Effect of an Epoxy-Based Bonding Agent on the Cure Characteristics and Mechanical Properties of Short-Nylon-Fiber-Reinforced Acrylonitrile–Butadiene Rubber Composites

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ABSTRACT: The cure characteristics and mechanical properties of short-nylon-fiber-reinforced acrylonitrile–butadiene rubber composites with and without an epoxy resin as a bonding agent were studied. The epoxy resin was a good interfacial-bonding agent for this composite system. The minimum torque showed a marginal increase with the resin concentration. The maximum–minimum torque showed only a marginal change with the resin. The scorch time decreased with the fiber concentration and resin content. The tensile strength and abrasion resistance were improved and the tear resistance and resilience were reduced with the resin concentration. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 532–539, 2006

Key words: composites; fibers; mechanical properties; nylon; rubber

INTRODUCTION

Short-fiber-reinforced rubber composites have obtained much attention because of processing advantages and improved mechanical properties. The properties of short-fiber-reinforced composites mainly depend on the type and concentration of the fiber, the orientation and distribution of the fiber after mixing, the aspect ratio of the fiber, and the degree of adhesion between the fiber and the matrix.[1–8] The fiber–matrix interfacial bond has a decisive effect on the service properties of composites. The role of the interface in fiber-reinforced polymers with natural fibers was reported by Mukherjea et al.[9] Different techniques have been employed to achieve a strong interface or good adhesion between fibers and matrices. Studies on interfacial adhesion with different short fibers and matrices were carried out earlier.[10–12] Geethamma et al.[13] found that the natural rubber/coir fiber interface bond could be improved by the addition of a resorcinol/hexamethylene tetramine dry-bonding system. The effect of a urethane resin on short polyester fiber/polyurethane composites was studied by Suhara et al.[14–16] Sreeja and Kutty[17] reported the effect of a urethane-resin-based bonding agent on styrene–butadiene rubber whole tire reclaim/short nylon fiber composites.

Rajeev et al.[18] studied the effect of a dry-bonding system in improving the interfacial bond in short melamine fiber/acrylonitrile–butadiene rubber (NBR) composites. The effect of a urethane bonding agent on NBR/reclaimed rubber/nylon 6 composites was studied by Sreeja and Kutty.[19] The effects of the fiber length and curing agents on the properties of short nylon fiber/NBR composite were studied by Rajesh et al.[20] Epoxy resins are well known for their adhesive properties, and their use as bonding agents in short-fiber composites has not been explored yet. In this article, we report the effect of an epoxy-based bonding agent on the cure characteristics and mechanical properties of short nylon 6 fiber/NBR composites.

EXPERIMENTAL

Materials

An epoxy resin (Lapox A31) with a density of 1.16 g/cc and a viscosity of 28,000 cP and a hardener (Lapox K30) were procured from Cibatul Ltd. (Gujarat, India). NBR with 33% acrylonitrile was supplied by Apar Polymers, Ltd. (Bombay, India). Nylon fiber obtained from SRF, Ltd. (Madras, India), was chopped to a length of approximately 6 mm. Zinc oxide (ZnO) was obtained from M/s Meta Zinc, Ltd. (Bombay, India). Stearic acid was procured from Godrej Soap (Pvt.), Ltd. (Bombay, India). Dibenzothiazyl disulfide (MBTS) was obtained from Bayer India, Ltd. (Bombay, India). Tetramethyl thiuramdisulfide (TMTD) was

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TABLE I
Formulation of the Mixes

Ingredient	Mix											
	A	B	C	D	E	F	G	H	I	J	K	L
NBR	100	100	100	100	100	100	100	100	100	100	100	100
Nylon	0	10	20	30	0	10	20	30	0	10	20	30
Resin[a]	0	0	0	0	3	3	3	3	5	5	5	5

[a] Epoxy resin formed by a 1 : 0.5 equiv combination of epoxy resin and amine-type hardener; zinc oxide (5 phr), stearic acid (4 phr), sulhur (0.7 phr), MBTS (1 phr), and TMTD (1.8 phr) were common to all of the mixes.

supplied by Nocil (Bombay, India). Sulfur was supplied by Standard Chemical Co. Private, Ltd. (Madras, India).

Processing

The formulation of the mixes is given in Table I.

The mixes were prepared according to ASTM Standard D 3182 (1989) on a two-roll, laboratory-size mixing mill. All the mixes were vulcanized at 150°C in an electrically heated hydraulic press to their respective cure times, as obtained from a Goettfert model 67.85 elastograph (Buchen, Germany). The cure rate was determined from the peak value of the first derivative plot of the cure curve. For thicker samples, sufficient extra cure time was given. Test pieces for tensile and tear properties were punched from the molded sheets along and across the grain direction. A schematic representation of the fiber orientation along and across the grain direction is shown in Figure 1. All the tests, except for the resilience and compression set, were carried out both along and across the direction of preferred orientation.
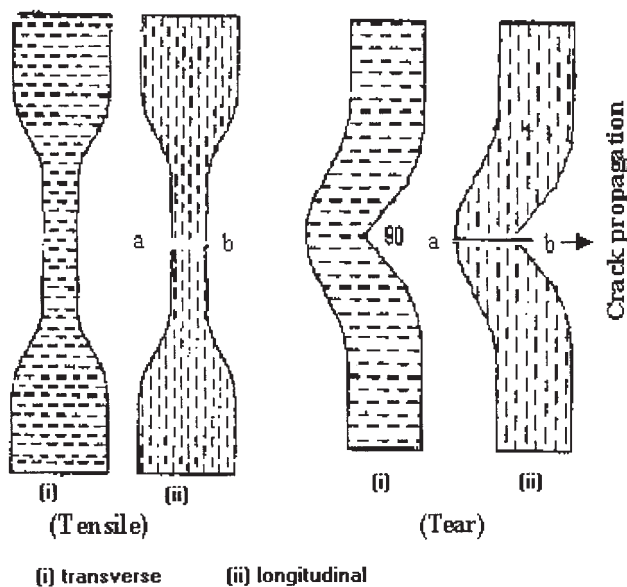
RESULTS AND DISCUSSION

Cure characteristics

Minimum torque

The variation of the minimum torque with the resin concentration at various fiber loadings is shown in Figure 2. The minimum torque shows only a marginal increase with increasing resin concentration for all fiber loadings (0–30 phr). This indicates that the processability of the composites is not much affected by the incorporation of the resin. Similar results have been reported earlier for short polyester fiber/polyurethane elastomer composites with a urethane bonding agent.[15]

Maximum–minimum torque

Upon the introduction of the resin, the maximum–minimum torque increases for all fiber loadings (Fig. 3). This may be due to better interaction of the fiber and matrix in the presence of the epoxy resin. At a 5 phr resin loading, there is a minor decrease in the maximum–minimum torque values. This may be due to the lower level of crosslinks formed in the presence of excess resin. The adverse effect of the resin at the 5 phr level on the cure is also reflected in the cure rate,
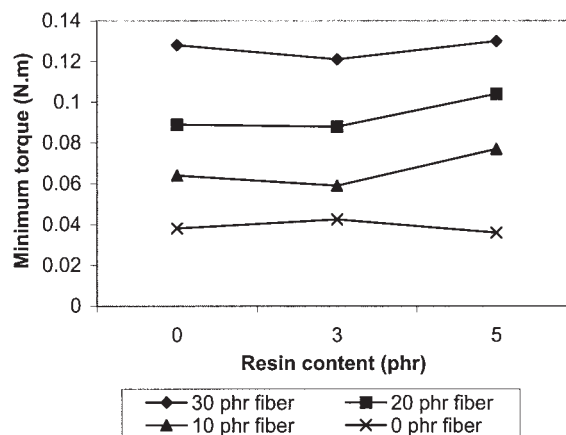

Figure 1 Schematic representation of the fiber orientation.

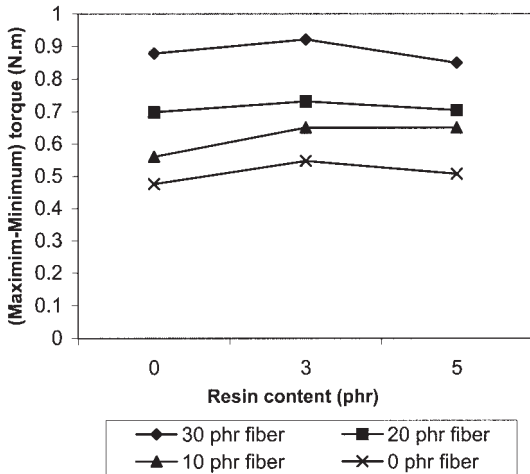**Figure 2** Variation of the minimum torque with the resin concentration.

Figure 3   Variation of the maximum–minimum torque with the resin concentration.
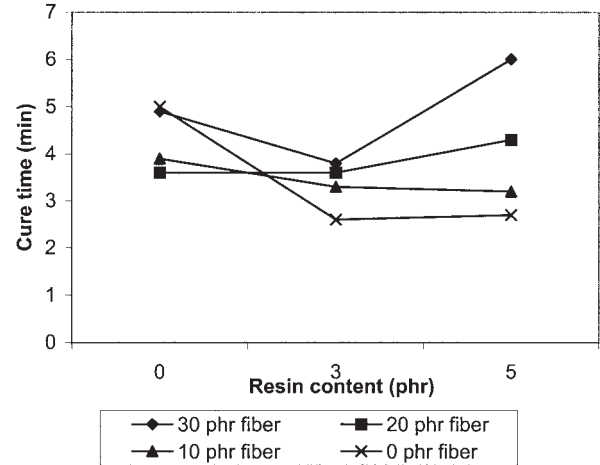

Figure 5   Variation of the cure time with the resin concentration

the increase in the elongation at break, and the lower resilience.

Scorch time and cure time

Figure 4 shows the variation of the scorch time with the resin content at different fiber loadings. The scorch time decreases sharply when the resin is introduced for all fiber concentration, and a further increase in the resin concentration causes only a slight decrease. The scorch time decreases from 2.9 to 1.7 min when the fiber concentration is increased from 0 to 30 phr in the absence of the resin. However, in the presence of 5 phr resin, all the composites have almost the same scorch time (0.8 min).

The cure time shows a drop at a 3 phr resin loading in all fiber loadings (Fig. 5). However, at a 5 phr resin
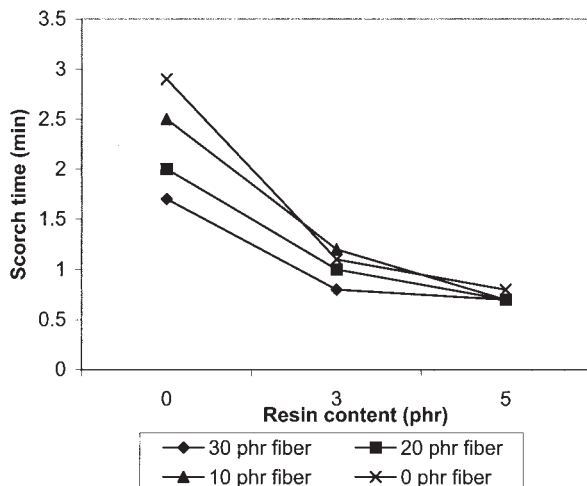
loading, the cure time is unaffected for the gum compound, whereas it increases for the composites. This effect is more pronounced in composites containing a higher proportion of fibers. At the 5 phr level, the resin is marginally in excess, and there seems to be some interference with the cure reaction resulting in a lower rate of cure and a higher cure time. The rate of the cure reaction shows a trend just the opposite of the cure time, with respect to an increasing resin loading (Fig. 6).

Mechanical properties

Tensile strength

The variation of the tensile strength with the resin concentration at various fiber loadings in longitudinal and transverse orientations of the fiber is shown in Figure 7(a,b), respectively. For the 30 phr fiber loaded composites, a resin concentration of 5 phr (mix L)
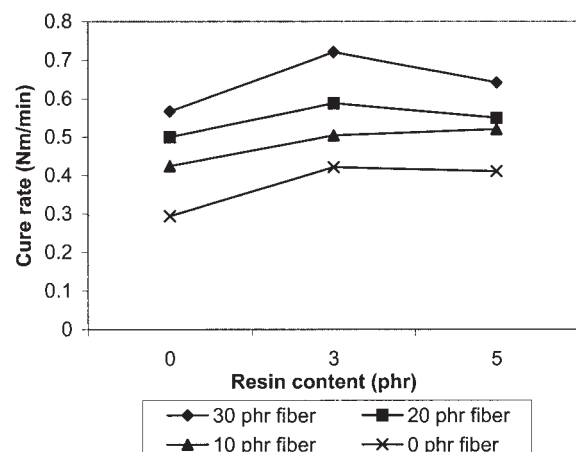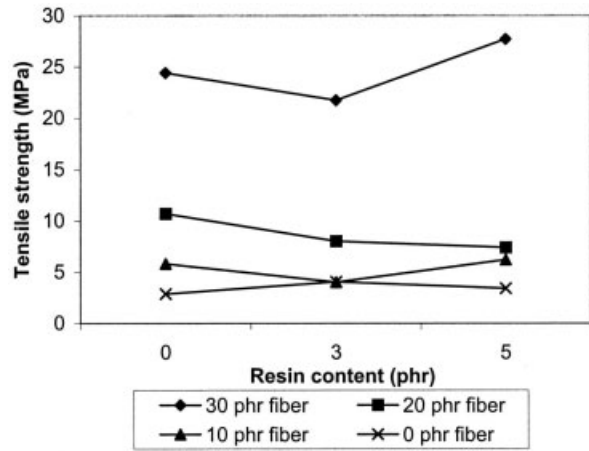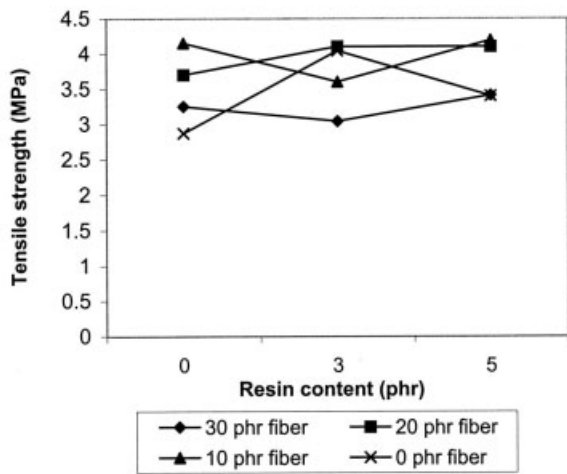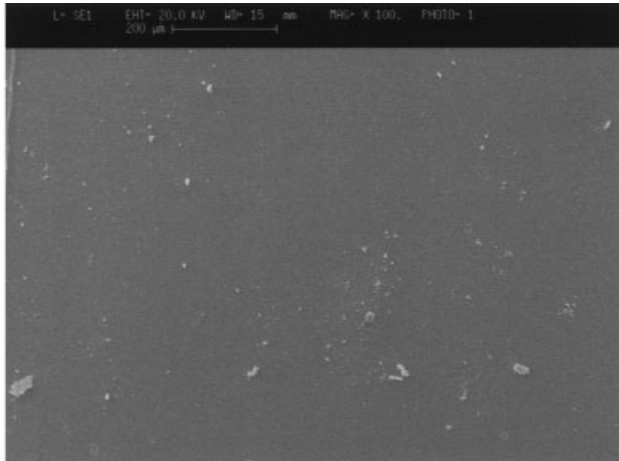

Figure 4   Variation of the scorch time with the resin concentration.

Figure 6   Variation of the cure rate with the resin concentration.
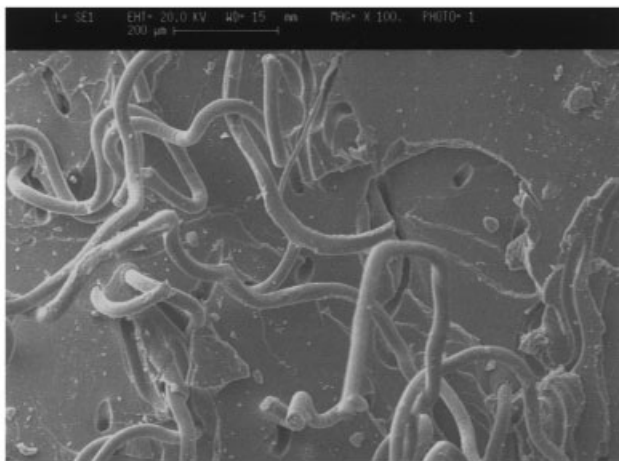
(a)

(c)

(b)

(d)

(e)

Figure 7 Variation of the tensile strength [(a) longitudinal and (b) transverse] with the resin concentration and SEM photographs of the tensile fracture surface of (c) mix A (original magnification = 100×, marker = 200 μ), (d) mix J (original magnification = 100×, marker = 200 μ), (e) mix J (original magnification = 500×, marker = 50 μ), (f) mix B (original magnification = 100×, marker = 200 μ), (g) mix B (original magnification = 500×, marker = 50 μ), and (h) mix L (original magnification = 100×, marker = 200 μ).

(f)

(g)
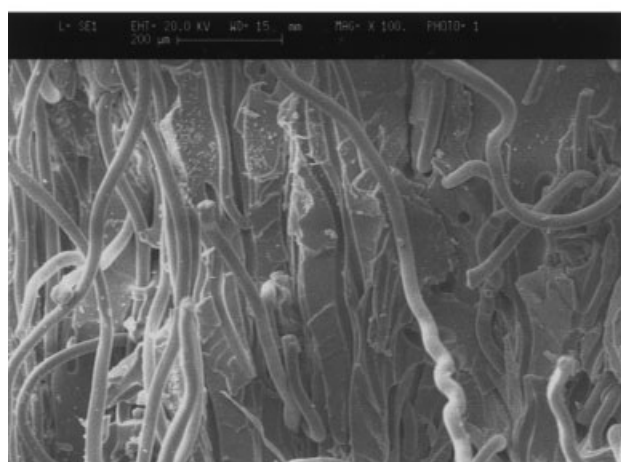
(h)

Figure 7 (*Continued from the previous page*)

gives maximum tensile strength. A similar trend is shown by the 10 phr fiber loading. This indicates that the epoxy resin provides effective interfacial bonding

for this composite. A proposed mechanism of bonding between the fiber and matrix in the presence of the resin is given in Scheme 1.

The marginal reduction in the tensile strength in the case of the 20 phr fiber loaded sample seems more from a scatter of experimental data points. In all cases, the tensile strength in the longitudinal direction is more than that in the transverse direction [Fig. 7(b)]. In the transverse direction, the fibers are less effective in restraining the matrix.

Figure 7(c) shows the scanning electron microscopy (SEM) photograph of the tensile fracture surface of gum vulcanizate. The fracture surface is smooth and has no crack propagation lines. This pattern is typical of weak matrices.

Figure 7(d,e) shows the SEM photographs of the tensile surface of the 10 phr fiber loaded sample containing 5 phr epoxy resin as a bonding agent (mix J) in the longitudinal orientation of the fibers, and Figure 7(f,g) shows the SEM photographs of the 10 phr fiber loaded compound without the resin (mix B). A large number of fiber ends and fiber pulled-out holes are visible in the case of mix J. The fibers are more firmly adhered to the matrix. Moreover, the fibers protruding out in the case of mix J are not clean. Some portion of the matrix is sticking to the surface of the fiber. However, in the case of mix B, the fiber surface is smooth and relatively clean, and the matrix is less mutilated. This suggests better fiber–matrix interfacial bonding in the presence of the resin and supports the higher tensile strength of mix J compared with that of mix B.

The tensile fracture surface of mix L with fibers in the transverse direction is shown in Figure 7(h). The fibers oriented in the horizontal plane are clearly visible in the figure. The channels formed by the fiber removal during fracture can be seen in the figure. This indicates that the fracture occurs by interface failure.
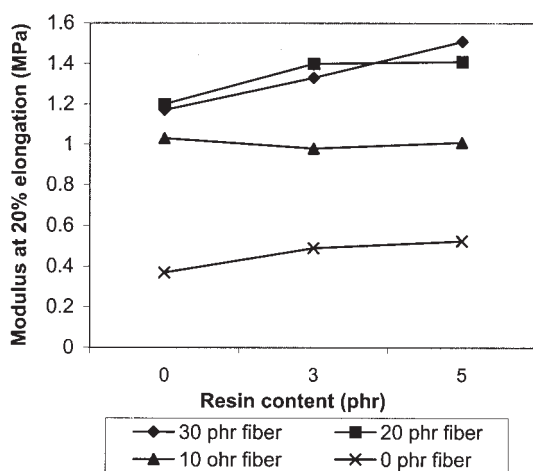
Modulus

The modulus at 20% elongation in the longitudinal orientation of the fiber increases as the resin concen-
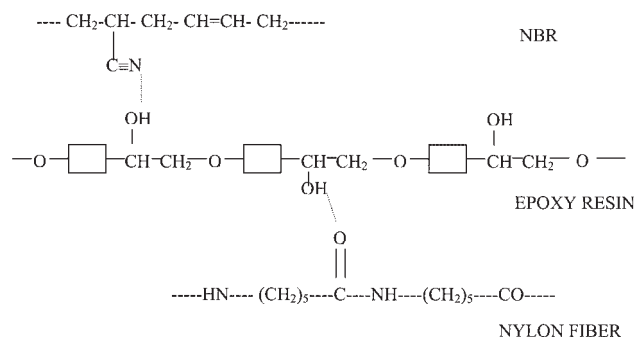
Scheme 1
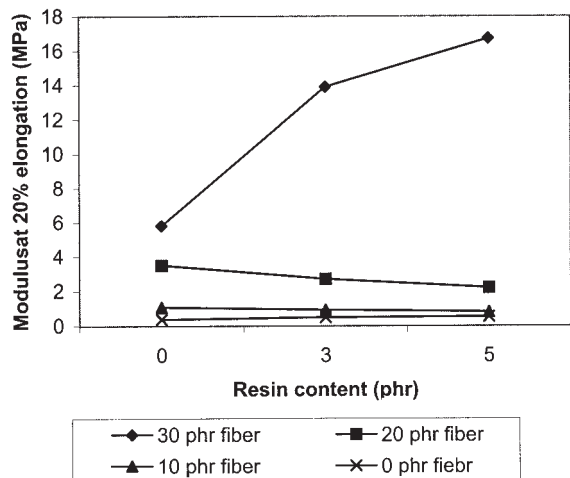
(a)

(b)

Figure 8 Variation of the modulus [(a) longitudinal and (b) transverse] with the resin concentration.

tration increases for a 30 phr fiber loading; this indicates a better restraint of the matrix by the improved fiber–matrix interfacial bond in the presence of the resin [Fig. 8(a)]. For a 0–20 phr fiber loading, the modulus remains more or less constant with the resin concentration. The modulus in the transverse direction does not show much variation with the resin content for all fiber concentrations [Fig. 8(b)].
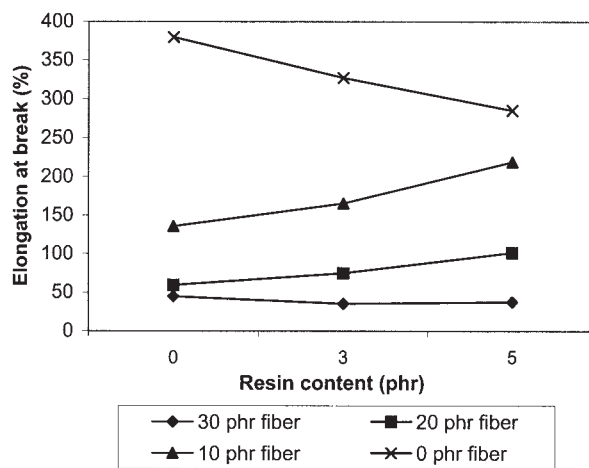
The variation of the elongation at break with the resin concentration in the longitudinal and transverse orientations of the fiber is shown in Figure 9(a,b), respectively. In the case of the composite, the elongation at break is marginally increased at a higher resin loading. As the fiber concentration increases, the effect of the resin loading on the elongation at break becomes insignificant, and the elongation at break remains constant at all resin loadings. This may be attributed partly to the plasticizing effect of the resin in the composites. At a lower fiber loading, the resin is in excess at 5 phr.

Tear resistance

The variation of the tear strength with the resin concentration in both the longitudinal and transverse directions is shown in Figure 10(a,b), respectively. The tear resistance decreases when the resin is introduced to a 30 phr fiber loaded composite, and upon a further rise in the resin concentration, the tear resistance remains unchanged. The tear strength is not much affected by the addition of the resin in the case of composites having a fiber loading of 0–20 phr.

Resilience

The resilience, an indication of material elasticity, shows a marginal decrease with the resin concentration for all fiber loadings (Fig. 11). The resilience decreases as the fiber concentration increases. The dissipation of energy at the fiber–matrix interface results in
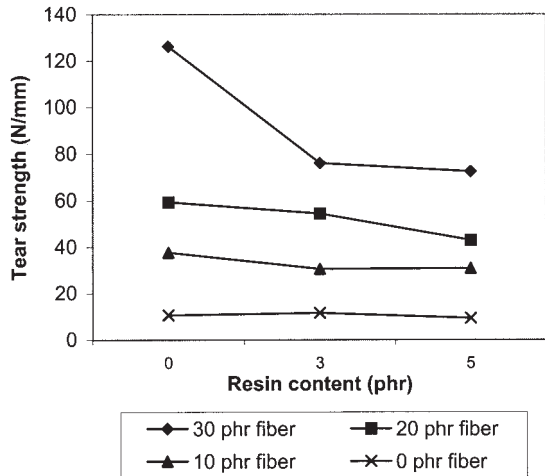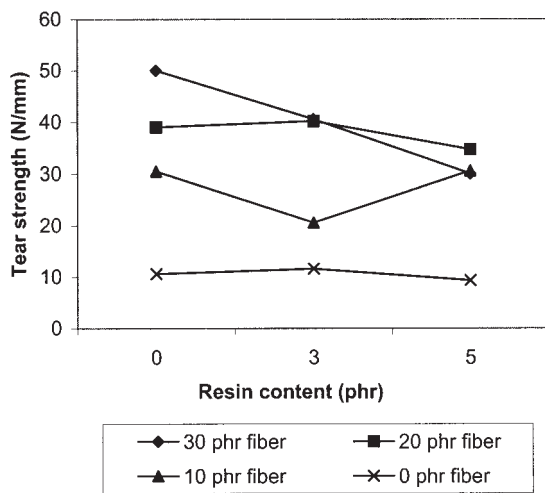

(a)
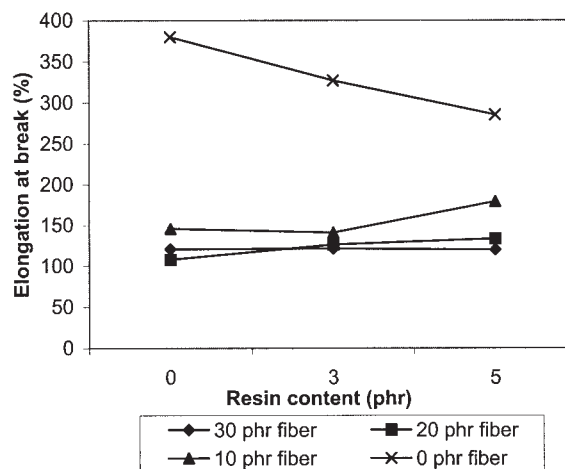
(b)

Figure 9 Variation of the elongation at break [(a) longitudinal and (b) transverse] with the resin concentration.

(a)

(b)

Figure 10 Variation of the tear strength [(a) longitudinal and (b) transverse] with the resin concentration.
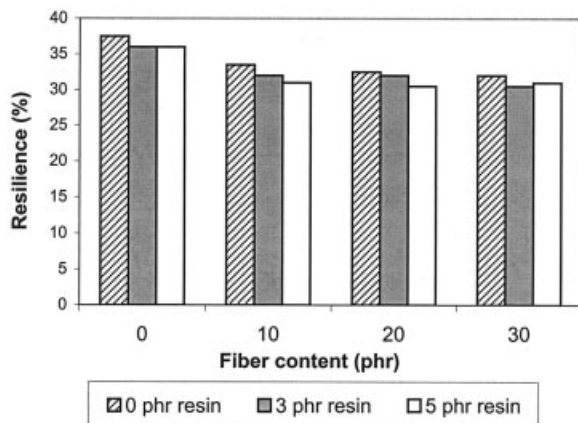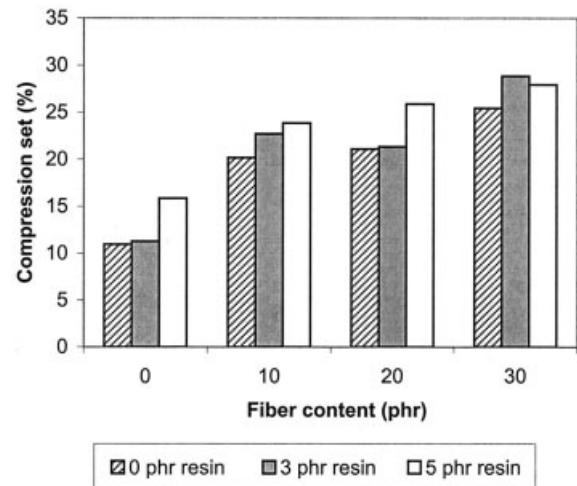

Figure 12 Variation of the compression set with the resin concentration.

a lower resilience value in the case of the composites. The compression set values increase with the resin concentration for all fiber concentrations (Fig. 12). This is in agreement with decreased resilience values.

Hardness

The hardness improves marginally with the resin concentration for composites with different fiber loadings (Fig. 13). It remains more or less constant in the case of a gum compound.

Abrasion loss

Figure 14(a,b) shows the variation of the abrasion loss with the resin concentration in the longitudinal and transverse orientations of the fiber, respectively. The
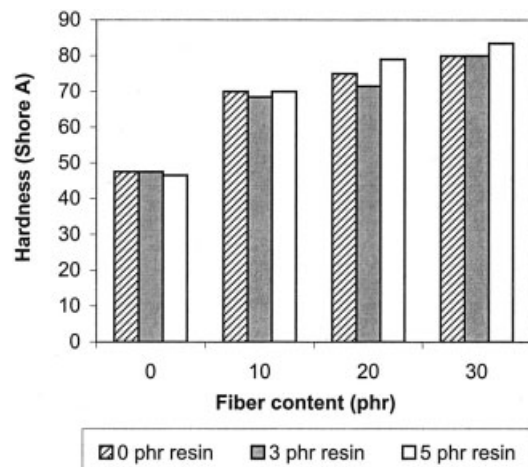

Figure 11 Variation of the resilience with the resin concentration.

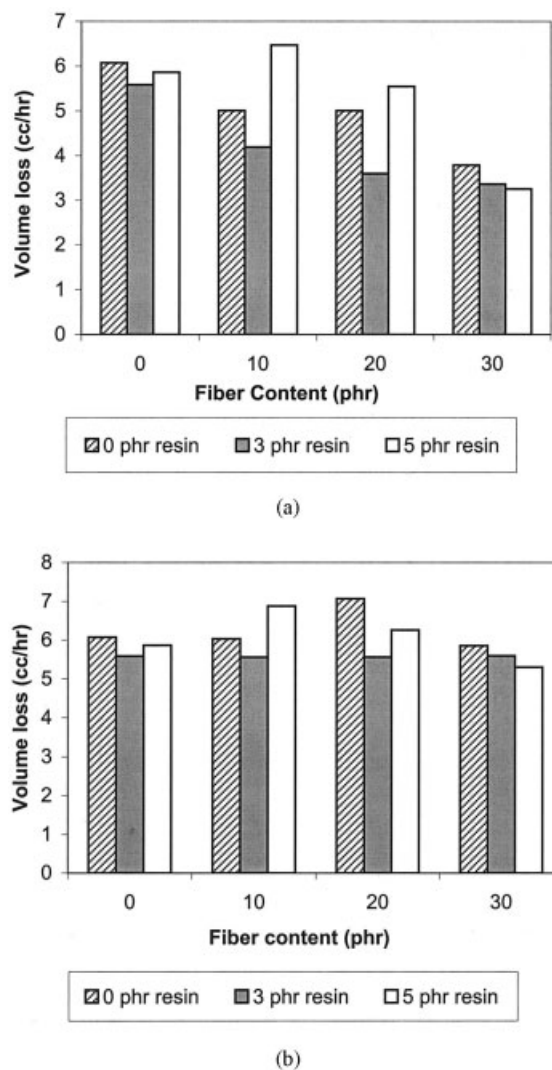**Figure 13** Variation of the hardness with the resin concentration.

Figure 14 Variation of the abrasion loss [(a) longitudinal and (b) transverse] with the resin concentration.

abrasion resistance is improved in the presence of the resin. Up to a 3 phr resin loading, the abrasion loss decreases in both the longitudinal and transverse directions for all fiber concentrations, indicating the formation of good interfacial bonding between the fiber and matrix, which resists the debonding of the fiber. However, a further increase in the resin content shows an increase in the abrasion loss at lower fiber concentrations (0–20 phr) in both the transverse and longitudinal directions, whereas at a 30 phr fiber loading,

the abrasion loss decreases with the resin concentrations. This indicates that for a lower fiber loading, 5 phr resin is excess.

CONCLUSIONS

An epoxy resin is an effective interfacial-bonding agent for short nylon 6/NBR composites. The mechanical properties of the composite are, in general, improved in the presence of an epoxy resin. The maximum–minimum torque changes only marginally with the resin concentration, whereas the scorch time decreases with the resin concentration. The minimum torque is not much affected by the presence of the resin. The tensile strength and modulus increase with the resin content. The abrasion loss decreases with an increase in the resin concentration. The tear and resilience decrease and the compression set increases as the resin content increases.

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