

Physicochemical Characterization of the Filler–Matrix Interface in Elastomer-Encapsulated Fly Ash/Polyester Particulate Composites

S. Guhanathan, M. Saroja Devi

Department of Chemistry, Anna University, Chennai 600 025, India

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ABSTRACT: An attempt was made to improve the toughness of fly ash (FA)/general-purpose unsaturated polyester resin (GPR) composites. Elastomer [styrene–butadiene rubber (SBR) or acrylic copolymer (AC)]-encapsulated fillers (FA or CaCO₃) were made through the coagulation of the emulsified elastomer containing the filler with constant stirring. The elastomer-encapsulated fillers were added to GPR at concentrations as high as 15 wt % to make FA/SBR or AC/GPR composites. The mechanical properties (i.e., the tensile strength, tensile modulus, tensile elongation, flexural strength, flexural modulus, impact strength, and hardness) of FA/GPR, FA/SBR/GPR, and FA/AC/GPR composites

were studied. The tensile-fractured surfaces of all the composites were studied with scanning electron microscopy. The thermal stability was studied with thermogravimetric analysis. An analysis of the results indicate that this modification technique is rather easy and more economical than the chemical modification of filler surfaces with functional silane coupling agents. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 171–184, 2005

Key words: fly ash; elastomer; polyester composites; characterization

INTRODUCTION

General-purpose unsaturated polyester resin (GPR) is one of the most important matrices for composite applications.^{1,2} They are particularly useful in sheet-molding compounds and bulk-molding compounds for manufacturing automotive parts.^{3,4} Like other thermosets, they are intrinsically brittle. The well-developed techniques of rubber toughening have had very limited success with GPR because of the reduced solubility of the rubber component in the unreacted resin and the poor chemical reactivity of the rubber with the polyester functionalities.

Using fillers for composites has long been a practice in the plastics industry either to reduce the cost or to impart certain properties. Unfortunately, the better stiffness obtained through filling is often accompanied by drawbacks such as worse processibility and lower toughness. To overcome these problems, a variety of methods have been adopted, including the choice of processing aids and the modification of the filler surface.⁵ Because of the reasoning that a properly tailored interface leads to improved toughness without much affecting the strength, the past decades have seen active efforts to develop new coupling agents and elas-

tomers for improving the interface between matrices and resins,^{6–10} and many have yielded plastics with balanced performance. Academic and industrial interest in filled polymers is steadily increasing as a result of the appreciable cost reduction and the opportunity to produce materials with a new set of selected properties. Filled elastomer technology is currently based on the dispersion of a low level of a filler [e.g. calcium carbonate (CaCO₃), quartz, or silica mica], which reduces the tensile strength and hardness. In contrast, the addition of mineral fillers to a semicrystalline thermoplastic such as polyolefin or polyamide is associated with a detrimental effect on the mechanical performance because of weak interfacial adhesion. Actually, the mechanical properties of composites depend on a complex interplay of the characteristic features of the filler (nature, shape, size, and size distribution) and the polymer matrix (nature, melting temperature, degree of crystallinity, ductility, molecular weight, and polydispersity), the filler content, the dispersion technique, and, above all, the interfacial adhesion.

The preparation of composites through the melt blending of a polymer matrix and a filler is a straightforward procedure but is not efficient with respect to the properties of the resulting composites. To overcome these limitations, a strategy has been proposed that is based on filler encapsulation by a polymer coating.¹¹ Another approach relies on the chemical

Correspondence to: M. Saroja Devi (msrde2000@yahoo.com).

TABLE I
Characterization of the Latices

Latex	pH	Viscosity (cP)	Color	Density (kg/m ³)	Solid content (%)
SBR	7.54	223	Milky white	1069.32	60.63
AC	7.46	256	Milky white	1046.48	59.42

modification of the filler surface by functional silanes and titanate esters, which are able to promote adhesion to polymers.^{6,7,12,13} In addition to these two rather complex and expensive techniques, Enikolopian¹⁴ and Howard and coworkers^{15–19} developed polymerization-filling techniques. They involve attaching a Ziegler–Natta catalyst to the surface of an inorganic filler so that olefin can be polymerized from the filler surface,^{20–23} this allows very high filler loadings (up to 95 vol %) to be reached together with acceptable mechanical properties. The adhesion of metals to the surface of fillers is also a widely applied technique. On the basis of this concept, the adsorption of polymers onto the surface of fillers has been carried out to impart mechanical properties. Little success has been reported for the preparation of mica-based composites by the direct adsorption of Mg-containing compounds on the surface of mica. Very low cost efficiency has been reported for the approach, which disregards the hydroxyl functions present on the filler surface.

The objective of this work was to produce homogeneous composites by the encapsulation of the filler surface by novel styrene–butadiene rubber (SBR) and acrylic copolymer (AC) latices at the surface of fly ash (FA) and CaCO₃ and by the subsequent filling of these encapsulated particles in GPR and to study the effects on the mechanical, thermal, and morphological properties.

EXPERIMENTAL

The resin was uncured GPR kindly supplied by Naphtha Chemicals Ltd. (Bangalore, India). The resin was available either as a solution containing 35% styrene

or in the form of the neat prepolymer without a solvent. The polyester prepolymer had a number-average molecular weight of 1800 g mol⁻¹. The acid number, defined as the amount (mg) of KOH used for the titration of 1 g of prepolymer, was 33.3. The OH number, obtained by the titration of the excess acetic anhydride used to esterify fully the hydroxyl groups, was 40.0. The OH functionality evaluated from this titration corresponded to 1.1. In the GPR formulation, 0.1 wt % hydroquinone was employed as an inhibitor to prevent premature curing. Methyl ethyl ketone peroxide in dibutylphthalate was used as a room-temperature curing agent. Cobalt naphthenate was used as an accelerator for GPR curing.

SBR latex and AC latex were kindly supplied by Protektol Anticorrosive, Ltd. (Chennai, India; Table I). FA was obtained from the Ennore Thermal Power Plant (Chennai, India). CaCO₃ was obtained from Sakthi Fiberglass Ltd. (Chennai, India). Magnesium sulfate was acquired from Oscar Chemicals Ltd. (Bombay, India).

Encapsulation of the filler with the elastomer

The required amount of dry FA (or CaCO₃) was placed in a 2-L beaker containing 750 mL of double-distilled water. The required amounts of SBR or AC latex were added, and the mixture was heated with stirring for approximately 35–40 min. The electrolyte solution containing MgSO₄ was then added to break the emulsion when the elastomeric layer was deposited on the surface of the filler. The aqueous layer was removed by filtration. The elastomer-encapsulated filler was washed with hot water three times and then dried *in vacuo*. The formulation and notation for the formation of elastomer-encapsulated FA and CaCO₃ are given in Table II. The elastomer-encapsulated FA and CaCO₃ were added to GPR in specified amounts and cast into sheets.

Fabrication of the composite sheets

For casting, two iron sheets 6 mm thick (30 cm × 30 cm) were used. One side of each of the iron sheets was

TABLE II
Compositions and Notations Used in Elastomer Encapsulation for the Fillers

Sample	Latex (mL)	Water (mL)	Elastomer content (g)	Filler (FA or CaCO ₃ ; g)	Notations	
1	15	750	9.1	80	SBF15	SBC15
					ACF15	ACC15
2	7.5	750	4.6	80	SBF7.5	SBC7.5
					ACF7.5	ACC7.5
3	3.75	750	2.3	80	SBF3.75	SBC3.75
					ACF3.75	ACC3.75
4	2	750	1.2	80	SBF2	SBC2
					ACF2	ACC2

TABLE III
Compositions and Notations Used in Elastomer-Encapsulated FA/GPR
and CaCO₃/GPR Composites

Sample	Type of filler	GPR (wt %) ^a	Filler (wt %) ^a	Notation
1	SBF 15	60	40	FA/SBR15/GPR
2	SBF 7.5	60	40	FA/SBR7.5/GPR
3	SBF 3.75	60	40	FA/SBR3.75/GPR
4	SBF 2.0	60	40	FA/SBR2.0/GPR
5	ACF 15	60	40	FA/AC15/GPR
6	ACF 7.5	60	40	FA/AC7.5/GPR
7	ACF 3.75	60	40	FA/AC3.75/GPR
8	ACF 2.0	60	40	FA/AC2.0/GPR
9	SBC 15	60	40	CaCO ₃ /SBR15/GPR
10	SBC 7.5	60	40	CaCO ₃ /SBR7.5/GPR
11	SBC 3.75	60	40	CaCO ₃ /SBR3.75/GPR
12	SBC 2.0	60	40	CaCO ₃ /SBR2.0/GPR
13	ACC 15	60	40	CaCO ₃ /AC15/GPR
14	ACC 7.5	60	40	CaCO ₃ /AC7.5/GPR
15	ACC 3.75	60	40	CaCO ₃ /AC3.75/GPR
16	ACC 2.0	60	40	CaCO ₃ /AC2.0/GPR

^a Resin/accelerator/catalyst = 100:1 mL of 1% solution:1 mL of 1% solution.

coated with Teflon, and high-viscosity silicone oil was spread over each of the Teflon-coated surfaces as a releasing agent. A square aluminum frame (0.3 cm × 28 cm × 28 cm) with one side open was placed on the Teflon-coated surface of one of the iron plates, and the second iron plate was placed above the frame in such a way that the Teflon-coated surface was facing the frame. Then, the two iron sheets were held tightly together by bolts and nuts. The appropriately formulated GPR resin (Table III) was stirred for 20 min and degassed for 10 min by the application of a vacuum to remove the air bubbles formed during stirring and then was poured into the mold. The mold was allowed to stand for 12 h for the complete curing of the resin. After that, the sheet was taken out and cut to the required specimen size according to ASTM specifications for tensile, flexural, impact, and hardness tests.

FA was dried at 120°C in a hot-air oven for 6 h before use to remove the moisture, and it was cooled in a desiccator; however, CaCO₃ was used as provided. In either case, the filler was mixed with the resin–accelerator mixture and stirred at room temperature for 20 min with a mechanical stirrer at 250 rpm to ensure the complete wetting of the filler particles. Then, the required quantity of the catalyst was added, and the mixture was stirred again and poured into the mold. At least six specimens of each type were made and subjected to testing to obtain the average value for the studied properties and to avoid possible errors due to the nonuniform distribution of the fillers.

Techniques

Thermogravimetric analysis (TGA)

The weight-loss measurements as a function of the temperature were carried out with a Mettler TA 3000

system at a heating rate of 20°C/min in air. The weight of the material was 6–9 mg, and TGA was run up to 800°C.

Scanning electron microscopy (SEM)

For the nonconducting samples before the SEM pictures were taken, the surfaces to be photographed were sputter-coated with gold, which provided a conductive coating. In this investigation, sputter coating was performed with a sputter coater. A Hitachi, Ltd. (Tokyo, Japan), S-415A was used to examine the tensile fracture surface of various filled and modified polymeric systems at 25 k, and the magnification was as high as 500×.

Testing of the composites

Six different specimens were tested for each composition, and the average of the values was taken. The mechanical properties, such as the tensile strength, flexural strength and modulus, impact strength, and hardness, were studied according to ASTM standards. Each test was carried out on at least six specimens, and the average value was taken.

Tensile strength

The tensile properties (ASTM D 638) were determined with a universal testing machine (HTE-S series H 50K-S, Hounsfield Test Equipment, Ltd., UK) at a crosshead speed of 0.5 mm/min.

Flexural strength and modulus

The flexural properties were determined by the application of a three-point-bending load to a rectangular

specimen (ASTM D 790), which rested on a block at both ends.

Impact strength

The impact strength was determined with an impact tester (type 1997, S.N.117, International Engineering Industries, Bombay, India). The impact strength was determined by the striking of a rectangular bar-shaped specimen with a hammer according to ASTM D 265.

Hardness

The hardness (ASTM D 2240) of the composites was studied with a Tree durometer/Shore D hardness tester (Blue Steel Engineer's Pvt., Ltd., Bombay, India). Five measurements of the hardness were taken at different positions on the specimen at least 6 mm apart, and the arithmetic mean was taken.

RESULTS AND DISCUSSION

Attempts were made in our study to improve the deteriorated properties of FA-filled GPR:

- By improving the interfacial bond between FA and GPR with coupling agents.²⁴
- By improving the inherent toughness of the resin through interpenetrating network formation with the addition of castor-oil-based polyurethane²⁵ to the GPR matrix.

Yet another way of improving the properties of FA/GPR composites is to deposit elastomeric layers on the filler surface by the mixing of the required amount of the dried filler with the emulsion of the elastomer and coagulation with continuous stirring. This leaves the filler particles encapsulated with the elastomeric polymer. When this encapsulated filler is added to the GPR matrix and cured, there is expected to be better adhesion between the filler and matrix through chemical bonding between the pendant double bonds in the elastomeric polymer on FA in GPR. A similar procedure was adopted to make an elastomer-encapsulated filler, and the effect of adding this elastomer-encapsulated CaCO₃ to GPR was studied and compared with the effects of FA/SBR and AC/GPR.

Mechanical properties

The interface between the filler particles and the matrix has a great influence on the mechanical properties of a composite. The mechanical properties can, therefore, give indirect information about the interfacial behavior. If there is insufficient adhesion between the filler and the matrix, the interface will be susceptible

to attack by water or any environment, and this will result in loss of strength.

The resistance of the matrix–filler interface is ultimately responsible for the properties of these materials. For this reason, the primary goal of this research is to obtain a strong interface. An adhesive system, commonly of the filler–elastomer matrix type, which acts positively with most of these materials, is generally incorporated to increase the resistance of the interface. It should be repeated, however, that the ideal system would be the one that would yield true covalent bonds between the elastomer-modified filler and matrix. Accordingly, the purpose of this work is to create an interface, formed by covalent bonds between the matrix and filler, that can advantageously replace the conventional adhesive system with relatively expensive silane based coupling agents, which will act as molecular bridges between both phases.

In the first stage of our research, we attempted to show that the incorporation of rubber molecules by encapsulation onto the filler surface by coagulation from its emulsion was capable of creating matrix–filler (elastomer) bonds and thus improving all mechanical properties.

Tensile strength

If there is good adhesion between the matrix and filler, the following aspects should be observed:

1. A rise in the moduli or stress at a particular deformation.
2. A drastic reduction in the elongation at break.

The effect of the encapsulation of fillers by elastomers on the tensile strength of GPR composites is shown in Figures 1–4. The incorporation of the elastomeric phase resulted in significant improvements in the tensile strength of FA/GPR and CaCO₃/GPR composites. The higher tensile strength of SBR-treated FA/GPR clearly indicates that SBR was more efficient in improving the filler–matrix interaction. This may be attributed to the better interaction of the vinyl group of styrene in the GPR matrix and the double bonds in SBR, in contrast to the acrylic group in AC. However, the encapsulation of both SBR and AC resulted in a significant improvement in the tensile strength of FA/GPR composites. For CaCO₃/GPR composites, AC encapsulation resulted in higher strength than SBR encapsulation. Increasing the elastomer concentration at a constant filler percentage produced a significant increase in all mechanical properties, including the tensile and flexural modulus. The increases were significant, particularly for 40% FA in GPR. A 2% SBR inclusion in 40% filler (FA) improved the tensile strength by 8.39 and 68.15% over that of neat GPR and FA/GPR, respectively. Similarly, when the elastomer

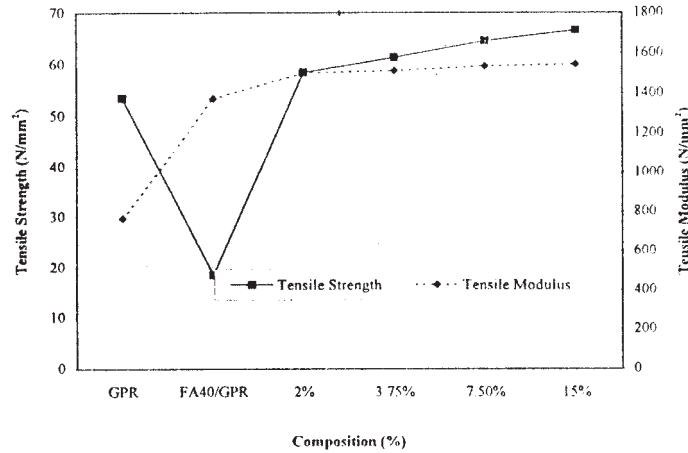


Figure 1 Effect of the elastomer concentration on the tensile properties of FA/SBR/GPR composites.

concentration (SBR) was increased by 3.75, 7.5, and 15% the tensile strength was increased by 12.7, 17.05, and 19.6% and 69.6, 71.2, and 72% over that of GPR and FA/GPR, respectively. Similar behavior was observed for AC-encapsulated systems also, but the increase was found less than that of the SBR-encapsulated systems. This may be due to better resistance offered by the filler–matrix interface in the latter materials. Therefore, the tensile test results seem to indicate that an elastomeric coating for fillers or an encapsulation of fillers improves significantly the properties of polyester resins. It can be concluded that the elastomer-encapsulated FA particles are perfectly compatible with the polymer resin. In this case, the volume fraction of the dispersed phase becomes significant.

The tensile modulus of the composites increased with increasing elastomer concentration. A soft elastomeric interface around the filler should have enhanced the modulus of the composites even at low elastomer concentrations.^{26–29} However, the results indicated that the tensile modulus increased by 48.8

and 8.4% over that of GPR and FA/GPR, respectively, with 2% SBR inclusion. The tensile modulus of the matrix was improved by approximately 9% with 3.75% elastomer concentration (SBR and AC in FA and CaCO₃). This suggests that SBR and AC form an interface with a reinforcing effect around the FA or CaCO₃ particles. An elastomeric interface around the filler particles has been shown to cause an increased modulus in the composite with respect to the case in which the elastomer exists as discrete domains in the matrix.^{27,29}

Fillers that have higher stiffness than the matrix can increase the modulus of composites and generally cause a dramatic decrease in the elongation at break. Almost all of the elongation occurs in the matrix if the filler is rigid. If there is good adhesion between the filler and the matrix, a still further reduction of the elongation at break will be observed. In the system under study, the tensile elongation decreased in comparison with that of the neat resin, but this decrease

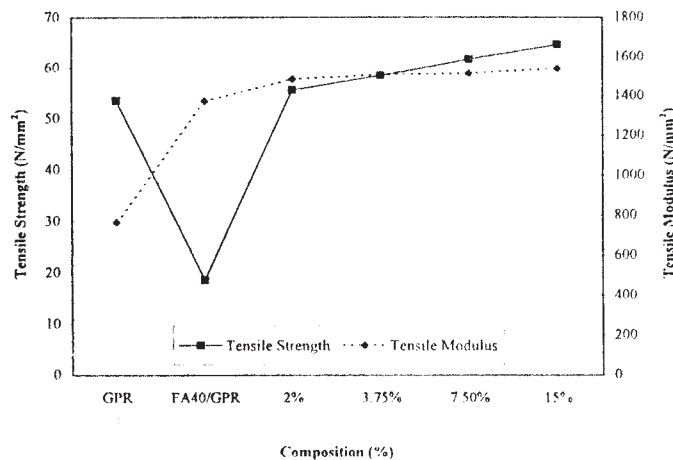


Figure 2 Effect of the elastomer concentration on the tensile properties of FA/AC/GPR composites.

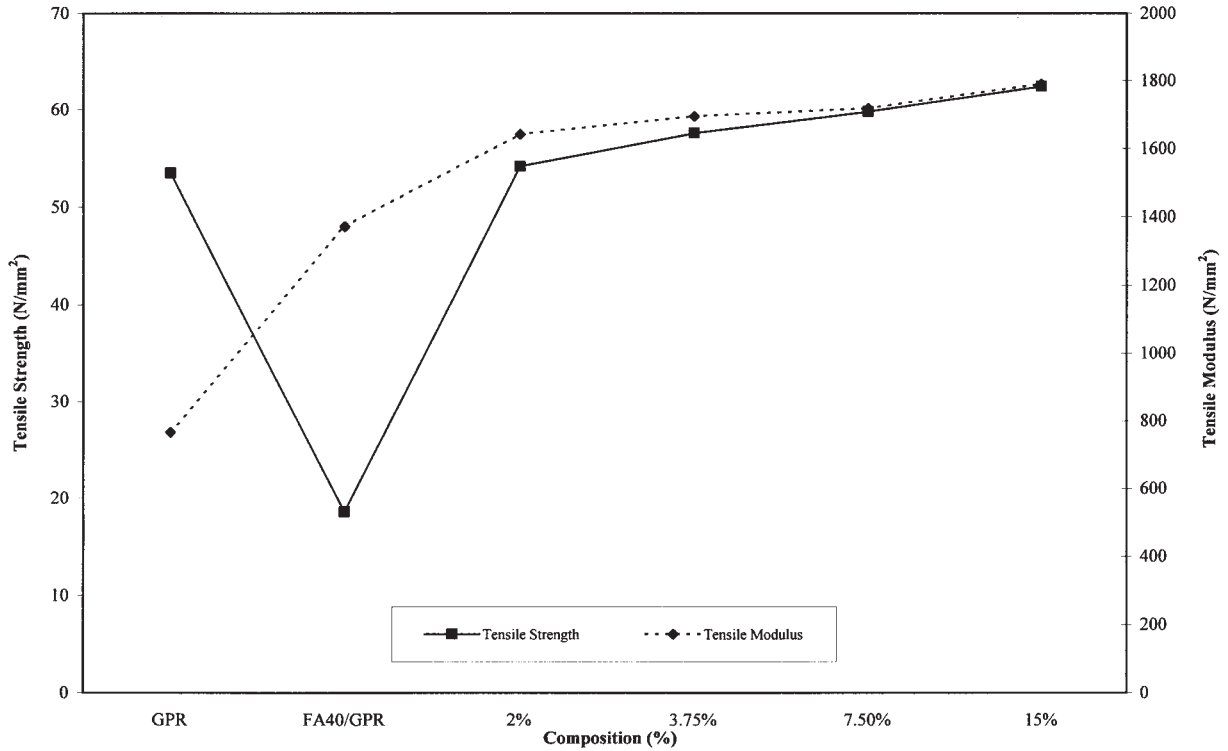


Figure 3 Effect of elastomer concentration on the tensile properties of CaCO₃/SBR/GPR composites.

was enhanced further by an increase in the elastomer concentration (Fig. 5).

Flexural strength and flexural modulus

To explore the effect of SBR or AC encapsulation on the adhesive bonding between FA and GPR in SBR- or

AC-encapsulated FA- or CaCO₃-filled GPR matrices with pull-off experiments, we recorded the flexural properties by performing a three-point-bending test (Figs. 6–9). The flexural studies show that the specimens coated or encapsulated with SBR or AC had improved properties. The maximum increase in the flexural strength was approximately 25%, and this

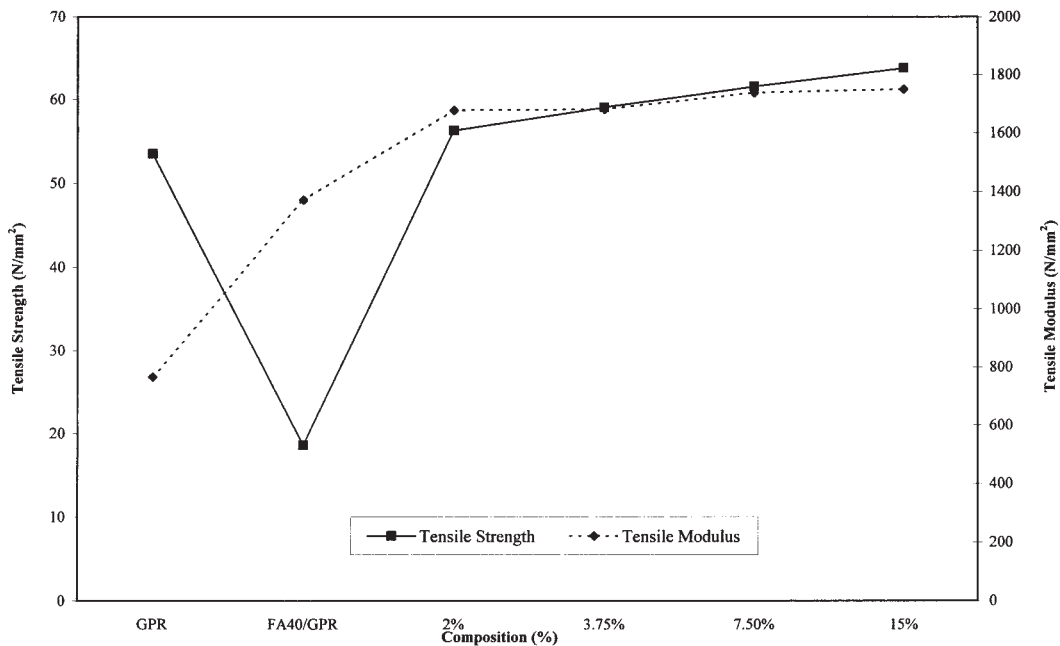


Figure 4 Effect of elastomer concentration on the tensile properties of CaCO₃/AC/GPR composites.

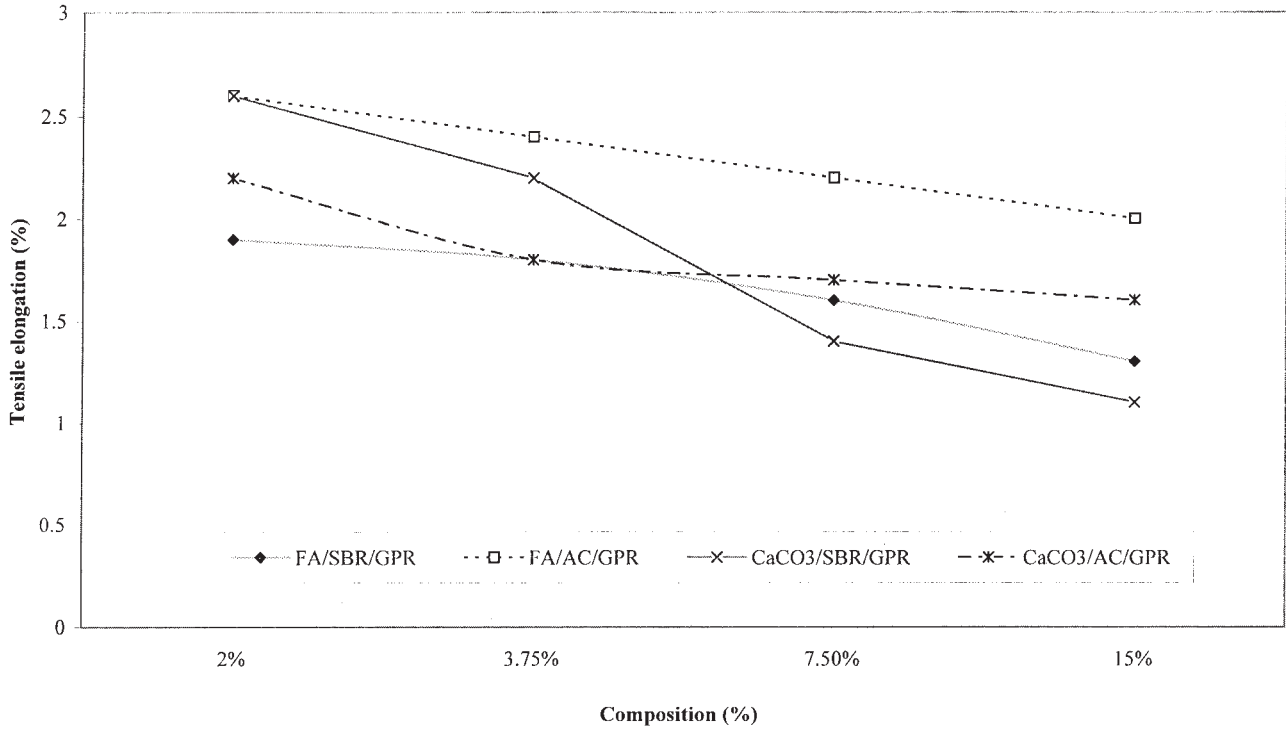


Figure 5 Tensile elongation of FA/SBR/GPR, FA/AC/GPR, CaCO₃/SBR/GPR, and CaCO₃/AC/GPR composites.

indicated that there was sufficient interfacial bonding for the transfer of the load from the matrix to the encapsulated fillers. The improvements in the flexural properties with increasing elastomer concentration could be explained by the enhanced interfacial properties of the surface-coated/encapsulated FA or CaCO₃ by SBR or AC due to surface roughening after the treatment. This interaction between the filler and

the matrix GPR resulted in changes in the failure mechanism of the composite specimens. According to Jang,³⁰ the increased flexural strength of composites with an elastomer-treated filler can also be partly attributed to a lower degree of compressive filler buckling due to enhanced interfacial bonding.

The trend of the flexural modulus was identical to that of the tensile modulus (Figs. 6–9). Similarly to our

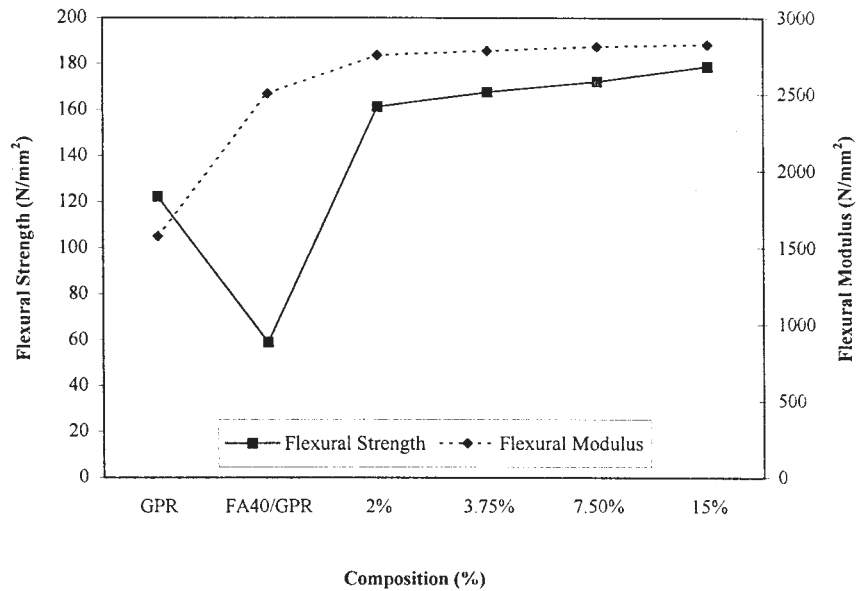


Figure 6 Effect of the elastomer concentration on the flexural properties of CaCO₃/SBR/GPR composites.

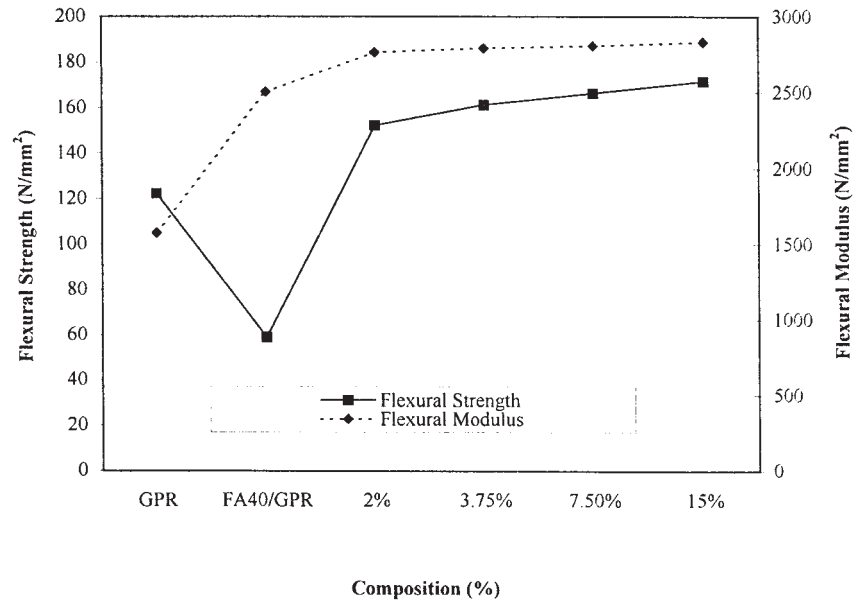


Figure 7 Effect of the elastomer concentration on the flexural properties of CaCO₃/AC/GPR composites.

report, Rana et al.³¹ reported on the effect of a compatibilizer for jute-fiber-reinforced polypropylene composites. The flexural modulus values were calculated from the slopes of the linear elastic portions of the load–deflection curves. The flexural modulus was controlled by the tensile and compressive properties of the filler and matrix, which in turn were governed by interfacial properties.³²

However, it has been reported that for a very low ratio of the loading span to the depth, the beam deflection may contain shear and bending components, and this gives an apparent flexural modulus lower

than the true flexural modulus.³³ However, the flexural modulus is believed to be due to the complex contribution of the stiffness of the GPR network and SBR- or AC-encapsulated FA and the strength of the interfacial bond.

Impact strength

The impact strength of the elastomer-encapsulated FA- or CaCO₃-filled GPR composites was significantly better than that of GPR and FA/GPR (Fig. 10–13). However, with SBR, the improvements in the impact

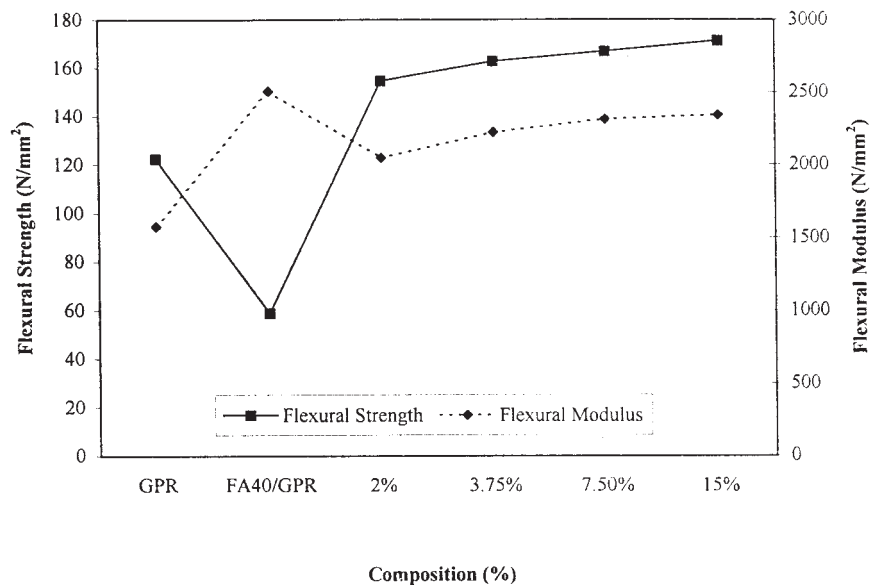


Figure 8 Effect of the elastomer concentration on the flexural properties of FA/SBR/GPR composites.

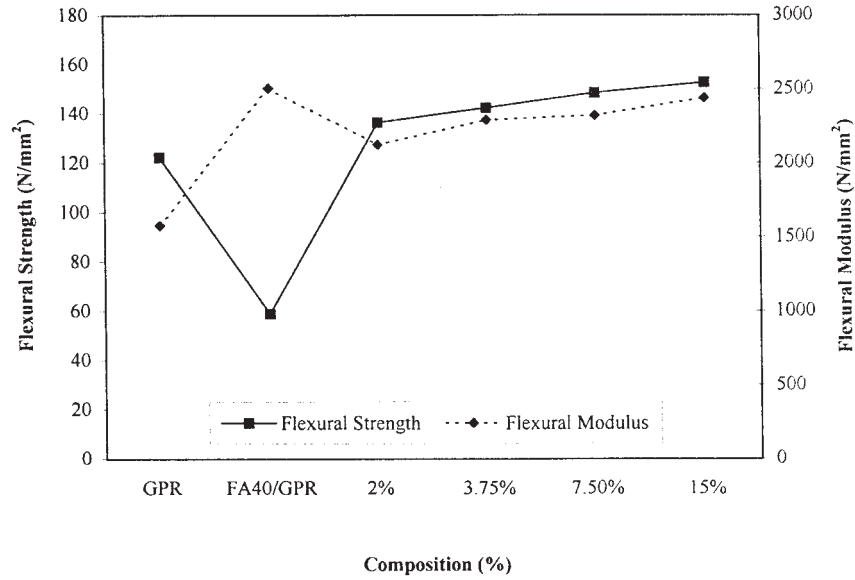


Figure 9 Effect of the elastomer concentration on the flexural properties of FA/AC/GPR composites.

strengths were rather marginal. The results indicate improved adhesion as a result of the encapsulation of the fillers by SBR or AC. Moreover, there was an increase of approximately 15.7% with 15% elastomer (SBR or AC) in the filler–matrix interface. This can be attributed to an increase in the adhesion between the matrix and filler and to the role played by the elastomer to improve the dispersion of the filler with the matrix and reduce the tendency for the fillers to agglomerate. However, both SBR and AC produced significant improvements for both FA- and CaCO₃-filled GPR composite systems.

A 2 wt % SBR concentration in the FA/GPR composites increased the impact strength from 8.88

(FA40/GPR) to 34.41 J/mm (74%), and increasing the SBR concentration to 15 wt % produced an improvement from 8.88 to 39.58 J/mm (77%). Similarly, a 2 wt % AC concentration in the FA/GPR composites produced an improvement from 8.88 to 34.23 J/mm (74%), and increasing the AC concentration to 15 wt % produced a 76.5% improvement (i.e., from 8.88 to 39.52 J/mm). The effect seen with the elastomer concentration was probably due to interfacial effects because the elastomer encapsulation could affect the matrix properties to such an extent. The improved tensile and impact strength suggests a strong interfacial adhesion between the matrix and filler interface, by which stresses could transfer from the matrix to the

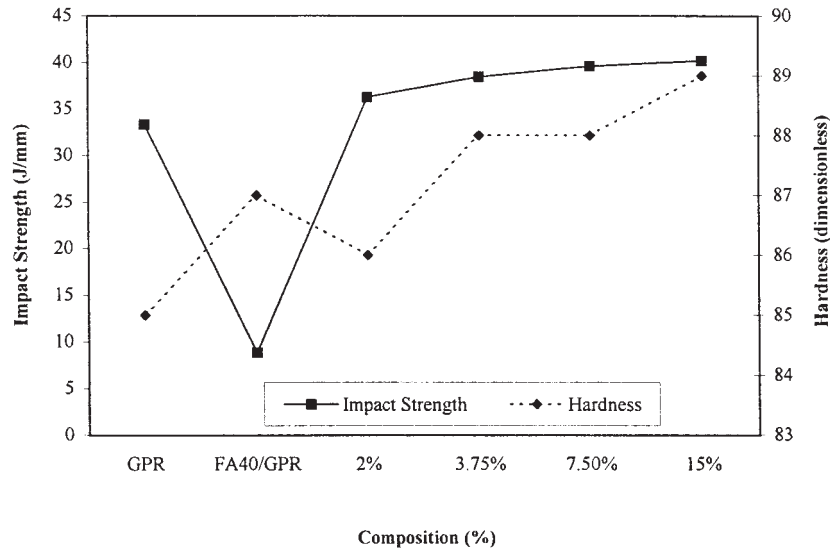


Figure 10 Effect of the elastomer concentration on the impact and hardness properties of CaCO₃/SBR/GPR composites.

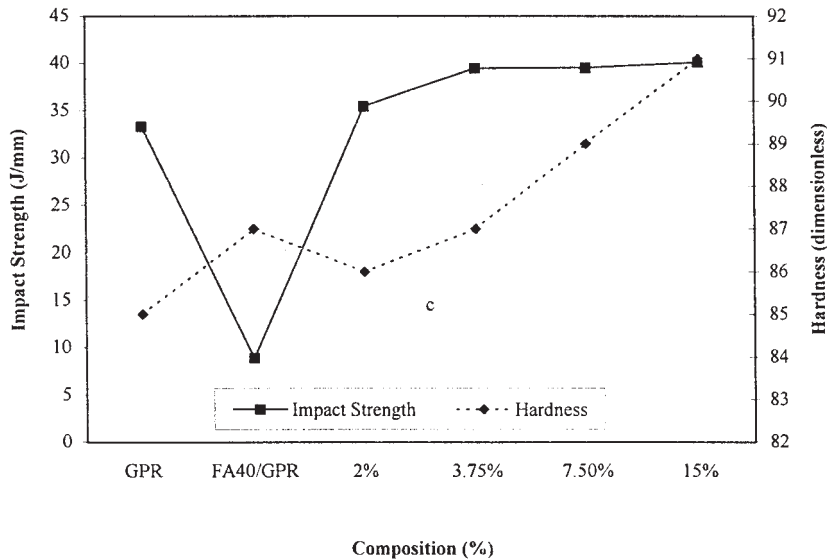


Figure 11 Effect of the elastomer concentration on the impact and hardness properties of CaCO₃/AC/GPR composites.

FA or CaCO₃ particle, and this resulted in a composite for which more energy was needed to start crack propagation.

The positive effects on the mechanical properties, even with small additional percentages of the elastomers, are interesting. One explanation is that the interfacial energy gap between the hydrophilic filler and hydrophobic polymer as well as the viscosity differences can lead to the thermoplastic elastomer preferring to be located at the FA particle surface instead of being dispersed in the polymer matrix during molding.

The low impact strength at a high filler concentration in FA/GPR might be due to the presence of too much filler within the body of the composites, and this could cause crack initiation and, therefore, potential composite failure³⁴ and lower impact strength. The addition of higher concentrations of the fillers also increased the probability of filler agglomeration,³⁵ and this created regions of stress concentrations that required less impact energy to initiate a crack. Similar observations have been reported elsewhere.²⁴ However, in the presence of the elastomer at the interface between the filler and matrix, the microstructure of the

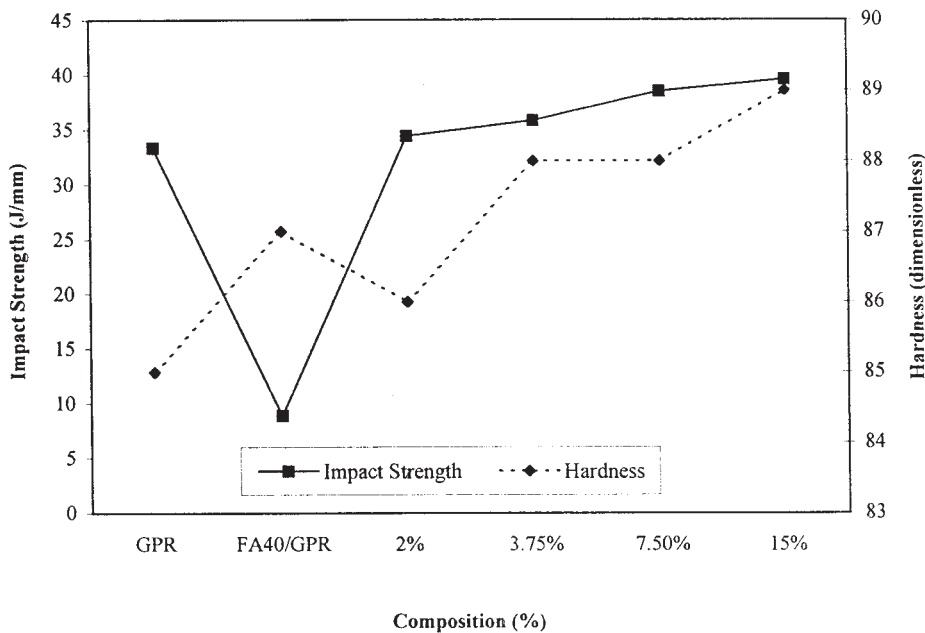


Figure 12 Effect of the elastomer concentration on the impact and hardness properties of FA/SBR/GPR composites.

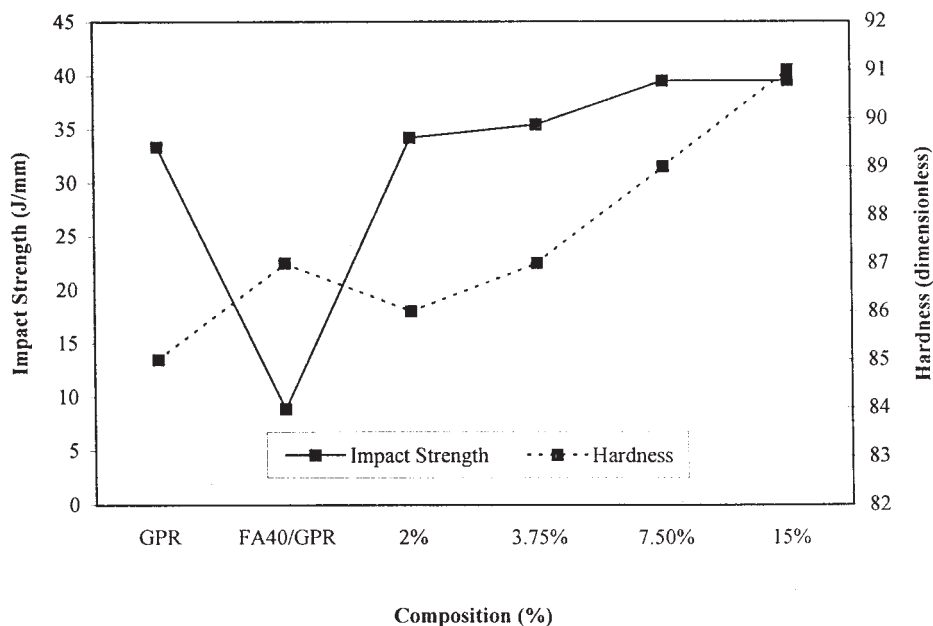


Figure 13 Effect of the elastomer concentration on the impact and hardness properties of FA/AC/GPR composites.

interface is modified and so there is a sharp increase in the impact strength. With 40% FA and 7.5% SBR, the impact strength was more or less equivalent to that of 40% CaCO_3 -filled GPR with 15% AC (i.e. FA-40/SBR 7.5/GPR had an impact strength equivalent to that of CaCO_3 -40/AC15/GPR). This shows that SBR, which has a vinyl group and hence more double bonds than AC, reacts extensively with the GPR matrix.

Hardness

The hardness measurements for the FA/GPR and SBR- or AC-encapsulated FA/GPR and CaCO_3 /GPR are presented in Figures 10–13. The values indicate that the mineral-filled composites were harder than the unfilled composites. The surface modification by the elastomer encapsulation of the filler further increased the hardness. This observation is in agreement with the fact that the hardness is a measure of resistance to penetration. It is generally known that both the hardness and tensile strength are improved by an increase in the crosslinking density. The hardness can be taken as the index of the crosslinking density at the surface of the composite, whereas the tensile strength can be taken as the index of the crosslinking density through the bulk of the entire composite. In this case, the encapsulation of fillers (FA and CaCO_3) by SBR and AC formed highly crosslinked networks during the curing of GPR. Therefore, the hardness of the composite increased.

Interfacial morphology

Morphological studies on FA/GPR, CaCO_3 /GPR, FA/SBR/GPR, FA/AC/GPR, CaCO_3 /SBR/GPR, and

CaCO_3 /AC/GPR composites were undertaken to correlate the mechanical properties. The morphology and mechanical properties of the elastomer-encapsulated filler/resin systems have been studied extensively in the literature.^{36,37} The SEM photographs of the tensile-fractured surfaces of the composites shown in Figures 14–19 reveal that the morphologies of the broken sections of FA/SBR/GPR and FA/AC/GPR were quite different from that of FA/GPR. For FA/GPR, the fractured surfaces were evidence of poor interfacial adhesion between the matrix and filler. For the FA/SBR/GPR and FA/AC/GPR composites with elastomer concentrations of 2–15% in the matrix, rough surfaces that formed because of the deposition of SBR or AC can be seen. This phenomenon should be responsible for the perfect blending of SBR and AC with the GPR matrix because of the enhanced compatibility between the two faces. It is believed that after filler encapsulation failure, initiation increased interfacial friction as a result of the rough filler surface.

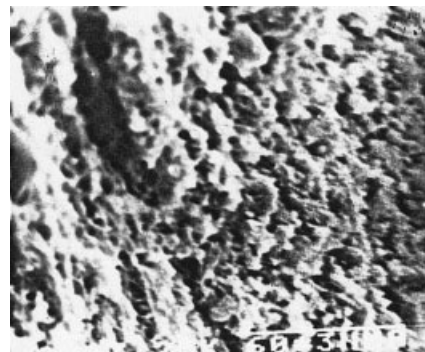


Figure 14 Microstructure of the FA/GPR composite.

Figures 14 and 15 show the microstructures of the FA/GPR and CaCO_3 /GPR composites, respectively. The FA particles were embedded in the GPR matrix and the cavities because of particle pullout. This particle pullout may have been due to the clean and smooth surface of the FA particle, which led to poor adhesion between the filler and matrix surfaces and subsequent crack propagation through the weak interface.

Figures 16 and 17 show the microstructures of FA/SBR/GPR and FA/AC/GPR. Good adhesion between the FA particle and polymer matrix is demonstrated because there is not much particle pullout and subsequent cavity formation. Figures 16 and 17 also show that the FA surface was not as clean and smooth as that of FA/GPR (Fig. 14), and the elastomers coated on the FA samples are believed to have been located on the FA surface and not dispersed in the GPR matrix. This observation supports the composite's mechanical properties shown in Figures 1–13. The SBR or AC encapsulator was capable of improving the interfacial adhesion between FA and GPR and resulted in better impact strength.

Figures 16–19 show the microstructures of the aforementioned composites with the SBR or AC concentration increased; they explore the interface region between FA or CaCO_3 and the polymer matrix. The micrographs show good interfacial adhesion between FA or CaCO_3 /GPR with SBR or AC. It is difficult to differentiate the FA particles from the polymer matrix, and the fracture paths passed either through the FA particles or through the polymer matrix and not in the interface between these. The FA particle surfaces were covered by SBR or AC and also by the GPR matrix. This confirmed that SBR and AC acted as coupling agents/compatibilizers or encapsulators in the FA/GPR and CaCO_3 /GPR composites.

Thermal stability

The thermal stability of SBR- and AC-encapsulated FA/GPR was studied with TGA. The TGA results are

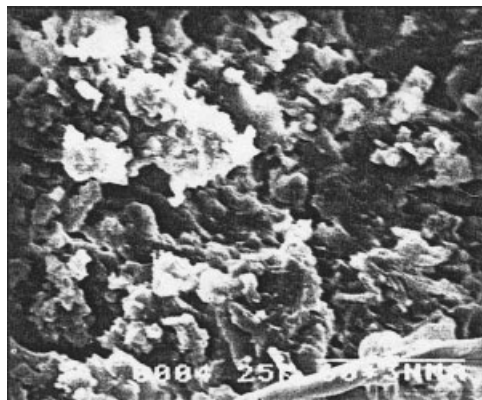


Figure 16 Microstructure of the FA/SBR/GPR composite.

shown in Table IV. The TGA curves for these composites with 2, 3.75, 7.5, and 15% elastomer-treated FA and CaCO_3 /GPR show two-stage decomposition. The elastomer-encapsulated (SBR or AC) FA or CaCO_3 /GPR samples showed almost higher first-stage decomposition than the GPR, FA/GPR, and CaCO_3 /GPR composites. A similar trend was also observed for second-stage decomposition, except for GPR. The first-stage decomposition occurred at 420°C for 2% SBR-encapsulated FA/GPR samples, but 2% SBR-encapsulated CaCO_3 samples decomposed at 430°C. For 15% SBR-encapsulated FA-40/GPR, the first-stage decomposition occurred at 423°C, but 15% SBR-encapsulated CaCO_3 -40/GPR made the composites undergo decomposition at 410°C. This occurred because, for 2% encapsulation of CaCO_3 , the particles were wetted more than FA in the GPR matrix, whereas at a higher percentage of elastomer encapsulation, there was better compatibility for both FA and CaCO_3 with GPR. Therefore, its first-stage decomposition took place at a higher temperature. A similar trend was observed for second-stage decomposition of SBR-encapsulated FA/GPR and CaCO_3 /GPR samples.

For the AC-encapsulated FA/GPR and CaCO_3 /GPR samples, the aforementioned behaviors were also



Figure 15 Microstructure of the CaCO_3 /GPR composite.



Figure 17 Microstructure of the FA/AC/GPR composite.

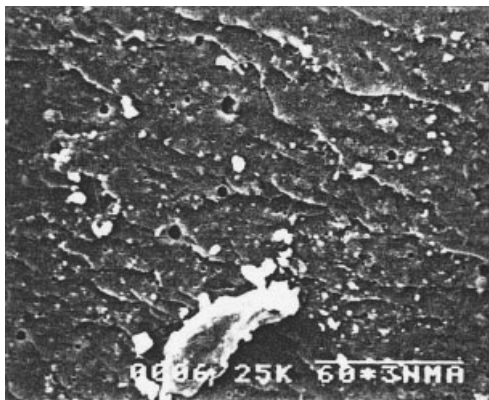


Figure 18 Microstructure of the CaCO₃/SBR/GPR composite.

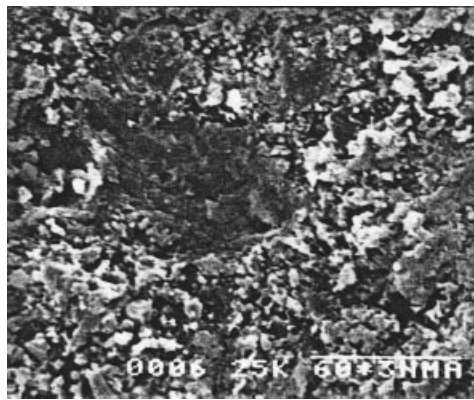


Figure 19 Microstructure of the CaCO₃/AC/GPR composite.

observed. This may be explained as follows. The mineral filler with a higher percentage of encapsulated polymers made the GPR composite decompose more easily than those with a lower percentage of encapsulated polymers. However, it may be concluded that with all modifications, there is only a minor effect on the thermal stability.

CONCLUSIONS

1. The elastomer encapsulation of the fillers (CaCO₃ and FA) resulted in significantly improved tensile and flexural strength and modulus, impact strength, and hardness for FA/GPR and CaCO₃/GPR. The tensile elongation decreased with in-

creasing elastomer concentration from 2 to 15 wt % in the GPR matrix.

2. FA/SBR/GPR had higher tensile and flexural strength than the FA/AC/GPR composites. However, the impact strengths for both systems were comparatively equal.
3. Comparing the CaCO₃/SBR/GPR and CaCO₃/AC/GPR composites, we found that AC-encapsulated CaCO₃/GPR showed higher tensile and flexural properties, whereas the impact strengths were almost equal.
4. The 2% SBR-encapsulated CaCO₃/GPR system had higher tensile elongation than all the other elastomer-encapsulated filled systems. However, 15% SBR-encapsulated FA/GPR had higher tensile and flexural properties.

TABLE IV
Thermal Stability of Elastomer-Encapsulated FA/GPR and CaCO₃/GPR Composites

Sample	System	Temperature (°C)	
		First-stage decomposition	Second-stage decomposition
1	GPR	406	538
2	FA40/GPR	390	520
3	CaCO ₃ -40/GPR	400	473
4	FA40/SBR2/GPR	420	526
5	FA40/SBR3.75/GPR	416	530
6	FA40/SBR7.5/GPR	423	533
7	FA40/SBR15/GPR	423	526
8	FA40/AC2/GPR	403	526
9	FA40/AC3.75/GPR	399	531
10	FA40/AC7.5/GPR	400	536
11	FA40/AC15/GPR	386	526
12	CaCO ₃ -40/SBR2/GPR	430	526
13	CaCO ₃ -40/SBR3.75/GPR	420	500
14	CaCO ₃ -40/SBR7.5/GPR	417	520
15	CaCO ₃ -40/SBR15/GPR	410	520
16	CaCO ₃ -40/AC2/GPR	469	516
17	CaCO ₃ -40/AC7.5/GPR	406	520
18	CaCO ₃ -40/AC15/GPR	395	527
19	CaCO ₃ -40/AC15/GPR	390	520

5. The impact strength and hardness properties of both SBR- and AC-encapsulated FA and CaCO₃/GPR were comparable.
6. The effect of the thermal stability was low for all chemical modifications.
7. The microstructures clearly showed that the filler particles were encapsulated by elastomers.

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