Effect of the Particle Size and Acid Pretreatments on Compatibility and Properties of Recycled HDPE Plastic Bottles Filled with Ground Tyre Powder

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ABSTRACT: With the growing emphasis on decreasing the accumulation of the used tyres in land fills, there has been significant scientific and technological interest to provide with solutions to their recovery and reuse. A new composite material based on reused tyre powder as reinforcement and recycled high-density polyethylene as matrix was studied in this work. The effect of chemical acidic pretreatments performed on the rubber and of the particle size on the behavior of the composite material were evaluated. Powder of reused tyres resulting from industrial grinding processes was separated by sieving in three particle size categories: below 200 μm, between 200–500 μm and over 500 μm. Pretreatments using H_2SO_4, HNO_3, or a 50% mix of H_2SO_4 and HNO_3 were carried out over the rubber before composite preparation. Mechanical tensile properties were evaluated to determine the effect of particle size and acid pretreatments on composite properties. Fracture surfaces of composite samples were also evaluated by scanning electron microscopy. Overall, all pretreatments improve the mechanical behavior of the obtained materials. This improvement is attributed to the development of a surface of the rubber, more suitable for mechanical adhesion. The effect of the particle size has a stronger influence in the properties of the material than the acidic pretreatments. J Appl Polym Sci 112: 1882–1890, 2009

Key words: reused tyres (A); recycling (A); interface (B); mechanical properties (B); surface analysis (D)

INTRODUCTION

The important issue of the accumulation of the used tyres in land fills[1–3] has impelled the efforts of the scientific community to provide with solutions to their recovery and reuse. Nowadays most of the end-of-life tyres, around 60%, end up in land fills. Some countries have developed special regulations designed to the control of used tyres.

The present ways to recover tyre waste include: reuse, rethreading, recycling, energy recovering, and dumping in landfills. Improving and widening these possibilities constitutes an environmentally important challenge. Some of the strategies include compounding rubber with several materials as concrete[4–6] natural rubber vulcanizates[7] and blends with polymers.[8–13]

This last aforementioned way seems quite reasonable, since many plastic materials include elastomers to improve their tenacity. In general, a thermoplastic or thermoset polymer acts as matrix and the rubber as disperse phase. These blends are biphasic and show improved resistance to impact and toughness. If the matrix is constituted by a polymer of general use and great production and, such as in this study, is recycled, the approach could suppose an alternative and effective reduction of the plastic waste. On the other hand, as in other biphasic polymer blends, interfacial compatibility of the components is important to achieve the desired properties.[14] In case of reclaimed rubber, when is blended with high-density polyethylene (HDPE), the compatibility is expected to be low. One way to increase the compatibility between both components is to reduce the degree of crosslinking of the reused tyres by devulcanization. The devulcanization may achieve by thermomechanical[15] or thermochemical treatments.[16] The rubber obtained by this process is called reclaimed tyre rubber.[17,18] In addition, grafting of polymers and compatibilizing agents have been used on tyre powder to obtain useful materials, improving the interfacial adhesion. Several methods were considered in modifying the properties of rubber, such as treatment using acrylamide, submitted to ultraviolet radiation using maleic anhydride-grafted polypropylene as compatibilizer,[19] or using

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glycidyl methacrylate and methacrylic acid trough photo initiated grafting.[20] These procedures improved the adhesion between components, resulting materials with good mechanical properties. In these cases, it is important to point out that the use of a relatively uncomplicated pretreatment process is critical to obtain economically attractive materials.

The possibilities of achieving a good biphasic blend with reasonable compatibility between phases obtained by a relatively uncomplicated process have lead to the use of several pretreatments.[21,22] The acid pretreatment produces by reaction a microporous surface that is useful for applications related to adsorption. In many cases, porosity developed in polymers has characteristics suitable to improve mechanical adhesion. The chemical attack leads to cavities that allow a good interlocking with adhesives.[23,24] With these antecedents, the feasibility of achieving appropriate rubber morphology, providing improved interfacial adhesion in rubber/recycled HDPE biphasic blends, combined with a relatively easy application with simple equipment seem a profitable way to obtain industrial products with adequate properties.

The particle size of the disperse phase also plays an important role in the mechanical properties of a biphasic blend. However, the size category of rubber powder available in the market is limited by the technical procedures of grinding. To preserve the costs of production low, it would be desirable not to process the powder supplied to further grinding which would require more sophisticated equipment, such as cryogenic processes. To evaluate the influence of the particle size on the properties of the material, a study is required. Results will allow deciding whether the final material behavior is highly improved by using an appropriate size.

A simple method to achieve smaller particle size without further grinding of the rubber is by sieving. Of course, sieving process results in using only a part of the total rubber amount and it could make the process financially not viable.

In this article, a new composite material based on reused tyre powder as a reinforcement and recycled HDPE matrix was studied, thereby providing another way of reducing the stock of used tyres and HDPE waste. The effect of the rubber content and chemical acidic pretreatments (nitric and sulphuric acids and their blends), performed to improve rubber/matrix compatibility, on the mechanical tensile properties of the composite were investigated. In addition, to elucidate the effect of particle size on mechanical properties of composite, the nontreated and treated powder rubber was separated by sieving in several particle sizes categories. Moreover, the HDPE/rubber interphase has been studied previously by scanning electron microscopy (SEM) and FTIR spectroscopy.[25] To improve the understanding of the HDPE/rubber composite material, a calorimetric analysis was also performed.

METHODOLOGY

Materials

HDPE recycled from water bottles, with a melt flow index of 1.35 g/min and density of 960 kg/m^3 was used. Commercial ground reused tyres were obtained from industrial rubber recycle plant.

The original rubber powder was separated by sieving in three particle size categories: <200 μm, 200–500 μm, and >500 μm.

Acid pretreatments were carried out with two oxidant acids in aqueous solution: H_2SO_4 density, 50% *v*/*v*, HNO_3, 50% *v*/*v*, and a blend of 50% *v*/*v* of them. All chemicals were of analytical grade.

Preparation of the blends

The powder of reused tyre was dried in an oven at 100°C for 24 h. For each particle size category and reused tyre pretreatment four compositions have been studied: 5, 10, 20, and 40% weight of rubber. Above 40%, the blend was difficult to process and homogenize. A control untreated sample was also used as a reference.

The acid pretreatments were carried out by immersion of reused tyre samples for 2 min in sulphuric acid (50% *v*/*v*), nitric acid (50% *v*/*v*), and sulphuric-nitric 50% *v*/*v* solutions. The etching treatment was followed by reaction in air for 5 min, neutralization with 3*M* NaOH and rinsing the sample with distilled water at room temperature until pH 7. To ensure that no significative reduction of the particle size after the acid pretreatment was produced, a new sieving of every size category was performed. The lost of material through the related mesh was >1% in every case.

The reused tyre was mixed with the recycled HDPE in a CollinW100T two-roll mixer at 153°C. To avoid polymer degradation, the mixing time was restricted to 3 min. The blend was then consolidated at 100 kN and 170°C for 15 min in a hot square (150 × 150 × 2 mm^3) plates press (Collin mod. P200E). The cooling process is carried out under pressure and using cool water for refrigeration for 5 min. Test samples were properly shaped according to the ASTM-D-412-98 specifications. Plain HDPE without reused tyre was also treated the same way as the filled materials to obtain suitable reference samples.

Mechanical testing

Tensile tests were carried out in an universal machine Instron 3366 following the specifications of the ASTM-D-412-98. Speed of the test was set at 20 mm/min. Testing temperature was 23 ± 2°C and the relative humidity of 50 ± 5%. Studied properties include Young's modulus, toughness, tensile strength, and the percentage of breaking deformation versus tyre-rubber content, surface modification, and particle size category.

Qualitative toughness of samples was calculated from measurements of the area of strength-strain curves to compare results. Statistical analysis was conducted on the mechanical testing data to determine the significance of the values. Five specimens were analyzed, and average and standard deviation were calculated.

Calorimetric analysis

The dynamic thermal behavior of the samples was analyzed using heat flow DSC. The measurements were made with a Mettler TA4000 thermoanalyzer coupled with a DSC 30 apparatus. The sample mass was between 3.0 and 3.5 mg, and it was small enough to avoid problems caused by heat and material transfer. Temperature and enthalpy were calibrated using In and Pb as standards. Samples were heated from 40 to 200°C at a heating rate of 10 K/min and using synthetic air as purging gas at a flow rate of 40 mL/min.

Scanning electron microscopy

SEM was used to qualitatively examine the fracture surface of the broken samples from mechanical testing. By observing the environment of the reused tyre particles it was possible to analyze the effects of the treatments and the adhesion of the filler to the matrix. Several images of every sample were studied.

The microscope used was a JEOL 5610 and previously to the observations, the samples were coated with a thin layer of carbon, to increase their conductivity.

RESULTS AND DISCUSSION

Mechanical properties

Figures 1–4 show the results of the mechanical properties determined by tensile test. These mechanical properties were analyzed with percentage of tyre content, chemical reused tyre pretreatment, and particle size category.

Overall, it was found that addition of reused tyre powder to the HDPE produces a decrease of the tensile strength (Fig. 1). This behavior is associated to the poor HDPE/ reused tyre interphase adhesion. The tensile strength was found to decrease when increasing the tyre content. Acidic pretreatments

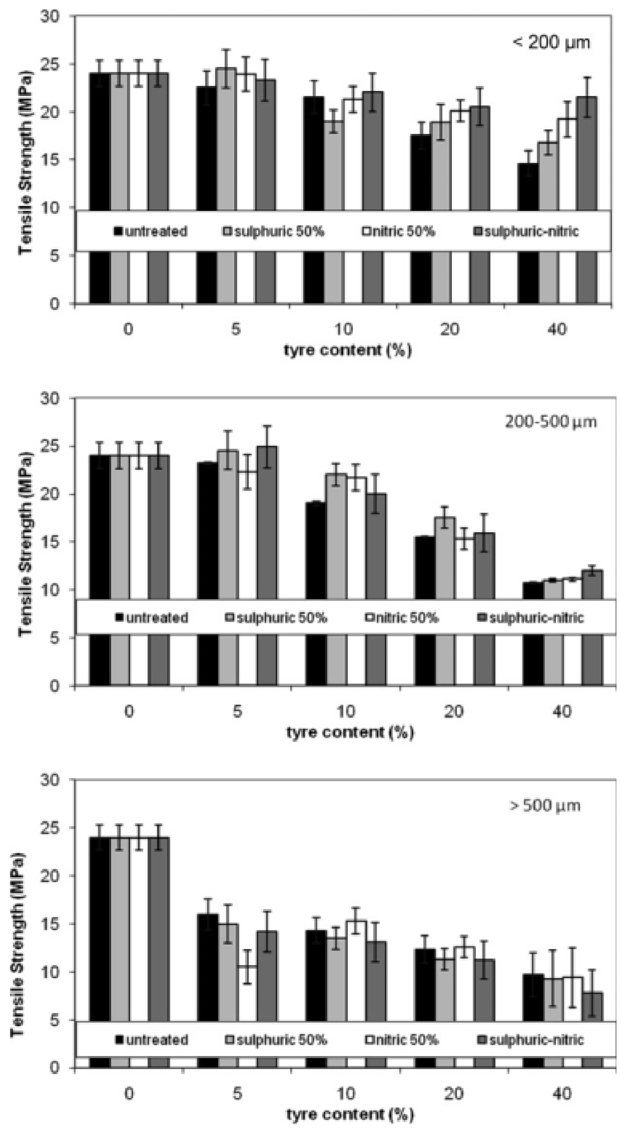

Figure 1 Tensile strength versus tyre content for untreated, treated with H_2SO_4 (50%), HNO_3 (50%), and H_2SO_4–HNO_3 (50%). HDPE-reused tyre composites with several rubber particle sizes.

were found to increase the tensile strength in most cases when particle size is below 500 μm. The effect of the acidic pretreatment[26–28] is related to the etching of the reused tyre surface, the elimination of moieties and additives and the achievement of a microporous surface more suitable for mechanical adhesion. The acid pretreated samples show similar behavior, obtaining for the 50% sulphuric–nitric solution better results than the nitric or sulphuric acid pretreatment, for the lowest particle size and highest reused tyre content.

As expected, particle size plays an important role in the tensile strength.[29] A minor decrease of the tensile strength at high tyre contents was obtained for small particle size category. The effect of particle size is clearly observed when comparing the three categories. Bigger particles provide a higher probability of failure cracks, whereas smaller particles may develop small microcracks with dimensions below the critical length. Quite obvious is the case of particles above 500 μm, showing a significant drop of the mechanical properties values for all studied cases. Also, the possibility of achieving a bigger particle size by conglomeration of particles during the process of blending should be considered. The agglomeration of particles would decrease the mechanical performance. However, the classification of particles may not be economically viable, since the increase of the composite properties is not worth the lost of tyre material that implies.

In addition, the effect of acids on tensile properties seems to be related to the particle size. It was observed that acid pretreatments improve the composite tensile strength specially when the smaller particle size category was treated, whereas in particles with size higher than 500 μm, the effect of acid pretreatment do not improve significantly the studied property. For example, the tensile strength was found to decrease about 25% (untreated) for compositions of 20% reused tyre when particle size is below 200 μm, meanwhile the same particle size pretreated with sulpho–nitric blend (20% reused tyre) showed only a decrease of 13%. A significant decrease of the tensile strength was observed for a composite reused tyre content of 10% *w*/*w* with particle size higher than 200 μm. In case of particle sizes over 500 μm, for a reused tyre content of 5%, a 25% of decrease of the tensile strength was resulted.

Considering acid pretreatments as a surface etching of the reused tyre, the acid treatment effect is higher when increasing the surface area. In case of small particles, the increase of surface area allows a more extensive etching of the acid. At the same time, since the etching produced should be, in terms of depth, equivalent in all cases, the roughness relative to the particle size should be more important, improving the reused tyre/matrix mechanical adhesion.

Composites with low reused tyre content and particle size below 200 μm, resulted in an increase (1–5%) of the stiffness (Young's modulus) compared with neat HDPE (Fig. 2). In contrast with other materials based on the addition of elastomers, the addition of high concentration of tyre rubber acts decreasing the deformation ability of the ductile and plastic HDPE matrix. Even without pretreatment, it was observed than Young's modulus of the composites was higher than the original HDPE without reused tyre, for composites with a low reused tyre content (5%) and particle size comprised between 200 and 500 μm. When the content of reused tyre increases the poor interfacial adhesion causes a decreasing of the stiffness for similar reasons to the exposed when considering the tensile strength. Also,

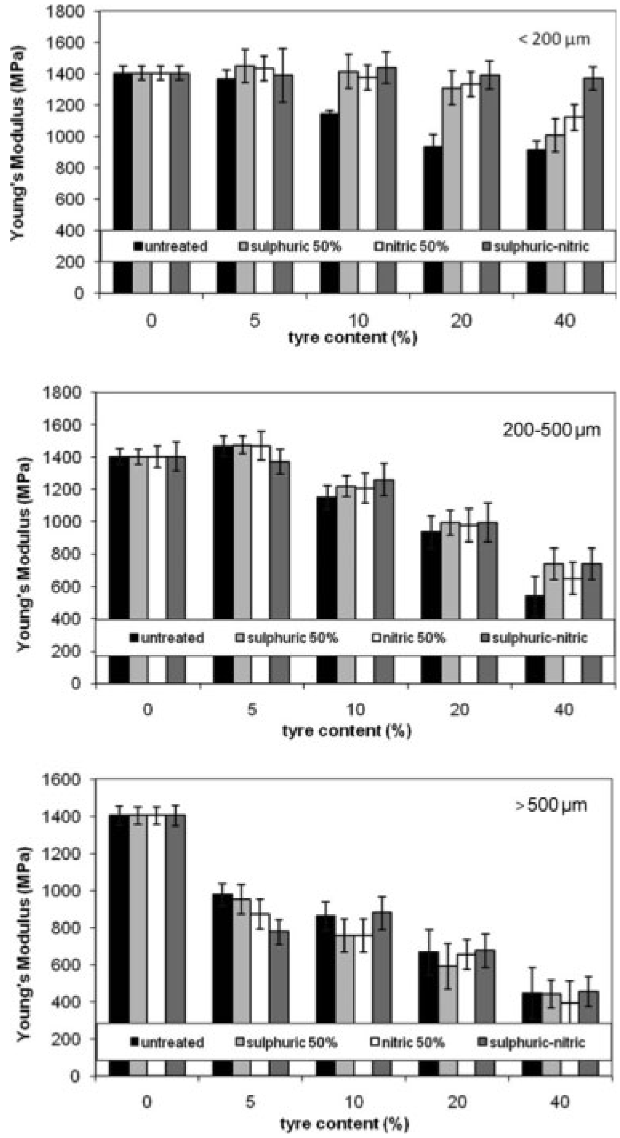

Figure 2 Young modulus versus tyre content for untreated, treated with H_2SO_4 (50%), HNO_3 (50%) and H_2SO_4–HNO_3 (50%). HDPE-reused tyre composites with several rubber particle sizes.

the decrease of the Young's modulus value is more drastic when using bigger particle size.

The effect of the acid pretreatment on Young's modulus is clearly visible in Figure 2. The etching of the acid acts promoting mechanical adhesion, but also rigidizes the rubber by extracting the substances that may act as a plasticizer. The acid treated reused tyre has a rigid nature as it has been also observed in studies by other authors.[30,27,28] Then, reused tyre obtained with previous acid etching are usually stiffer than not treated ones. The sulpho–nitric mixture seems to provide the best results, but in general all acids have an improving effect. As exposed previously for tensile strength composite properties, the effect of acid treatments in Young's modulus was higher when adding smaller particle size.

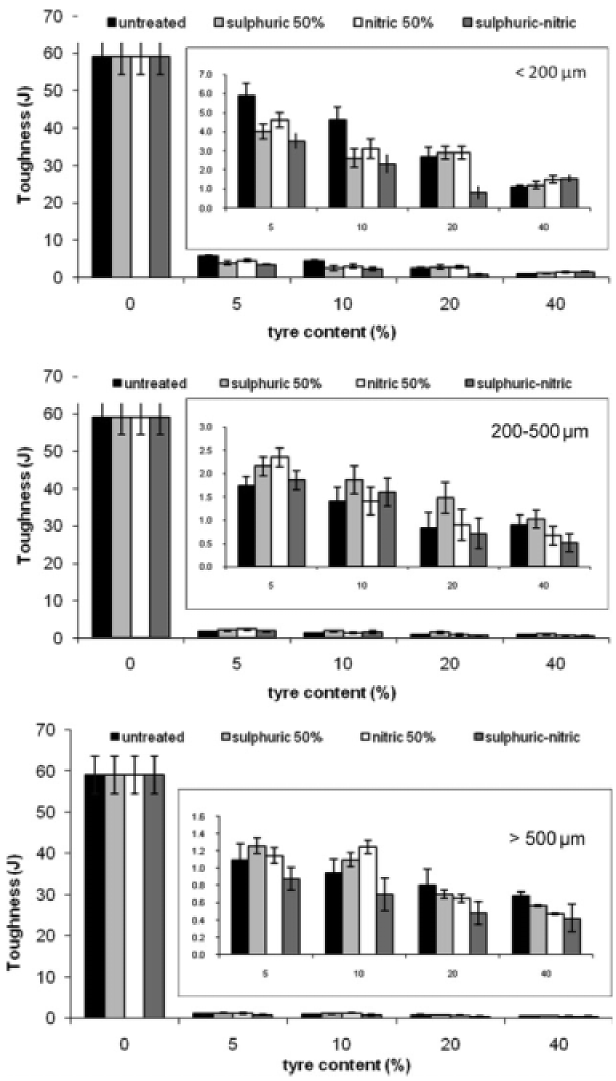

Figure 3 Toughness versus tyre content for untreated, treated with H_2SO_4 (50%), HNO_3 (50%), and H_2SO_4–HNO_3 (50%). HDPE-reused tyre composites with several rubber particle sizes.

The addition of reused tyre in all prepared composites produce a drastic fall of the toughness (Fig. 3) and elongation at break (Fig. 4). Toughness and elongation at break for reused tyre based composites show lower values than that of pure HDPE matrix, considerations about the particle size and type of pretreatment are not relevant in that case. The decrease of elongation at break is related to the imperfect interfacial adhesion between components. The incidence of the poor adhesion between phases on this property is especially important. On the other hand, the compatibilizing effect achieved by the acid pretreatments is counteracted by the increase of the stiffness of the rubber. As discussed previously, the extraction of additives, oligomers, or plasticizers of the rubber by the acid produces a rigid material. The reduction of the ability of deformation of the rubber influences the decrease of elongation and subsequently the decrement of the toughness.

Calorimetric study of the samples

Calorimetry applied to composite materials has been used as a tool to detect possible changes in crystallinity or microstructure of the matrix when adding a second component as reinforcement. By measuring the melting temperatures and the enthalpy of melting of the composites, such changes can be followed. The enthalpy and melting temperature of the samples are shown in Figures 5 and 6, respectively.

From the results obtained for enthalpy of the composites (Fig. 5), it was observed that the values remain approximately constant for all composite compositions, regardless of the pretreatment and particle size. That should be related to the poor interfacial adhesion between reused tyre particles and

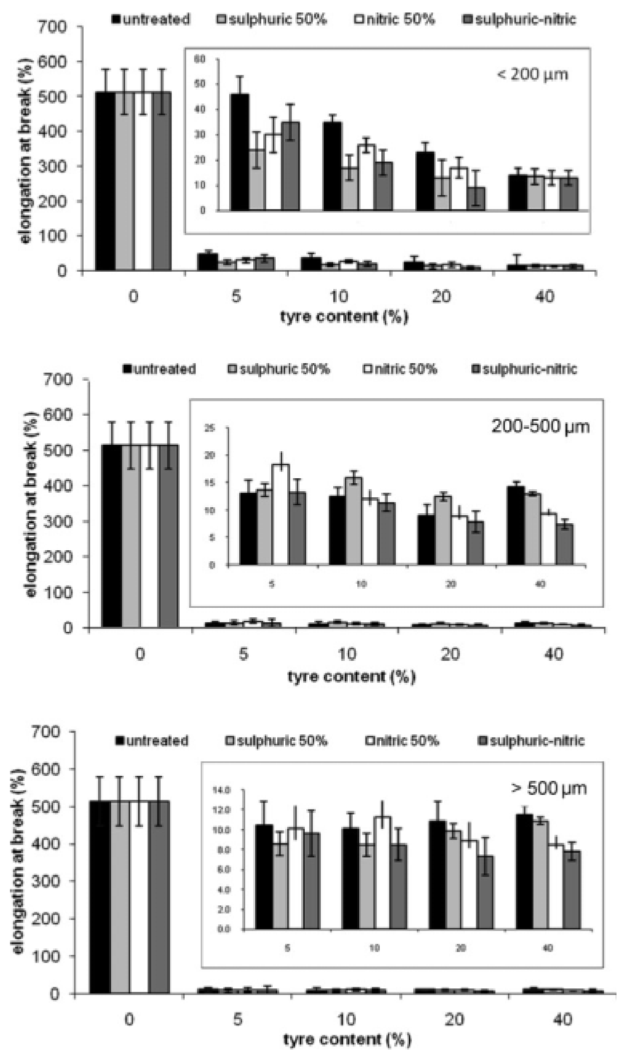

Figure 4 Elongation at break versus tyre content for untreated, treated with H_2SO_4 (50%), HNO_3 (50%), and H_2SO_4–HNO_3 (50%). HDPE-reused tyre composites with several rubber particle sizes.

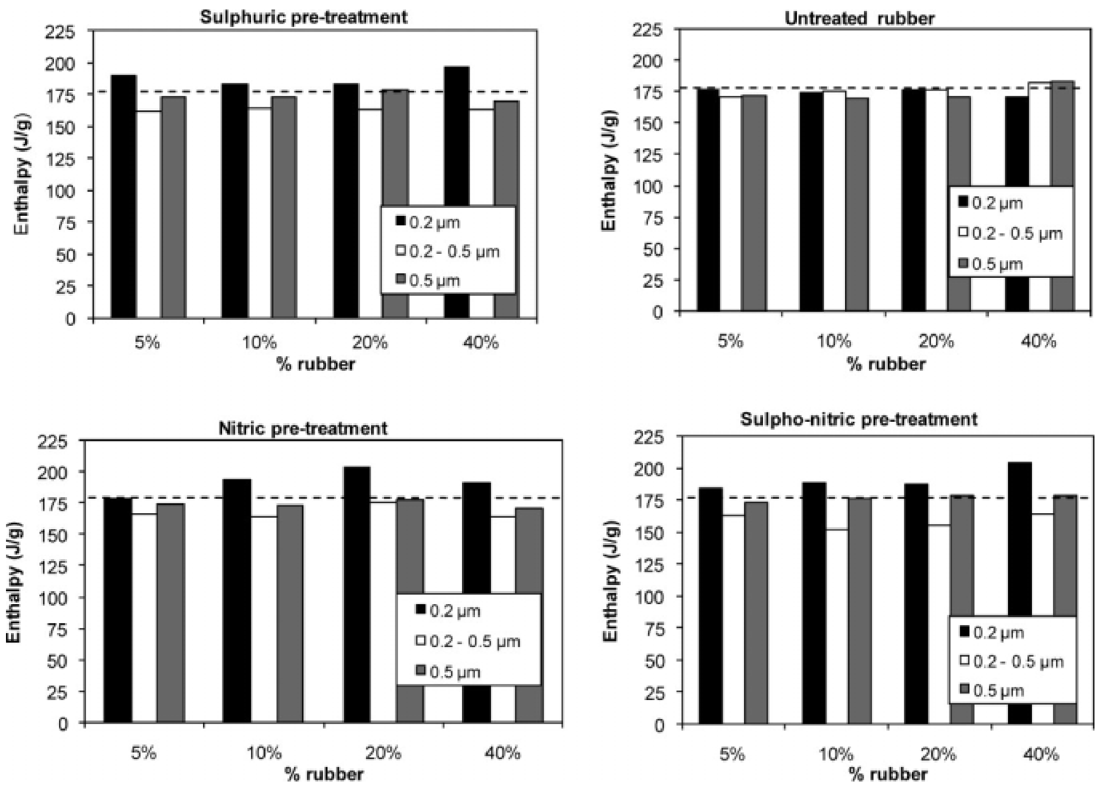

Figure 5 Melting enthalpy versus tyre content for untreated, treated with H_2SO_4 (50%), HNO_3 (50%), and H_2SO_4–HNO_3 (50%). HDPE-reused tyre composites with several rubber particle sizes in micrometer.

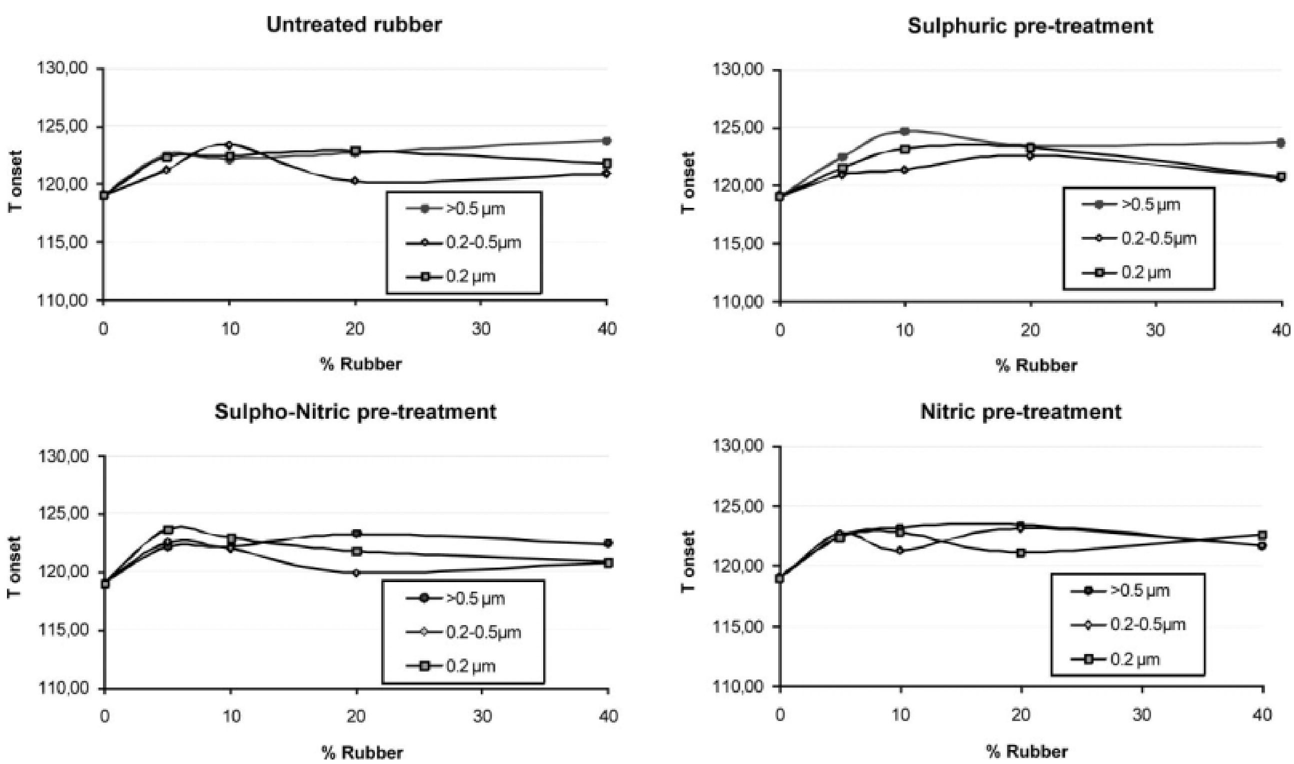

Figure 6 Onset temperature versus tyre content for untreated, treated with H_2SO_4 (50%), HNO_3 (50%), and H_2SO_4–HNO_3 (50%). HDPE-reused tyre composites with several rubber particle sizes in micrometer.

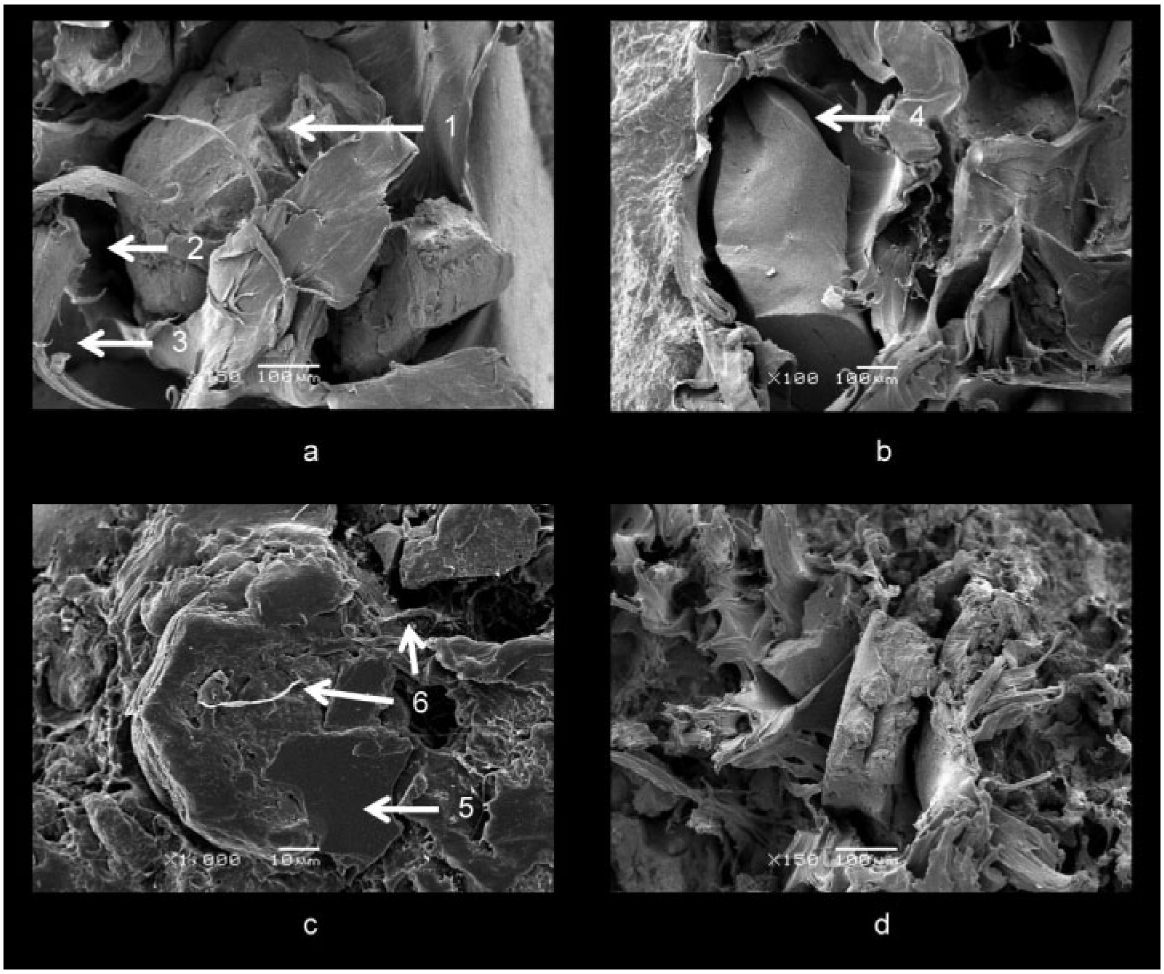

Figure 7 SEM microphotographies of different fracture surfaces of ground tyre/recycled HDPE: (a) particle size higher than 500 μm treated with H_2SO_4, (b) particle size lower than 500 μm treated with HNO_3, (c) particle size lower than 200 μm treated with H_2SO_4, (d) particle size between 200 and 500 μm treated with H_2SO_4–HNO_3 (50%).

HDPE matrix. Enthalpy tends to increase slightly for acid pretreated reused tyre for composites with the particles size below 200 μm. In addition, the enthalpy of melting seems to increase when increasing the amount of reused tyre in the composites. This phenomenon is related to the nucleation effect of the reused tyre particles in the interior of the HDPE during the preparation of the samples by melting. The small particles of tyre powder act as nucleating agents increasing the compactness of the structure in their boundaries. The promotion of the crystallization results in an increase of melting enthalpy that is also related to the best performance in mechanical terms, such as tensile strength and Young's modulus.

Particle sizes above 200 μm results always in a decrease of the enthalpy of melting. Big particles treated with acids become cracked, rough, and have pores where HDPE can enter in the process of melting. When pore size is big enough, a significant amount of the HDPE in contact with the reused tyre becomes affected by this fractured surface being disturbed in the possibilities of forming a compact structure, promoting the amorphous state in this space close to the particle surface. The nucleation effect would not be present in this case because of the big size of the particles.

Calorimetric data related to the melting temperature of the samples are shown in Figure 6. An increase in the melting temperature could be associated to a more compact crystalline structure. In this case, results show that there is a trend to higher onset temperatures in samples including tyre rubber, except in the case of sulpho–nitric treatment. However, the differences in temperature are not significant and it was difficult to conclude about the effect of reused tyre particles on HDPE microstructure. Overall, small particle sizes tend to result in higher melting temperature.

Scanning electron microscopy

Some microphotographies depicting the fracture surface of the reused tyre based composites are shown in Figure 7.

The images show different levels of magnification, which allows the comparison of the different particle sizes. The picture "a" shows a composite sample containing sulphuric treated reused tyre particle sizes above 500 μm. In the centre appears a big particle (1), showing some cracks and pores big enough to be observed at this level of magnification. The particle is unlinked to the matrix, as it can be observed by the deep voids around its contour (2). The tyre seems to be resting on the HDPE, without being properly attached to it. On the other hand, the matrix has been strained and deformed plastically (3). Microphotography "b" from a sample including particles with sizes below 500 μm pretreated with HNO_3 shows similar features. The interaction between both components of the composite is not good and there are many cavities (4) around the reused tyre particle. Image "c" shows a different situation, since magnification is 10 times higher, particle is much smaller. The particle seems much more integrated in the matrix, and there is an area on the right with a clean cut that indicates that the particle itself has been broken instead of detached (5), which proves the good performance of the interfacial contact, when the particles has been treated with H_2SO_4. The contour of the particle does not show voids around, instead some fragments of HDPE sprout from the reused tyre showing points of good attachment between both components (6). The high magnification allows the appreciation of the roughness achieved by the pretreatment. Picture "d" shows particles (size between 200 and 500 μm) treated with H_2SO_4–HNO_3 (50%). Several medium size particles appear showing different levels of attachment.

CONCLUSIONS

From the study of the mechanical properties it is concluded that: (i) in most cases, acidic pretreatments act improving the compatibility of the components resulting in better mechanical properties that untreated samples, (ii) acid pretreatments act over the reused tyre particles causing etching of the surface and improving mechanical adhesion, (iii) for small particle sizes, the pretreatment with sulpho–nitric mixture gives the best results in terms of mechanical properties, but H_2SO_4 has also a very positive effect, (iv) smaller particle size produces a composite with higher tensile strength and stiffness, (v) the results of the particle sizes below 200 μm, and between 200 and 500 μm are both acceptable in terms of balance properties/amount of useful reused tyre, whereas particles bigger than 500 μm produce a drastic reduction of mechanical properties, and (vi) the effect of the acidic pretreatment is more intense when using smaller particle sizes.

Calorimetric studies show differences in melting enthalpy of the materials studied. This leads to the following conclusions: (i) melting enthalpy is constant for untreated samples in every particle size, that means the matrix is not altered by the presence of the reused tyre in terms of crystalline structure, (ii) enthalpy of melting tends to be higher for the pretreated composites with particle size below 200 μm, because of the nucleation effect of the reused tyre in the interior of the HDPE, this effect, may also be a cause of the better mechanical performance achieved with these samples, (iii) the enthalpy of melting for the pretreated composites with particles size below 200 μm also increases with the percent of tyre, and (v) particle sizes above 200 μm cause a decrease of the melting enthalpy.

SEM microphotographs show differences relative to the particle size: small particles are more attached to the matrix because of the high relative roughness and relative magnitude of pores and cracks. The etched surface achieved by acids may not be enough to effectively link bigger particles to the matrix.

The results achieved for the proposed composite materials, obtained exclusively from polymeric discarded waste, allow considering them as a real alternative to future applications. However, further studies are still needed to achieve the best possible features.

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