determined by Soxhlet extraction using *o*-xylene. The extraction was carried out for 16 h (~ 10 times circulation of solvent/h), followed by drying the samples in an air oven

(50°C for 24 h) before weighing. The *o*-xylene insoluble fraction was considered to correspond to the residual gel content.

RESULTS AND DISCUSSION

Tensile properties

Tensile properties, of the GTR-containing compositions produced by different mastication methods (cf. Table II), are shown in Table IV. The experimental data clearly demonstrate the beneficial effect of bituminous treatment of GTR and its dependency on the mastication method chosen. One can see that GTR-containing TPEs with suitable tensile properties can be obtained for all recipes used by choosing the proper production methods. Based on the above-mentioned definition of TPEs (see introduction), one can conclude that samples B3–B6, B10, B11, B14, and B15–B18 satisfy qualifying standards for TPEs. Note that compression set values are not reported here, although the related values were below 50%.

It is clearly seen that the requisite condition for producing GTR-containing TPEs with suitable properties is preheating the GTR/bitumen blend before mastication with the other blend components in a Brabender plasticorder or extruder. Sol–gel analysis has shown that this heating treatment of GTR leads to decreasing gel-fraction content by about 8% (compared to initial GTR), which is a result of partial devulcanization of GTR. Further decrease of the gel-fraction content, up to about 13%, is observed for the GTR/bitumen blend after its preheating (calculation was done with respect to GTR content). It can be concluded that in such a case bitumen acts as a softening and devulcanizing agent, breaking-up the sulfuric crosslinks in GTR, and therefore leading to activation and functionalization of, at least, its surface. The reactive sulfur released from GTR and sulfur of bitumen components (cf. Table I) further take part in covulcanization of preheated GTR/bitumen blend with fresh rubber (EPDM) in the revulcanization step.

Indeed it can be seen that the tensile strength and ultimate elongation are higher for all TPEs produced by methods that included the procedure of GTR/bitumen pretreatment compared to those produced by the other methods. This suggests an effective interfacial stress transfer between the matrix and the GTR particles¹⁴ attributed to better entanglement of the partly devulcanized GTR rubber chains into the surrounding matrix.

One can see that the higher the GTR content in TPEs, the lower are the tensile properties of the product. Additional homogenization, by rolling preheated GTR/bitumen blend and/or final product (cf. Table II), further improved the tensile strength and, especially, ultimate elongation of the resulting TPEs. This

TABLE IV
Tensile Properties of Individual Polymers and Blends Produced

Blend code	Composition	Code of producing method	Tensile strength ^a (MPa)	Ultimate elongation ^a (%)	Hardness (Shore A)
Mastication by using Brabender plasticorder					
Recipe "a"					
B1	HDPE ^R /EPDM	A	13.0 (20.0)	840 (754)	93
B2	HDPE ^R /EPDM/GTR	A	4.4 (6.7)	114 (120)	96
B3	HDPE ^R /EPDM/(GTR/bitumen)	A	4.1 (6.5)	168 (176)	94
B4	HDPE ^R /EPDM/(GTR/bitumen)	B	4.9 (8.0)	528 (536)	93
B5	HDPE ^R /EPDM/(GTR/bitumen)	C	6.0 (10.2)	540 (535)	93
B6	HDPE ^R /EPDM/(GTR/bitumen)	D	6.1 (10.7)	615 (590)	93
Recipe "b"					
B7	HDPE ^R /EPDM	A	11.6 (17.9)	750 (593)	90
B8	HDPE ^R /EPDM/GTR	A	3.7 (6.7)	46 (58)	95
B9	HDPE ^R /EPDM/(GTR/bitumen)	A	3.9 (7.0)	85 (97)	93
B10	HDPE ^R /EPDM/(GTR/bitumen)	B	4.0 (5.2)	127 (194)	93
B11	HDPE ^R /EPDM/(GTR/bitumen)	C	5.9 (5.3)	377 (325)	92
Recipe "c"					
B12	HDPE ^R /SBR ^b	A	6.8	265	83
B13	HDPE ^R /SBR ^b /GTR	A	7.0	18	79
B14	HDPE ^R /SBR ^b /(GTR/bitumen)	C	8.4	355	84
Mastication by using single-screw extruder					
Recipe "a"					
B15	HDPE ^R /EPDM/(GTR/bitumen)	E	7.5	270	88
B16	HDPE ^R /EPDM/(GTR/bitumen)	F	9.0	300	89
B17	HDPE ^R /EPDM/(GTR/bitumen)	G	9.8	425	86
B18	HDPE ^R /EPDM/(GTR/bitumen)	H	13.6	515	86

^a The data in parentheses represent the properties after ageing at 70°C for 24 h.

^b Curing system used, phr per 100 phr of SBR in mix formulations: sulfur, 0.9; tetramethylthiuram disulfide, 0.1; ZnO, 5.0; stearic acid, 2.0; 2-mercaptobenzothiazole, 1.0.

fact is evidence of effective compatibilization of the TPE blend components.²²

To check the compatibilization efficiency of bitumen in rubber/polyolefin blends, TPES containing SBR were selected (samples B15–B17). Note that SBR is far less compatible with HDPE than with EPDM. It can be seen that tensile characteristics of HDPE^R/SBR TPE (sample B12) are inferior to those of HDPE^R/EPDM TPE (sample B1). Introduction of GTR into the HDPE^R/SBR formulation (sample B13) leads to a dramatic reduction in ultimate elongation compared to that of the HDPE^R/EPDM/GTR blend (sample B2).

However, after bituminous treatment of GTR and further melt production of HDPE^R/SBR/(GTR/bitumen) TPE (sample B14) the tensile properties were substantially improved over those of the reference HDPE^R/SBR blend (sample B13). It can thus be concluded that bitumen acts as an effective compatibilizer for polyolefins and rubbers in TPES.

Extrusion technology is economically favored and technologically sound for GTR-containing TPE production. It can be seen, from the data presented in Table V, that even after six cycles of reprocessing, the HDPE^R/EPDM/(GTR/bitumen) TPE (sample B17) re-

TABLE V
Effect of Reprocessing on Tensile Properties, Gel Fraction Content, and Flow Activation Energy of HDPE^R/EPDM/(GTR/bitumen) = 40/35/25(1/1) TPE Produced by Method "G"

Blend code	Reprocessing cycle	Tensile strength (MPa)	Ultimate elongation (%)	Gel fraction content (%)	Flow activation energy (kJ/mol)
B17	0 (primary)	9.8 ± 0.3	425 ± 16	9.6 ± 0.6	28.7
	1st	9.9 ± 0.4	432 ± 23	10.5 ± 0.7	29.1
	2nd	10.1 ± 0.5	457 ± 24	11.6 ± 0.8	29.2
	3rd	10.0 ± 0.2	474 ± 13	13.3 ± 0.7	29.7
	4th	10.9 ± 0.7	493 ± 17	10.8 ± 0.8	31.3
	5th	11.3 ± 0.8	458 ± 20	10.5 ± 0.7	36.3
	6th	11.1 ± 0.6	455 ± 15	10.1 ± 0.5	28.2

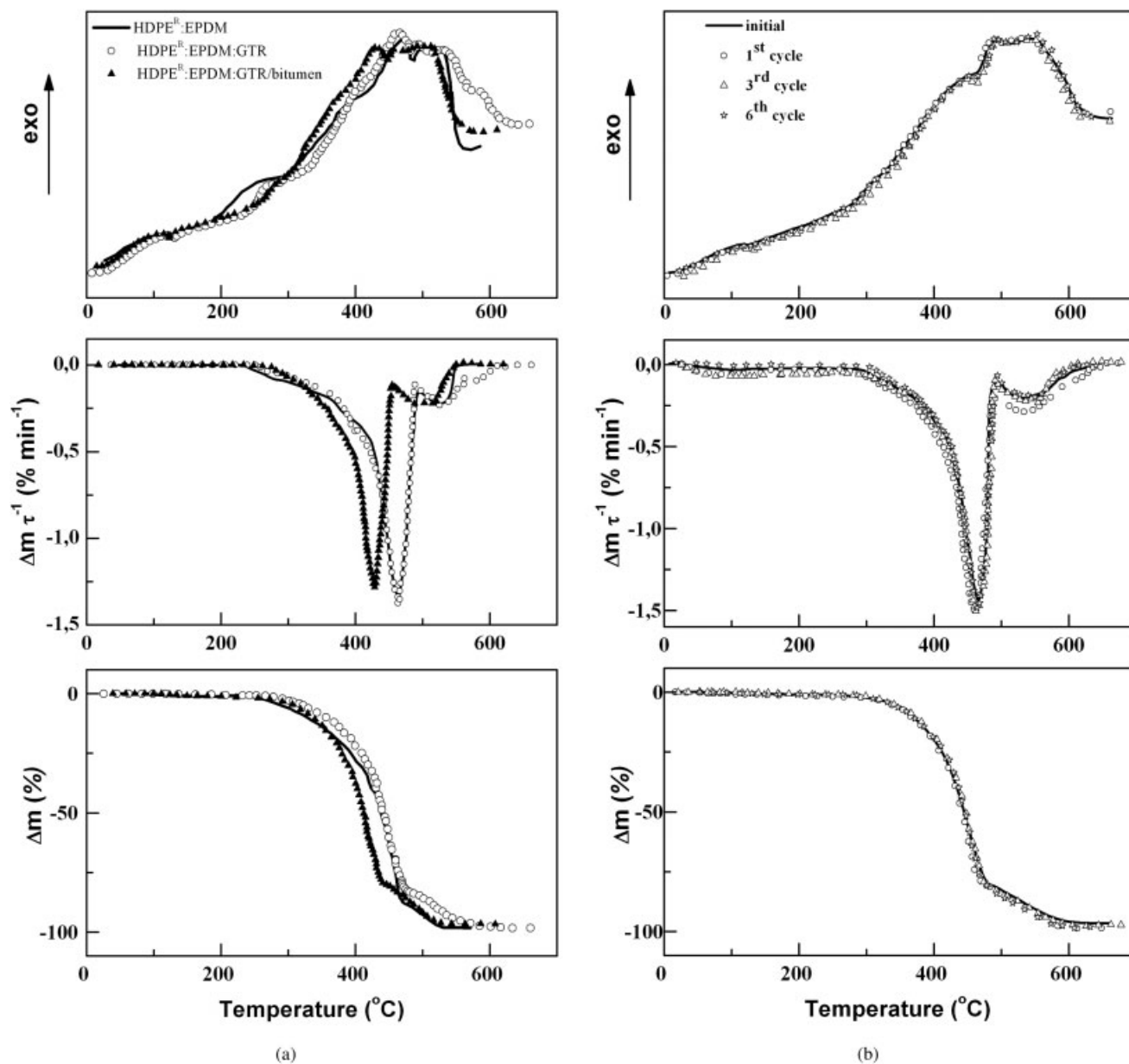


Figure 1 Thermogravimetric analysis of the blends: (a) (—) HDPE^R/EPDM (sample B1); (○) HDPE^R/EPDM/GTR (sample B2), and (▲) HDPE^R/EPDM/(GTR/bitumen) (sample B6). (b) HDPE^R/EPDM/(GTR/bitumen) TPE (sample B17) as well as after the 1st, 3rd, and 6th reprocessing cycles in a single-screw extruder. Sample codes correspond to the blends in Table IV.

tains tensile properties at a suitable level (also see section on rheological properties).

Note that all EPDM-based compositions exhibit similar hardness values, which are near or above 90 Shore A units, whereas the SBR-based compositions exhibit lower hardness values, which are around 80 Shore A units.

Table IV indicates some increase of tensile properties for most of the compositions studied as a result of thermal ageing. It can be concluded here that all the investigated blends were remarkably stable with respect to ageing. As shown¹⁴ the enhancement in tensile strength and marginal change in ultimate elonga-

tion suggest the formation of some additional crosslinks (postcuring). On the other hand, the increase of both tensile strength and ultimate elongation, observed for samples B2–B5 and B8–B10, suggest that postcuring occurs mainly in the rubber phase.

Thermogravimetric analysis (TGA)

The thermal stability of a GTR-containing composition (sample B2) and a GTR/bitumen-containing blend (sample B6) was studied by TGA and compared to that of the reference HDPE^R/EPDM TPE (sample B1); the corresponding curves are shown in Figure 1(a). It

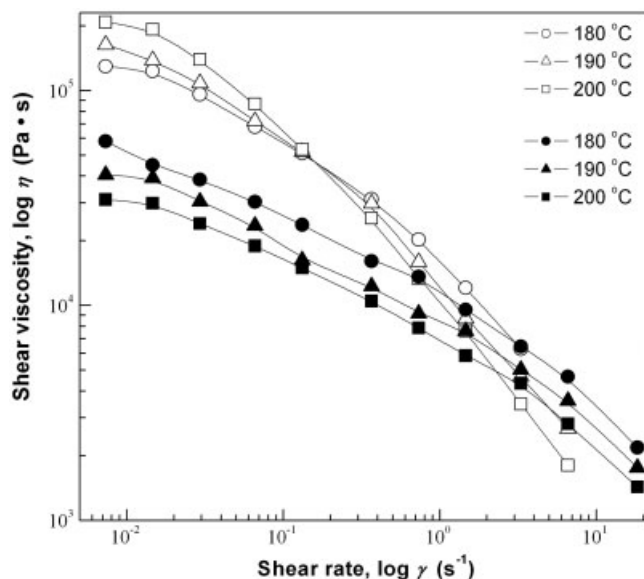


Figure 2 Shear viscosity (η) versus shear rate (γ) plots for HDPE^R/EPDM (sample B1, open symbols) and for HDPE^R/EPDM/(GTR/bitumen) TPE (sample B6, solid symbols) obtained at different temperatures (indicated in the plot). Sample codes correspond to the blends in Table IV.

can be seen that introduction of GTR into the basic HDPE^R/EPDM blend is not accompanied by significant changes in thermal stability. Some shift to higher temperatures is observed for the stages of intensive decomposition $\geq 500^\circ\text{C}$ only, although, finally, char residue values are nearly the same for both samples: 1.77% for the reference HDPE^R/EPDM (sample B1) and 1.67% for the HDPE^R/EPDM/GTR (sample B2). In addition, one can see that the stage of thermal oxidative destruction at $150\text{--}250^\circ\text{C}$, characteristic for the basic HDPE^R/EPDM blend, disappears completely for the GTR-containing samples.

The thermal behavior of GTR/bitumen-containing TPE (sample B6) in the temperature region $\leq 340^\circ\text{C}$ is quite similar to that of the GTR-containing blend (sample B2). However, some depression, by about $28\text{--}33^\circ\text{C}$ in the temperature of the maximal rate of decomposition in the region from about 340 to 460°C , was observed for the sample B6 compared to that of both the other samples (B1 and B2). In the temperature region $\geq 460^\circ\text{C}$ the thermal behavior of sample B6 is quite similar to that of reference sample B1.

Thermal stability of the favored TPE (sample B17), before and after reprocessing in a single-screw extruder, was also studied, and the corresponding curves are shown in Figure 1(b). No significant changes in thermal stability of the reprocessed samples were observed after six reprocessing cycles. This fact is in harmony with the high residual tensile properties of B17 (see section on tensile properties). Further, the exceptional thermal stability suggests that no additional stabilizer need be added to the TPES produced.

Rheological properties

The rheological properties of the HDPE^R/EPDM/GTR (sample B2) and HDPE^R/EPDM/(GTR/bitumen) (sample B6) were studied and compared with those of the reference HDPE^R/EPDM (sample B1). The dependency of shear viscosity (η) versus shear rate (γ), obtained at different temperatures, is shown in Figure 2. It should be noted that measurements were not possible with HDPE^R/EPDM/GTR blends because of their very high viscosity ($>10^5 \text{ Pa s}^{-1}$), caused by the introduction of crosslinked GTR particles. A significant decrease in the melt viscosity was observed for GTR/bitumen-containing TPE (sample B6) compared to that of the reference HDPE^R/EPDM (sample B1) at a given temperature and shear rate (except the region of the highest shear rate). Undoubtedly, this is mainly attributed to the low molecular weight of bitumen, which acts as an effective plasticizer in the TPE studied.

For both samples B1 and B6 the viscosity decreases with increasing shear rate at a fixed temperature. Shear thinning is typical for most thermoplastic polymers.⁸ However, a viscosity increase was observed for sample B1 with rising temperature in the low shear-stress region. On the other hand, in the high shear-stress region, the opposite tendency is obvious. The above-mentioned increase in viscosity can be explained by postcuring of the TPE (sample B1) during rheological measurement (i.e., thermally induced crosslinking of the EPDM). It is intuitive that the higher the temperature, the higher is the crosslinking

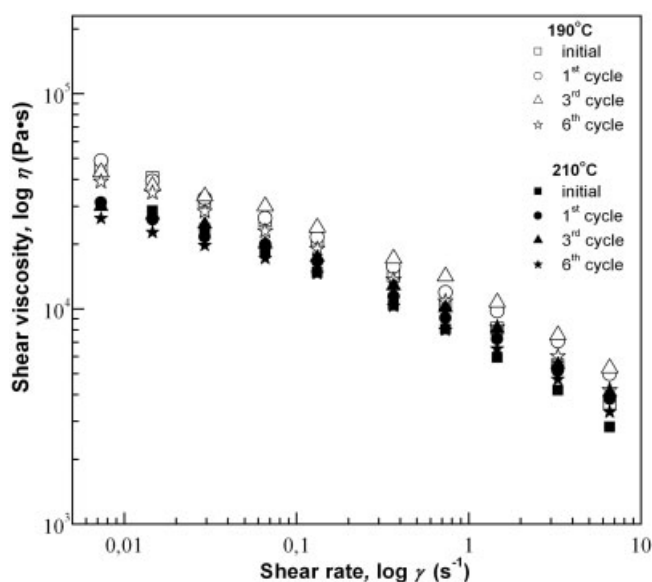


Figure 3 Shear viscosity (η) versus shear rate (γ) plots for the primary HDPE^R/EPDM/(GTR/bitumen) TPE (sample B17, cf. Table IV) as well as after the 1st, 3rd, and 6th reprocessing cycles in a single-screw extruder. The temperatures of melt-flow measurements are indicated in the plot.

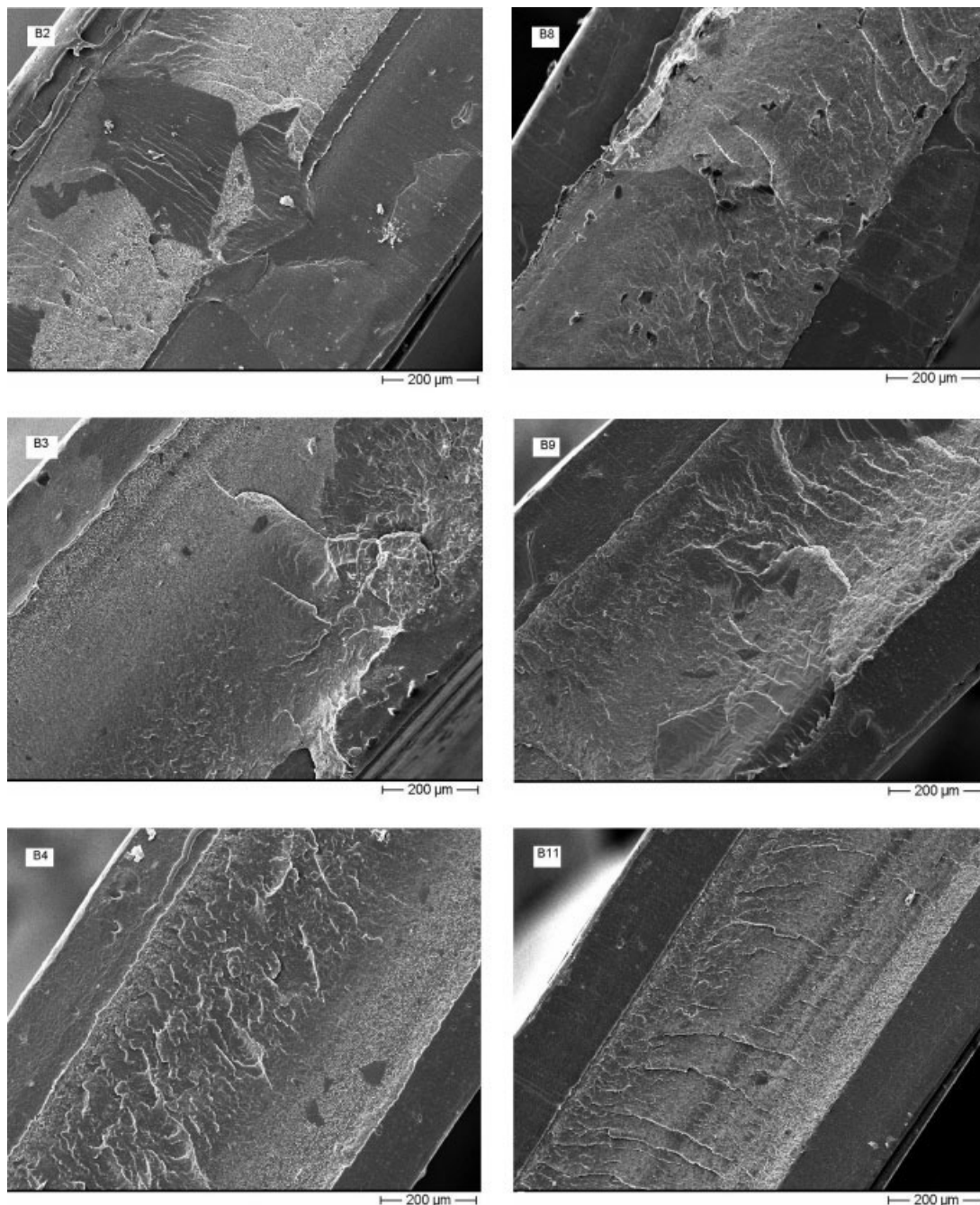


Figure 4 Typical SEM photomicrographs of cryofractured cut surfaces of TPEs of recipes “a” (samples B2, B3, and B4) and “b” (samples B8, B9, and B11). Sample codes correspond to the blends in Table IV.

of the product.²³ Note that the gel fraction of sample B1 increased from zero (before mastication) up to about 16% (after mastication); also note the substantial influence of the rubber component on the flow behavior of blends, exactly in the range of the low shear-stress region, where relaxation processes take place²⁴ and some agglomerated structures can be formed.^{25,26} Logically, in the high shear-stress region the influence of the rubber component on flow behavior of the TPE is insignificant because of the absence of relaxation

processes and destruction of agglomerated structures.²³

The rheological properties of the multireprocessed (six cycles) HDPE^R/EPDM/(GTR/bitumen) TPE (sample B17) were studied and typical dependency, of $\eta = f(\dot{\gamma})$ obtained at 190 and 210°C after the 1st, 3rd, and 6th reprocessing cycles, is shown in Figure 3. In all cases the viscosity decreases with increasing shear rate at a fixed temperature and, with increasing temperature at a fixed shear rate, the viscosity first slightly

increases before slightly decreasing. Thus, during the first three processing cycles some postcuring reactions should dominate. This conclusion agrees with the gel fraction data presented in Table V. However, virtually no significant changes in viscosity of the samples can be observed during six reprocessing cycles, which means that the TPES under investigation can be easily reprocessed by different industrial melt-processing technologies (extrusion, injection molding, etc.).

Scanning electronic microscopy (SEM)

Figure 4 shows SEM photomicrographs taken from the cryogenically fractured surfaces of the sheets of some blends. They were produced according to recipes "a" (samples B2, B3, and B4) and "b" (samples B8, B9, and B11) by different methods. Sample codes correspond to the blends in Table IV. One can clearly see that GTR particles, directly dispersed in HDPE^R/EPDM blends (samples B2 and B8), are very poorly bonded to the matrix: many large and small GTR particles are observed outside the matrix, indicating a lack of interaction between them. Sample B8, produced with the higher GTR content (35 wt %), is characterized by deteriorated homogeneity of the surface compared to that of sample B2; that is, an increase of apparent size of debonded GTR particles and the presence of cracks (or holes) are observed. Both samples exhibit unacceptably low tensile properties (cf. Table IV), especially sample B8.

It can be seen that the surface of the HDPE^R/EPDM/(GTR/bitumen) blends, produced by mastication of compositions by a Brabender plasticorder (samples B3 and B9, method "A"), look more homogeneous. Furthermore, the apparent size of the GTR particles is reduced and the small GTR particles are well incorporated into the matrix, whereas the larger particles partially protrude outside the fracture surface; moreover, there are no visible holes or cracks as there were in the corresponding bitumen-free samples. It can be concluded that, in such a case, bonding between GTR particles and the thermoplastic matrix is improved, resulting in increasing elongation at break (cf. Table IV). However, the homogeneity level achieved does not provide the high level of tensile properties for samples B3 and B9 (cf. Table IV). We consider that no significant interfacial layer between GTR particles and thermoplastic matrix is formed.

A superior degree of bonding between GTR particles and matrix was achieved for samples B4 and B11, produced by methods "B" and "C," respectively (cf. Table III), where the partial devulcanization of GTR under the preheating of GTR/bitumen blend occurred. Surfaces of samples B4 and B11 were characterized by a higher level of homogeneity compared to that of the other samples, which can be explained by the formation of a significant interfacial layer of par-

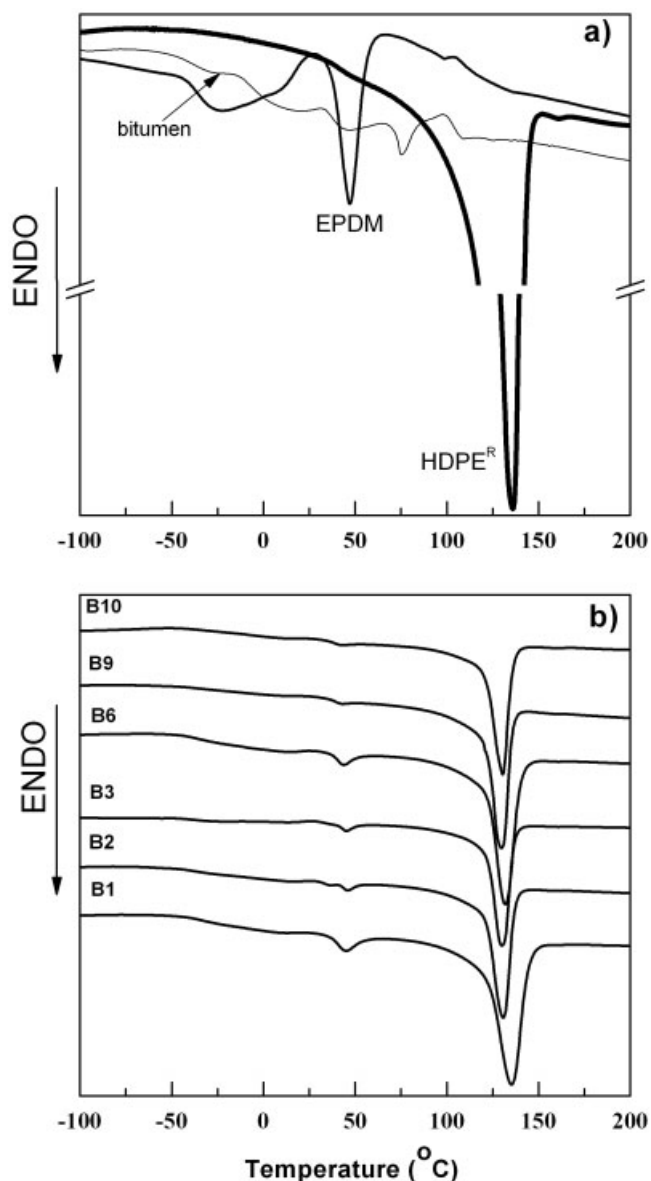


Figure 5 Typical DSC traces for (a) individual HDPE^R, EPDM, and bitumen and for (b) TPES produced by different methods. The codes of the curves correspond to the formulation codes in Table IV.

tially devulcanized GTR, bitumen, and other components of the blends. Understandably, samples B4 and B11 exhibit high tensile properties (cf. Table IV), especially with respect to sample B4.

Differential scanning calorimetry (DSC)

Typical DSC curves, for the individual polymers and for TPES produced, are shown in Figure 5(a) and (b), respectively, and the corresponding thermal characteristics are summarized in Table VI. Both components (EPDM and HDPE^R) retain their own amorphous and crystalline phases in TPES produced, although some

TABLE VI
DSC Characteristics for Individual Components and Blends Produced

Blend code	Composition	T_m (°C)		$T_{m\text{onset}}/T_{m\text{end}}$ (°C)		X_c^a (%)	
		EPDM	HDPE ^R	EPDM	HDPE ^R	EPDM	HDPE ^R
	HDPE ^R	—	136	—	37/160	—	65
	EPDM	47	—	28/65	—	12	—
	Recipe "a"						
B1	HDPE ^R /EPDM	45	135	26/69	73/156	6	57
B2	HDPE ^R /EPDM/GTR	46	131	26/57	73/145	4	63
B3	HDPE ^R /EPDM/(GTR/bitumen)	45	130	27/65	73/143	3	61
B4	HDPE ^R /EPDM/(GTR/bitumen)	44	129	29/58	73/143	3	56
B6	HDPE ^R /EPDM/(GTR/bitumen)	44	132	29/65	70/147	4	62
	Recipe "b"						
B7	HDPE ^R /EPDM	45	135	27/70	73/158	4	60
B8	HDPE ^R /EPDM/GTR	45	132	36/57	70/146	3	65
B9	HDPE ^R /EPDM/(GTR/bitumen)	42	130	29/64	70/142	2	64
B10	HDPE ^R /EPDM/(GTR/bitumen)	42	131	28/70	73/144	2	50
B11	HDPE ^R /EPDM/(GTR/bitumen)	45	133	32/58	75/146	0	60

^a The X_c (crystallinity) values were calculated taking into account the weight fraction of PE in the EPDM ($\approx 71\%$) and that of EPDM in the blends; the enthalpy of melting of PE with 100% degree of crystallinity was taken as 283 J/g.

reduction in the crystallinity (X_c) can be observed, especially for the EPDM component. The dramatic reduction in X_c values of the EPDM component can be explained in its crystallization is hampered because of the presence of HDPE^R crystallites and intermingling of several EPDM chains with those of the HDPE. The outcome of the latter is a "mixed amorphous phase" for HDPE^R/EPDM.

Some depression of the melting temperature (T_m) values of both EPDM and HDPE^R components of the TPEs, compared to that of the individual polymers, was observed. This depended on the composition and processing conditions used. It is known that the depression of T_m of polymers in the blends is caused by the formation of less-perfect crystallites or crystallites having a smaller size.²⁷ Irrespective of which mechanism is at work, the decrease in T_m is always evidence of improved blend compatibility.

In addition, for the HDPE^R matrix, a significant shift of onset of melting temperature ($T_{m\text{onset}}$) toward higher temperature and narrowing of a region of crystallites melting ($T_{m\text{end}} - T_{m\text{onset}}$) is observed in all the blends (cf. Table VI) compared to that of the individual HDPE^R. The growth of $T_{m\text{onset}}$ can be caused by disappearance of smaller, less-perfect crystallites attributed to their evolving into the amorphous phase and narrowing of the crystallite region: melting is a result of decreasing crystallite dimension dispersion.

Dynamic mechanical thermal analysis (DMTA)

Temperature dependencies of loss modulus (E''), storage modulus (E'), and loss factor ($\tan \delta$) for individual HDPE^R and EPDM, as well as for some blends produced, are shown in Figures 6, 7, and 8, respectively. Values of the glass-transition temperature (T_g), de-

fining as the temperature position of the E'' peak, and corresponding E'' values at those T_g 's are listed in Table VII. EPDM has one sharp relaxation peak at -36°C (α -transition), corresponding to the T_g of its amorphous phase (cf. Fig. 6). Some increase in E' and $\tan \delta$ values, around 50°C (cf. Figs. 7 and 8), can be attributed to the melting of residual polyethylene crystallites, confirmed by the above DSC data. HDPE^R has two broad relaxation peaks (cf. Fig. 6) at -15°C (β -transition), assigned to the T_g of its amorphous

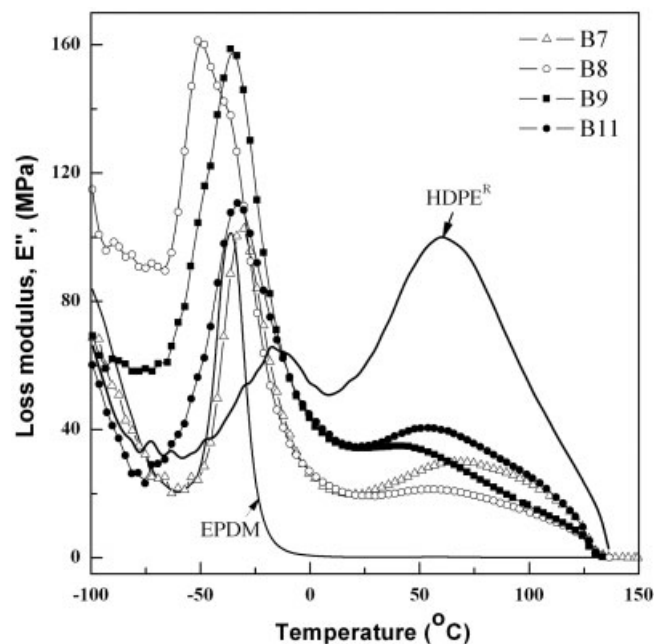


Figure 6 Temperature dependency of loss modulus (E'') for HDPE^R, EPDM, and TPEs produced. The codes of the curves correspond to the formulation codes in Table IV.

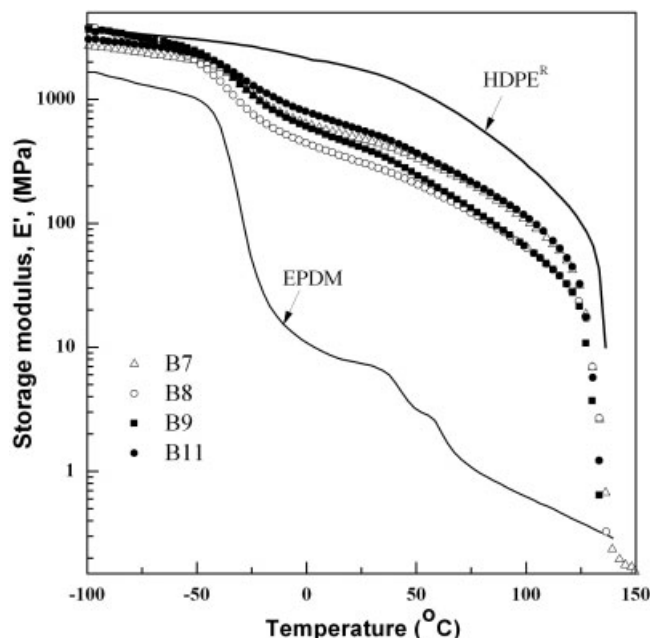


Figure 7 Temperature dependency of storage modulus (E') of individual HDPE^R, EPDM, and TPEs produced. The codes of the curves correspond to the formulation codes in Table IV.

phase, and the peak around approximately 60°C (α_c -transition), relating to the vibration and rotational motion of $-\text{CH}_2-$ groups in the crystalline phase, ascribed to recrystallization of the smaller, less-perfect crystallites.²⁸ For both EPDM and HDPE^R the low temperature transition below -100°C is observed as the result of the crankshaft motion of $-\text{CH}_2-\text{CH}_2-$ polyethylene chain segments.²⁹

The character of $E'(T)$ plots (cf. Fig. 7) of all the blends studied is quite similar to the HDPE^R, which means that HDPE^R forms a continuous thermoplastic phase (matrix), whereas the dispersed phase is formed by the EPDM/GTR mixture.

The introduction of GTR into HDPE^R/EPDM TPE (sample B8) results in essential changes in its viscoelastic properties. A new, sharp relaxation transition around -50°C (T_{g1}) appears (cf. Figs. 6 and 8) that is characteristic for the rubber component of GTR.²¹ A substantial decrease, by 9–14°C in both T_g values (cf. Table VII), as well as some downtrend in the $E' = f(T)$ curve and uptrend in the $\tan \delta = f(T)$ and $E'' = f(T)$ curves were observed compared to those of the GTR-free sample B7 (cf. Figs. 6–8). All these changes suggest a significant growth of chain flexibility of the components of the GTR-containing sample B8, attributed to disorder of the thermoplastic matrix by dispersed crosslinked GTR particles caused by poor interphase adhesion between the components.^{18,19} The tensile characteristics of sample B8 are much lower than those of the GTR-free sample B7 (cf. Table IV).

Introduction of bitumen into the HDPE^R/EPDM/GTR blend (sample B9) yields a convergence between T_{g2} and T_{g4} values (cf. Table VII) and growth by about 80% in ultimate elongation value compared to that of sample B8 (cf. Table IV), which can be interpreted as improved “mixing” of the blend components. However, the disordering of the thermoplastic matrix by dispersed rubber particles is high, as reflected by the high values of E'' and $\tan \delta$ (cf. Figs. 6 and 8, respectively). As a result, the tensile properties of sample B9 (cf. Table IV) do not satisfy qualifying standards for TPES.²² It can be concluded that, in such a case, the processing conditions used (method “A”) do not provide the required devulcanization degree of GTR and interfacial adhesion between the components. Some growth in the crosslinking degree of the amorphous phase of the blend occurs, which is confirmed by both the downtrend of $E'' = f(T)$ curve in the temperature region $\leq -50^\circ\text{C}$ and the uptrend of the $E' = f(T)$ curve (cf. Figs. 6 and 8, respectively). We consider this to be a result of dynamic vulcanization of the dispersed rubber phase inside the plastic matrix. Thus, the bitumen can act as an additional curing agent. This is the reason that the term dynamic vulcanization can be used, although bitumen is not at all a traditional curative for rubbers.

The HDPE^R/EPDM/(GTR/bitumen) blend (sample B11), produced by method “C,” is characterized by significant reductions of E'' and $\tan \delta$ values (cf. Figs. 6 and 8) as well as a further uptrend of the $E' = f(T)$ curve (cf. Fig. 7) compared to those of sample B9.

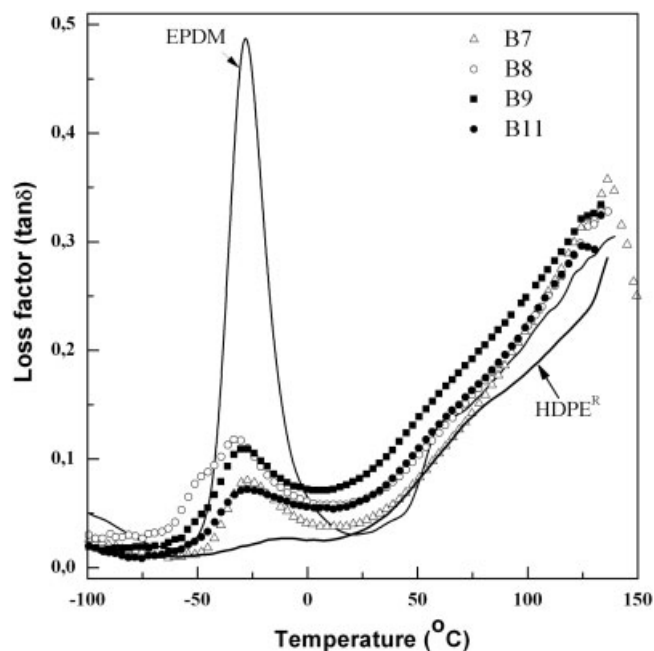


Figure 8 Temperature dependency of loss factor ($\tan \delta$) for HDPE^R, EPDM, and TPEs produced. The codes of the curves correspond to the formulation codes in Table IV.

TABLE VII
DMTA Data for Individual Components and Blends Produced

Blend code	Composition	T_g (°C)/ E''^a (MPa) for phases rich in:			
		GTR	EPDM (amorphous)	HDPE ^R (amorphous)	HDPE ^R (crystalline)
		T_{g1}/E''	T_{g2}/E''	T_{g3}/E''	T_{g4}/E''
	HDPE ^R	—	—	—15/65	60/100
	EPDM	—	—36/102	— ^b	—
B7	HDPE ^R /EPDM	—	—31/134	— ^b	68/30
B8	HDPE ^R /EPDM/GTR	—50/160	—42/150	— ^b	54/21
B9	HDPE ^R /EPDM/GTR/bitumen	—49/121	—35/158	— ^b	42/35
B11	HDPE ^R /EPDM/GTR/bitumen	—48/63	—33/110	— ^b	53/41

^a E'' value taken at T_{gi} .

^b T_{g3} is overlapped with T_{g2} .

Undoubtedly, such changes evidence further growth in the crosslinking degree of the dispersed EPDM/GTR rubber phase in sample B11 compared to that of B9. However, based on the increasing ultimate elongation value of sample B11 (cf. Table IV) improved interfacial adhesion between the components can be unequivocally posited. We consider that this is a consequence of the higher degree of bitumen-induced devulcanization of GTR, with preheating of the GTR/bitumen blend before mastication, additionally reflected by the significant decrease of T_{g1} onset of the rubber phase (cf. Fig. 6) from -65°C (for sample B9) to -75°C (for sample B11). This result agrees well with the conclusions made on the basis of sol-gel analysis (see section on tensile properties). As was noted above the (re)covulcanization of partly devulcanized GTR with EPDM and bitumen occurred during mastication of composition in the Brabender plasticorder and, finally, sample B11 exhibited high values of tensile strength and ultimate elongation (cf. Table IV). Certainly, this is a result of the improved compatibility of the blend components.

Based on analysis of the DMTA data it can be concluded that, in producing a GTR/bitumen-containing TPE by method "C," the bitumen first acts as a devulcanizing agent for GTR and then, simultaneously, as an effective curing agent for dispersed EPDM/GTR rubber phase and as a compatibilizer for blend components, thus improving the interfacial adhesion between the dispersed rubber phase and plastic HDPE^R matrix.

CONCLUSION

Based on this study, dedicated to producing thermoplastic elastomers (TPEs) using ground tire rubber (GTR), the following conclusions can be drawn:

- Bitumen is a suitable reclaiming agent for GTR under the treatment conditions used. During fur-

ther melt processing it acts as a curing agent for the rubber components of TPEs and also works as an effective compatibilizer for HDPE^R/EPDM/GTR compositions.

- TPEs, containing GTR pretreated by bitumen, show outstanding mechanical properties, high thermal stability, and good reprocessability. In addition, TPE grades containing GTR and recycled HDPE can be produced not only in batches but also continuously at an industrial scale.
- The performance of TPEs mainly depends on conditions of GTR reclamation by bitumen, type of the rubber used, and melt-processing parameters.
- Investigations of the structure-property relationships of TPEs, carried out by SEM, DSC, and DMTA methods, clearly confirm the improvement in interfacial adhesion between the GTR particles and surrounding thermoplastic matrix when the GTR was partially devulcanized in bitumen.

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