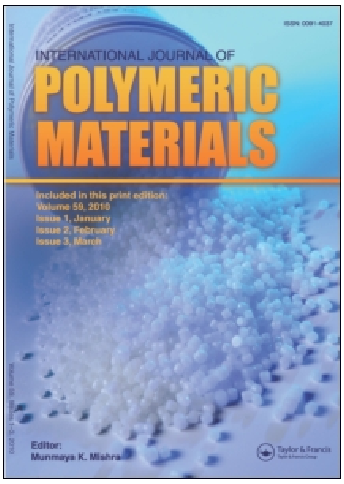
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Effects of Scrap Rubber Particles on the Mechanical Behavior of Epoxy

C. Kaynak[a][b]; E. Sipahi-Saglam[a]; G. Akovali[a]
[a] Department of Polymer Science and Technology, Middle East Technical University, Ankara, Turkey [b] Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey

Online publication date: 27 October 2010

To cite this Article Kaynak, C. , Sipahi-Saglam, E. and Akovali, G.(2002) 'Effects of Scrap Rubber Particles on the Mechanical Behavior of Epoxy', International Journal of Polymeric Materials, 51: 1, 133 — 150
To link to this Article: DOI: 10.1080/00914030213028
URL: http://dx.doi.org/10.1080/00914030213028

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Journal of Polymeric Materials, 51:133–150, 2002

0091-4037/02 $12.00 + .00

Effects of Scrap Rubber Particles on the Mechanical Behavior of Epoxy*

C. KAYNAK [a, b, †], E. SIPAHI-SAGLAM [a] and G. AKOVALI [a]

[a]*Department of Polymer Science and Technology,*
[b]*Department of Metallurgical and Materials Engineering,*
Middle East Technical University, TR-06531 Ankara, Turkey

(Received 13 November 2000; In final form 6 January 2001)

In this work changes in the mechanical properties of epoxy resin modified with scrap car tire rubber particles were examined. Different surface modification techniques were used to improve the compatibility at the interface between the rubber particles and the epoxy matrix. The treatments applied to surfaces of rubber particles were: the silane coupling agents, plasma surface modification and acrylic acid/benzoylperoxide. First, rubber parts of ground scrap car tires, with or without surface treatment, were mixed with epoxy. Then, this mixture was poured into molds to obtain mechanical test specimens. After curing, mechanical tests were performed and the fracture surfaces of the specimens were examined under scanning electron microscope. Changes in mechanical properties were evaluated with respect to the different surface treatment processes applied on rubber particles. Generally, decreases in tensile properties and impact resistance were observed compared to the unmodified epoxy. On the other hand, increases in fracture toughness values were obtained in all surface treated cases. 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.

Keywords: Epoxy resin; Scrap tire rubber; Mechanical properties; Surface modification

---

* Dedicated to Professor S. Fakiror on the occasion of his 65th birthday.

[†] Corresponding author. Tel.: +(90) 312-210 5920, Fax: +(90) 312-210 1267, e-mail: ckaynak@metu.edu.tr

INTRODUCTION

Scrap tires have become a symbol of the global waste problem, despite their accounting only for about 2% of the total amount of waste. 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.

Scrap rubber to be used as a filler and toughening agent in epoxy resin is recently under consideration, because epoxides are 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. However, neat epoxies are among the most brittle polymeric materials.

Rubber modification, *i.e.*, addition of a second dispersed rubbery particulate phase of several microns insize, has been successfully applied to overcome the brittleness of many epoxies. There are two approaches for rubber modification of epoxies. The first approach is based on using reactive liquid elastomers [1 – 7]. 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. Volume fraction and size of the rubber domains are controlled by the degree of compatibility of the phases and the kinetics of gelation. Butadiene-acrylonitrile based rubbers are the principal liquid elastomers used for toughening of epoxies.

The second approach of the rubber modification of epoxies, recently under research, is based on using pre-formed rubber particles [8, 9] instead of reactive liquid elastomer. The advantage of this approach is that particle size and volume fraction of the second phase is usually not varied by the resin type and by processing conditions. Compatibility with the epoxy resin and adhesion to the matrix can be achieved by applying various surface treatments to the rubber particles.

The main objective of this work is to explore the feasibility of using coarse sized recycled rubber particles of 355 – 500 μm with and without surface treatment in epoxy. It is also aimed to evaluate the influences of rubber modification on the mechanical properties of epoxy resin.

EXPERIMENTAL

Materials

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^{TM}, Turkey). 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.

Surface Treatment of Rubber Particles

Surface treatment methods applied to the scrap tire rubber particles were: (1) use of silane coupling agents, (2) use of acrylic acid/benzoylperoxide, and (3) treatment with non-equilibrium plasma. In this context, the following seven different sets of procedures were used, in three groups of experiments.

In the first group, two different silanes as coupling agents were applied separately in diethyl ether as a solvent. As the first silane coupling agent, vinyltriethoxysilane (Fluka) $[CH_2{=}CHSi(OC_2H_5)_3]$ was used in three different weight percentages; 1%, 2% and, 4% with respect to the amount of rubber particles. 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) $[H_2NCH_2CH_2CH_2\,Si(OC_2H_5)_3]$, at 2% by weight.

In the second group of surface treatment experiments, RF (13.56 MHz) plasma treatments were carried out with a power of 50 W for 15 minutes; by use of either direct application of oxygen or nitrogen plasma on rubber particles or by application of oxygen plasma to the 2% wt. vinyltriethoxysilane treated rubber regrinds.

In the third group of experiments, direct chemical modification of rubber surfaces was attempted, either by using acrylic acid (Merck) [$CH_2{=}CHCOOH$], 5% by weight with respect to the rubber; or by applying a mixture of acrylic acid and benzoylperoxide (Merck) [$(C_6H_5COO)_2$], the latter being 5% by weight with respect to the acrylic acid, in order to facilitate the polymerization of acrylic acid to polyacrylic acid. All of these were applied in diethyl ether as the solvent.

Specimen Preparation

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 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 hours 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 moulds to obtain specimens for mechanical tests, and cured for 1 hour at 140°C.

Mechanical Tests

In this study, tension, impact and, fracture toughness tests were performed according to ASTM D638, D256, and D5045 standards, respectively; in order to evaluate the mechanical properties of rubber-modified and unmodified epoxy resin. For tension tests M-III type specimens with gage length, width and thickness of 10 × 5 × 4 mm were used. For the charpy impact tests unnotched bars of 50 × 6 × 4 mm were used. For the plane strain fracture toughness tests single edge notched bend specimen of 44 × 10 × 5 mm were used. Tension and fracture toughness tests were performed using a screw-driven universal testing machine (Lloyd). The machine had a constant crosshead speed with a loading rate of 10 mm/min. Unnotched charpy specimens were tested by using a pendulum impact tester (Coesfeld Materialtest). All specimens were tested at room temperature. For each testing condition, at least 6 specimens were used.

SEM Studies

Fracture surfaces obtained from tensile, charpy impact, and plane-strain fracture toughness tests were examined under scanning electron microscope (JEOL JSM-6400). Samples were coated with a thin layer of gold before examination, not only to improve the conductivity but also to protect the fracture surfaces from the beam damage and the charge build-up.

RESULTS AND DISCUSSION

Tension Tests

Test data of recycled-rubber-modified and unmodified epoxies are evaluated as tensile properties of *Elastic Modulus*, *Tensile Strength*, and *Strain at Failure* values in Table I.

Table I indicates that tensile strength of the epoxy decreased somewhat with the addition of rubber; both for treated and untreated rubber cases. Neat epoxies have high tensile strength values because of the crosslinks in their structure. The decrease in tensile strengths of the epoxy resin rubber system used in this study can be due either/or to the size of rubber particles used as well as their rather inhomogeneous distribution in the matrix. On the other hand, if compared to the data of untreated-rubber-modified epoxies; it is seen that surface treatments applied increased the tensile strength values to some extent, due to the improved interfaces. This effect is especially observed by 2% vinyltriethoxysilane and benzoylperoxide/acrylic acid treatments.

Elastic modulus, which is the ratio of stress to strain in the linear elastic region of the stress-strain curve, is known to be related to the stiffness of the polymer and is expected to be influenced by the existence of rubber in the system. Due to the higher elasticity of the rubber particles, modulus of the epoxy decreased monotonically by the increase of the rubber content. As seen in Table I, epoxy

TABLE I Tensile, Charpy Impact, and Plane-Strain Fracture Toughness test results

*Materials designation**	*Elastic modulus* (MPa)	*Tensile strength* (MPa)	*strain at Failure*	*Impact toughness* (kJ/m^2)	*Fracture toughness* ($MPa\sqrt{m}$)
E	616 ± 3	76 ± 3	0.12 ± 0.01	7,4 ± 0,7	0,98 ± 0,23
5R	564 ± 4	37 ± 3	0.07 ± 0.01	2,7 ± 0,4	
10R	470 ± 2	32 ± 4	0.07 ± 0.01	2,8 ± 0,2	
PO5R	257 ± 5	39 ± 3	0.15 ± 0.01	3,3 ± 0,6	
PN5R	254 ± 6	31 ± 4	0.12 ± 0.01	3,1 ± 0,7	
1VS5R	302 ± 2	40 ± 4	0.13 ± 0.01	2,9 ± 0,6	1,12 ± 0,11
2VS5R	342 ± 3	49 ± 2	0.16 ± 0.02	4,1 ± 0,4	1,13 ± 0,06
4VS5R	179 ± 3	28 ± 6	0.16 ± 0.02	3,8 ± 0,6	1,06 ± 0,12
2AS5R	180 ± 1	36 ± 7	0.21 ± 0.02	4,1 ± 0,7	1,43 ± 0,25
PS5R	299 ± 4	33 ± 2	0.11 ± 0.02	4,0 ± 0,2	1,02 ± 0,13
A5R	352 ± 3	42 ± 6	0.12 ± 0.02	3,5 ± 0,6	1,26 ± 0,08
BA5R	412 ± 4	45 ± 3	0.11 ± 0.01	3,2 ± 0,6	1,54 ± 0,19
BA25R	244 ± 3	22 ± 2	0.10 ± 0.01	2,3 ± 0,4	1,05 ± 0,04
2AS25R	131 ± 3	18 ± 2	0.14 ± 0.03	2,2 ± 0,3	1,05 ± 0,05

* Materials Designation E: Neat epoxy resin; 5R: Epoxy with 5% vol. untreated rubber; 10 R: Epoxy with 10% vol. untreated rubber; PO5R: Epoxy with oxygen plasma treated 5% vol. rubber; PN5R: Epoxy with nitrogen plasma treated 5% vol. rubber; 1VS5R: Epoxy with 1% wt. vinyltriethoxysilane treated 5% vol. rubber; 2VS5R: Epoxy with 2% wt. vinyltriethoxysilane treated 5% vol. rubber; 4VS5R: Epoxy with 4% wt. vinyltriethoxysilane treated 5% vol. rubber; 2AS5R: Epoxy with 2% wt. 3-Aminopropyltriethoxysilane treated 5% vol. rubber; PS5R: Epoxy with oxygen plasma/2% wt. vinyltriethoxysilane treated 5% vol. rubber; A5R: Epoxy with 5% wt. acrylic acid treated 5% vol. rubber; BA5R: Epoxy with 5% wt. acrylic acid/benzoylperoxide treated 5% vol. rubber; BA25R: Epoxy with 5% wt. acrylic acid/benzoylperoxide treated 25% vol. rubber; 2AS25R: Epoxy with 2% wt. 3-Aminopropyltriethoxysilane treated 25% vol. rubber.

blended with untreated rubber particles, has higher modulus as compared to those with surface treated rubber particles.

Strain at failure data in Table I also indicate that strain values decreased for the epoxy modified with untreated rubber particles. However, these values are seen to increase somewhat if surface treated rubber particles are used. The limited or non-existing bonds between untreated rubber particles and epoxy can be the main reason for the behaviour of the untreated rubber case, and any improvement in these interactions are reflected in strain at break values directly. The highest strain at failure values were obtained with 2% wt. 3-aminopropyltriethoxysilane surface treatments, where the long organic 3-aminopropyl groups probably provided some additional flexibility.

Charpy Impact Tests

Charpy impact test results are also presented in Table I as *Impact Toughness* values. In impact tests, the loading rate is very high as compared to other static mechanical tests, thus it makes the interface a very critical issue; a weak interface leads to sudden fracture. The incompatibility of untreated rubber with epoxy, in fact; caused considerable decreases in the impact toughness values. After surface treatments, these results were slightly improved. However, one should also point out that, the level of surface treatment is also a very critical issue. When the surface treatment is insufficient (*e.g.*, in the case of 1% wt. silane treatment), it does not give satisfactory results. On the contrary, too much surface treatment can cause the system to become even more brittle (*e.g.*, in the case of 4% wt. silane treatment). The optimum silane percentage observed in these studies was 2% wt.

Fracture Toughness Tests

The fracture toughness test results are listed in Table I as *Plane-Strain Fracture Toughness* (K_{IC}) values. Contrary to the tensile and impact test results, fracture toughness values of rubber modified epoxy samples are better than the neat epoxy, in general. This improvement in fracture toughness is mainly due to the prevention of the crack growth to some extent by the rubber particles in the matrix. The main toughening mechanisms responsible for this crack growth retardation, observed with fractographic studies under scanning electron microscope, were ‘‘crack deflection’’, ‘‘shear deformation’’ and some ‘‘debonding’’ at the interface.

It is seen that fracture toughness of epoxy modified with surface treated scrap rubber particles are somewhat increased. These increases in each surface treatment method are not very different. However, for the epoxy with 5% vol. rubber, two of the surface treatments methods, 2% wt. 3-aminopropyltriethoxysilane and 5% wt. acrylic acid/benzoyl-peroxide, resulted in higher K_{IC} values than the others. These treatments increased the fracture toughness of neat epoxy by as much as 50%.

Interface Studies

It is clear that epoxy resin (with lyophilic groups) is incompatible with the untreated rubber particles from scrap tires (mostly lyophobic). First of all, in order to observe this incompatibility, epoxy matrix was mixed with untreated scrap tire rubber particles at 5% vol. concentration. Specimens obtained from this mixture were fractured, and fracture surfaces were examined under the scanning electron microscope. Figure 1 shows typical fractographs, indicating the large amount of separation at interfaces due to incompatibility or lack of adhesion.

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 modification, surfaces of recycled rubber particles were treated by three groups of methods, with seven different procedures, as mentioned before. The first method involved the use of two silane coupling agents.

Organosilicon compounds were first developed as 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,

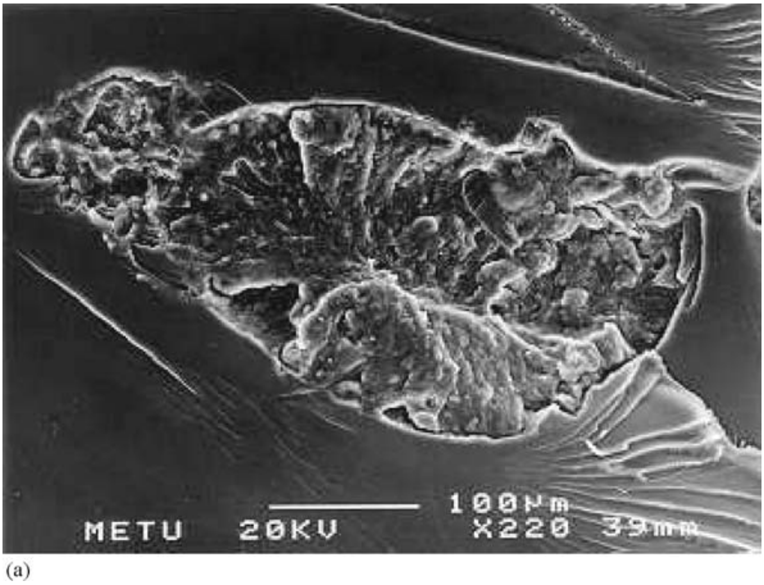


FIGURE 1 Micrographs showing incompatible interfaces between epoxy and untreated rubber particles due to weak adhesion.

(b)

FIGURE 1 (Continued).

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 second one was 3-aminopropyltriethoxysilane. Only 2% wt. was chosen because of the best fracture toughness value (Tab. I) of the previous treatment. The influences of these treatments are indicated in Figures 2(a) and 2(b), respectively. These figures show the fractographs of interfaces with better adhesion after these treatments.

In the second group of experiments, plasma treatment was applied. It is known that the molecules, atoms, and ions in electronically excited states in plasma, in addition to the 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

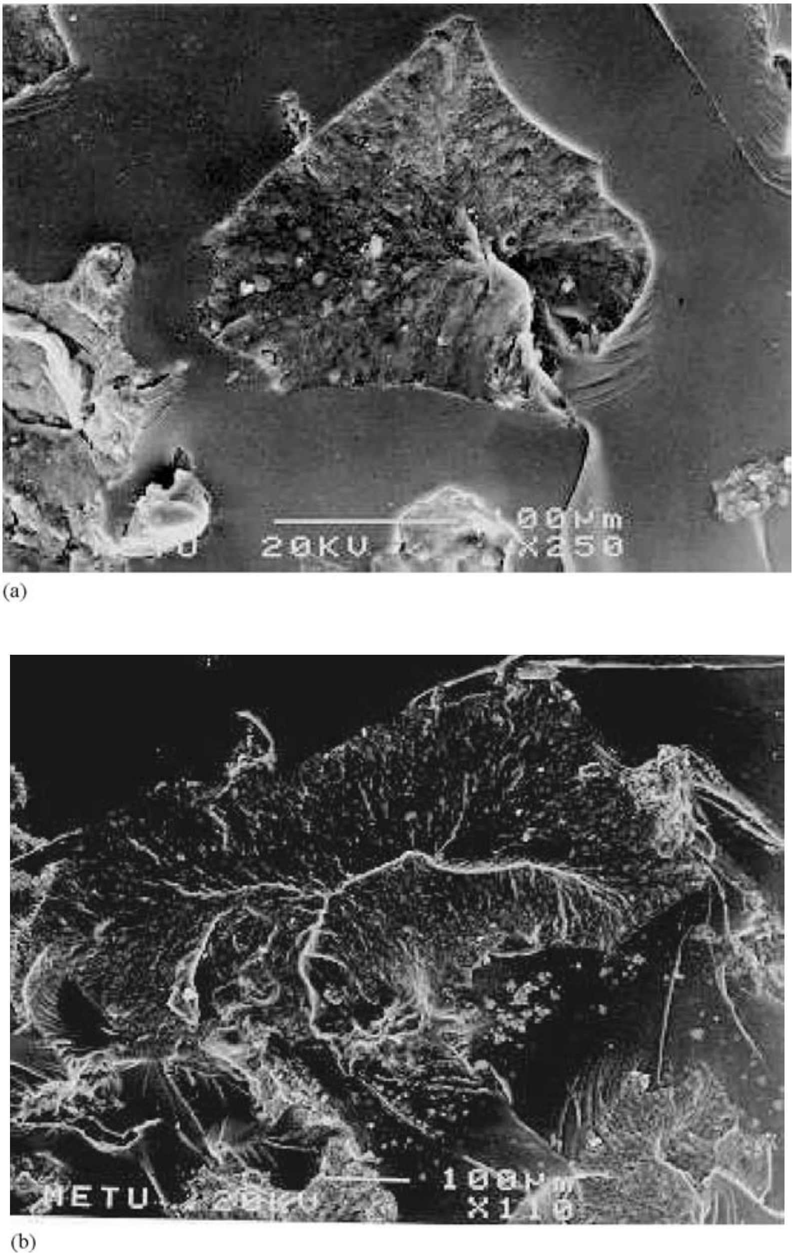


FIGURE 2 Micrographs of compatible interfaces between epoxy and surface treated rubber particles showing better adhesion. (a) after 2% wt. vinyltriethoxysilane treatment (b) after 2% wt. 3-aminopropyltriethoxysilane treatment (c) after oxygen plasma treatment (d) after nitrogen plasma treatment.

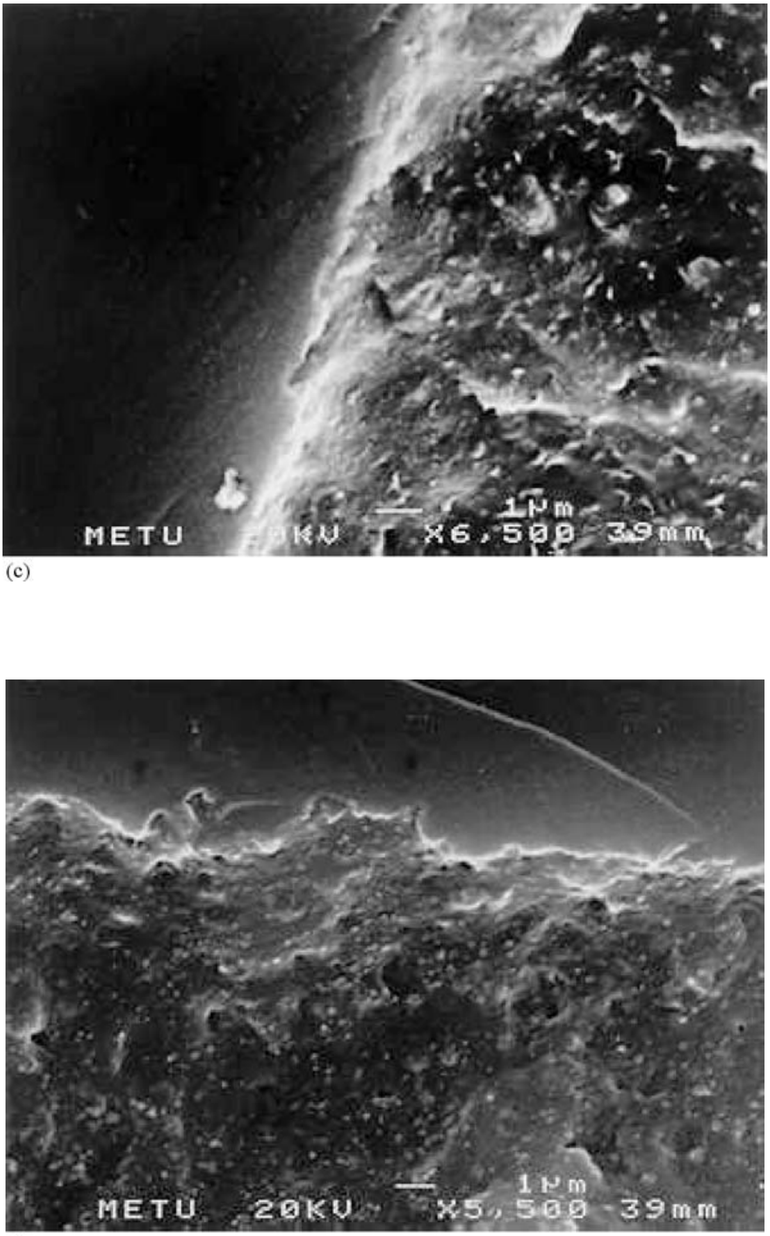


FIGURE 2 (Continued).

and/or on surfaces, and lead to film building on the substrate surfaces. Plasma can provoke reactions even with compounds which are totally inert under normal conditions.

In this group oxygen and nitrogen plasma were applied, and as an alternative plasma method, oxygen plasma was also applied to the surfaces of rubber particles treated with 2% wt. vinyltriethoxysilane. Figures 2(c) and 2(d) indicate the effects of these treatments, which are very similar to the previous cases. Again, a much better adhesion at the interfaces is very clear in the fractographs.

Another surface treatment method in the third group 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 as 5% by weight with respect to rubber particles. Additionally, as the last surface treatment method; benzoylperoxide was added at 5% by weight with respect to the acrylic acid in order to initiate the polymerization of acrylic acid to polyacrylic acid. These treatments resulted in influences similar to other cases as explained before.

After improvement of interfaces between epoxy and recycled rubber particles by these seven different surface treatment methods as shown by the fractographs of Figures 2, 3 and 4, the main rubber toughening mechanism observed was *crack deflection* due to the nonlinear crack front, resulting from prevention and retardation of crack growth rate, and/or crack tip blunting, when the main crack crosses the rubber particles with better adhesion to the epoxy matrix.

Fractographic examinations also indicate that surface treated rubber particles initiate shear deformations at the interface as shown in Figures 3(a), 3(b), 3(c) and 3(d) for different surface treatments, respectively. 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 together with some debonding are indicated in Figures 4(a), 4(b), 4(c) and 4(d) for different treatments, respectively. The slightly debonded interfaces create new surfaces, which need more energy absorption from the system leading to higher toughnesses again. Therefore, a secondary

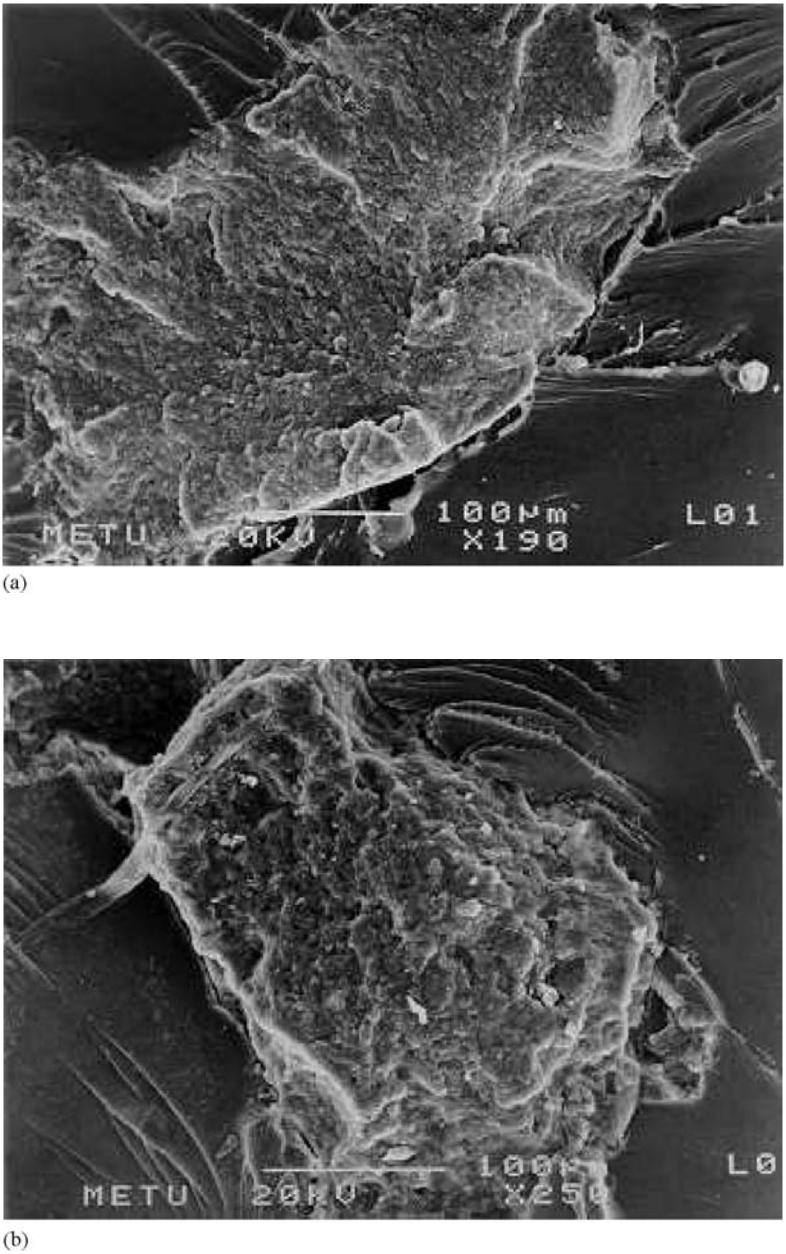
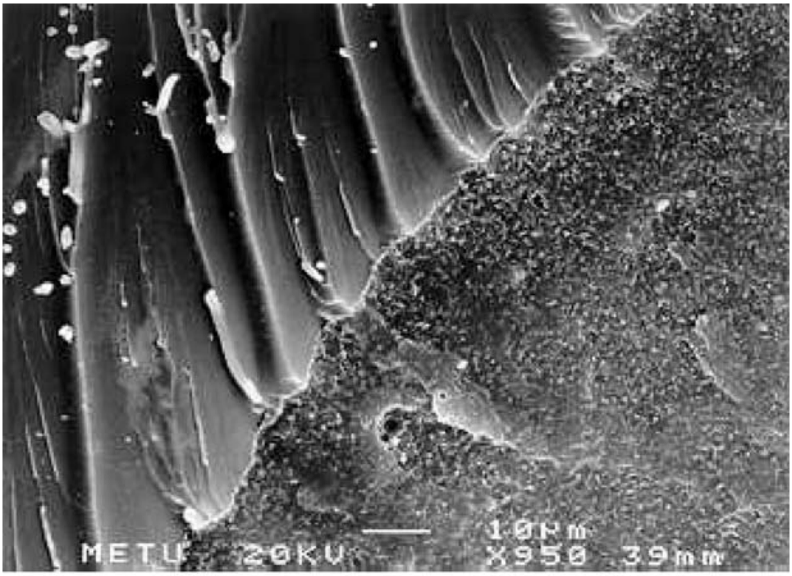
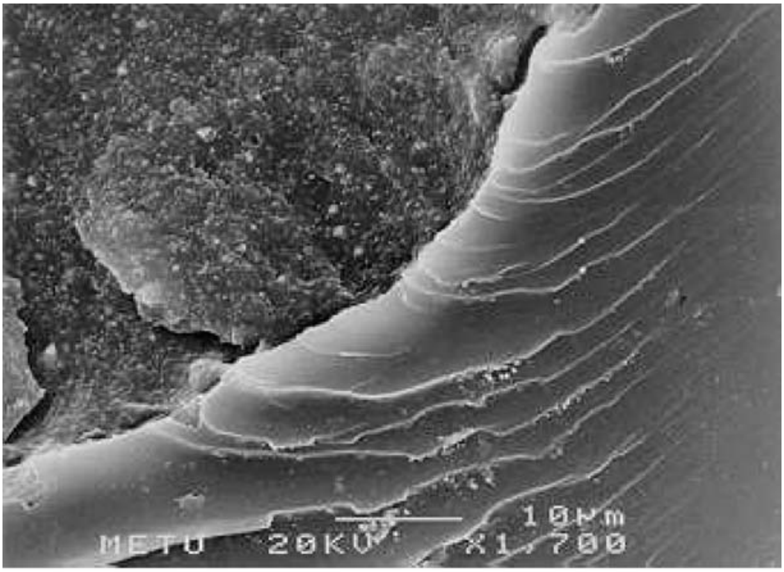


FIGURE 3 Micrographs of interfaces between epoxy and surface treated rubber particles showing shear deformation lines (a) after 2% wt. vinyltriethoxysilane treatment (b) after 2% wt. 3-aminopropyltriethoxysilane treatment (c) after oxygen plasma treatment (d) after nitrogen plasma treatment.



(c)



(d)

FIGURE 3 (Continued).

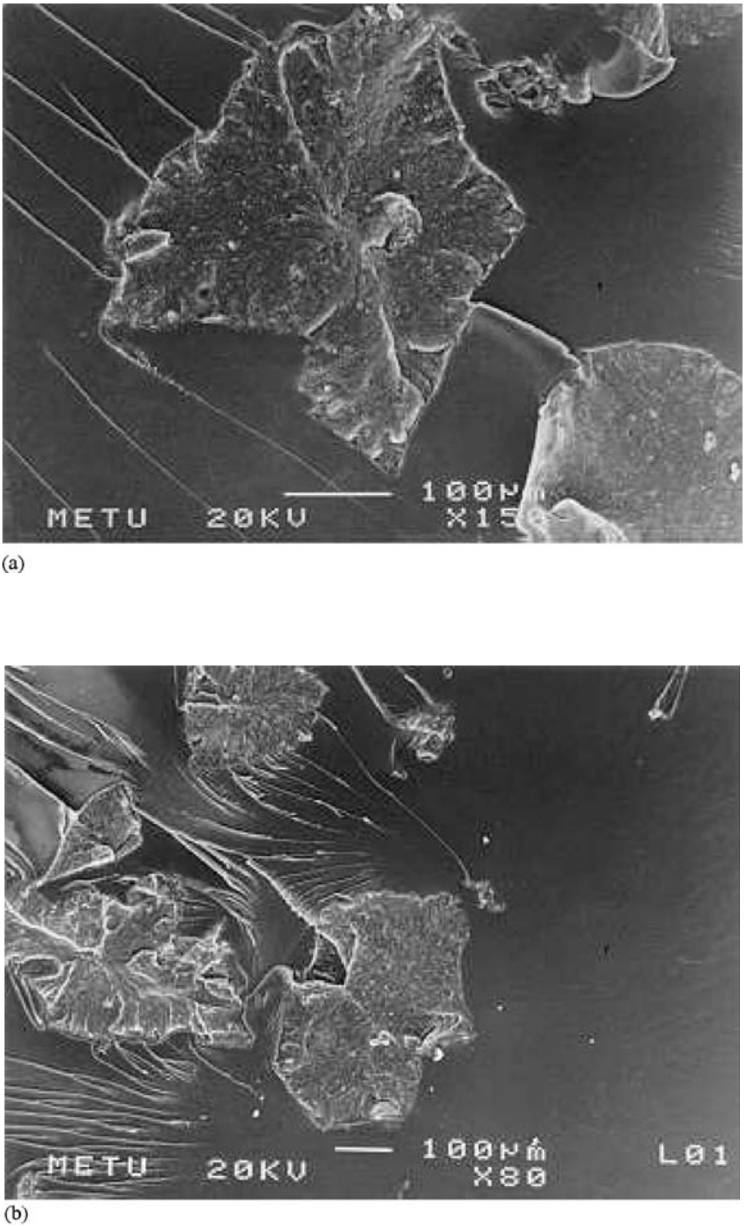
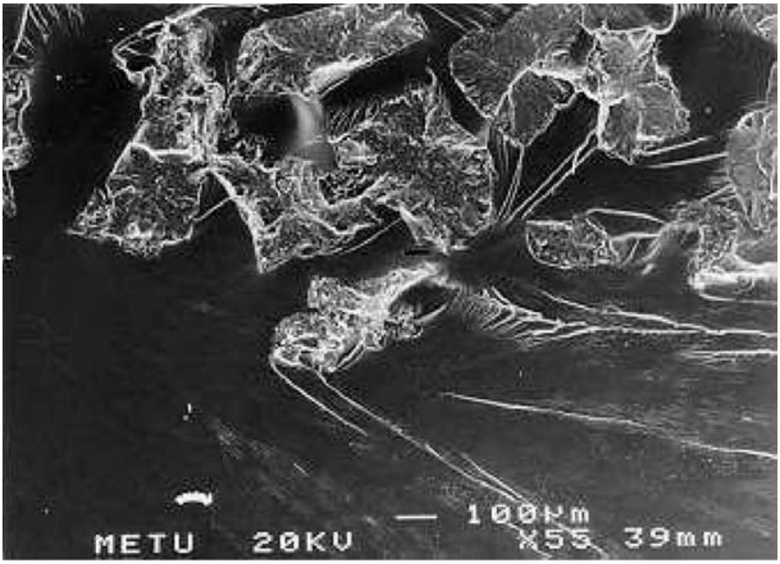
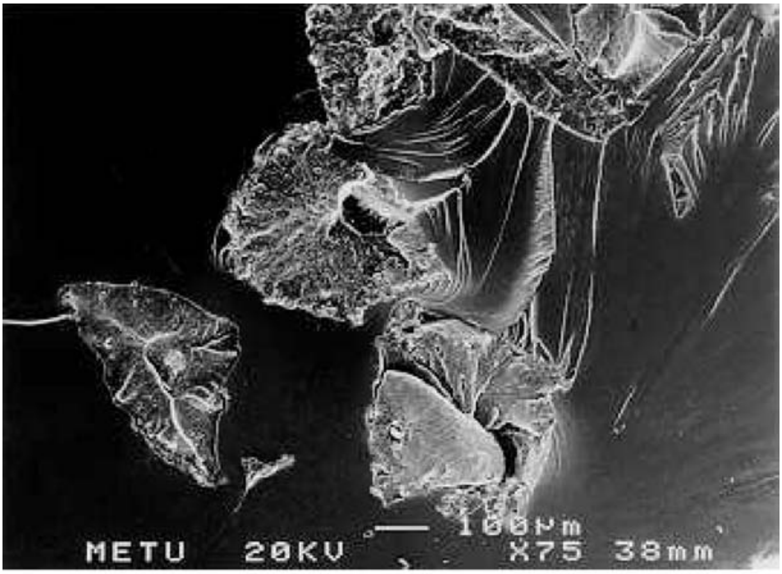


FIGURE 4 Micrographs of interfaces between epoxy and surface treated rubber particles showing shear deformation lines started at the interface with some debonding (a) after 2% wt. vinyltriethoxysilane treatment (b) after 2% wt. 3-aminopropyltriethoxysilane treatment (c) after oxygen plasma treatment (d) after nitrogen plasma treatment.



(c)



(d)

FIGURE 4 (Continued).

toughening mechanisms of recycled surface treated rubbers in epoxy might be *shear deformation* and some *debonding*.

CONCLUSIONS

Tensile and impact test data indicated that the mechanical performance of epoxy decreases when modified with scrap tire rubber regrinds. On the other hand, surface treatment of scrap rubber regrinds resulted in slight increases in tensile strength, strain at break, and also impact toughness values of the rubber-modified epoxy as compared to the epoxy samples modified with untreated rubber particles. The highest increase was achieved with 2% wt. vinyltriethoxysilane treatment most probably due to better adhesion created at interfaces. However, these increases led to considerable reductions in the stiffness, *i.e.*, elastic modulus values, of the epoxy resin.

Contrary to the tension and impact test results, fracture toughness of neat epoxy was improved when the epoxy was modified by any surface treated rubber regrinds. The best K_{IC} values were obtained with 2% wt. 3-Aminopropyltriethoxysilane and acrylic acid/benzoylperoxide treatments. The increment in K_{IC} value can be as much as 50%. Fractographic examinations indicated that the main toughening mechanism was crack deflection due to better adhesion at the interface, while secondary mechanisms were shear deformations and some debonding.

In summary, this study evaluates the feasibility of blending epoxy with surface-treated recycled scrap tire regrinds. Although the tensile and impact properties are decreased, fracture toughness of the epoxy may be improved considerably, in addition to cost and environmental savings.

References

[1] Bagheri, R. and Pearson, R. A. (1995). *J. Appl. Polym. Sci.*, **58**, 427.
[2] Sue, H. J. (1991). *Polym. Eng. Sci.*, **31**, 275.
[3] Yee, A. F. and Pearson, R. A. (1986). *J. Mater. Sci.*, **21**, 2462.
[4] Kinloch, A. J., Shaw, S. J., Tod, D. A. and Hunston, D. L. (1983). *Polymer*, **24**, 1355.
[5] Kunz-Douglas, S., Beaumont, P. W. R. and Ashby, M. F. (1980). *J. Mater. Sci.*, **15**, 1109.

[6] Bascom, W. D., Cottington, R. L., Jones, R. L. and Peyser, P. (1975). *J. Appl. Polym. Sci.*, **19**, 2425.

[7] Sultan, J. N., Liable, R. C. and McGarry, F. J. (1971). *Polym. Symp.*, **16**, 127.

[8] Boynton, M. J. and Lee, A. (1997). *J. Appl. Polym. Sci.*, **66**, 271.

[9] Bagheri, R., Williams, M. A. and Pearson, R. A. (1997). *Polym. Eng. Sci.*, **37**, 2.