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Flexibility improvement of short glass fiber reinforced epoxy by using a liquid elastomer

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Abstract

In certain applications of fiber reinforced polymer composites flexibility is required. The aim of this study was to improve flexibility of short glass fiber reinforced epoxy composites by using a liquid elastomer. For this purpose, diglycidyl ether of bisphenol-A (DGEBA) based epoxy matrix was modified with hydroxyl terminated polybutadiene (HTPB). A silane coupling agent (SCA) was also used to improve the interfacial adhesion between glass fibers and epoxy matrix. During specimen preparation, hardener and HTPB were premixed and left at room temperature for an hour before mixing with epoxy resin to allow possible reactions to occur. In order to compare flexibility of the specimens flexural tests were conducted and the data were evaluated numerically by using a derived relation. Test data and scanning electron microscope analysis indicated that surface treatment of glass fibers with SCA, and HTPB modification of epoxy matrix improved flexural properties especially due to the strong interaction between fibers, epoxy, and rubber. It was also observed that HTPB modification resulted in formation of relatively round rubber domains in the epoxy matrix leading to increased flexibility of the specimens.

Keywords: Epoxy resin; Short glass fibers; HTPB (Hydroxyl Terminated Polybutadiene)

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1. Introduction

Epoxy resins are a class of high performance thermosetting polymers widely used as matrix resins for advanced composite materials for application in the automotive, construction and aerospace industries. Typical epoxy resin types used in industry are; epichlorohydrin and bisphenol A derived (the most widely used one), epoxy cresol-novalak, epoxy phenol-novalak, polynuclear phenol-glycidyl ether-derived, and cycloaliphatic epoxy [1]. In this study, epichlorohydrin and bisphenol A derived epoxy resin was chosen.

The strength and stiffness of short glass fiber reinforced composites depend on fiber volume fraction, orientation and aspect ratio (length/diameter). First, strength and stiffness of the composite are related to the glass fiber content, and they may be increased 400% by increasing glass fiber content from 20 to 80%. Orientation is difficult to control. It is strongly influenced by processing methods and by local flow conditions, for instance, in injection-molded parts. As a result, changes in volume fraction and aspect ratio will change the degree of orientation [2].

Glass fiber reinforced composites perform well only when stress can transfer efficiently across the interphase between the fibers and matrix. In order to improve fiber wettability or to enhance affinity between fiber and matrix, modification of the fiber surface can be done by coating fiber with: (a) a silane with reactive end groups, (b) a rubber emulsion, (c) a solution of different polymers such as polyurethane, polystyrene, etc. [3]. Today, glass fibers are commonly treated with silane coupling agents (SCA).

In 1992 Kaushal [4] studied the flexural behavior of glass/epoxy composites toughened by a liquid rubber. In this investigation, E-glass fabric reinforced epoxy matrix resin was modified by amine terminated copolymer of butadiene and acrylonitrile (ARBN). It was reported that rubber toughening by ARBN also resulted in flexibility improvement. Bussi et al. [5] in 1994 studied the flexural properties of blends of DGEBA based epoxy resin and hydroxyl terminated, internally epoxidized polybutadiene rubber. In order to improve flexibility and also toughness, the epoxidized polybutadiene rubber was prereacted with excess diepoxide to achieve better bonding between the

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rubber particles and epoxy matrix. Then, Tong and his co-workers [6] used polysiloxanes as flexibilizer for epoxy resin. They reported that flexibility was increased by increasing molecular weight and concentration, and decreasing particle size of the polisiloxane particles.

In 1995 Matheswaran and Padmanabhan [7] used specimens of DGEBA type epoxy resin matrix reinforced with glass fiber fabric. They indicated that addition of plastisol and polycarbonate independently to the glass fiber-epoxy system increases flexibility and also toughness. Then, amine terminated polysulfone (ATPS) was used by Ratna et al. [8] in 1997 as a modifier for DGEBA type epoxy resin. They observed that ATPS forms a compatible blend with epoxy, and due to the presence of the flexible ether and sulfone linkages, ATPS increased flexibility of the epoxy matrix.

Shih et al. [9] in 1999 used a synthesized polydimethylsiloxane containing isocyanate group to improve the flexibility of *o*-cresol formaldehyde novalac epoxy resin. They showed that modified epoxy resin had flexibility improvement with increasing modifier content. Nigam et al. [10] also reported that if epoxy cresol novalac resin was modified with carboxyl terminated copolymer of butadiene acrylonitrile (CTBN), then flexibility of the system could be improved due to the possible chemical interaction between the oxirane ring of epoxy and carboxyl function of the CTBN. Then, Barcia and his researchers [11] used hydroxyl terminated polybutadiene (HTPB) to modify the surfaces of carbon fibers. They observed that HTPB formed a flexible interface between carbon fibers and epoxy matrix increasing the toughness and flexibility of the system.

In 2001, Ozturk, Kaynak and Tincer [12,13] used HTPB and a special SCA to improve flexural properties of a DGEBA type epoxy resin. It was shown that by using certain orders of mixing of constituents flexibility could be improved. In the present study it was aimed to observe whether the same procedures would be again also effective or not when epoxy was reinforced with short glass fibers.

2. Experimental

The liquid epoxy resin used was solvent-free diglycidyl ether of bisphenol A (DGEBA) type (Ciba-Geigy/Araldite CY225) which was hardened by using a liquid, modified and preaccelerated anhydride curing agent (Ciba-Geigy/Hardener HY925). The liquid elastomer modifier chosen was low molecular weight HTPB. For fiber reinforcement, chopped E-glass fibers (Camelyaf/Turkey) with a length and diameter of 3 mm and 13 μm, respectively, were used. Glass fiber surfaces were sized with a SCA of Polyvest 25 (Huls-Veba/Germany). The amount of this SCA used was about 2 wt% with respect to the amount of glass fibers. The surface treatment was carried out in a slurry mixture of required compositions where the solvent was diethylether. The slurry was left at room temperature for 24 h in order to remove diethylether. Then glass fibers were put in an oven at 60 °C for 3 h and then kept at room temperature.

Specimens were prepared in four different mixing and moulding procedures. In the first way, non-treated fibers were mixed with epoxy/hardener mixture directly. In the second one, fiber surface was treated with SCA before mixing with epoxy system. In the third method, non-treated fibers were mixed with epoxy/hardener mixture modified by HTPB. In the fourth mixing and moulding procedure, SCA treated fibers were mixed with epoxy/hardener system modified by HTPB. In each method three different short glass fiber concentrations (10, 20, and 30 wt%) were used. Therefore, testing specimens were prepared in 12 different conditions, and their designations are described in Table 1 in detail.

Epoxy and hardener were mixed with a ratio of 100:80 parts by weight and liquid rubber modification was performed as 1% by weight of total epoxy/hardener mixture. The slurry mixtures were poured into moulds designed for test specimens. Bending tests were performed by using Lloyd universal testing machine with a cross-head speed of 1.7 mm/min. Bar shaped samples with dimensions of 80 × 10 × 4 mm were used according to the Test Method-I Procedure A mentioned in ASTM D790M-92 Standard. Fractographic observations were also conducted under Jeol JSM-6400 scanning electron microscope (SEM) to evaluate

Table 1
Specimen designations used for 12 different mixing and moulding methods

Specimen designations	Mixing and moulding methods
E	Neat epoxy/hardener mixture
10 GF/E	10 wt% non-treated glass fiber mixed with epoxy/hardener mixture
20 GF/E	The same method with 20 wt% fiber
30 GF/E	The same method with 30 wt% fiber
10 GF-S/E	10 wt% SCA treated glass fiber mixed with epoxy/hardener mixture
20 GF-S/E	The same method with 20 wt% fiber
30 GF-S/E	The same method with 30 wt% fiber
10 GF/E-R	10 wt% non-treated glass fiber mixed with epoxy/hardener mixture modified with 1 wt% HTPB[a]
20 GF/E-R	The same method with 20 wt% fiber
30 GF/E-R	The same method with 30 wt% fiber
10 GF-S/E-R	10 wt% SCA treated glass fiber mixed with epoxy/hardener mixture modified with 1 wt% HTPB[a]
20 GF-S/E-R	The same method with 20 wt% fiber
30 GF-S/E-R	The same method with 30 wt% fiber

[a] 1 wt% HTBP was first premixed with hardener, and then after 1 h epoxy was added to this mixture.

the effects of SCA sizing on fiber surfaces and the formation of rubber domains in the epoxy matrix modified with HTPB.

3. Results and discussion

The SCA used in this study has a reactive polybutadiene group with *n* from 8 to 10 and hydrolysable methoxy end groups. During the application of SCA, slow hydrolysis of methoxy groups with residual water on the glass surface produce silanols followed by oxygen linkages with the glass fiber. Yet due to its long reactive polybutadiene group both hydrolysis and condensation observed in common SCAs, is very slow or not observed in this SCA. Reactive polybutadiene, organofunctional group may interact to form a chemical bond with epoxy molecule resulting in adhesion between fiber and matrix. The amount of SCA used is important to improve the adhesion at the glass fiber-epoxy matrix interface. Generally, a range of 0.2–2% by weight of the sizing layer was used. In this study, SCA concentration was kept as 2% for all conditions.

In order to improve flexibility, usually long chain and reactive molecules were used. Since anhydride curing agent and HTPB are very reactive materials, they were premixed and left for one hour to allow possible reactions to occur. The reaction between hydroxyl end groups of rubber and hardener, a ring opening reaction, may lead to chain extension in the system. Therefore, an increase in flexibility is expected. Moreover, double bond in the HTPB backbone may open, and reaction may proceed from this site leading to crosslinking. Liquid rubber modification may also increase the degree of entanglement between epoxy resin and HTPB due to their long chain structures. In order to determine the system functionality, the exact chemical reactions that occurred should be known. However, it is very difficult to predict these reactions since resin mixture contains very reactive chemicals. Furthermore, the addition of HTPB having functional groups in the presence of SCA leads to changes in system functionality.

The flexural behavior showed by 3-point bending tests of all specimens is given in Fig. 1(a)–(c) separately according to their glass fiber content. Then, the flexural strength, flexural strain at break, and flexural modulus values of all specimens determined from these stress–strain curves were tabulated in Fig. 2(a), (b), and (c), respectively. Stress–strain curves (Fig. 1(a)–(c)) indicate that untreated short glass fiber reinforcement of unmodified epoxy leads to very linear flexural behavior up to the fracture point. Due to the plasticization effects of SCA and HTPB, surface treatment of glass fibers and modification of epoxy resulted in some non-linear plastic behavior. However, in 30% GF specimens all flexural stress–strain curves were linear due to the higher content of stiff glass fibers.

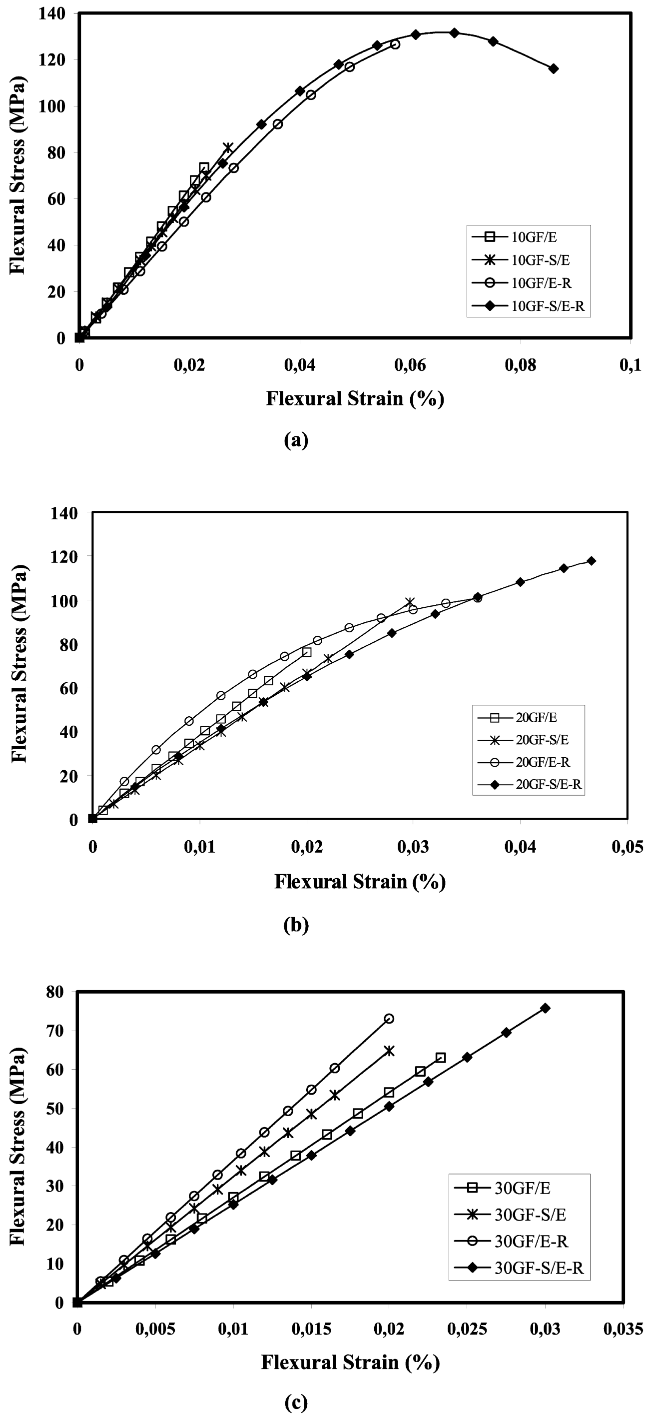
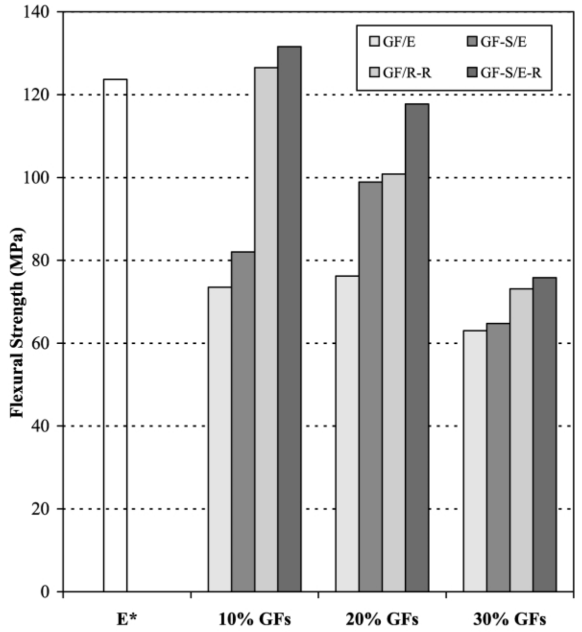


Fig. 1. Flexural stress–strain curves of specimens reinforced with (a) 10 wt% GFs; (b) 20 wt% GFs; (c) 30 wt% GFs.

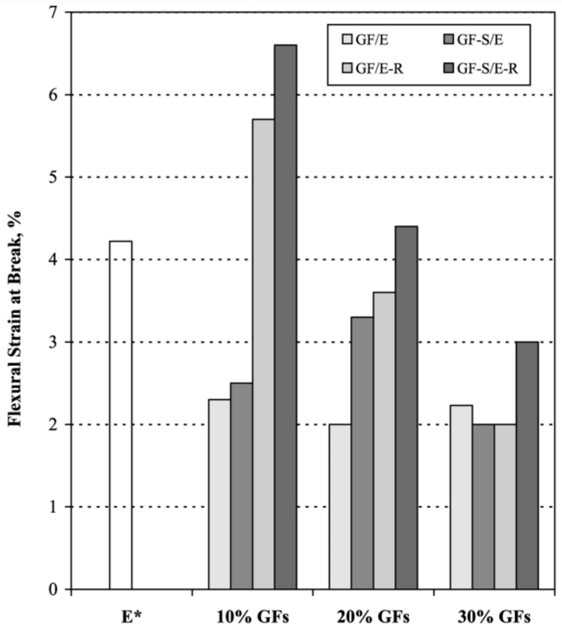
Fig. 2(a) indicates that with increasing glass fiber content flexural strength decreased with respect to the value of neat epoxy system. This decrease can be related with the uneven and random fiber orientation, relatively low volume percentages, and short lengths of the fibers. However, the effect of silane treatment of fibers leading to increased flexural strength values were clearly observed in this figure. For instance, in 10% GF specimens, flexural strength increased 12% with SCA treatment of fibers. Similarly,



Flexural Strength (MPa)	10 GF/E	10 GF-S/E	20 GF/E	20 GF-S/E	30 GF/E	30 GF-S/E
Epoxy without modification	74 ±3	82 ±3	76 ±6	99 ±8	63 ±3	65 ±3
Epoxy with 1% HTPB modification	127 ±3	132 ±3	101 ±4	118 ±5	73 ±3	76 ±1

* For neat epoxy system Flexural Strength (MPa) = 124 ± 6

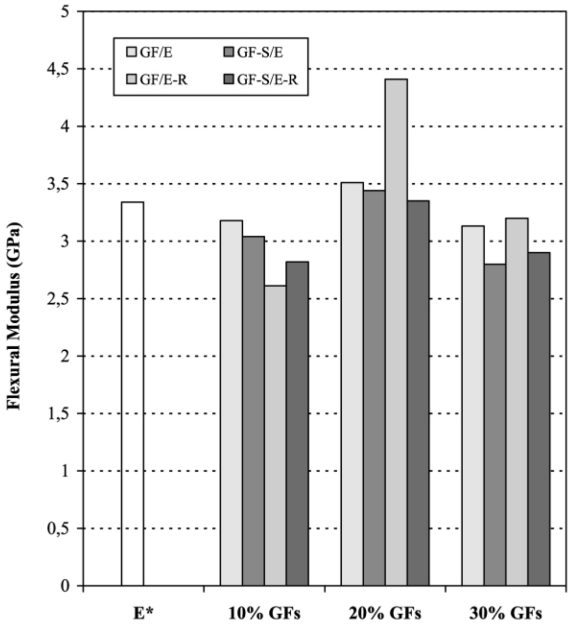
(a)



Flexural Strain at Break (%)	10 GF/E	10 GF-S/E	20 GF/E	20 GF-S/E	30 GF/E	30 GF-S/E
Epoxy without modification	2.3 ±0.1	2.5 ±0.1	2.0 ±0.1	3.3 ±0.3	2.2 ±0.1	2.0 ± 0.1
Epoxy with 1% HTPB modification	5.7 ±2.3	6.6 ±2.7	3.6 ±0.2	4.4 ±0.4	2.0 ±0.1	3.0 ±0.1

* For neat epoxy system Flexural Strain at Break (%) = 4.2 ±0.1

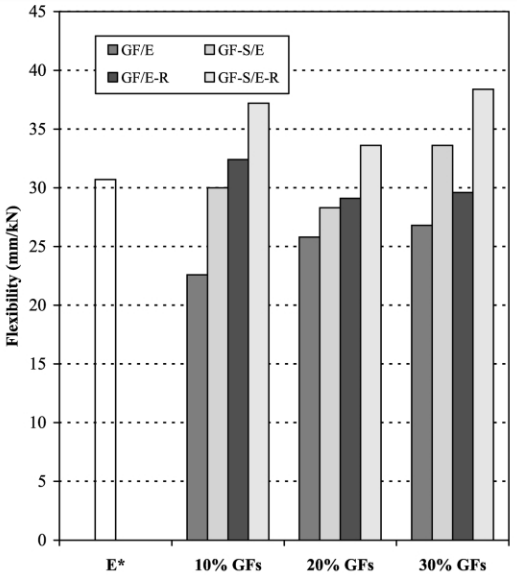
(b)



Flexural Modulus (GPa)	10 GF/E	10 GF-S/E	20 GF/E	20 GF-S/E	30 GF/E	30 GF-S/E
Epoxy without modification	3.2 ±0.1	3.0 ±0.2	3.5 ±0.4	3.5 ±0.2	3.1 ±0.5	2.8 ±0.1
Epoxy with 1% HTPB modification	2.6 ±0.3	2.8 ±0.1	4.4 ±0.1	3.4 ±0.4	3.2 ±0.1	2.9 ±0.2

* For neat epoxy system Flexural Modulus (GPa) = 3.3 ± 0.1

(c)



Flexibility (mm/kN)	10 GF/E	10 GF-S/E	20 GF/E	20 GF-S/E	30 GF/E	30 GF-S/E
Epoxy without modification	22.6	30.0	25.8	28.3	26.8	33.6
Epoxy with 1% HTPB modification	32.4	37.2	29.1	33.6	29.6	38.4

* For neat epoxy system Flexibility (mm/kN) = 30.7

(d)

flexural strength of 20% GF specimens increased as much as 30% with surface treatment. This is mainly due to better interfacial adhesion between fibers and matrix.

Fig. 2(a) also shows that flexural strength values increased with HTPB modification of epoxy in all specimens. In 10% GF specimens, the maximum value of flexural strength (132 MPa) was obtained in HTPB modified epoxy reinforced with SCA treated glass fibers. This was higher than the value for neat epoxy system. In 20 and 30% GF specimens, flexural strength values also increased with HTPB modification. This should be a result of premixing HTPB with hardener leading to improved interaction between HTPB domains and epoxy resin. This is discussed in the previous studies [12,13] in detail.

On the other hand in Fig. 2(b), the flexural strain at break values decreased with increasing fiber content in the matrix, but increased with surface treatment of fibers. Addition of stiff glass fibers decreased the flexural strain at break value by almost 50% compared with the neat epoxy system. However, SCA treatment of fibers increased the flexural strain at break values in 10 and 20% GF specimens. Fig. 2(b) also indicates that when epoxy was modified with HTPB, percentage flexural strain at break value increased abruptly as 2.5 times in 10% non-treated fiber reinforced specimens. It was further increased with SCA treatment. Likewise, in 20 and 30% GF specimens, strain at break values also increased with rubber modification of matrix.

In Fig. 2(c) it is shown that in all specimens, the flexural modulus values decreased with surface treatment of fibers. The flexural modulus values of 20% GF specimens were higher than other specimens. In 10% GF specimens, it was decreased with rubber modification as expected, since flexural elastic strain increased. For the flexibility improvement, increase in elastic strain and decrease in flexural modulus was desired. Similarly in 30% GF specimens, rubber modification decreased flexural modulus.

'Flexibility' is difficult to be quantified, thus in order to compare the flexibility of the specimens a relation was assessed by using the following procedure assuming that flexibility is directly proportional or approximately equal to the 'flexural compliance' of the specimens. Compliance is the reciprocal of the stiffness, and the flexural stiffness is the ratio of the applied load (P) to the amount of elastic deflection (δ). Elastic deflection of specimens under three point bending loading with rectangular cross sections can be determined by

$$\delta = \frac{Pl^3}{48EI} \tag{1}$$

where l, w and t are length, width and thickness, respectively; E, elastic modulus; and I, moment of inertia for rectangular cross sections. Since $I = wt^3/12$, then

$$\text{Flexural stiffness} = \frac{P}{\delta} = \frac{48EI}{l^3} = \frac{4Ewt^3}{l^3} \tag{2}$$

Therefore

$$\text{Flexibility} \approx \text{Flexural compliance} = \frac{1}{\text{Flexural stiffness}} = \frac{1}{E}\,\frac{l^3}{4wt^3} \tag{3}$$

In this relation, it can be seen that flexibility depends on geometry (l, w, t) and flexural modulus (E) of the specimens, where E is the slope of the linear part of the flexural stress vs. strain curve. Flexibility of the specimens were evaluated by using this relation, and given in Fig. 2(d) with the derived unit of mm/kN.

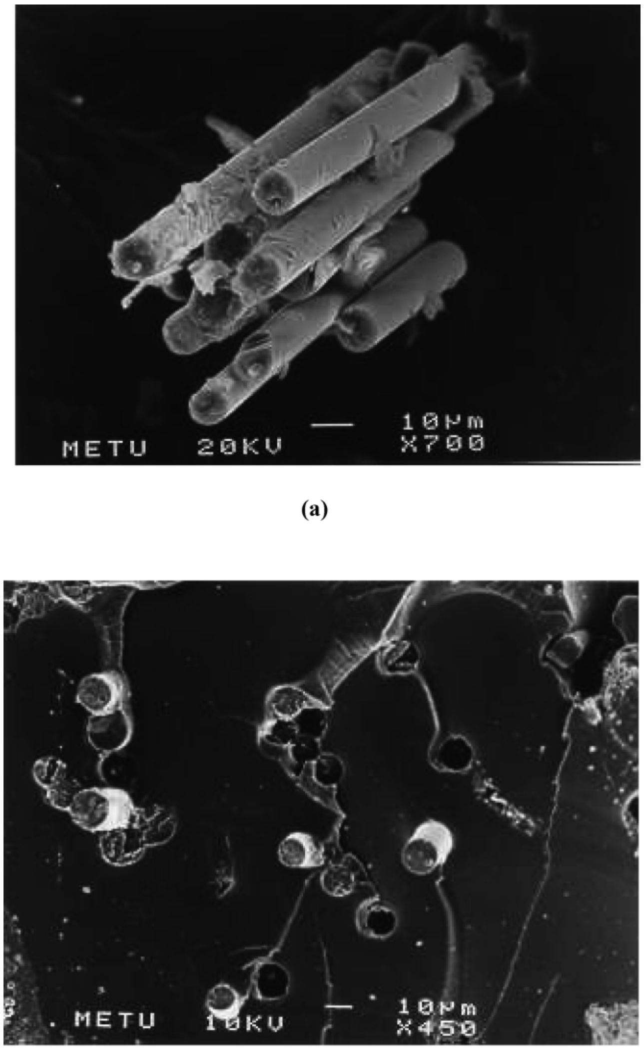
Fig. 2(d) shows that fiber reinforcement decreased flexibility of neat epoxy due to the stiffening effect of the high modulus glass fibers. However, surface treatment of glass fibers by SCA resulted in substantial improvement in the flexibility of all specimens. In 10% GF specimens, SCA treatment of fibers increased flexibility as much as 33%, while in 20% GF specimens this increase was nearly 10%. There was also a sharp increase in flexibility, around 25%, in 30% GF specimens with fiber surface treatment. This should be due to improved adhesion at the fiber/matrix interface.

Fig. 2(d) also shows that HTPB modification of epoxy improved flexibility of all specimens. In 10% non-treated GF specimens, flexibility increased by 5.5%, and with SCA treatment of fibers, a further increase of 21% was obtained compared with the neat epoxy system. In the case of 20 and 30% SCA-treated GF specimens, flexibility values increased 9.5 and 25%, respectively.

Premixing HTPB with hardener improved flexibility. Because, rubber molecules might react with hardener fully, leading to strong interaction with epoxy. Therefore, the load transfer from epoxy matrix to rubber particles may occur easily. If there were not enough interactions between chemicals, flexibility would decrease. In this study, HTPB concentration was kept as 1%. Because, increasing rubber content results in improper mixing due to the incompatibility between rubber and epoxy resin as discussed in the previous studies [12,13]. Achieving improvements in proper mixing processes and also better interactions at the epoxy-rubber interface may allow the use of higher HTPB concentrations for possible higher flexibility values.

SEM studies were also conducted to observe the influences of SCA treatment of fiber surfaces, and morphology of the rubber domains formed due to HTPB modification of the epoxy system. Effects of non-treated fiber reinforcement are shown in Fig. 3. Fig. 3(a) indicates that when glass fibers were not treated with SCA, their

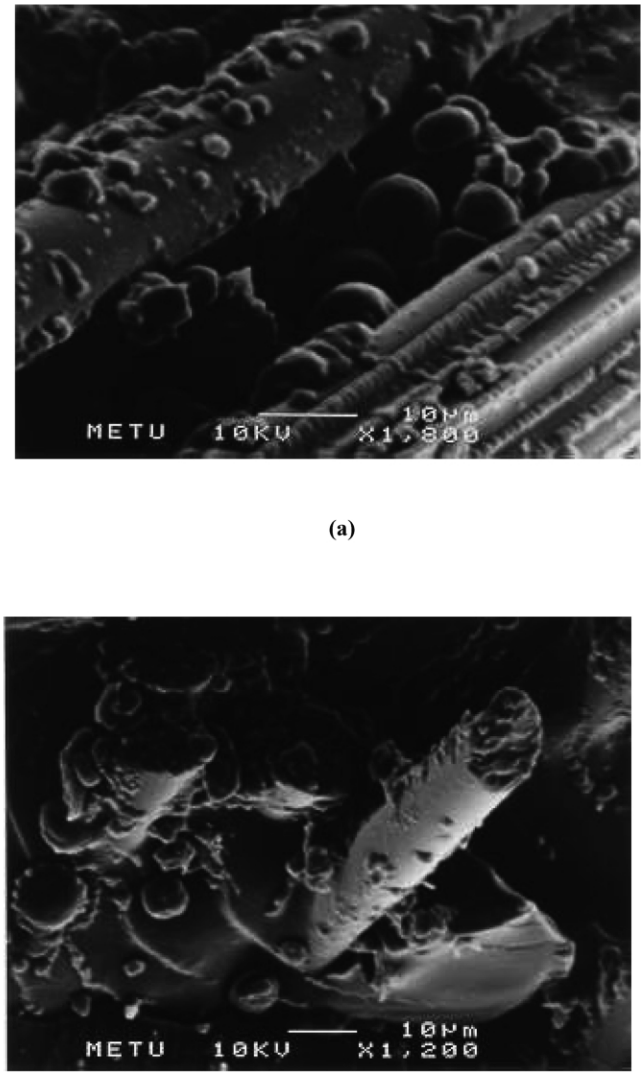
Fig. 2. Flexural properties of all specimens. (a) Flexural strength; (b) flexural strain at break; (c) flexural modulus; (d) flexibility.



(a)

(b)

Fig. 3. Effects of non-treated fiber reinforcement (a) Smooth glass fiber surfaces due to little interfacial adhesion; (b) Holes due to fiber pull-outs.



(a)

(b)

Fig. 4. Effects of SCA treated fiber reinforcement (a) and (b) rough glass fiber surfaces due to improved matrix adherence.

surfaces were rather smooth which indicates insufficient adherence to the epoxy matrix, while Fig. 3(b) shows ‘fiber pull-outs’ occurred due to the weak interface between epoxy and non-treated glass fibers.

SCA treatment of glass fiber surfaces resulted in rather higher wettability leading to improved interfacial bonding with the epoxy matrix. Fig. 4(a) and (b) indicate the rough surfaces of fibers due to the improved adherence with the epoxy matrix leading to increased flexibility.

Effects of HTPB modification of epoxy matrix are indicated in Fig. 5(a) and (b), which show formation of the rubber domains in the matrix. Rubber domains increased flexibility due to mainly flexible nature of HTPB. These domains also increased toughness of the specimens. Fig. 5(a) shows that rubber domains were homogenously dispersed, and had relatively round shapes with a fine size of less than 10 μm. On the other hand, some rubber domains were larger (Fig. 5(b)). This should be due to the possible coalescences of smaller rubber domains.

Fig. 6(a) and (b) show that some rubber domains acted as coupling agent and adhered to the glass fiber surfaces. Therefore, this also increased the interaction at the fiber/epoxy matrix interface. In Fig. 6(a) and (b), silane-treated fibers having rough surfaces and dispersed rubber domains in the epoxy matrix were shown. Rough surfaces were due to silane treatment and rubber adhesion to the fiber surfaces. Specimens having silane-treated fibers and HTPB modified epoxy resulted in the highest flexibility values. This may be associated with the flexible interface consisting rubbery SCA and HTPB domains which were both able to dissipate the energy.

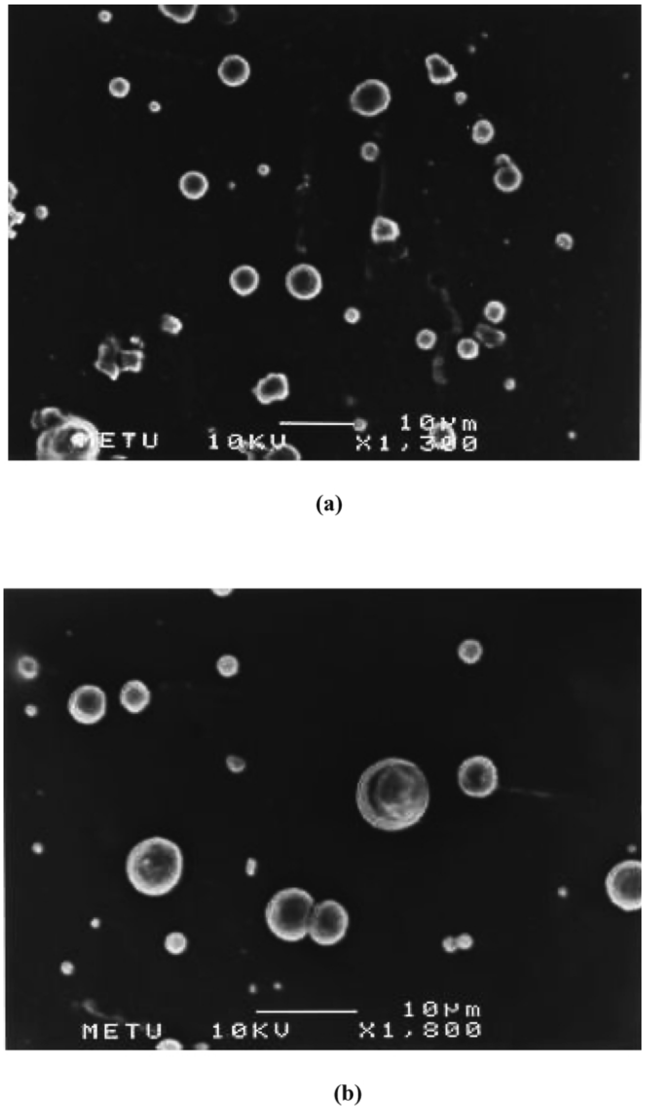


Fig. 5. Effects of HTPB modification of epoxy matrix (a) finely dispersed rubber domains; (b) larger rubber domains due to coalescence.

4. Conclusion

Flexibility of short glass fiber reinforced epoxy was improved first with HTPB modification. The reason of the flexibility increase should be due to the procedure of premixing HTPB with hardener before epoxy addition which changes the path of the curing reactions. Because, these reactions between hydroxyl end groups of rubber and hardener (a ring opening reaction) may lead to chain extension in the system. Secondly, surface treatment of glass fibers with SCA also improved flexibility especially due to enhanced interaction at the fiber/epoxy matrix interface.

It can be concluded that a high mechanical performance and flexibility of epoxy based composites can be achieved by employing short glass fibers treated with a suitable SCA together with rubber (e.g. HTPB) domains dispersed in epoxy matrix, and when the dispersed particle size becomes smaller and more uniform, then flexibility will be improved more.

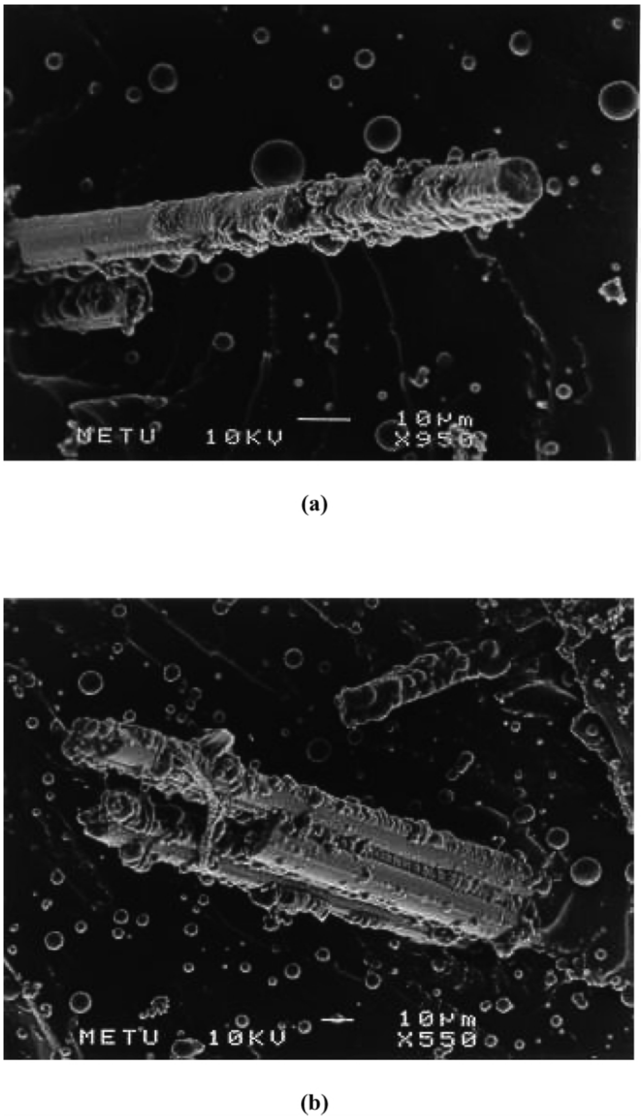


Fig. 6. Effects of both SCA treated fiber reinforcement and HTPB modified epoxy matrix (a) and (b) rubber domains and rough fiber surfaces.

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