Partial Replacement of EPDM by GTR in Thermoplastic Elastomers Based on PP/EPDM: Effects on Morphology and Mechanical Properties

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ABSTRACT: The formulation of recycled thermoplastic elastomeric materials (TPE) based on ground tyre rubber (GTR), generated from end of life tyres, can be an alternative strategy to deal with a type of waste responsible for increasingly environmental problems over the past decades. The incompatibility of GTR with thermoplastics places several issues on the formulation of these materials, which this study tries to overcome. An encapsulation strategy of the GTR by an elastomeric phase is proposed in this work to overcome the lack of adhesion between the materials. Ternary blends, composed of a highly flowable polypropylene homopolymer, an ethylene propylene diene monomer (EPDM) and GTR were formulated and their morphology and mechanical properties analyzed. The morphology of the blends showed interaction between the materials, revealing that the encapsulation of GTR by a rubber phase can be an adequate strategy to formulate recycled-based TPE materials, if the dimension of the GTR particles is controlled and taken into consideration. The mechanical properties revealed the replacement effect of EPDM by GTR, and its dependence on the amount of that replacement. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40160.

INTRODUCTION

Waste generated from end of life vehicles has contributed on the past years to several worldwide environmental problems. In order to deal and prevent this specific problem, as well as to save the raw materials, waste management regulations have been imposed, promoting the reuse and recycling of the waste products.[1] Waste rubbers from end of life tyres (ELT) are a major part of this environmental problem. The Portuguese organization for collection and disposal of ELT, collected 90.372 tons of ELT in 2011, mainly for retread, recycling and energy recovery purposes.[2] Upcycling this type of waste is a current relevant subject and strategies and techniques are under development for new value-added applications, like synthetic turf, shock-absorbing surfaces or moulded objects.[3–7] The injection moulding industry is currently looking at ground tyre rubber (GTR), originated from mechanical shredding and grinding of tires in recycling plants, as a material that can be used in injection moulding applications. However, some compatibility issues must be resolved, because vulcanized GTR acts as semirigid filler, with poor adhesion to the thermoplastic matrix, which leads to a reduction on the mechanical properties of the material,

especially of the elongation at break and impact resistance.[8,9] Since thermoplastic elastomers (TPE) have the advantage of large-scale processing as well as recyclability, TPE based on GTR (TPE^GTR) are a possible alternative to existing commercial TPE. Polypropylene is often used as a thermoplastic phase on TPE since it is a low-cost material with balanced mechanical and physical properties as well as easy processability. However, the formulation of TPE^GTR materials with lack of compatibility, leads to blends with properties that do not fulfil the specifications required for a TPE, like elongation at break and compression.[10]

Several studies have been developed to enhance the compatibilization between the materials, predominantly acting on the nature of the GTR particles or on the interface between the polyolefin matrix and GTR.[11–15] Reversing the chemical structure of the rubber material to an unvulcanized state is one of the strategies on rubber recycling. Most of the research in this area has been directed to the development of different techniques and materials capable of reclaiming or devulcanizing the rubber material. Physical processes, like microwave and ultrasound techniques, and mechanochemical processes have been used.

Surface functionalization of GTR is another research focus. Sung et al.[16] used allylamine to modify the surface of GTR with the grafting reaction being induced by UV radiation. Peroxide was also used to promote an *in-situ* compatibilization between a polyolefin and GTR.[17–19] The use of compatibilizing agents to promote the adhesion between the thermoplastic and the elastomeric phase is another pursued strategy to improve the behavior of TPE[GTR] blends. Maleic anhydride (MA) grafted materials like SEBS, ethylene propylene diene monomer (EPDM) and PP were used as compatibilizing agents. Kim et al.[20] study the effect of ultrasonic treated GTR and SEBS-g-MA on polyolefinic blends. Zhang et al.[21] studied the effect of bitumen treated GTR with SEBS-g-MA or EPDM-g-MA. Both works lead to promising results toward the formulation of TPE[GTR]. The partial substitution of virgin elastomer by GTR is also an alternative strategy to obtain a TPE[GTR].[22–25] Grigoryeva et al.[26] successfully incorporated reclaimed GTR with bitumen on HDPE/EPDM blends, establishing a relationship between the process and the properties of the blend. Kumar et al.[27] developed thermoplastics vulcanizates (TPV) based on GTR through dynamic vulcanization of fresh rubber, with sulfur or peroxide, in a LDPE matrix. This vulcanization during the mixing process enabled a fine and uniform dispersion of the crosslinked rubber in the thermoplastic matrix and a significant improvement of these blends mechanical properties. In spite of this better behavior of TPV blends, the formulation of TPE[GTR] without the use of thermochemical methods still remains a relevant subject of interest and for ecological, energetic, and industrialization reasons can contribute to a significant enhancement on the process of ELT recycling. To achieve it, GTR encapsulation by fresh rubbers as well as GTR reclaiming procedures must be considered in new design experiments.[28]

This work intends to contribute to the definition of adequate strategies, techniques and materials for the formulation of TPE[GTR] by the injection moulding industry without the use of thermochemical methods that imply time and energy consuming procedures. Upcycling the use of GTR material in new added-value technical applications is another research focus. The use of a high melt flow polypropylene, suitable for the injection moulding of thin complex parts, will be the base for the TPE[GTR] and the effect of different fresh rubbers will be thoroughly analyzed.

This article presents the first part of this work, studying the morphology and mechanical properties of binary and ternary mixtures with EPDM, as the fresh rubber, due to its reasonable compatibility with polyolefin materials.[27,29] The blends were submitted to tensile, hardness, and impact tests. Dynamic scanning calorimetry (DSC) was used to assess the effect of crystallinity on the TPE[GTR] blends. Scanning electronic microscopy (SEM) was used to analyze the blends morphology, namely the dispersion and adhesion ability of the thermoplastic and elastomeric phases and also a possible encapsulation effect of GTR by EPDM.

EXPERIMENTAL

Materials
The elastomeric materials used on the blends formulation are as follows: a recycled rubber powder (GTR), from mechanical ground scrap tyres, FB 00-08, from Biosafe S.A., Portugal, obtained by an ambient grinding process, sieving class 635 to 20 Mesh and density from 0.6 to 0.7 g/cm^3; and a commercial available EDPM, Buna EP G2470 from Lanxess, suitable for injection moulding, with 69% ethylene weight content (wt %), 4.2 wt % content of ethylidiene norbornene, as diene, 0.86 g/cm^3 density, Money viscosity (ML(1+4) at 125°C) of 22 MU and a MFI of 0.5 g/10 min (230°C, 2.16 kg). For the thermoplastic phase, it was used a polypropylene homopolymer, PPH10060 supplied by Total Petrochemicals, especially suited for injection moulding of very thin and complex parts, with a MFI of 35 g/10 min (230°C, 2.16 kg) and density of 0.9 g/cm^3.

Set of Experiments
An experimental procedure was established to evaluate the effect of EPDM and GTR in polypropylene based blends (Figure 1). A first set of experiments was performed to study the effect of the fresh rubber content, EPDM, on the morphology and mechanical properties of PP based blends [Figure 1(b)]; a second set to study the effect of GTR and EPDM on a PP based binary blend [Figure 1(c)]; finally, an evaluation of the EPDM replacement by GTR was made by varying the weight content of EPDM, on the rubber phase, between 70 and 30 wt %, [Figure 1(d)]. Blends compositions are listed in Table I.

Melt Mixing and Sample Preparation
Binary and ternary blends were prepared by melt mixing on a Brabender type internal mixer. For ternary blends, the blending process was carried out in two stages. A first mixing stage of EPDM with GTR was made to promote a better encapsulation of the GTR particles by EPDM. To be able to achieve a homogeneous mixture of the injection grade EPDM with GTR, this operation was performed at 180°C during 8 min. This mixture was then milled to obtain the granules for the next blending stage. On a second stage PP was placed in the mixing equipment at 180°C and 60 rpm rotor speed and after 2 min GTR/EPDM mixture, prepared on the first stage, was added and mixed at 60 rpm for an additional 8 min period. Some structural changes could occur in GTR at this temperature, but they were not detected in this work. Additionally, it must be referred
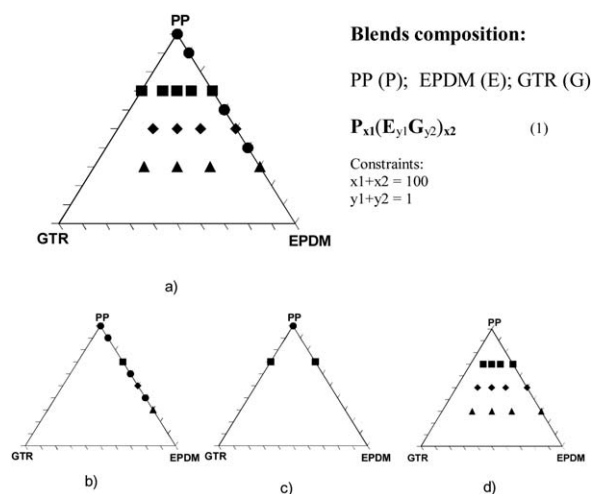

Blends composition:

PP (P); EPDM (E); GTR (G)

$$P_{x1}(E_{y1}G_{y2})_{x2} \qquad (1)$$

Constraints:
x1+x2 = 100
y1+y2 = 1

Figure 1. Set of experiments: ternary diagrams.

Table I. Blends Composition

Blends		Designation	PP (wt %)	EPDM (wt %)	GTR (wt %)
PP (**P**); EPDM (**E**); GTR (**G**)		P_{100}	100	0	0
Binary blends $P_{x1}(E_{y1}G_{y2})_{x2}$ x_1 = (90;70;60;50;40;30) y_1 = (0; 1)	$P_{x1}E_{x2y1}$ with: y2=0	$P_{90}E_{10}$	90	10	0
		$P_{70}E_{30}$	70	30	0
		$P_{60}E_{40}$	60	40	0
		$P_{50}E_{50}$	50	50	0
		$P_{40}E_{60}$	40	60	0
		$P_{30}E_{70}$	30	70	0
	$P_{x1}G_{x2y2}$ with: x1=70 and y1=0	$P_{70}G_{30}$	70	0	30
Ternary blends $P_{x1}(E_{y1}G_{y2})_{x2}$ x_1 = (70; 50; 30) y_1 = (0.3; 0.5; 0.7)	$P_{70}(E_{y1}G_{y2})_{30}$	$P_{70}(E_{0.7}G_{0.3})_{30}$	70	21	9
		$P_{70}(E_{0.5}G_{0.5})_{30}$	70	15	15
		$P_{70}(E_{0.3}G_{0.7})_{30}$	70	9	21
	$P_{50}(E_{y1}G_{y2})_{50}$	$P_{50}(E_{0.7}G_{0.3})_{50}$	50	35	15
		$P_{50}(E_{0.5}G_{0.5})_{50}$	50	25	25
		$P_{50}(E_{0.3}G_{0.7})_{50}$	50	15	35
	$P_{30}(E_{y1}G_{y2})_{70}$	$P_{30}(E_{0.7}G_{0.3})_{70}$	30	49	21
		$P_{30}(E_{0.5}G_{0.5})_{70}$	30	35	35
		$P_{30}(E_{0.3}G_{0.7})_{70}$	30	21	49

that similar conditions were also considered in other works without report of any thermal degradation of the materials.[26,29]

The final blend composition was then milled into granules. For injection moulding a 65 tons injection moulding machine, Inauton D65, was used with the following parameters: 220°C injection temperature, 35 bar holding pressure and mould temperature of 40°C.

Morphological Characterization
Morphological studies of the blends were carried out using a SEM Hitachi S-4100. The moulded specimens were broken in liquid nitrogen to avoid damage or phase deformation. The cryogenic fracture surfaces were etched with xylene, at 50°C for 15 min, for selective extraction of the uncured rubber phase. The samples were then dried and subsequently assembled on aluminum stubs and sputter-coated with a thin layer of gold to avoid electrostatic charging during SEM analyzes.

Mechanical Testing
The tensile properties of the blends, such as tensile strength and strain, were measured on a universal testing machine Autograph AG-IS, from Shimadzu, using a 10kN load cell. Tensile tests (type I specimens) were made at a constant crosshead speed of 500 mm/min in accordance with ASTM D412. Elongation was measured by a noncontact video extensometer, Shimadzu DVE-

201, coupled to the universal testing machine. Hardness (shore D) of the samples was measured with a Teclock Hardness Tester accordingly to ASTM D 2240. Izod impact tests were performed on a Ray Ran universal pendulum impact system. Impact specimens were prepared with a length of 57 mm, 13 mm width, and 3.2 mm thickness. A notch dept of 2.4 mm with an angle of 45° was made on the specimens for impact testing. All measurements were done at ambient temperature and the reported results are averaged values of at least five samples.

Dynamic Scanning Calorimetry
The crystallinity of the materials was obtained on a Shimadzu equipment DSC-60, at a scan rate of 20°C/min. Samples of about 10 mg were used in this study. Two heating cycles were used in a temperature range between -120°C and 200°C, under nitrogen atmosphere. The samples were heated in the first cycle to 200°C and held for 1 min to eliminate the influence of thermal and mechanical history. Then they were cooled until -120°C, and heated again to 200°C. The melting behavior was recorded during the second heating scan. Heat of fusion (ΔH_m) was calculated under the area of the endothermic peak and crystallinity (X_c) was obtained from the relationship:

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_0} \times 100 \qquad (1)$$

where ΔH_0 is the heat of fusion of 100% crystalline PP, taken as 209 J/g.[30]

For comparative purposes, the crystallinity takes in consideration the weight content of PP in the blend [eq. (2)].

$$\text{Corrected crystallinity}: X_c^c(\%) = \frac{\Delta H_m}{(1-\phi)\Delta H_o} \times 100 \qquad (2)$$

Where: ϕ is the weight fraction of rubber in the blend.

RESULTS AND DISCUSSION

Phase Morphology

The morphology of this type of blends is strongly dependent on the viscosity ratio, blend ratio, interfacial tension, and processing conditions.[31]

The PP/EPDM blends show a uniform dispersion of EPDM in the PP matrix, revealing an adequate experimental mixing pro-

cess (Figure 2). Blends up to 50 wt % EPDM show a homogeneous dispersed rubber phase in a continuous thermoplastic matrix. Above 50 wt % EPDM, $P_{40}E_{60}$ and $P_{30}E_{70}$, a cocontinuous morphology is formed in the material. In blends with continuous-disperse morphology, the dimensions of the spherical rubber domains increase up to 30 wt % EPDM [Figure 2(b)], due to the coalescence of the dispersed rubber particles. Badhane et al.[32] also reported that for low EPDM contents particles assume the form of spherical droplets. Above 30 wt % EPDM there is a transition on the rubber particle size toward a finely dispersed morphology in the blend and with a more elongated shape, as seen in the $P_{50}E_{50}$ blend [Figure 2(d)]. For higher contents of EPDM and under specific shear stress conditions, induced during the injection moulding process, there is deformation and breakup of the rubber particles in to small domains. The viscosity ratio between the disperse phase (EPDM, 0.5 g/10 min) and the continuous phase (PP, 35 g/10 min) may be inducing this type of morphology, normally obtained in thermoplastic elastomeric vulcanizates (TPV), on which the dynamic
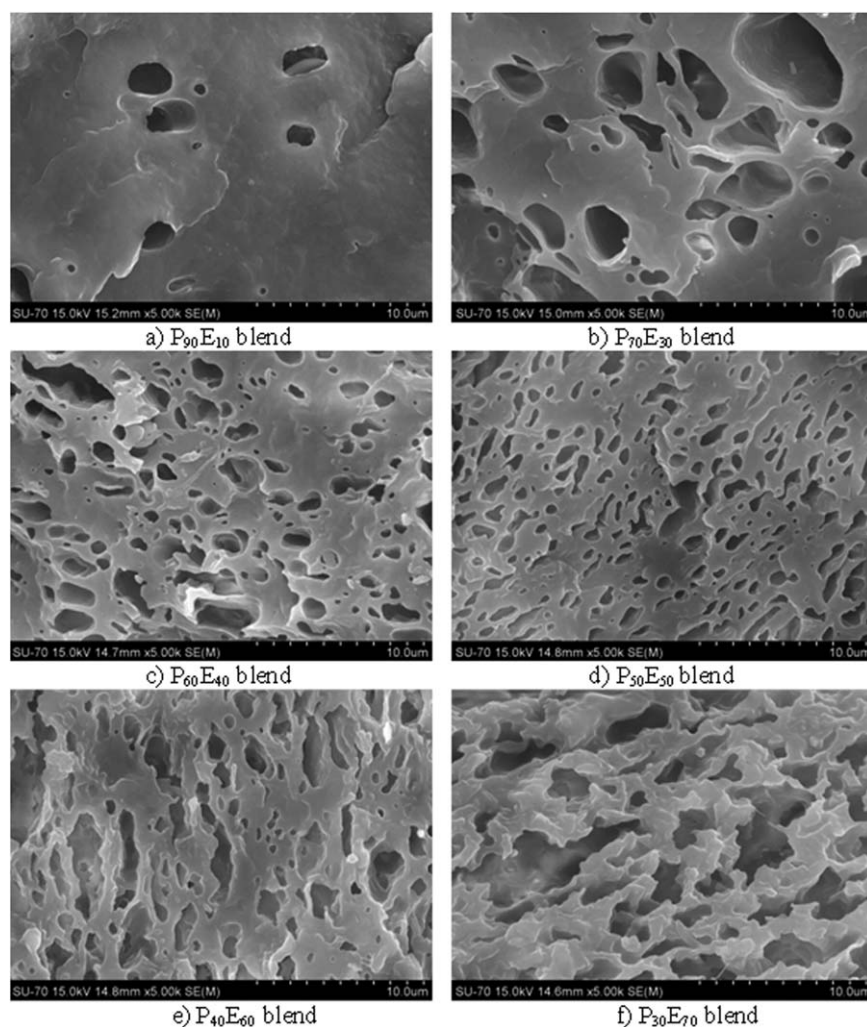

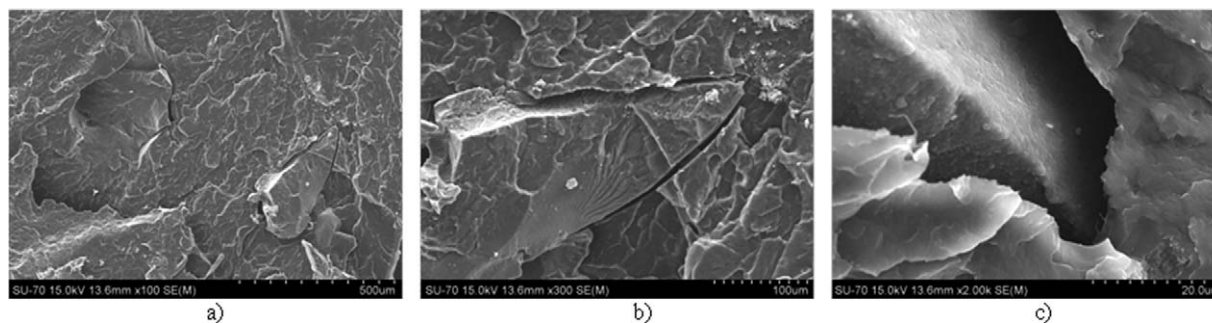**Figure 2.** SEM micrographs of PP/EPDM blends, etched with xylene (15 min, 50°C).

Figure 3. SEM micrographs of $P_{70}G_{30}$ blend, etched with xylene (15 min, 50°C).

vulcanization leads to an increase of the EPDM viscosity and shear stress to a breakup of the EPDM domains.

These changes on the size, shape, and number of rubber domains and thus on the overall morphology, from a continuous-dispersed to a cocontinuous one, may contribute for changes on the mode of failure of the material and, consequently, on the mechanical behavior.

As previously described, due to the different solubility parameters of PP and rubber, xylene was used to dissolve the elastomeric EPDM material. However, Scholz et al.[18] referred that xylene has also a slight dissolving effect, about 5%, in the GTR

particles, which can lead to their size reduction. In blends with poor compatibility between phases this contraction can lead to a gap between GTR and PP matrix (Figure 3).

For a blend with compatibility between the different phases, the contraction of the rubber material will be more difficult to occur. In those blends, a fibrillar type interface layer is expected to be formed.[18] These fibrillar structures are probably created by the entanglement of EPDM with polypropylene, pulled from the matrix during the shrinkage process. SEM images of the ternary blends reveal these fibrillar structures, being more visible for blends with higher contents of EPDM (Figures 4–6).
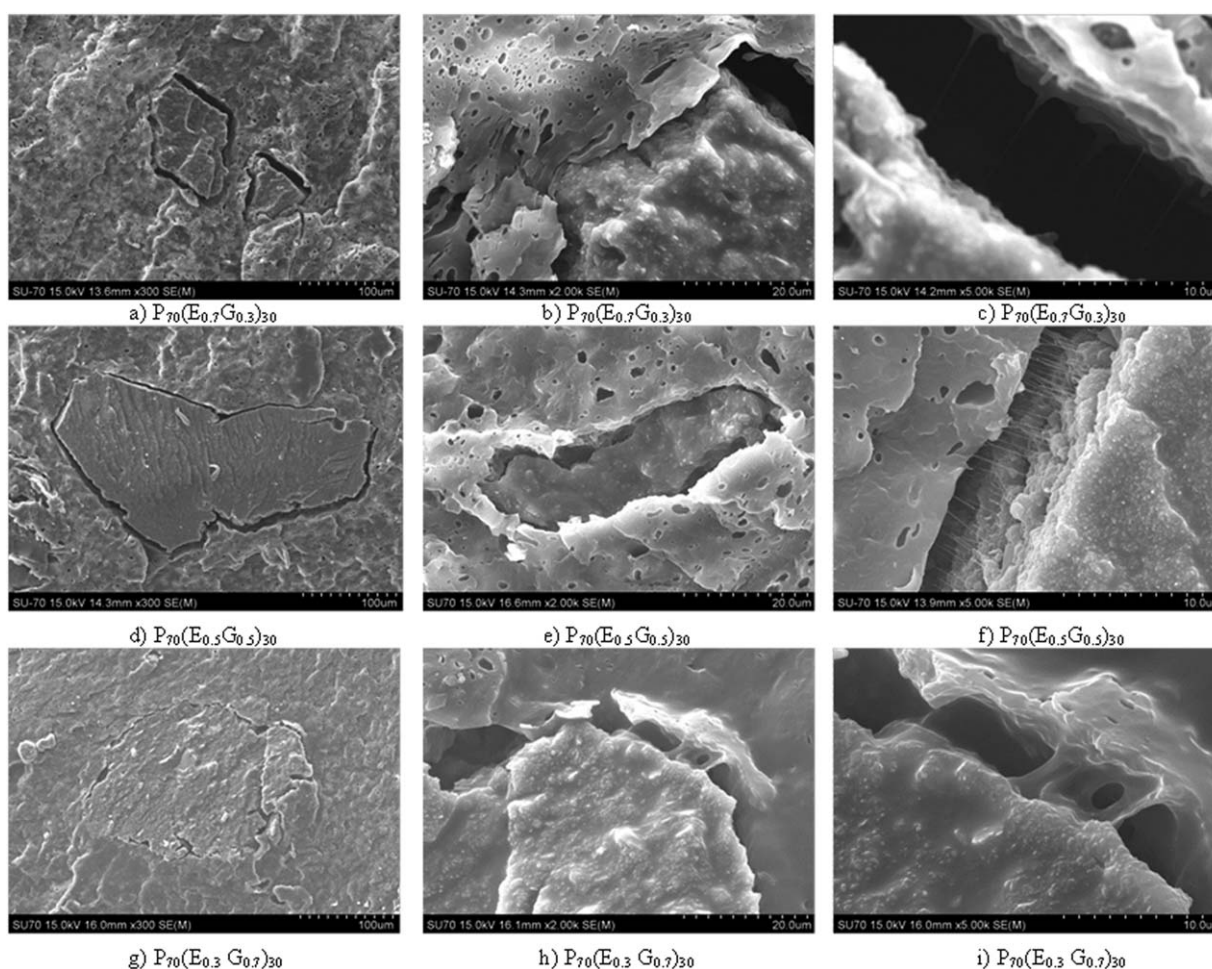

Figure 4. SEM micrographs of $P_{70}(E_{y1}G_{y2})_{30}$ blends, etched with xylene (15 min, 50°C).
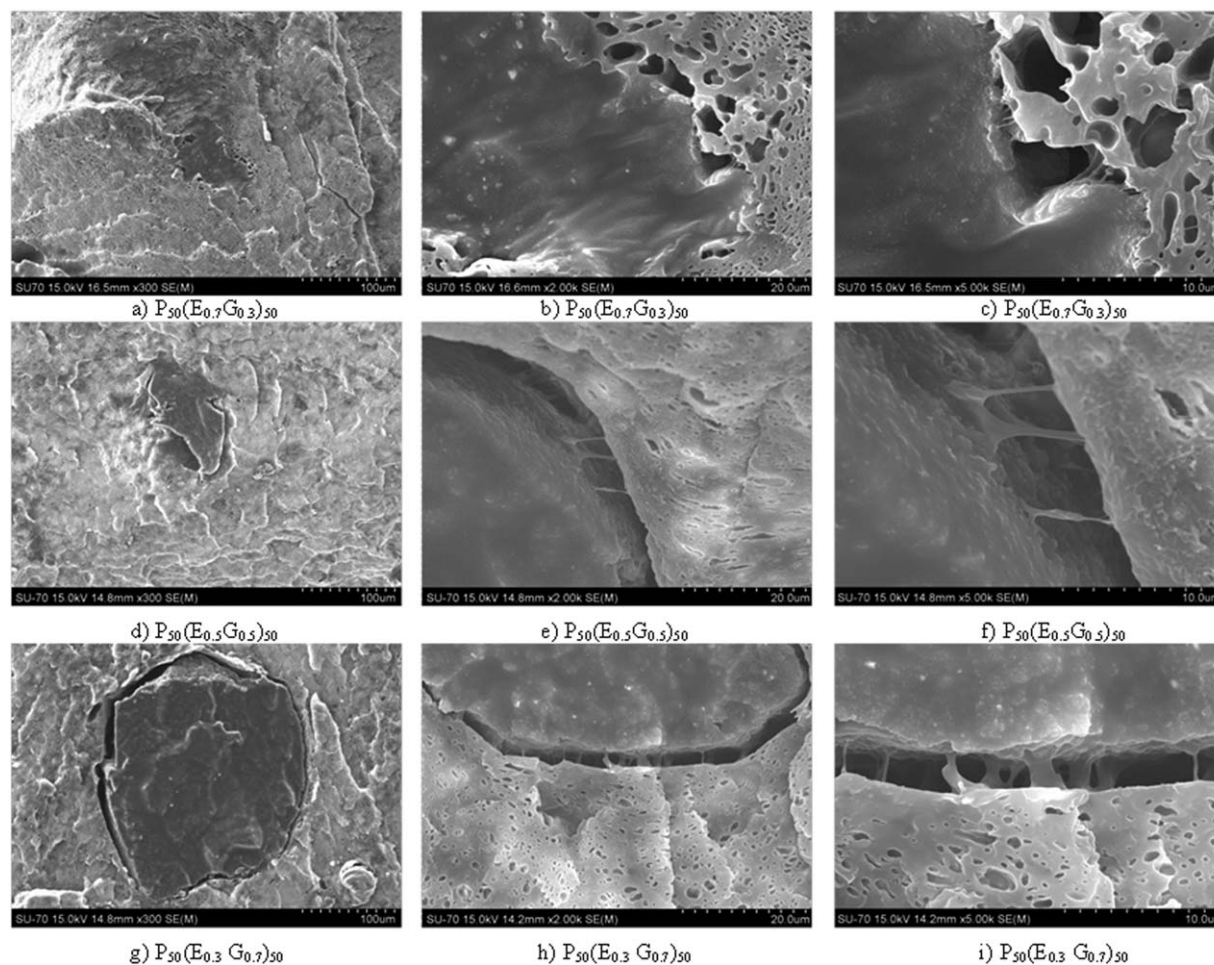
Figure 5. SEM micrographs of $P_{50}(E_{y1}G_{y2})_{50}$ blends, etched with xylene (15 min, 50°C).

Almost all the ternary blends show a continuous-disperse morphology, with a homogeneous dispersion of GTR particles and EPDM domains. The exceptions are for the $P_{30}(E_{0.7}G_{0.3})_{70}$ and $P_{30}(E_{0.5}G_{0.5})_{70}$ blends [Figure 6(a,d)] that show a cocontinuous morphology due to a higher content of EPDM, with embed GTR particles.

The strategy of GTR encapsulation by EPDM seems to be more effective on the blends with smaller particles size and on the blends with higher EPDM contents, [Figures 5(a), 6(g)]. The existence of a bigger gap between the PP matrix and GTR particles of higher dimensions suggests that EPDM layer around GTR will probably have a lower thickness or that it cannot totally encapsulate the GTR particle. Thereby, EPDM will not be able to promote an effective bonding between the two materials.

Mechanical and Thermal Properties
The mechanical and thermal properties of the formulated blends are listed in Table II.

Tensile Properties and Hardness
Effect of EPDM Content in the PP/EPDM Binary Blends.
Elongation at break of the PP/EPDM binary blends show a significant increase, being more pronounced above 30 wt %

EPDM (Figure 7). The tensile strength, Young modulus, and hardness properties show a gradual decrease with increasing EPDM content, Table II. The results reveal only a slight influence of the EPDM content on the matrix crystallinity, leading to the conclusion that these changes are related with the mechanical properties of EPDM.[33–35]

Effect of GTR and EPDM on the 70/30 Binary Blends. Taking polypropylene as the reference material (P_{100}), binary blends with 70 wt % PP content [Figure 1(c)] show 45% decrease on the tensile strength for $P_{70}E_{30}$ and 49% for $P_{70}G_{30}$. $P_{70}E_{30}$ shows a 63% increase on elongation and $P_{70}G_{30}$ an 84% decrease. These results seem to indicate some compatibility between PP and EPDM, mostly due to the existence of a low interfacial tension between the two components.[36,37] The existence of some stress transfer between the materials and the deformation capability of EPDM allows significant changes in the elongation at break of the blend. Conversely, vulcanized GTR behaves as a semirigid filler with very poor compatibility with the PP matrix. This significantly changes the mode of failure of PP, through the formation of voids and cracks in the blend, leading to a significant decrease of the elongation at break.[24] The results also show that GTR has a lower effect on the reduction of hardness
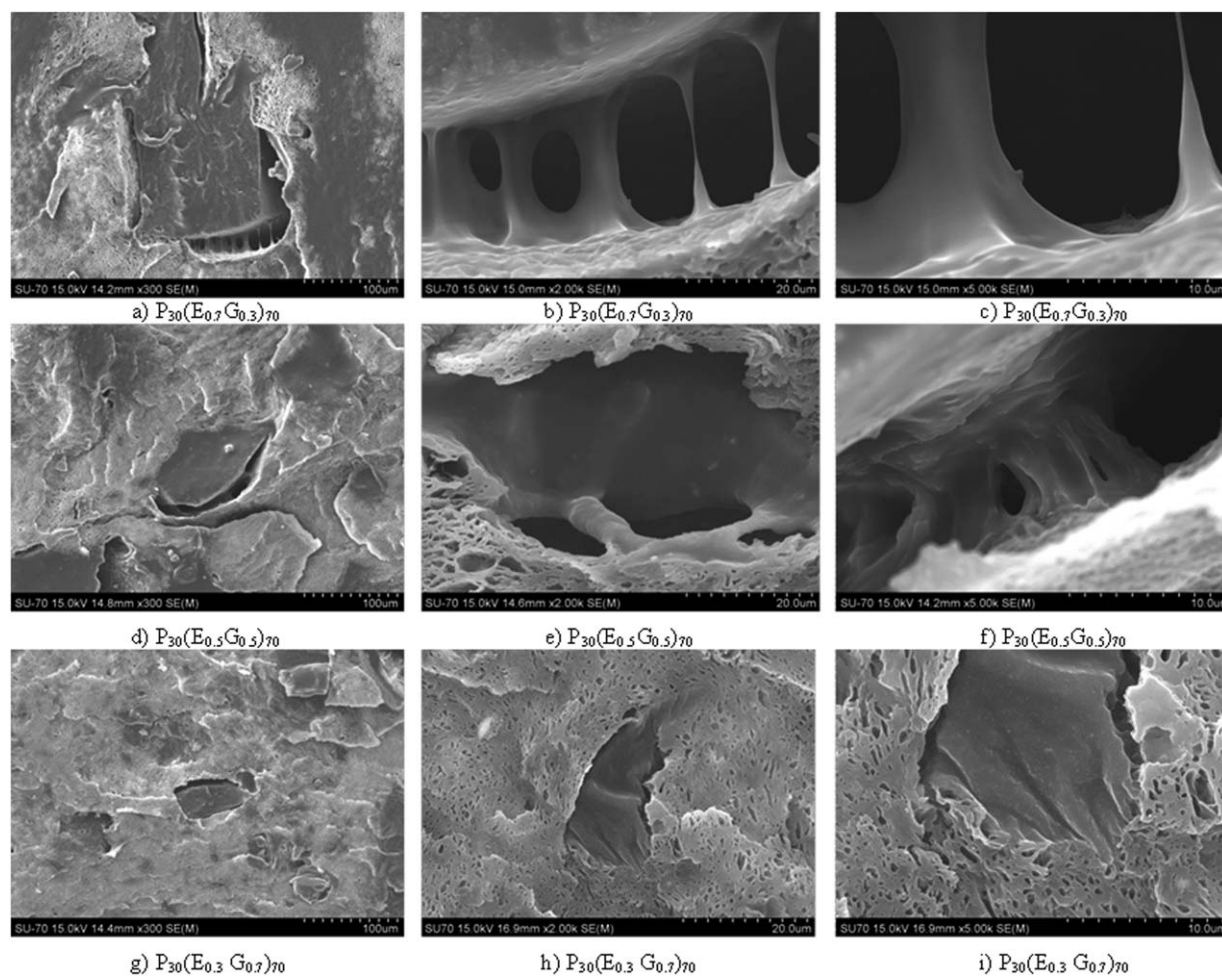
Figure 6. SEM micrographs of $P_{30}(E_{y1}G_{y2})_{70}$ blends, etched with xylene (15 min, 50°C).

than EPDM. $P_{70}E_{30}$ has an 18% inferior hardness result and $P_{70}G_{30}$ a 7% reduction.

Effect of EPDM replacement by GTR The effect of EDPM replacement by GTR is more pronounced in the elongation behavior (Figure 8). A 30 wt % replacement of EPDM by GTR, on the rubber phase, leads to a decrease of 80% on $P_{70}(E_{y1}G_{y2})_{30}$, 89% on $P_{50}(E_{y1}G_{y2})_{50}$ and 59% on $P_{30}(E_{y1}G_{y2})_{70}$ ternary blends. These results seem to indicate that a complete encapsulation of all the GTR particles by EPDM was not successfully achieved on GTR particles with larger dimensions, as previously reported. Due to the existence of GTR particles with incomplete or inexistent encapsulation by EPDM, the lack of adhesion between GTR and PP leads to a strong decrease of the elongation. The results also show that GTR has an insignificant effect on tensile strength, indicating that the thermoplastic matrix plays a dominant role. An increase in hardness with increasing GTR content in the ternary blend is also observed, which agrees with the effect of GTR detected on the binary blends. The increase on PP crystallinity with the GTR content, Table II, is attributed to its nucleation effect, but has no significant influence on the tensile properties of the ternary blends.

Impact Properties

The elastomeric phase in TPE has a toughening effect on the blend that can be explained by the deformation mechanisms of crazing and shear yielding and also by cavitation and deformation. Shear yielding occurs by the effect of the rubber in the PP matrix. Rubber inclusions induce stress concentration regions that can lead to a shear band effect in the material, responsible for inhibiting the crazes growth process. The dominant energy absorbing process is also dependent on the composition of the PP/rubber blends and on the resultant morphology, especially above certain rubber contents in the blend, as showed in the morphological analyses. By enhancing the shear band effect in the matrix, the dispersed elastomeric particles may prevent crazes, growing from the GTR surface, from becoming unstable, thus increasing the ductility of the material. Adhesion also plays a significant role on this toughening behavior. If debonding of different materials occurs during the deformation process, there is a relief of the stress field and the occurrence of voids or flaws, which leads to an inferior impact behavior.[38] Encapsulation of the GTR particles by an elastomeric layer may also contribute to change the major local failure mechanism from crazing to shear yielding, by the relief of triaxial stresses at the filler surface.[39]

Table II. Mechanical and Thermal Properties of the Blends

Blend	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore D)	Young Modulus (MPa)	Impact strength – IZOD (kJ/m^2)	Fusion enthalpy ΔHm (J/g)	Crystallinity X_c (%) (corrected)
P$_{100}$	36.5 ± 0.4	79.7 ± 7.9	66.5 ± 0.6	428.9 ± 20.4	4.1 ± 0.3	98.1 ± 3.2	47.0 ± 1.5
P$_{90}$E$_{10}$	28.7 ± 0.3	89.7 ± 9.9	62.9 ± 1.2	343.5 ± 10.5	5.0 ± 0.3	86.5 ± 1.9	46.0 ± 1.0
P$_{70}$E$_{30}$	20.2 ± 0.8	130.0 ± 12.7	54.8 ± 0.3	249.2 ± 8.8	5.6 ± 0.4	73.9 ± 1.4	47.9 ± 0.9
P$_{60}$E$_{40}$	15.8 ± 0.2	420.0 ± 53.6	47.4 ± 0.7	189.8 ± 4.1	17.9 ± 06	60.5 ± 1.4	48.2 ± 1.14
P$_{50}$E$_{50}$	12.4 ± 0.1	464.6 ± 60.0	41.0 ± 0.8	123.4 ± 8.1	53.9 ± 1.9	52.3 ± 0.9	50.0 ± 0.9
P$_{40}$E$_{60}$	9.1 ± 0.1	487.7 ± 56.4	33.0 ± 0.5	68.9 ± 5.5	64.6 ± 2.0	43.2 ± 0.8	51.7 ± 0.9
P$_{30}$E$_{70}$	6.1 ± 0.1	554.9 ± 28.2	25.6 ± 0.4	32.6 ± 1.2	NB	30.4 ± 0.4	48.5 ± 0.7
P$_{70}$G$_{30}$	18.8 ± 0.1	12.5 ± 0.2	62.1 ± 0.7	224.1 ± 2.2	2.9 ± 0.1	86.7 ± 2.0	59.9 ± 1.4
P$_{70}$(E$_{0.7}$G$_{0.3}$)$_{30}$	19.3 ± 0.3	26.1 ± 3.7	55.3 ± 0.9	231.1 ± 5.5	5.2 ± 0.5	87.6 ± 1.9	52.2 ± 1.3
P$_{70}$(E$_{0.5}$G$_{0.5}$)$_{30}$	20.0 ± 0.2	19.2 ± 2.9	56.6 ± 1.1	241.8 ± 5.2	4.8 ± 0.4	76.4 ± 1.5	52.3 ± 1.1
P$_{70}$(E$_{0.3}$G$_{0.7}$)$_{30}$	20.3 ± 0.1	20.3 ± 2.6	58.4 ± 0.6	246.5 ± 7.9	3.5 ± 0.2	75.9 ± 1.9	52.4 ± 1.3
P$_{50}$(E$_{0.7}$G$_{0.3}$)$_{50}$	12.9 ± 0.0	52.7 ± 7.5	43.8 ± 1.0	136.8 ± 10.7	25.1 ± 2.8	55.0 ± 1.1	52.6 ± 1.0
P$_{50}$(E$_{0.5}$G$_{0.5}$)$_{50}$	12.8 ± 0.0	37.6 ± 4.6	46.2 ± 0.8	130.6 ± 3.2	15.9 ± 1.1	55.4 ± 1.6	52.9± 1.5
P$_{50}$(E$_{0.3}$G$_{0.7}$)$_{50}$	12.7 ± 0.1	26.9 ± 3.5	49.2 ± 0.8	145.9 ± 5.1	5.6 ± 0.2	55.4 ± 1.4	53.0± 1.3
P$_{30}$(E$_{0.7}$G$_{0.3}$)$_{70}$	7.2 ± 0.1	229.4 ± 18.2	28.3 ± 0.4	38.9 ± 3.2	29.6 ± 1.5	33.2 ± 1.1	52.9 ± 1.8
P$_{30}$(E$_{0.5}$G$_{0.5}$)$_{70}$	7.5 ± 0.1	160.8 ± 24.9	31.2 ± 0.6	43.4 ± 3.9	26.9 ± 1.6	35.5 ± 1.2	56.5 ± 1.8
P$_{30}$(E$_{0.3}$G$_{0.7}$)$_{70}$	7.7 ± 0.1	96.1 ± 13.3	36.1 ± 0.7	52.8 ± 4.7	18.2 ± 0.1	36.2 ± 1.4	57.8 ± 2.2

Effect of EPDM Content on the PP/EPDM Binary Blends. The impact strength of PP/EPDM blends increases smoothly from 4.13 to 5.61 kJ/m^2 as the EPDM rubber increases from 0 to 30 wt % content in the blend. Between 30 and 40 wt % content a significant increase is observed (Figure 9). Above 40 wt % content, EPDM may be inducing a predominantly shear yield mechanism in the material, rather than crazing, which leads to a more effective dissipation of the impact energies and may explain the differences on the impact resistance of the materials. An increase on the number and density of the shear bands is probable to occur for higher contents of EPDM, enhancing the
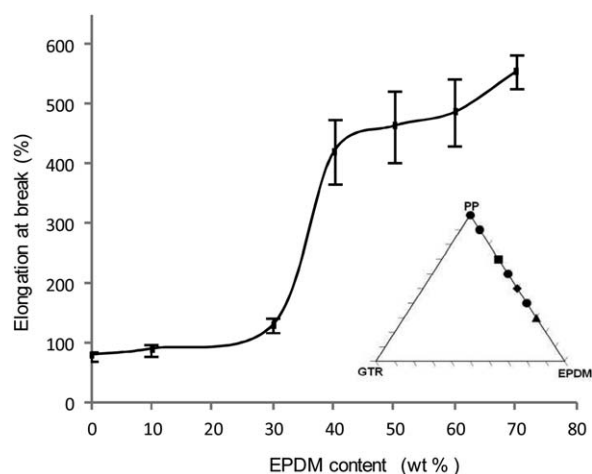
shear band effect and, therefore, the impact resistance.[40] The blends with a cocontinuous morphology, above 50 wt % EPDM, by having a more elastomeric nature, show the highest impact strength results.

Effect of GTR and EPDM on the 70/30 Binary Blends. On the 70/30 binary blends, P$_{70}$E$_{30}$ has an impact resistance 36% higher than PP and P$_{70}$G$_{30}$ 29% lower. These results may indicate some rigidity of the vulcanized GTR rubber and the lack of adhesion between PP and GTR. This low interfacial bonding can induce the existence of voids at the interfaces which may lead to a predominantly crazing deformation mechanism responsible for a decrease of the impact resistance. Conversely,
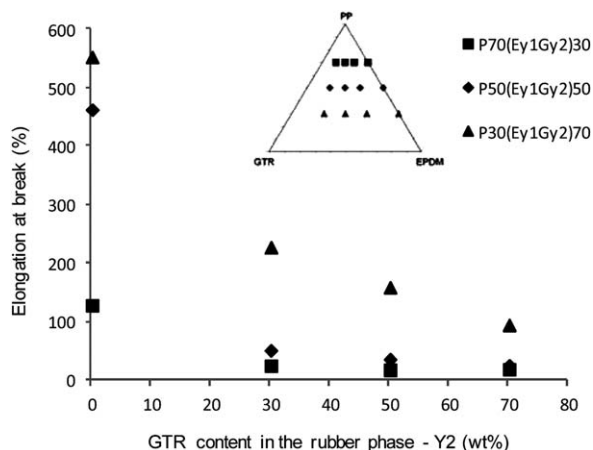

Figure 7. Effect of EPDM content in elongation at break of PP/EPDM blends.

Figure 8. Effect of EPDM replacement by GTR in elongation at break.
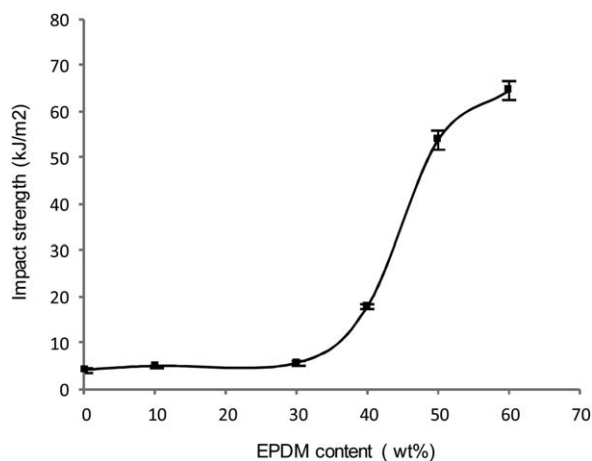
Figure 9. Effect of EPDM weight content on impact strength of PP/EPDM blends.

the compatibility of the materials, the resultant continuous-disperse morphology and the rubber behavior of EPDM, can be responsible for improving the impact performance of $P_{70}E_{30}$ blend.

Effect of EPDM Replacement by GTR on Impact Resistance. The effect of EDPM replacement by GTR on the impact resistance is more pronounced on the ternary blends above 30 wt % rubber phase, $P_{50}(E_{y1}G_{y2})_{50}$ and $P_{30}(E_{y1}G_{y2})_{70}$, (Figure 10). A 30 wt % replacement of EPDM by GTR, in the rubber phase, leads to a 7% decrease on the $P_{70}(E_{0.7}G_{0.3})_{30}$ blend and to a 54% decrease on the $P_{50}(E_{0.7}G_{0.3})_{50}$ blend. Impact specimens of $P_{30}E_{70}$ did not break and, so, no reference data was possible to obtain.

The reduction of the impact strength with increasing GTR content can be explained by the nature of the GTR particles, by the reduction of EPDM content and also by an inferior encapsulation effect of the GTR particles.

CONCLUSIONS

The formulation of TPE^{GTR} without the use of thermochemical methods can contribute to a significant enhancement on the process of ELT recycling.
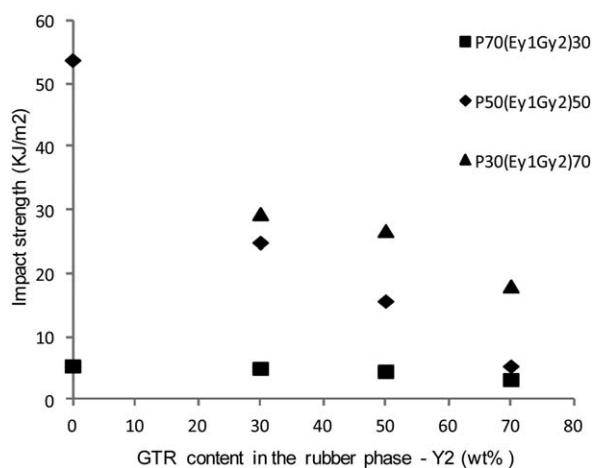

Figure 10. Effect of EPDM replacement by GTR on the impact strength.

In TPE blends GTR behaves as semirigid filler, with little or no adhesion to PP, leading to a lower mechanical performance of the material.

The use of EPDM as fresh rubber on TPE^{GTR} allowed a significant improvement on the toughness of the material, making it an adequate choice to technologically compatibilize GTR with polyolefin materials.

This study showed that a successful encapsulation is dependent on the correlation between the dimensions of the GTR particles and the EPDM/GTR content ratio. A complete encapsulation can be achieved with smaller particles of GTR and/or for higher EPDM contents.

Detailed analysis of the crystallization behavior in TPE^{GTR} blends must be developed for a better understanding of the GTR and fresh rubber effects on their final properties.

For industrialization and environmental reasons, the development of TPE^{GTR} formulations, must take in consideration their processability by injection moulding technologies as well as their recyclability and, therefore, this research fields should be considered in future work.

REFERENCES

1. Fontaine, N.; Védrine, H. in Directive 2000/53/CE; Council, E. P., Ed., Official Journal of the European Union: 2000, p 18.

2. Pneu, V. in Relatório anual e contas; Valor Pneu, Ed.: 2012.

3. Radeshkumar, A.; Karger-Kocsis, J. *Plast. Rubber Compos.* **2002**, *31*, 99.

4. Jana, G. K.; Das, C. K. *Prog. Rubber Plast. Recycling Technol.* **2005**, *21*, 319.

5. Isayev, A. I.; Yushanov, S. P.; Kim, S. – H., Levin; V. Y. *Rheol. Acta.* **1996**, *35*, 616.

6. Guo, X.; Xiang, D.; Duan, G.; Mou, P. *Waste Management.* **2010**, *30*, 4.

7. De, D.; Das, A.; De, D.; Dey, B., Debnath, S. C., Roy, B. C. *Eur. Polym. J.* **2006**, *42*, 917.

8. Ismail, H.; Awang, M.; Hazizan, M. A. *Polym. Plast. Technol. Eng.* **2006**, *45*, 463.

9. Scaffaro, R.; Dintcheva, N. T.; Nocilla, M. A.; La Mantia, F. P. *Polym. Degrad. Stab.* **2005**, *90*, 281.

10. Datta SA-Sa, S. In Polymer blends: Performance. Buknall DRPaCB, Eds.; Wiley: New York, **2000**; p 517–56.

11. Grigoryeva, O.; Fainleib A.; Grenet J.; Saiter JM. *Rubber Chem. Technol.* **2008**, *81*, 737.

12. Wagenknecht, U.; Wiessner, S.; Heinrich, G.; Michael, H.; Zichner, M. *Plast. Rubber Compos.* **2006**, *35*, 393.

13. Zhang, X.; Chen, C.; Lu, C. *Prog. Rubber Plast. Recycling Technol.* **2012**, *28*, 81.

14. Zhang, X.; Lu, C.; Liang, M. *J. Appl. Polym. Sci.* **2011**, *122*, 2110.

15. Zhang, X.; Lu Z.; Tian, D.; Li, H.; Lu, C. *J. Appl. Polym. Sci.* **2013**, *127*, 4006.

16. Sung Hyo, L.; Shanmugharaj, A. M.; Sridhar, V.; Zhen Xiu, Z.; Jin Kuk, K. *Polym. Adv. Technol.* **2009**, *20*, 620.

17. Naskar, A. K.; Bhowmick, A. K.; De, S. K. *Polym. Eng. Sci.* **2001**, *41*, 1087.

18. Scholz, H.; Pötschke, P.; Michael, H.; Mennig, G. *Kaut. Gummi Kunstst.* **2002**, *55*, 584.

19. Wiessner, S. W. U.; Zichner, M.; Michael, H.; Heinrich, G. Effects of Interface Reactions in Compatibilised Rubber Powder-Polypropylene–TPEs; Polymer Processing Society: Leipzig, **2005**.

20. Kim, J. K.; Lee, S. H.; Balasubramanian, M. *Polímeros* **2006**, *16*, 263.

21. Zhang, S. L.; Xin, Z. X.; Zhang, Z. X.; Kim, J. K. *Waste Management* **2009**, *29*, 1480.

22. Costa, H. M.; Ramos, V. D. *Polym. Test.* **2008**, *27*, 27.

23. Halimatuddahliana Ismail, H. *Polym. Plast. Technol Eng.* **2009**, *48*, 34.

24. Majid Rezaei, A.; Azam Jalali, A.; Hossien, N. *J. Appl. Polym. Sci.* **2010**, *115*, 2416.

25. Mészáros, L.; Tábi, T.; Kovács, J. G.; Bárány, T. *Polym. Eng. Sci.* **2008**, *48*, 868.

26. Grigoryeva, O. P.; Fainleib, A. M.; Tolstov, A. L.; Starostenko, O. M.; Lievana, E.; Karger-Kocsis, J. *J. Appl. Polym. Sci.* **2005**, *95*, 659.

27. Kumar, C. R.; Fuhrmann, I.; Karger-Kocsis, J. *Polym. Degrad. Stab.* **2002**, *76*, 137.

28. Karger-Kocsis, J.; Mészaros, L.; Bárány, T. *J. Mater. Sci.* **2013**, *48*, 1.

29. Lievana, E. J. Recycling of Ground Tyre Rubber and Polyolefin Wastes by Producing Thermoplastic Elastomers; Technical University of Kaiserslautern: Kaiserslautern, **2005**.

30. Gottfried, W.; Ehrenstein, G. R.; Pia Trawiel. Thermal Analysis of Plastics; Theory and Pratice; Hanser Gardner Publications: München, **2004**.

31. Babu, R.; Singha, N.; Naskar, K. *Polym. Bull.* **2011**, *66*, 95.

32. Bhadane, P. A.; Champagne, M. F.; Huneault, M. A.; Tofan, F.; Favis, B. D. *Polymer* **2006**, *47*, 2760.

33. Van der Wal, A.; Mulder, J. J.; Oderkerk, J.; Gaymans, R. J. *Polymer* **1998**, *39*, 6781.

34. Lampman, S. Characterization and Failure Analysis of Plastics. ASM international, Materials Park: **2003**.

35. Gupta, N. K.; Jain, A. K.; Singhal, R.; Nagpal, A. K. *J. Appl. Polym. Sci.* **2000**, *78*, 2104.

36. Sengupta, P. Morphology of Olefinic Thermoplastic Elastomer Blends. A Comparative Study into the Structure-Property Relationship of EPDM/PP/Oil Based TPVs and SEBS/PP/Oil Blends; University of Twente: Enschede, **2004**.

37. Brown, S. B. In Polymer Blends Handbook, Utracki L. A., Eds.; Kluwer Academic: Dordrecht, **2003**.

38. D. R. Paul, C. B. Bucknall, Polymer Blends: Performance, Vol. 2; John Wiley & Sons: New Jersey, **2000**.

39. D. Nwabunma, Thein Kyu. Polyolefin Blends; John Wiley & Sons; New York, **2008**.

40. Jain, A. K.; Nagpal, A. K.; Singhal R.; Gupta N. K. *J. Appl. Polym. Sci.* **2000**, *78*, 2089.