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Structure and properties of blends based on ground rubber tires and thermoplastics

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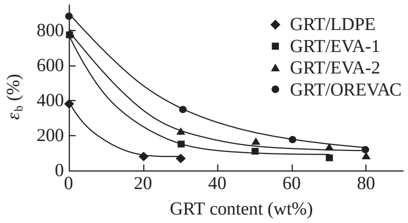
The blends of ground rubber tires (> 50 wt%) and thermoplastics have been obtained under conditions of high temperature shear deformation and characterized. The elongation at break of the blends is higher than 100%.



The utilization of waste rubber is an important ecological problem. The grinding of waste rubber is an economically suitable method of recycling because rubber tire is a thermoset material, which cannot be processed like thermoplastics.[1–3] Among the most promising methods of rubber waste treatment is high temperature shear deformation (HTSD).[3] This method allows one to produce ground rubber tire powder (GRT) for its incorporation into thermoplastics to obtain blends with high mechanical properties. One of main requirements to these blends is elongations at break, which should exceed 100%, but such compositions were not obtained up to now. Recently, a comprehensive review was published,[2] in which the difficulties in production of the high quality GRT-filled compounds were considered. However, the effect of the functional polymer components of GRT/polymer blends, which could improve their mechanical properties, was not discussed.

The blending of thermoplastic polymers and GRT and the grinding of truck tire treads to prepare GRT were carried out under HTSD conditions at 160 °C. The GRT incorporation meets no difficulties even at high filler loadings in polymer matrices.[3,4]

The aim of this work was to investigate the influence of high GRT contents (> 50 wt%) on the mechanical properties, melt flow index (MFI) and morphology of blends based on different functional polymers.[†]

The incorporation of GRT in a polymer matrix leads to a decrease in Young's modulus E, tensile strength σ_b and elongation at break ε_b for all blends. Thus, for the GRT/LDPE = 30/70 blends, $E \approx 0.79E_0$ and $\sigma_b \approx 0.53\sigma_{b0}$ (E_0 and σ_{b0} are the Young's modulus and the tensile strength of LDPE, respectively). The values of E, σ_b and ε_b differ significantly depending on the polymer matrix. The GRT/LDPE blends have very poor mechanical properties, especially elongation at break: $\varepsilon_b \approx 80$ and 70% at 20 and 30 wt% filler, respectively (Figure 1). Blends based on LDPE with > 30 wt% GRT cannot be obtained. The poor interfacial interaction between GRT and LDPE favours crack propagation accompanied by a significant decrease in the mechanical properties.

Figure 1 shows the elongations at break as a function of the GRT content for samples prepared *via* compression molding. The GRT/OREVAC blend has the highest value of ε_b. This fact is explained by the presence of maleic anhydride in OREVAC. Most probably, maleic anhydride enhances the adhesion of the OREVAC molecules to rubber powder particles and increases the interfacial interaction that leads to a higher elongation at break. At the same time, an increase in the concentration of vinyl acetate from 10 to 30 wt% has a weaker effect on ε_b (Figure 1, curves *2* and *3*).

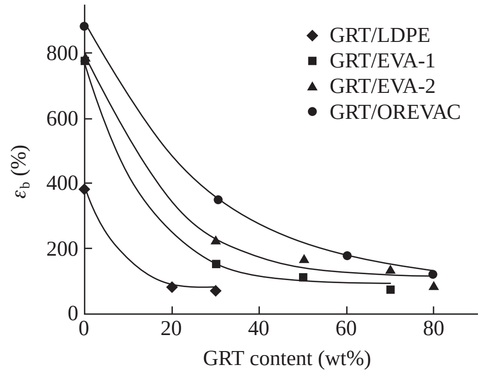


Figure 1 Elongation at break of thermoplastic/GRT blends as a function of GRT content.

[†] The following commercial polymers were used: low density polyethylene (LDPE), ethylene–vinyl acetate copolymer with 10–14 wt% vinyl acetate (EVA-1), ethylene–vinyl acetate copolymer with 24–30 wt% vinyl acetate (EVA-2), and a random terpolymer of ethylene, vinyl acetate and maleic anhydride (maleic anhydride content of 1600 ppm) (OREVAC). The rubber powder with a particle size of 0.315–0.63 mm was obtained by sieving.[5]

On the grinding of rubber waste under HTSD conditions, rubber degradation occurred with the formation of free radicals followed by their recombination resulting in double bonds. The content of double bonds on the GRT surface determined by ozonolysis on an ADS-1 instrument was approximately 8×10^{-6} mol g^{-1}.[5–7]

The mechanical properties of the blend samples obtained by injection molding or cut off from compression moulded sheets were measured on an Instron 1122 tensile test machine.

Table 1 Mechanical properties of blends obtained by different molding methods.

Composition GRT/Polymer (w/w)	Molding method	E/MPa	σ_b/MPa	ε_b (%)	MFI/ g per 10 min
GRT/EVA-2	Compression	6.4	2.5	135	1.0
(70/30)	Injection	6.6	2.7	140	1.0
GRT/EVA-2	Compression	4.3	1.6	100	0.1
(80/20)	Injection	5.1	2.2	110	no flow
GRT/OREVAC	Compression	11.0	3.8	130	0.3
(70/30)	Injection	13.6	4.5	140	0.3
GRT/OREVAC	Compression	7.5	3.0	120	no flow
(80/20)	Injection	8.0	4.1	150	no flow

Thus, the addition of 30 wt% GRT to EVA-1, EVA-2, and OREVAC results in the blends with $\varepsilon_b \approx 155$, 230, and 380%, respectively. In other words, the elongations at break of GRT/EVA-1, GRT/EVA-2, and GRT/OREVAC blends exceed that of the GRT/LDPE blend by the factors of 2.2, 3.3, and 5.4, respectively (Figure 1).

Note that, at the GRT content of >50 wt%, all the test blends showed elongations higher than 100% (Figure 1).

Table 1 summarizes the data on mechanical properties of GRT/EVA-2 and GRT/OREVAC samples prepared by injection and compression molding from blends with GRT contents of >50 wt% obtained previously[3] and in this work. The Young's modulus and ultimate tensile strength of GRT/OREVAC compositions are higher than the corresponding values for GRT/EVA-2. At the same time, the elongations at break are almost independent of the sample preparation method. As can be seen, a gain in the GRT content up to 80 wt% results in a decrease of the mechanical characteristics for all compositions.

It is well known that the addition of a particle filler to polymer increases the melt viscosity.[8] It was shown that the melt flow index of GRT/OREVAC, GRT/EVA-2, and GRT/EVA-1 blends drops with an increase in the filler content due to the formation of an interfacial region. However, these materials demonstrate the fluidity only at the GRT content below 80 wt%. An insignificant increase in the MFI of GRT/LDPE blend is probably related to the absence of interfacial interaction.

The FTIR spectra (Figure 2) of two individual components (*1*, *2*) and of their blends with GRT (*4*, *5*) are identical to suggest the absence of chemical interactions between the components.

The morphology of the samples after the tensile fracture was examined on a JEOL JSM7001F scanning electron microscope. GRT particles had asymmetric shapes and well-developed surface areas (750–1200 cm^2 g^{-1}). Two characteristic regions with a distinct boundary were observed at the surface of particles: a region of plastic fracture with a developed surface and a region of brittle fracture with a smooth surface.

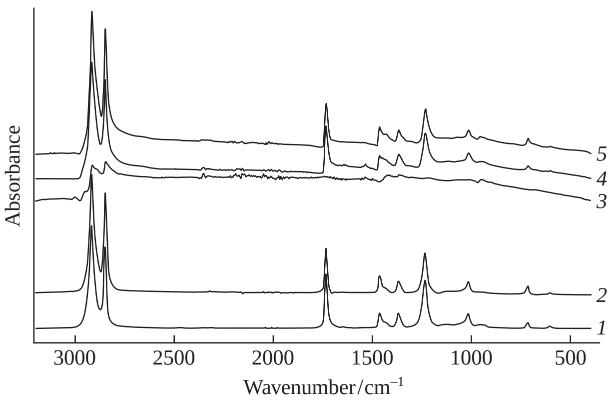


Figure 2 FTIR spectra of (*1*) EVA-2, (*2*) OREVAC, (*3*) GRT, (*4*) GRT/EVA-2 (70/30), and (*5*) GRT/OREVAC (70/30).

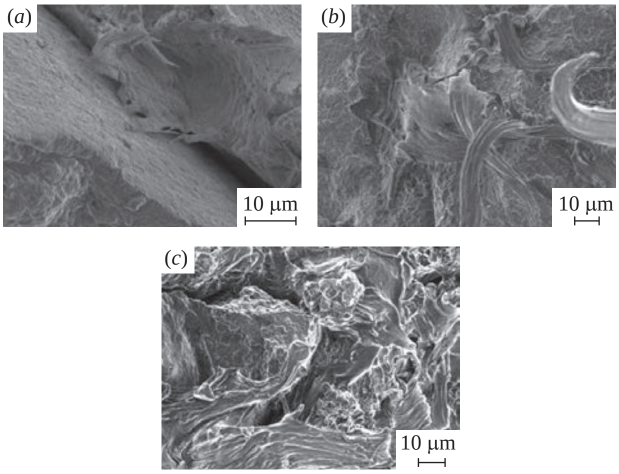


Figure 3 SEM micrographs of blend surfaces after tensile fracture: (*a*) GRT/LDPE (30/70), (*b*) GRT/EVA-2 (30/70), and (*c*) GRT/EVA-2 (70/30).

It is evident (Figure 3) that on the surface of the GRT/EVA-2 (30/70) sample, fibrous matrix formations fibrillated at large local deformations are clearly visible with the points of matrix attachment to the powder particles. Thus, a conclusion can be made that an interphase physical interaction between the matrix and the filler takes place [Figure 3(*b*)]. As the GRT content increases [GRT/EVA-2 (70/30)], the transverse dimensions of the fibrous formations diminish due to a decrease in the volume fraction of the matrix. The observed interactions result in large local deformations; moreover, they are responsible for high integral deformations [Figure 3(*c*)]. In the blend GRT/LDPE (30/70), there is no fiber formation [Figure 3(*a*)] since LDPE has no functional groups and, thus, the interphase interaction is absent.

Thus, the use of functional polymers as a matrix of blends makes it possible to extend the assortment of materials filled with rubber powder at filler contents of >50 wt%. These materials can be processed by traditional methods such as injection molding and extrusion.

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