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A fractographic study on toughening of epoxy resin using ground tyre rubber

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Abstract

This study is a fractographic examination of epoxy resin modified with scrap car tyre regrinds used as toughening phase. Five different surface treatment techniques, used to improve the compatibility at the interface between the rubber particles and the epoxy matrix, were: oxygen plasma, two silane coupling agents, acrylic acid and acrylic acid/benzoylperoxide mixture. Rubber parts of ground scrap car tyres with a size range of 355–500 μm after surface treatment were mixed with epoxy. This mixture was poured into molds to obtain fracture toughness test specimens. After curing, plane strain fracture toughness tests were performed and the fractured surfaces of the specimens were examined under the scanning electron microscope. Fractographic studies indicated that the increase in fracture toughness values were due to the improved interface leading to crack deflection as the main rubber toughening mechanism. Secondary rubber toughening mechanisms observed were shear deformation and some debonding initiated at the interface. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Recycled rubber; Rubber toughening mechanisms; Fracture toughness

1. Introduction

Scrap tyres have become a symbol of the global waste problem, despite their accounting only for about 2% of the total amount of waste. Every year 2 Mtonnes of tyres are scrapped in Europe and 2.8 Mtonnes in the USA [1]. There is a continuous effort on the recycling of scrap rubber. Rubber recycling has been extended to the use of rubber in asphalt, scrap rubber as fuel, rubber pyrolysis, tire splitting and other uses. Many scrap tires are chopped, ground, or powdered for use in a wide variety of products such as floor mats, adhesives, gaskets, shoe soles, and electrical insulators, or blended into asphalt for use in pavement binders and sealants, or as an aggregate substitute. Some of the chopped scrap tires become fill and cover material in construction and landscaping, artificial reefs and breakwaters for beach erosion control, playground surfacing material and equipment, sound barriers, boat dock shock absorbers, and even materials for building houses. The use of scrap tires as fuel increases every year, and it is currently the largest single use of scrap tires.

Scrap rubber to be used as a filler and toughening agent in epoxy resin is recently under consideration, because epoxides are the most widely used and studied thermosetting materials. They are used in a wide range of industrial applications such as coatings, as matrices for composites, as adhesives and as encapsulating materials. Neat epoxides however have a very low crack growth resistance and are amongst the most brittle polymeric materials.

Actually, addition of a second dispersed rubbery particulate phase with a particle size of several microns, i.e. rubber modification, has been successfully applied to overcome the brittleness of many epoxides over the past 25 years. However, these approaches were based on using reactive liquid elastomers [2–8]. The reactive liquid rubber used in this method is dissolved in the epoxy first. After adding curing agent, as the resin begins to cure and the molecular weight rises, the rubber precipitates out and forms the second phase particles. The volume fraction and size of the rubber domains are controlled by the degree of compatibility of the two phases and the kinetics of gelation. Butadiene–acrylonitrile based rubbers are the principal liquid elastomers used for toughening of epoxies.

In reactive liquid rubber toughening, especially for concentrations of more than 5 vol%, these studies [2–8] indicated that decreasing the size of the rubber domains down to a few microns in the epoxy matrix increased the effectiveness of the toughening process. For instance, in the

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work of Hwang et al. [8], two different reactive liquid rubbers, an amino-terminated butadiene acrylonitrile rubber (ATBN) and an epoxy-terminated butadiene acrylonitrile rubber (ETBN), used with a concentration of 15 phr (parts per 100 parts of resin) leading to a particle size range of 1–20 μm, increased impact strength, plane strain fracture toughness (K_{IC}) and fracture energy (G_{IC}). In these researches, two major toughening mechanisms were suggested; the increased size of the plastic zone at the crack tip and rubber-enhanced shear deformation of the matrix.

A recent study of Bagheri et al. [9] indicated that scrap rubber particles might also be used as toughening agents in epoxies. The advantage of this approach is that the particle size and volume fraction of the second phase is usually not affected by the resin type and by processing conditions. Compatibility with the epoxy resin and adhesion to the matrix can be achieved via chemical modification of the surfaces of the particles. Some of the methods used for rubber surfaces are plasma surface modification and silane coupling agent treatment.

The aim of this investigation was to explore the toughening mechanisms developed when coarser surface treated recycled rubber particles are used in epoxy matrix. For this purpose scanning electron microscopy was used on the fractured surfaces of plane strain fracture toughness test specimens.

2. Experimental

The epoxy resin used was a liquid diglycidylether of bisphenol A (DGEBA)-based epoxy resin (Ciba-Geigy/LY556). The hardener and the accelerator used were methyltetrahydrophthalicanhydride (Ciba-Geigy/HY917), and a tertiary amine (Ciba-Geigy/DY062), respectively. Rubber particles were obtained from used car tires (LASSA™). These scrap tires were cleaned with tap water and dried. After being cut into small flakes they were cryogenically and mechanically ground, and sizes between 355–500 μm were selected by sieve analysis. For the surface treatment of these rubber particles five different methods were used.

As the first silane coupling agent treatment vinyltriethoxysilane (Fluka) [$CH_2{=}CHSi(OC_2H_5)_3$] was used. In this treatment three different weight percentages: 1, 2 and, 4% with respect to the amount of rubber particles were applied. Since the 2% vinyltriethoxysilane resulted in the highest toughness values, further treatments were based on this amount. The second silane coupling agent used was 3-aminopropyltriethoxysilane (Fluka) [$H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$]. Only 2 wt% was used.

The third treatment used was oxygen plasma modification of the 2 wt% vinyltriethoxysilane treated rubber particles. As the fourth method, rubber particles were treated with acrylic acid (Merck) [$CH_2{=}CH\ COOH$]. The amount of acrylic acid selected was 5% by weight with respect to the rubber particles. In the fifth method, a mixture of acrylic acid and benzoylperoxide (Merck) [$(C_6H_5COO)_2$] was used. Benzoylperoxide was added at a concentration of 5% by weight with respect to the amount of acrylic acid, in order to initiate the polymerization of acrylic acid to polyacrylic acid.

These surface treatments were applied to mixtures of the required compositions in diethylether as solvent. The oxygen plasma treatments were carried out using an APS Advanced Plasma Systems (Model D Series 18, RF, 13.56 MHz) generator with a power of 50 W for 15 min.

The mixing ratio of the epoxy, hardener, and accelerator was kept constant for all experiments, at 10:9:0.2 by weight, respectively. The treated rubber particles were mixed with liquid epoxy resin mechanically at a concentration of 5% by volume. To observe the influence of higher rubber contents, 25 vol% was also used for only two different surface treatment methods. In order to provide better mixing and to prevent bubble formation, epoxy and rubber mixtures were preheated for 3 h at 90°C in the oven. Then the hardener and the accelerator were added in the given ratios to the rubber–epoxy mixture. The overall slurry mixture was poured into PTFE (polytetrafluoroethylene) moulds designed for fracture toughness test specimens and cured for 1 h at 140°C.

For the plane strain fracture toughness tests, single edge notched bend specimens measuring $44 \times 10 \times 5\ mm^3$ were used. Fracture toughness values were determined according to the procedure given in ASTM D5045 standard. Tests were performed using a Lloyd screw-driven universal testing machine. The machine had a constant crosshead speed with a loading rate of 10 mm/min. All specimens were tested at room temperature. For each testing condition, at least 6 specimens were used. Fractured surfaces obtained from plane-strain fracture toughness tests were examined at various magnifications using a JEOL JSM-6400 scanning electron microscope at an accelerating voltage of 20 kV. Samples were coated with a thin layer of gold before examination to protect the fracture surfaces from the beam damage and the charge build-up.

3. Results and discussion

It is clear that epoxy resin (with hydrophilic groups) is incompatible with the untreated rubber particles from scrap tyres (mostly hydrophobic). First of all, in order to observe this incompatibility, epoxy matrix was mixed with untreated scrap tyre rubber particles at a concentration of 5 vol%. Specimens obtained from this mixture were fractured using the Charpy impact test, because of its simplicity and short duration. Then fracture surfaces were examined under a scanning electron microscope. Fig. 1 shows typical fractographs, indicating the large amount of separation at the interface due to incompatibility or lack of adhesion.

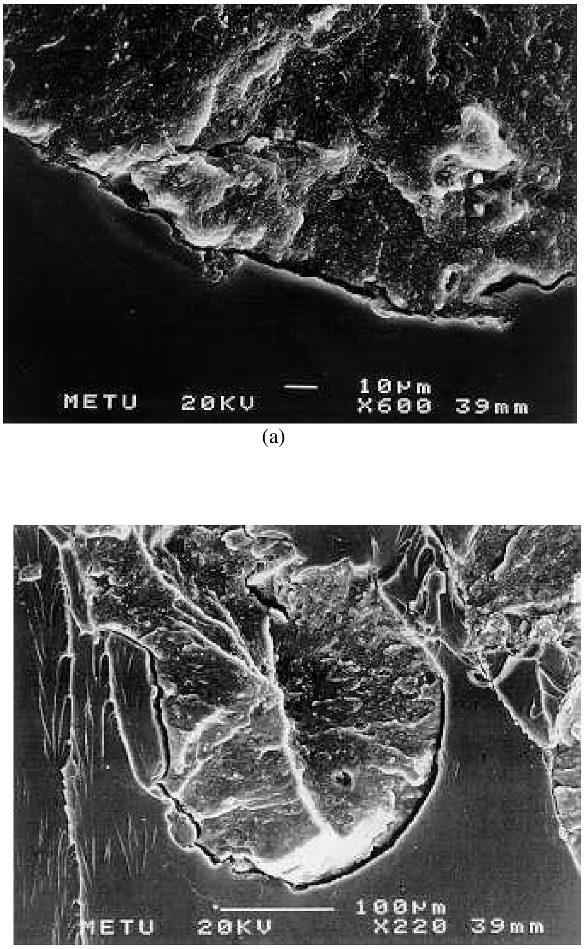


Fig. 1. Two examples (a) and (b) of SEM fractographs with incompatible interfaces between epoxy and untreated rubber particles showing lack of adhesion.

Over the years, several methods have been developed to modify polymer surfaces for improved adhesion, wettability, printability, dye uptake, etc. These include mechanical treatments, wet chemical treatments, exposure to flame, corona discharges, and glow discharge plasma. A basic objective of any such treatment is to remove loosely bonded surface contamination and to provide intimate contact between the two interacting materials on a molecular scale, for molecular energies across an interface decrease drastically with increasing intermolecular distance.

When two materials are incompatible it is often possible to bring about compatibility by introducing a third material that has properties intermediate between those of the other two. Therefore for better rubber toughening, surfaces of recycled rubber particles were treated by five different methods as mentioned before. The first two methods involved the use of silane coupling agents.

Organosilicon compounds were first developed in the 1940s as potential coupling agents for glass reinforced polymers since the silicon ends of the molecules are similar to glass, and organic groups on silicon could be synthesized for compatibility with organic polymers. Nowadays, they have various applications in the areas of reinforced composites, coatings, adhesives, paints, inks and elastomers. Silicon coupling agents have two types of components and their general structure is $R–Si–(OR')_3$ where R is the organofunctional group (e.g. vinyl, amino, mercapto), and OR' is a group capable of hydrolysis (e.g. ethoxy, methoxy, acetoxy).

The first silicon-coupling agent used was vinyltriethoxysilane with three different weight percentages: 1, 2 and 4%. The influences of this treatment are indicated in Figs. 2 and 3 through fractographs of the fracture toughness specimens. Fig. 2 shows the fractographs of interfaces with better adhesion after vinyltriethoxysilane treatment. Improved interface after this treatment will deflect the propagating main crack from its growth plane and/or lead to crack tip blunting. Therefore, *crack deflection* may be considered as the main rubber toughening mechanism. However, this was not possible to indicate on the SEM fractographs, which only shows fractured surfaces of the final failure stage. In

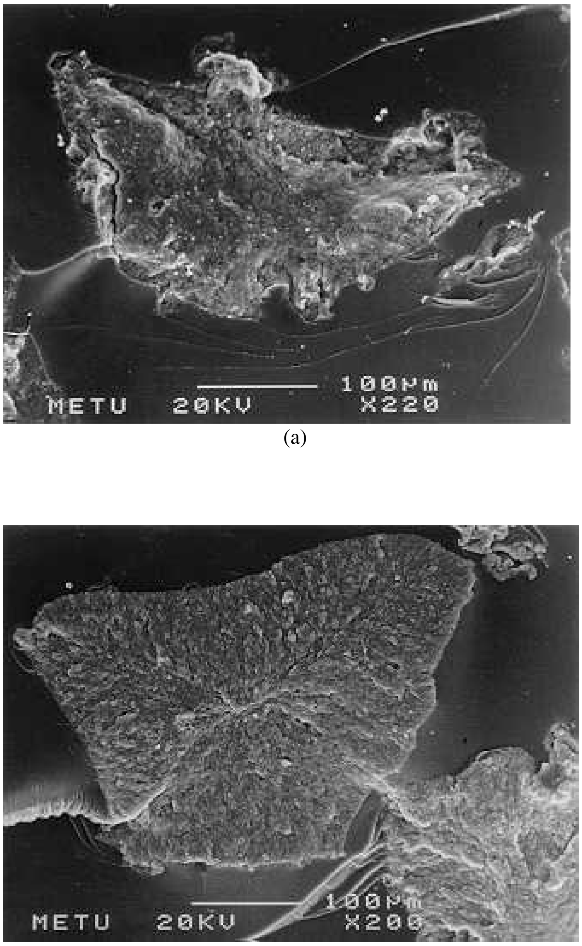
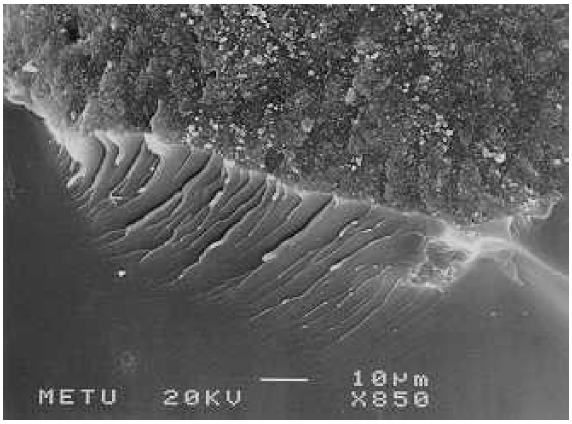
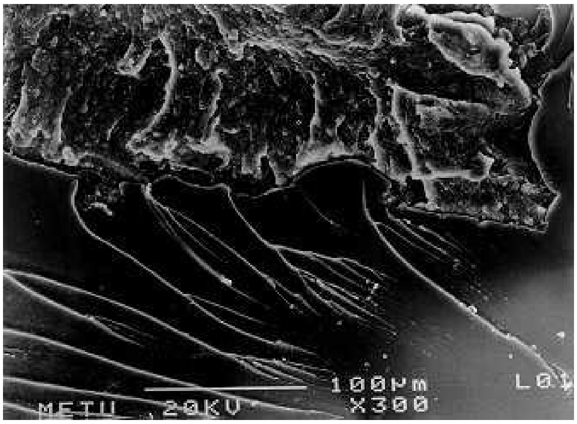


Fig. 2. SEM fractographs of compatible interfaces between epoxy and vinyltriethoxysilane treated rubber particles showing better adhesion: (a) with 4 wt%; and (b) with 2 wt%.



(a)



(b)

Fig. 3. SEM fractographs of interfaces between epoxy and vinyltriethoxysilane treated rubber particles showing shear deformation lines started at the interface with some debonding: (a) with 4 wt%, only deformation lines; and (b) with 2 wt%, deformation lines plus debonding.

further studies, in order to reveal this mechanism, surface microscopy should be used on the specimen surfaces before the final failure. Fig. 3a indicates shear deformation lines started at the interface, while in Fig. 3b there is some slight interface debonding together with shear deformations. This might be considered that *shear deformation* and slight *debonding* are secondary mechanisms of rubber toughening in epoxy.

The second silicon-coupling agent used was 3-aminopropyltriethoxysilane. Only 2 wt% was chosen because of the best fracture toughness value (Table 1) of the previous treatment. The effects of this treatment are indicated in Figs. 4 and 5. Similarly, Fig. 4 shows the fractographs of interfaces with better adhesion after 3-aminopropyltriethoxysilane treatment. Again, Fig. 5a indicates shear deformation lines started at the interface, while in Fig. 5b there is some slight interface debonding together with shear deformations.

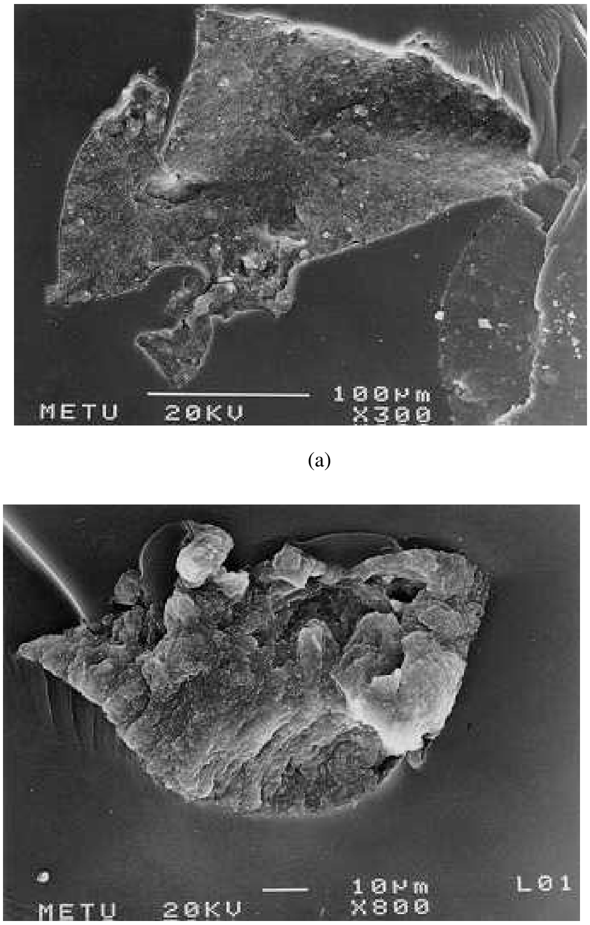
As the third treatment method plasma surface modification was applied. Plasma is partially or full ionized gases and vapors, with substantial proportion of the constituent particles (molecules, atoms, ions) being in excited states. Plasma can be ignited and supported with electromagnetic fields. They typically emit in a wide spectrum, including optical range, and so recognizable through their glow. The molecules, atoms, and ions in electronically excited states, UV and light emission, and high kinetic energy particles (especially ions) activate and/or etch surfaces, induce polymerization of many substances in the gas phase and/or on surfaces, and lead to film building on the substrate surface. Plasma can provoke reactions even with compounds, which are totally inert under normal conditions.

In plasma four major effects on surfaces are normally observed. Each is always present to some degree but one may be favored over the others, depending on the substrate and the gas chemistry, the reactor design, and the operating parameters. The four major effects are: (i) surface cleaning, that is removal of organic contamination from the surfaces; (ii) ablation, or etching of material from the surface, which can remove a weak boundary layer and increase the surface area; (iii) crosslinking or branching of near surface molecules, which can cohesively strengthen the surface layer; and (iv) chemical modification in which the

Table 1
Plane-strain fracture toughness test results

Materials	Fracture toughness K_{IC} (MPa$\sqrt{m}$)
EP[a]	0.98 ± 0.23
EP + 5 vol% R + 1 wt% VS[b]	1.12 ± 0.11
EP + 5 vol% R + 2 wt% VS[c]	1.13 ± 0.06
EP + 5 vol% R + 4 wt% VS[d]	1.06 ± 0.12
EP + 5 vol% R + 2 wt% AS[e]	1.43 ± 0.25
EP + 5 vol% R + OP/2 wt% VS[f]	1.02 ± 0.13
EP + 5 vol% R + 5 wt% AA[g]	1.26 ± 0.08
EP + 5 vol% R + 5 wt% AA/BP[h]	1.54 ± 0.19
EP + 25 vol% R + 5 wt% AA/BP[i]	1.05 ± 0.04
EP + 25 vol% R + 2 wt% AS[j]	1.05 ± 0.05

[a] Materials designation: EP: Neat epoxy resin.
[b] EP + 5 vol% R + 1 wt% VS: Epoxy with 5 vol% rubber treated with 1 wt% vinyltriethoxysilane.
[c] EP + 5 vol% R + 2 wt% VS: Epoxy with 5 vol% rubber treated with 2 wt% vinyltriethoxysilane.
[d] EP + 5 vol% R + 4 wt% VS: Epoxy with 5 vol% rubber treated with 4 wt% vinyltriethoxysilane.
[e] EP + 5 vol% R + 2 wt% AS: Epoxy with 5 vol% rubber treated with 2 wt% 3-aminopropyltriethoxysilane.
[f] EP + 5 vol% R + OP/2 wt% VS: Epoxy with 5 vol% rubber treated with oxygen plasma and 2 wt% vinyltriethoxysilane.
[g] EP + 5 vol% R + 5 wt% AA: Epoxy with 5 vol% rubber treated with 5 wt% acrylic acid.
[h] EP + 5 vol% R + 5 wt% AA/BP: Epoxy with 5 vol% rubber treated with 5 wt% acrylic acid and 5 wt% benzoylperoxide.
[i] EP + 25 vol% R + 5 wt% AA/BP: Epoxy with 25 vol% rubber treated with 5 wt% acrylic acid and 5 wt% benzoylperoxide.
[j] EP + 25 vol% R + 2 wt% AS: Epoxy with 25 vol% rubber treated with 2 wt% 3-aminopropyltriethoxysilane.



(a)

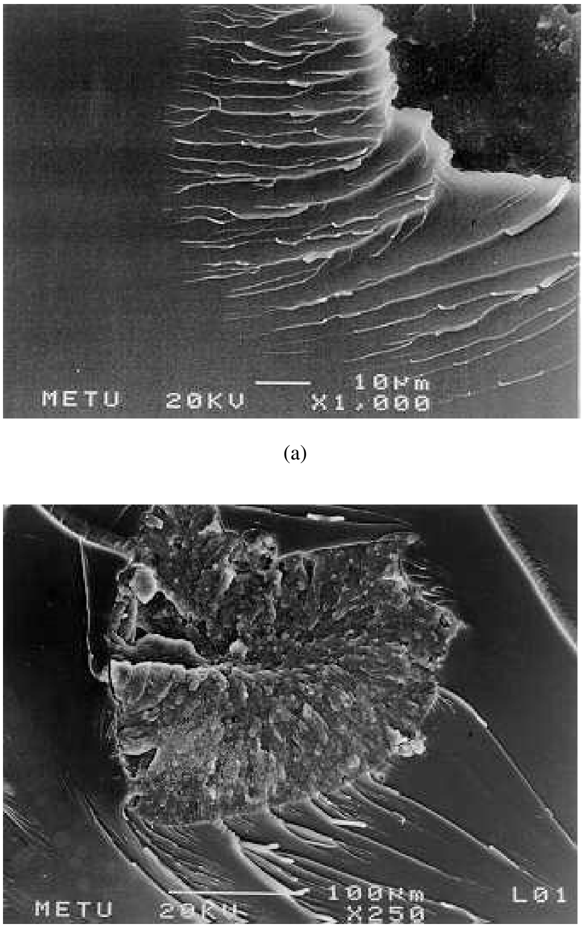
(b)

Fig. 4. SEM fractographs of compatible interfaces, (a) and (b), between epoxy and 3-aminopropyltriethoxysilane (2 wt%) treated rubber particles showing better adhesion.

surface region of the substrate is altered with new chemical functionalities (hydroxyl, amine, and carboxyl groups) capable of interacting with adhesives or materials deposited on the polymer.

In this study, oxygen plasma modification was applied to the surfaces of rubber particles treated with 2 wt% vinyltriethoxysilane before. Figs. 6 and 7 indicate the effects of this treatment, which are very similar to other cases. Again, much better adhesion at the interfaces is very clear as shown in Fig. 6, and some slight interface debonding together with shear deformations as indicated in Fig. 7.

The fourth rubber surface treatment method was the use of acrylic acid. Acrylic acid swells the rubber particles somewhat. Therefore it was used to improve the interface between the rubber particles and epoxy after its diffusion into rubber regions followed by polymerization while dispersed in epoxy matrix. The amount of acrylic acid was selected 5% by weight with respect to rubber particles. As the fifth and last surface treatment method benzoylperoxide was added 5% by weight with respect to the amount of acrylic acid in order to initiate the polymerization of acrylic acid to polyacrylic acid. These treatments resulted in similar influences with other cases as explained before.



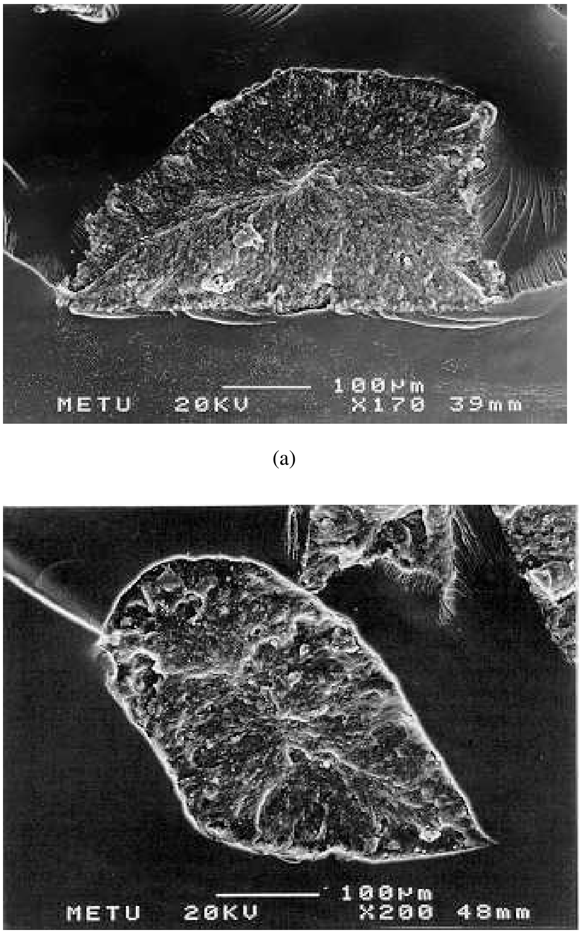
(a)

(b)

Fig. 5. SEM fractographs of interfaces between epoxy and 3-aminopropyltriethoxysilane (2 wt%) treated rubber particles showing shear deformation lines started at the interface with some debonding: (a) only deformation lines; and (b) deformation lines plus debonding.

For comparison, plane strain fracture toughness (K_{IC}) values for neat epoxy and all these different rubber surface treatments are tabulated in Table 1. It is seen that fracture toughness of epoxy modified with surface treated scrap rubber particles increases to a certain extent. This increase in each surface treatment method for 5 vol% rubber is not so different. However, two of the surface treatments methods, 2 wt% 3-aminopropyltriethoxysilane and 5 wt% acrylic acid/benzoylperoxide, resulted in higher K_{IC} values than the others. These treatments increased the fracture toughness of neat epoxy as much as 50%.

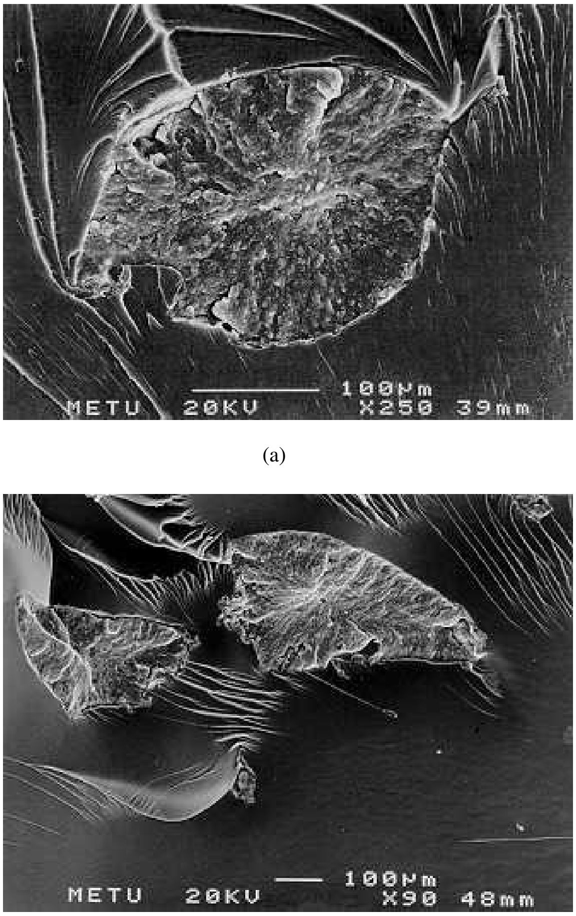
In order to observe the effects of higher rubber content, fracture toughness tests are also conducted for 25 vol% rubber. In this case only the best two surface treatment methods (2 wt% 3-aminopropyltriethoxysilane and 5 wt% acrylic acid/benzoylperoxide) were chosen. Table 1 indicates that fracture toughness values decreases slightly



(a)

(b)

Fig. 6. SEM fractographs of compatible interfaces, (a) and (b), between epoxy and oxygen plasma/vinyltriethoxysilane (2 wt%) treated rubber particles showing better adhesion.



(a)

(b)

Fig. 7. SEM fractographs of interfaces, (a) and (b), between epoxy and oxygen plasma/vinyltriethoxysilane (2 wt%) treated rubber particles showing shear deformation lines started at the interface with some debonding.

when rubber content is increased to 25 vol%, however it is still higher than the fracture toughness of neat epoxy.

This decrease in K_{IC} with 25 vol% rubber shows that the improvement in fracture toughness of epoxy resin by the addition of surface treated ground tyre rubber particles do not obey the Rule of Mixtures in terms of K_{IC} values. However, the main additive effect of the rubber particles may be due the their much higher tearing or fracture energy (G_{IC}) values than the epoxy resin. Therefore, in further studies, it is worth to examine the influence of rubber content on the toughness of epoxy resin by direct measurements of G_{IC} values in samples with different compositions.

After improvement of interfaces between epoxy and recycled rubber particles by these five different surface treatment methods as shown by the fractographs in Figs. 2, 4 and 6, the main rubber toughening mechanism observed was *crack deflection* due to the nonlinear crack front resulted from prevention and retardation of crack growth rate, and/or crack tip blunting, when the main crack crosses the rubber particle with better adhesion to the epoxy matrix.

Fractographic examinations also indicated that surface treated rubber particles initiate shear deformations at the interface as shown in Figs. 3a, 5a and 7a. These plastic deformation lines absorb some of the fracture energy of the propagating cracks leading to higher toughness values. In some cases shear deformations also started at the slightly debonded interface. These deformation lines are indicated in Figs. 3b, 5b and 7b. The slightly debonded interfaces create new surfaces, which need more energy absorption from the system leading to higher toughness again. Therefore, secondary toughening mechanisms of recycled surface treated rubbers in epoxy might be *shear deformation* and some *debonding*.

4. Conclusions

The interface between an epoxy resin matrix and recycled scrap car tire rubber particles can be improved by the modification of the surfaces of rubber particles. In this study, the treatments leading to better adhesion at the interface were vinyltriethoxysilane, 3-aminopropyltriethoxysilane, oxygen plasma with vinyltriethoxysilane, acrylic acid, and acrylic acid/benzoylperoxide mixture. These treatments increased the fracture toughness of neat epoxy resin blended with 5 vol% rubber. The increment in K_{IC} values can be as much as 50%. Increasing the rubber content to 25 vol% caused a slight decrease in fracture toughness as compared with 5 vol%, but it was still higher than for neat epoxy. Fractographic examination indicated that the main toughening mechanism was *crack deflection* due to better adhesion at the interface, while the secondary mechanisms were *shear deformations* and some *debonding*.

In summary, this study introduces an approach for rubber toughening of engineering epoxies by blending with surface-treated recycled scrap tire particles. In addition to cost and environmental savings, this approach results in improved fracture toughness values.

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