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Polyethylene/ground tyre rubber blends: Influence of particle morphology and oxidation on mechanical properties

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Abstract

Results concerning the influence of the modification of morphological and chemical characteristics of ground tyre rubber (GTR) powders on the mechanical properties of polyethylene (HDPE or LDPE)/GTR blends are given. In order to improve the interfacial adhesion between rubber particles and matrix, two oxidation treatments of the GTR powder by potassium permanganate (in solution) and γ -irradiation (in air) were performed. Then, the powder was incorporated in a HDPE matrix containing a small amount of maleic anhydride grafted polyethylene (MAGPE). The effect on the mechanical properties of the blends was studied. Since none of them was really effective, we conclude that oxidation cannot compensate for the lack of chemical reactivity of GTR powders.

Keywords: Recycling; Ground tyre rubber; Compatibilization; Oxidation

1. Introduction

For many years, the management of end-of-life tyres is a concern. For example, more than 250 million tyres are scrapped every year in the United States. In consequence, most developed countries have imposed regulations to forbid land filling of tyres. Waste management of end-of-life tyres requires profitable recycling solutions. The grinding of tyres and the incorporation of ground tyre rubber (GTR) powders in polymers or mortars seems to be one of the more advantageous ways. Nevertheless, in the case of a simple re-incorporation in polymer

matrices, the mechanical properties of the pure polymer tend to decrease drastically with the powder content, because of the lack of interfacial interactions due to the crosslinked structure of GTR particles [1–3].

In order to promote GTR compatibility with the matrix, modification of the powder seems to be required. A first approach is the control of the GTR particle size and morphology.

The influence of particle mean size (typically about several hundreds of micrometers) was studied by several authors [3–5]. Goncharuk et al. [4] observed that elongation at break of LDPE/GTR blends decreased with increasing particle mean size, while tensile strength was not affected by this parameter. Liu et al. [3] noted the same tendency in the case of PP/EPDM powder blends. Rajalingam et al. [5] showed that a decrease of particle size

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from 600 to 74 μm had a weak effect on impact energy of NR/GTR blends.

The influence of the particle shape and of the powder's specific surface area, which are controlled by the grinding process, was also investigated [4,6,7]. Goncharuk et al. [4] studied three methods of grinding: roller grinding, elastic-strain grinding and cryogenic grinding. The blends containing powders prepared by roller grinding exhibited the best properties. This was ascribed to a higher specific surface area. Liu et al. [7] observed that the elongation at break of PP/EPDM powder blends was higher with an ambient ground powder than with a cryogenic ground powder because the particles surface was less developed in this latter case.

However, all the authors agree about the necessity to perform chemical modification on GTR to obtain good adhesion with the polymer matrix and to improve mechanical properties.

According to this objective, numerous processes of devulcanization were considered, such as chemical [2,8,9], biological [10], ultrasonic [11,12] or microwave [13] processes. However, all these treatments take a long time and/or have pollution problems. Thermomechanical devulcanization of rubber powder in a counterrotating twin screw [14,15] is highly interesting because it is a fast and ecological method, but only poor results were obtained by the authors [15].

A third possibility for compatibilization consists of the oxidation of the GTR surface. Adhesion between rubber-like SBR and several polymers was highly enhanced by oxidation or chlorination treatments, according to chemical [16,17] or plasma [18] methods. Nevertheless, the incorporation of oxidized or chlorinated GTR in PE [19,20], PVC [21] or NR [22] matrix resulted in poor mechanical properties. No thermoplastic elastomer-like behaviour was reported. The improvement of Young's modulus, tensile strength and hardness was attributed to a rigid layer of degraded rubber on the particle surface. At the same time, elongation at break decreased.

Liu et al. proposed oxidization of EPDM powder by KMnO_4 to break unsaturated $\text{C}=\text{C}$ bonds of the rubber and to create hydroxyl groups. Then, the modified powder was incorporated into a PP matrix containing a small amount of maleic anhydride (MA) grafted chains [3,7]. These authors noted a significant improvement of elongation at break while tensile strength remained constant. They

explain these results considering that polar groups on the EPDM surface reacted with maleic anhydride to form covalent bonds.

Gamma Irradiation in air could provide another way of oxidation. Numerous studies show that the radiation energy can induce macromolecular chain scission [23]. Some of the created free radicals can also recombine together to crosslink [24,25], or with oxygen in air to create polar groups [26]. Nevertheless, no radiation method had been performed on GTR as far as we know.

In the present work, the objective was to evaluate the possibility of recycling high percentages of GTR into a recycled polyethylene matrix to obtain a 100% recycled blend with acceptable mechanical performance. The influence of GTR particle mean size and specific surface area on PE/GTR blend properties was first investigated. In a second step, two oxidation treatments were carried out to improve the compatibility between rubber particles and the recycled PE matrix, in which maleic anhydride grafted polyethylene (MAGPE) chains were added. The first treatment used KMnO_4 according to the earlier works carried on by Liu et al. through a wet process. The second was γ -irradiation in air according to a dry process.

2. Experimental

2.1. Materials

The LDPE and HDPE used were recycled materials and contained small amounts of PP impurities. The MAGPE was OREVAC 18302 from ATOFINA (0.5 wt% of maleic anhydride). GTR powders were provided by different European firms (Holland, Italy, Spain and France) and are designated in this study G, T5PL, T5, T6, T8, R8 and E. All powders are blends of car and truck tyres and contain a small amount of fibres, except T5PL which comes only from pure truck tyres and which is fibre free. Two of the GTR powders were ground in our laboratory through cryogenic and ambient conditions. Potassium permanganate (KMnO_4 ; purity of 99%) was provided by ACROS ORGANICS.

2.2. Processing and testing

2.2.1. Oxidation of GTR by KMnO_4

G powder was oxidized by a 2 wt% solution of KMnO_4 in water/acetone (90/10 in volume) for 4 h

according to Liu et al. [3,7]. Then, the by-product MnO_2 was removed by washing the GTR powders with a H_2O_2 (30 wt%) and H_2SO_4 (0.1 wt%) solution and then de-ionized water. GTR powders which were modified by KMnO_4 were designated GTR-K 2.

2.2.2. γ -Irradiation of GTR

γ -irradiation of G powder was performed by Ionisos SA (France), using a 2×10^6 Curie ^{60}Co source, under air atmosphere. Irradiation dose (15, 25, 50, 75 and 100 kGy) was controlled with a precision of $\pm 5\%$. Irradiation rate was 2000 Gy/h.

Irradiated powders were designated GTR-I 15, GTR-I 25, GTR-I 50, GTR-I 75 and GTR-I 100 according to irradiation dose.

2.2.3. Blend processing

The LDPE/GTR (GTR content between 0 and 70 wt%) and HDPE/MAGPE/GTR 65/5/30 blends were prepared in a Haake plasticorder Rheomix 3000p. LDPE was melted at 130°C and HDPE (with MAGPE) was melted at 145°C . When the torque was stabilized (after 4 min), the ground tyre rubber powder was added. The torque remained constant for about 6 min after the powder addition.

In a second series, several blends were performed in two steps in order to promote the reaction between oxidized GTR and MAGPE. In the first step, GTR was blended with HDPE/MAGPE in 22/11/67 proportions. In the second step, HDPE was added to obtain the same formulation as in the one step process (65/5/30).

The blends were then milled into small particles (5 mm) using a shredder/grinder (Rotoplex Alpine), then standard ISO 527-2 type 1A tensile test specimens were prepared by injection-moulding (Sandretto Otto 95 T) of these shredded particles at 170°C .

2.2.4. Characterisation of GTR powder

Particles size was measured using a laser granulometer LS Coulter 230 in dry conditions.

Specific surface area measurements were performed using a Coulter SA 3100 apparatus by low-temperature sorption of krypton from a krypton-helium mixture, according to the BET method.

Wettability tests were performed using a LPR 902 Powder Wettability Meter from KSV Instruments LTD, based on the following procedure: a solvent (ethanol) rises through a bed of powder, a laser

beam goes through the liquid and a detector measures the variation of intensity to determine the adsorbed volume of solvent. The squared adsorbed volume is plotted as function of time. The slope A of the curve is expressed by the formula:

$$A = \eta / (C^* \gamma_L^* \cos \theta),$$

where η is the liquid viscosity, C a constant independent of the used liquid (C depends on the porosity and the packing of the particles), γ_L is the free surface energy of the liquid, θ is the contact angle.

The evolution of the slope A quantifies the affinity between the powder and the solvent.

FTIR spectroscopy in HATR mode was achieved using a Perkin Elmer apparatus with a ZnSe crystal. Each analysis was an average of 10 scans.

2.2.5. Characterisation of polymer blends

Mechanical tests were performed using ADAMEL MTS and ZWICK Z010 testing machines according to ISO 178:1993 and ISO 527-1:1993 standards. Flexural moduli were measured at a speed of 2 mm/min. Tensile strength and elongation at break were measured at 100 mm/min. Charpy impact strength was measured on un-notched specimens for HDPE and notched specimens for LDPE (ISO 179) standard using a ZWICK 5101 pendulum (4 or 7.5 J for samples which did not break with the smallest pendulum).

Differential scanning calorimetry measurements were performed on a DSC Setaram 92 apparatus (temperature rate of $5^\circ\text{C}/\text{min}$ from ambient to 400°C , in air).

SEM observations were carried on by using a Quanta 200 FEG ESEM from FEI Company.

3. Results and discussion

3.1. PE/GTR blends

3.1.1. Influence of the powder content

3.1.1.1. *Mechanical properties.* As can be seen in Fig. 1, the tensile properties are strongly damaged by the incorporation of GTR (powder G, powder mean size = $380 \mu\text{m}$) in LDPE and these properties decrease proportionally with the powder content. Nevertheless, the elongation at break levels off at high loading, which could be ascribed to percolation phenomena of GTR particles. This drastic decrease of mechanical performances could be ascribed to

poor interfacial adhesion, as can be observed on ESEM fracture surface (Fig. 2). A similar trend is seen for HDPE/GTR blends (Fig. 3).

3.1.1.2. Microstructure. The microstructure of PE matrix is not much disturbed by the incorporation of powder because of the weak compatibility between the two phases. The decrease of the blend crystallinity index is in proportion to the increase of powder content (as observed in Fig. 4). So, the crystallinity index of the LDPE matrix is not reduced. On the contrary, the melting temperature decreases from 138 to 132 °C. From these results, it can be assumed that the crystallisation is perturbed by the presence of rubber particles at the matrix–particle interface.

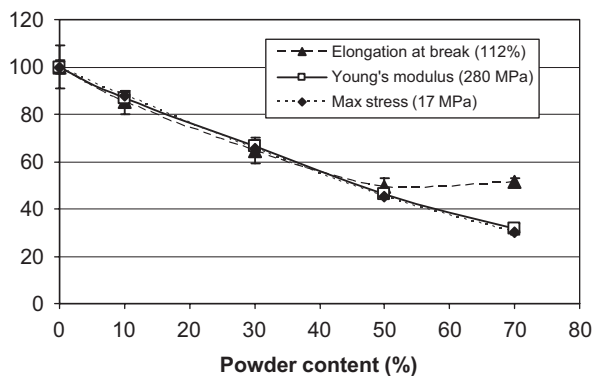


Fig. 1. Mechanical properties of LDPE/GTR blends relative to values of virgin LDPE (reference = 100); In brackets, the absolute values of virgin LDPE are given.

3.1.2. Influence of particles morphology

3.1.2.1. Particles mean size. The mechanical properties of blends LDPE/GTR 50/50 which were prepared with different powders are presented in Table 1. As powders differ mainly in the particle mean size, between 400 and 1200 μm, no significant variations of mechanical properties with particle size, were observed. Only the elongation at break, which decreases from 55% to 32%, seems to be slightly dependent on mean size.

3.1.2.2. Specific surface area. In order to study the effect of specific surface area on mechanical properties, two powders were ground by cryogenic and ambient grinding and sieved to obtain approximately the same particle size. The specific surface area was measured and compared to the specific

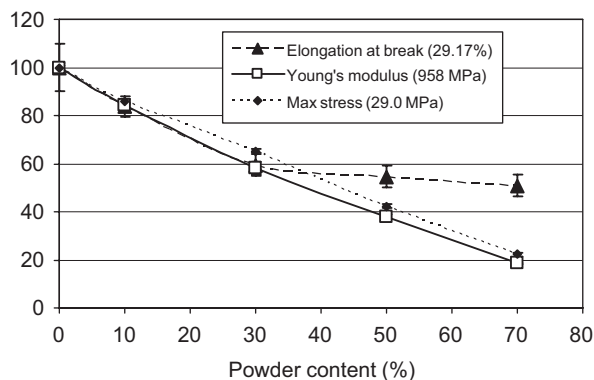


Fig. 3. Mechanical properties of HDPE/GTR blends relative to values of virgin HDPE (reference = 100); in brackets, the absolute values of virgin HDPE are given.

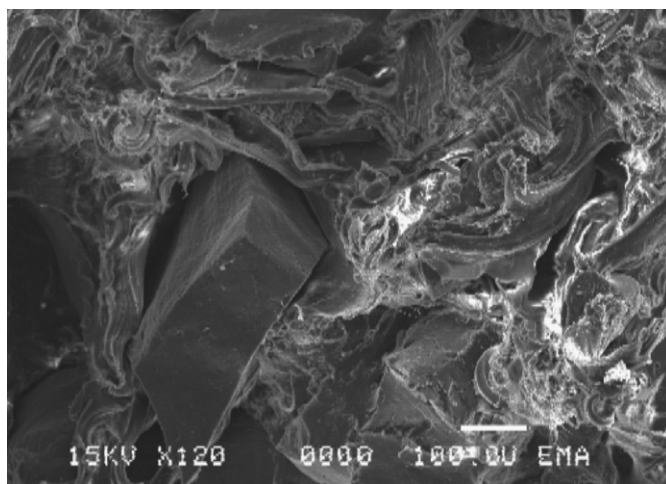


Fig. 2. Broken cross-section of a LDPE/GTR 50/50 blend.

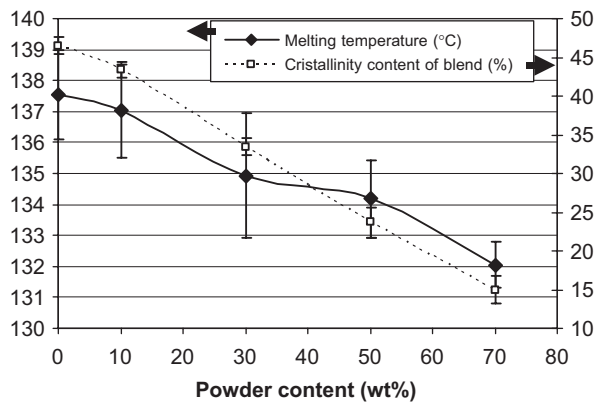


Fig. 4. Crystallinity index and melting temperature of LDPE/GTR (Powder G) blends.

Table 1

Mechanical properties of LDPE/GTR 50/50 blends with different GTR powders; standard deviations are given in brackets

Powder	Particles mean size (μm)	Young's modulus (MPa)	Max stress (MPa)	Elongation at break (%)	Impact energy (kJ/m^2)
G	380	130 (6)	7.7 (0.2)	55 (4)	2.4 (0.2)
T5PL	500	99 (5)	7.8 (0.1)	55 (4)	2.9 (0.2)
T5	520	107 (3)	8.0 (0.1)	44 (4)	2.5 (0.2)
T6	620	109 (6)	7.7 (0.2)	41 (3)	2.6 (0.2)
T8	690	111 (3)	7.9 (0.1)	43 (4)	2.6 (0.3)
R8	710	122 (5)	7.3 (0.2)	39 (4)	2.7 (0.2)
E	1200	155 (9)	7.5 (0.5)	32 (4)	/

Table 2

Mechanical properties of LDPE/GTR 70/30 blends with ambient and cryogenic ground powder; particles mean size is between 600 and 700 micrometers; Standard deviations are given in brackets

Mode of grinding	Specific surface area (m^2/g)	Specific surface areas ratio ^a	Young's modulus (MPa)	Max stress (MPa)	Elongation at break (%)	Impact energy (kJ/m^2)
Cryo	0.056	2.8	226 (6)	11.0 (0.2)	62 (5)	4.1 (0.4)
Ambient	0.051	3.6	255 (9)	11.2 (0.2)	63 (4)	3.7 (0.3)

^aRatio between the experimental specific surface area (measured by BET method) and the calculated specific surface area (calculated from size distribution of powder).

Table 3

Thermal properties of different blends LDPE/GTR 50/50; Standard deviations are given in brackets

Powder	Particles mean size (μm)	Melting temperature ($^{\circ}\text{C}$)	Crystallinity index (%)
G	383	134.6 (0.5)	22.4 (1)
T5	515	134 (1.1)	23.7 (1.7)
T8	692	134.4 (1.3)	24.3 (1.3)

surface area of a powder containing only spherical particles with the same size distribution. The specific surface area was very low for the two powders (Table 2), but it appeared that cryogenic ground particles surface was 30% less developed than ambient ground particles surface, as expected according to literature results.

Table 2 gives mechanical properties of LDPE/GTR blends 70/30 obtained with these two powders. It is obvious that no significant difference is noticeable between the two blends.

3.1.2.3. *Microstructure.* Particles mean size has no noticeable influence on microstructure of LDPE/GTR blends, as seen in Table 3. The crystallinity

ratio and the melting temperature are the same for the 3 LDPE/GTR 50/50 blends, independently of the particle mean size.

We conclude that the control of the morphology and the size of GTR particles cannot achieve a significant improvement in mechanical properties. The very low specific surface area, even with an ambient grinding process, and especially the weak adhesion between the rubber and the PE matrix, may explain these results. Consequently, the use of a surface treatment on particles is considered as a potential alternative to compatibilize both phases.

3.2. Oxidation treatments

Two oxidation treatments were performed: oxidation by KMnO_4 through a wet process and γ -irradiation according to a dry process. Oxidation efficiency and mechanical properties of HDPE/MAGPE/GTR blends were measured and compared.

3.2.1. Influence of the treatment on surface properties

Fig. 5 shows the results of wettability tests concerning the two types of oxidized GTR powders. The ethanol adsorption by the powder seems to be faster using the wet process (KMnO_4) than the dry one (irradiation) but the rate increases with the irradiation level. This result could be ascribed to enhanced oxidation for the GTR surface since ethanol is a polar solvent. Consequently, this method seems able to evaluate the degree of oxidation of powder surface.

For irradiated GTR powders, HATR-infrared spectroscopy analysis was carried out (Fig. 6)

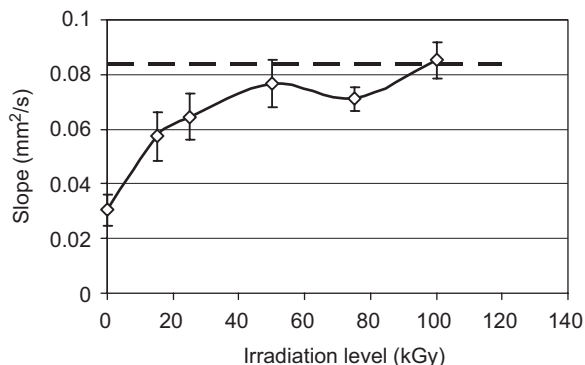


Fig. 5. Kinetics of ethanol adsorption by GTR powder as a function of the irradiation level (kGy) The broken line indicates the value for GTR oxidized by 2 wt% KMnO_4 .

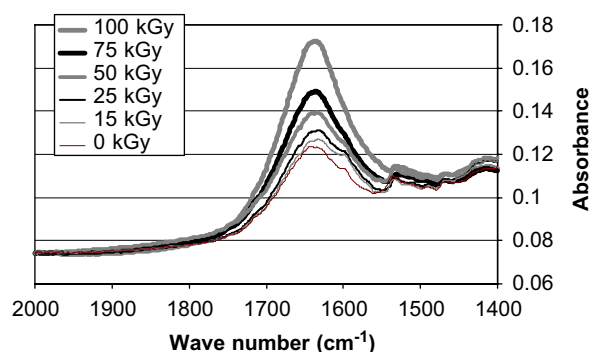


Fig. 6. HATR-infrared spectroscopy of irradiated GTR, between 1400 and 2000 cm^{-1} .

and shows that the intensity of the peak located at 1630 cm^{-1} , which is related to carbonyl groups vibrations, increases with the irradiation level. Therefore, all these results seem to be in agreement with the formation of polar (carbonyl) groups on GTR powders through both oxidation treatments.

3.2.2. Influence of GTR oxidation treatments on mechanical properties

HDPE/MAGPE/GTR (GTR-K 2, GTR-I 25 and GTR-I 100) 65/5/30 were blended in one step and compared to the same formulation with unmodified GTR. Mechanical performances are presented in Table 4. No improvement due to oxidation seems to be noticeable. It can be concluded that oxidation of GTR surface is not sufficient to enhance mechanical performance of blends.

Nevertheless, another explanation can be considered. Indeed, the dilution of maleic anhydride in the PE matrix may induce a too low probability for reactions between these groups and carbonyl groups on the GTR surface. In order to clarify this point, blending with irradiated GTR was performed in two steps as described in the experimental section.

3.2.3. Influence of the processing

Some HDPE/MAGPE/GTR-I 65/5/30 blends were performed in two steps. Table 5 shows the mechanical results with the same formulations obtained according to the one-step process (Table 4). No change was observed whatever the considered mechanical properties, as the irradiation level increased for a two-step process. Moreover, no significant difference was noticeable between the two processes.

Table 4

Mechanical properties of HDPE/MAGPE/GTR 65/5/30 with GTR, GTR-K 2, GTR-I 25 and GTR-I 100 performed in one-step process; standard deviations are given in brackets

Powder	Young's modulus (MPa)	Max stress (MPa)	Elongation at break (%)	Impact energy (kJ/m ²)
GTR	477 (14)	17.7 (0.2)	25 (1.8)	4.8 (0.7)
GTR-K 2	435 (16)	18 (0.2)	21.6 (2.1)	/
GTR-I 25	506 (11)	17.8 (0.1)	22.7 (1.9)	5.3 (1.3)
GTR-I 100	496 (11)	17.5 (0.1)	22.9 (1.6)	5.0 (0.8)

Table 5

Mechanical properties of HDPE/MAGPE/GTR-I 65/5/30 performed in two-step process; standard deviations are given in brackets

Powder	Young's modulus (MPa)	Max stress (MPa)	Elongation at break (%)	Impact energy (kJ/m ²)
GTR	501 (16)	17.2 (0.3)	23.7 (1.5)	4.8 (0.7)
GTR-I 15	494 (7)	17.4 (0.2)	24.3 (1.9)	5.2 (1.0)
GTR-I 25	491 (5)	17.2 (0.1)	24.6 (1.4)	5.2 (1.0)
GTR-I 50	503 (13)	17.3 (0.1)	24.8 (1.4)	4.7 (0.6)
GTR-I 75	495 (7)	17.2 (0.1)	24.1 (1.5)	5.0 (0.9)
GTR-I 100	496 (7)	17.5 (0.1)	23.4 (1.8)	4.6 (0.6)

4. Conclusion

First, it has been shown that the incorporation of a ground tyre powder into recycled polyethylene matrix led to a drastic decrease of the mechanical performance because of a too weak interfacial adhesion. Moreover, the mean size and the surface roughness of particles seem to have no significant influence on these properties.

In order to improve the interfacial adhesion, ground tyre powders were treated on one hand by potassium permanganate (wet process) and on the other hand by γ -irradiation (dry process) to oxidize particles surface and to compatibilize HDPE/MAGPE/GTR blends. The oxidation was confirmed by a specific wettability test and by FTIR spectroscopy. Nevertheless, the mechanical tests showed no significant improvement that could be ascribed to a promotion of interfacial adhesion, in comparison with a HDPE/MAGPE/GTR blend without previous oxidation of GTR particles.

These experiments have shown that surface treatments based on GTR oxidation were not effective enough to significantly improve the mechanical performances of blends with polyethylene. Consequently, we conclude that such a strategy for improving GTR reactivity towards a non-polar polymer matrix cannot be as effective as strategies

involving interfacial free radical co-crosslinking reactions in the blend (controlled dynamic vulcanization) [27–28].

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