

Studies on Acrylonitrile Butadiene Rubber – Short Nylon Fiber Composites

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ABSTRACT: Acrylonitrile butadiene rubber (NBR) matrix was reinforced with different levels of short nylon fiber loading. Cure characteristics and mechanical properties of composites in longitudinal and transverse directions have been studied. Cure time was reduced while processability, as indicated by the minimum torque, was marginally reduced with increase in fiber loading. Tensile and tear properties improved with fiber concentration and the values were higher in longitudinal direction of fiber orientation. Abrasion resistance, resilience and compression set were increased in presence of fibers. Elongation at break values showed a drastic drop on introduction of fibers. Heat build up was higher for composites.

KEY WORDS: acrylonitrile butadiene rubber, fiber, composite, cure characteristics, mechanical properties.

INTRODUCTION

THE REINFORCEMENT OF rubber with short fibers offers strength and stiffness compared to the soft and tough rubber matrix. Recently short fiber reinforced rubber has gained importance due to its advantages like design flexibility, anisotropy in technical properties, stiffness, damping and processing economy [1-9]. The properties of short fiber reinforced composites mainly depend on the type and concentration of the fiber, the orientation and distribution of the fiber

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after mixing, the aspect ratio of the fiber and the degree of adhesion between the fiber and matrix [10-18]. Short jute fiber reinforced rubber composites have been studied by Murty et al. [9]. Short silk fiber reinforced polychloroprene rubber and natural rubber have been studied by Setua et al. [19,20]. They have reported that the addition of fibers affects the processing characteristics of the composites and there is an improvement in tensile strength. Senapati et al. have studied the effect of fiber concentration, orientation and L/D ratio on the properties of short polyester fiber natural rubber composite [21]. Properties like tensile strength, abrasion resistance, hardness were increased with fiber content. Polyester fiber reinforced ethylene propylene rubber was studied by Furukawa et al. [22]. However, a systematic study of short fiber reinforced acrylonitrile butadiene rubber (NBR) composites is found to be lacking. In the present work, we investigate the cure characteristics and mechanical properties of short nylon fiber reinforced NBR composites.

EXPERIMENTAL

Materials

NBR used in this study was obtained from Apar Polymers Ltd., India. Nylon fiber obtained from SRF Ltd., Madras was chopped to approximately 6 mm length. Zinc oxide (ZnO) was obtained from M/s, Meta Zinc Ltd., Bombay. Stearic acid was procured from Godrej Soap (Pvt.) Ltd., Bombay, India. Dibenzothiazyl disulfide (MBTS) and 1,2-dihydro 2,2,4-trimethyl quinoline (HS) were obtained from Bayer India Ltd., Bombay. Tetramethyl thiuramdisulfide (TMTD) was supplied by NOCIL, Bombay, India. Sulfur was supplied by Standard Chemical Company Private Ltd., Madras.

Processing

Formulation of mixes is given in Table 1. The mixes were prepared as per ASTM 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 Goettfert Elastograph Model 67.85. For thicker samples sufficient extra cure time was given. Test pieces for tensile and tear properties were punched from the molded sheet along and across the grain direction. The schematic representation of fiber orientation along and across the grain direction

Table 1. Formulation of the mixes.

Ingredient	Mix No			
	A	B	C	D
NBR	100	100	100	100
Short nylon fiber	0	10	20	30

NBR-Acrylonitrile butadiene rubber. (Zinc oxide - 4 phr, Stearic acid - 2 phr, HS (1,2-dihydro 2,2,4-trimethyl quinoline) - 1 phr, MBTS (dibenzothiazyl disulfide) - 0.5 phr, TMTD (tetramethylthiuram disulfide) - 1.8 phr and Sulfur - 0.3 phr are common to all mixes).

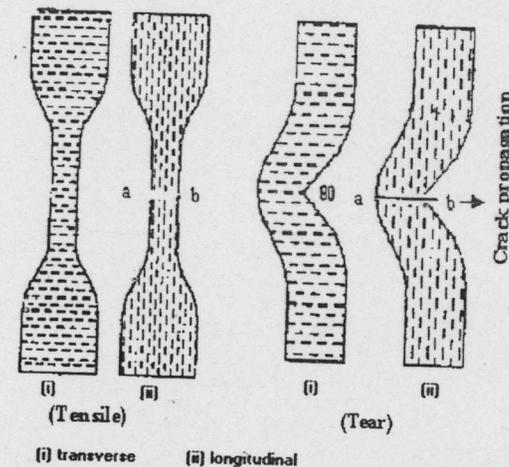


FIGURE 1. Schematic representation of fiber orientation.

are shown in Figure 1. All the tests except resilience and compression set were carried out both along and across the direction of preferred orientation. Tensile properties were determined using a Zwick Universal Testing Machine model 1445 according to ASTM D 412 (die E). Tear strength also was determined using Zwick UTM. Abrasion resistance was determined using a DIN abrader as per DIN 53516, using a sample of diameter 12 mm under a load of 10 N. Resilience was determined as per ASTM 2832-88 while the heat build up was determined according to ASTM D 623-78 method A. The compression set was determined as per ASTM D 395-86 method B. The samples were aged for 48 h at 70°C in an ageing oven to determine the ageing resistance of the composite.

RESULTS AND DISCUSSION

Cure Characteristics

MINIMUM TORQUE

The variation of minimum torque with fiber loading is shown in Figure 2. The minimum torque increases linearly with increase in fiber concentration, indicating that the processability of the composite is adversely affected by the introduction of fibers.

(MAXIMUM-MINIMUM) TORQUE

Figure 3 shows the variation of (maximum–minimum) torque values of the composites. The (maximum–minimum) torque values increase from 0.253 N m at 0 phr to 0.489 N m at 30 phr fiber, indicating a more restrained matrix in the case of composites.

SCORCH TIME AND CURE TIME

Scorch time showed a reduction from 2.85 min at 0 phr to 2.1 min at 30 phr (Figure 4). Cure time is reduced from 8 min at 0 phr to 5.85 min at 30 phr (Figure 5). The reduced cure time is accompanied by the increased cure rate values (Figure 6). The cure rate values increased from 0.0842 N m/min at 0 phr to 0.2256 N m/min at 30 phr. That both the scorch time and cure time are reduced indicates that the presence of

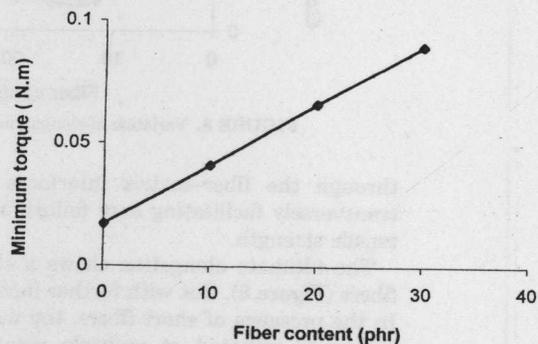


FIGURE 2. Variation of minimum torque with fiber loading.

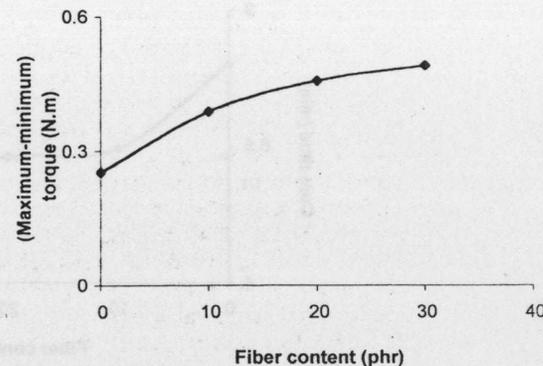


FIGURE 3. Variation of (maximum–minimum) torque with fiber loading.

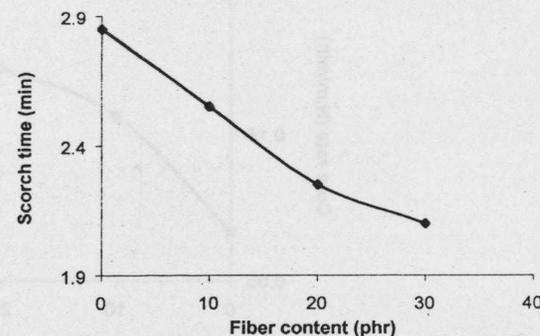


FIGURE 4. Variation of scorch time with fiber loading.

short nylon fibers is accelerating the cure reaction. This may be attributed to the possibility of generation of amines from nylon fibers by degradation at the curing temperature.

Mechanical Properties

Figure 7 shows the variation of tensile strength of NBR with different fiber content. The tensile strength is found to increase linearly with increase in fiber loading. This is in contrast to the pattern reported for short Nylon fiber – NR composites, where the tensile strength–fiber

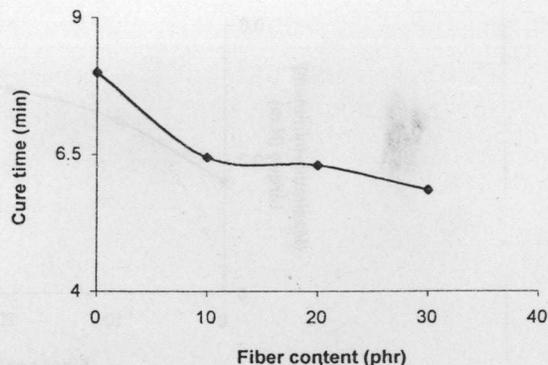


FIGURE 5. Variation of cure time with fiber loading.

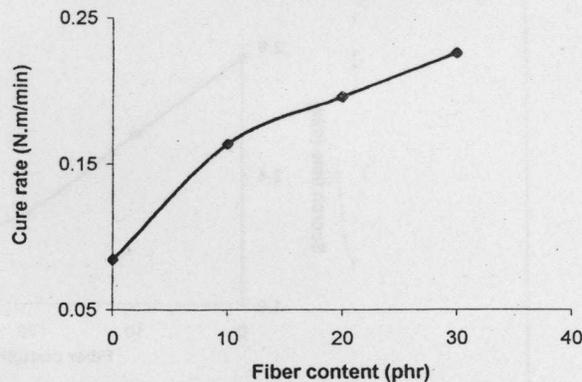


FIGURE 6. Variation of cure rate with fiber loading.

relationship was non-linear with a minimum at lower fiber concentrations. This arises mainly from the fact that NR matrix has high gum strength arising out of strain induced crystallisation whereas NBR has a relatively lower gum strength. In the former case, at lower fiber loadings, the dilution effect due to physical presence of short fibers contributes to the initial reduction in tensile strength whereas in the case of NBR the variation is linear. At any given fiber loading mixes with longitudinal fiber orientation show higher tensile strength than mixes with transversely oriented fibers. The growing crack can easily pass

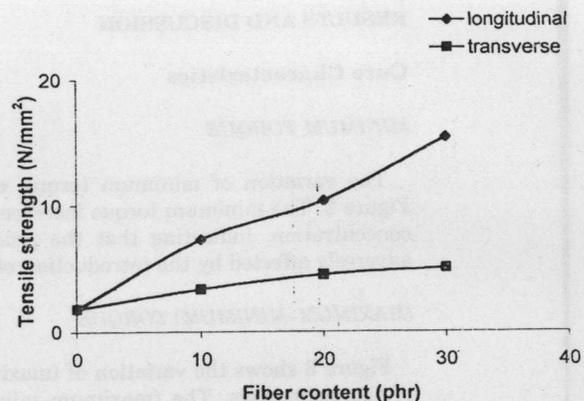


FIGURE 7. Variation of tensile strength with fiber loading.

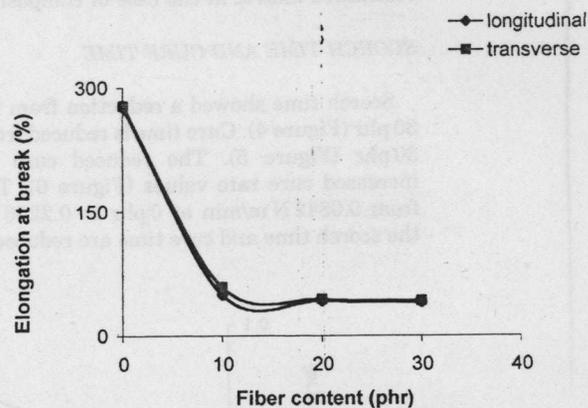


FIGURE 8. Variation of elongation at break with fiber loading.

through the fiber-matrix interfaces when the fibers are oriented transversely facilitating easy failure of the sample, resulting in lower tensile strength.

The ultimate elongation shows a sharp fall on the introduction of fibers (Figure 8). But with further increase, the values tend to stabilize. In the presence of short fibers, the matrix is more restrained and the failure is initiated at multiple points, resulting in lower ultimate elongation values.

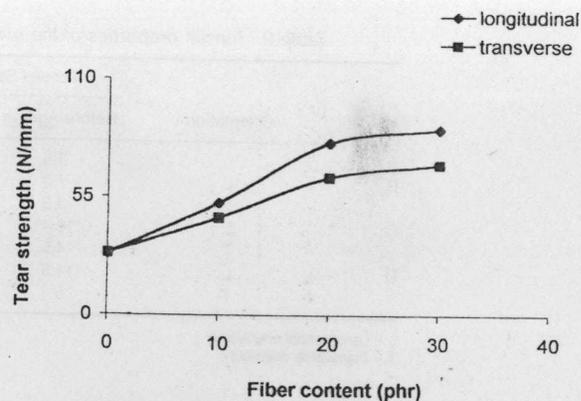


FIGURE 9. Variation of tear strength with fiber loading.

Tear strength is found to increase with fiber content in both the orientations of fibers (Figure 9). As fiber concentration increases, there is more and more hindrance to the propagating tear by the fibers and hence the improvement in tear strength. The tear strength values are higher in the longitudinal direction at all fiber loadings. In the case of transversely oriented fibers, most of them being parallel to the propagating crack front, offers less resistance to propagating tear and hence the lower tear strength values.

The heat build up values of the composites are given in Figure 10. The heat build up values in both the orientations of fibers increased with fiber content. At all fiber loadings, the heat build up was higher for the longitudinally oriented fiber samples than the samples with fibers oriented transversely. The higher heat generation in the longitudinally oriented fiber samples can be attributed to higher stiffness of the samples in that direction. In the case of 30 phr fiber loaded sample, where fibers are oriented transversely to the direction of strain, the crack generated inside could grow fast along the fiber-matrix interface as the matrix was soft. This resulted in the premature failure of the sample at 30 phr.

Resilience shows a marginal improvement on introduction of fibers (Figure 11). But with further increase in fiber loading, it remains unchanged. This may be attributed to the relatively lower elasticity of the gum compound. The acrylonitrile part of the NBR contributes to the lower resilience of NBR. The short fibers restrains the matrix and the resilience is improved marginally.

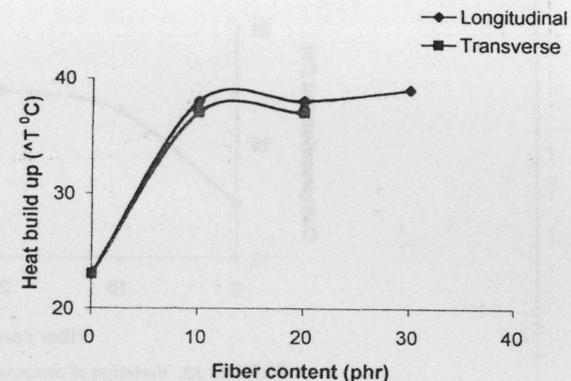


FIGURE 10. Variation of heat build up with fiber loading.

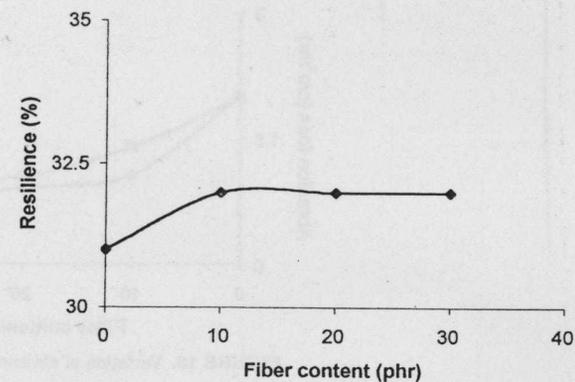


FIGURE 11. Variation of resilience with fiber loading.

Compression set increased with increase in fiber concentration (Figure 12). This trend is in contrast to the pattern observed in the case of resilience. This is because, the compression set test is conducted at elevated temperature whereas the resilience is a room temperature test.

The abrasion resistance registers an improvement with increasing fiber loading (Figure 13). This is due to the more restrained matrix in

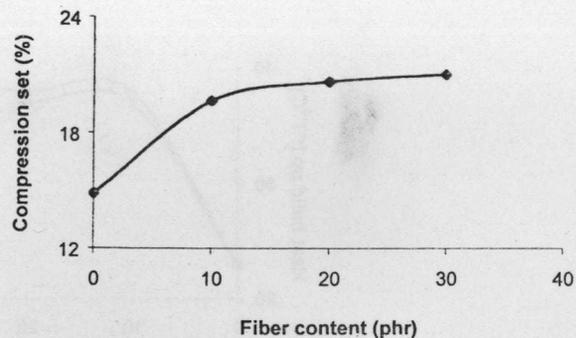


FIGURE 12. Variation of compression set with fiber loading.

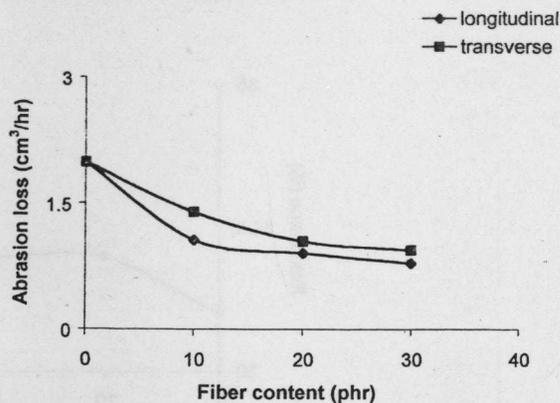


FIGURE 13. Variation of abrasion loss with fiber loading.

the case of composite. Abrasion loss is found to be higher in the case of longitudinally oriented specimens. In transverse direction, the fibers get debonded and separated from the matrix more easily than in samples with transversely oriented fibers while being abraded through the abrader surface.

Ageing Resistance

The tensile strength shows retention values above 100 (Table 2). This can be attributed to a post curing effect as the cure pattern of NBR is a

Table 2. Tensile properties of the mixes before and after ageing.

Mix No	Orientation	Tensile Strength (N/mm ²)		Percentage Retention
		Before Ageing	After Ageing	
A		1.8	2.2	120
B	L	7.3	11.2	154
	T	3.3	3.8	114
C	L	10.4	12.8	123
	T	4.5	6.0	135
D	L	14.3	16.4	117
	T	5	6.2	123

L - Longitudinal orientation.
T - Transverse orientation.

Table 3. Elongation at break values of the mixes before and after ageing.

Mix No	Orientation	Elongation at Break (%)		Percentage Retention
		Before Ageing	After Ageing	
A		278.0	292.0	105
B	L	49.0	52.4	107
	T	58.8	61.9	105
C	L	41.6	41.3	99
	T	43.9	37.4	85
D	L	40.1	43.2	108
	T	41.8	41.3	99

L - Longitudinal orientation.
T - Transverse orientation.

marching cure. The fiber filled mixes (mixes B-D) show retention values higher than that of the gum compound. This indicates an improvement in the fiber matrix interfacial bond during the ageing.

The elongation at break values of all the mixes are affected only marginally by ageing (Table 3).

The tear resistance of the gum compound (mix A) is reduced while that of all the fiber filled mixes (mixes B-D) are improved by ageing at elevated temperature (Table 4). This is because, the tear resistance of an elastomer is better when the matrix is slightly under cured. Since ageing leads to further cure in the case of NBR, the tear resistance of mix A is lower after ageing. For the fiber filled samples, since the fibers compensate for such losses with interfacial bonding that is improved during ageing, the retention values are better.

Table 4. Tear properties of the mixes before and after ageing.

Mix No	Orientation	Tear Strength (N/mm)		Percentage Retention
		Before Ageing	After Ageing	
A		28.9	21.5	74
B	L	52.2	71.3	136
	T	45.3	48.2	107
C	L	80.3	87.2	108
	T	64.3	66.8	104
D	L	86.6	92.1	106
	T	70.2	75.2	107

L - Longitudinal orientation.
T - Transverse orientation.

CONCLUSIONS

The introduction of short fibers to the NBR matrix increases the minimum torque, (maximum-minimum) torque and cure rate. Scorch time and cure time decrease with increase in fiber content. Mechanical properties of the composite vary with fiber concentration and orientation. Properties like tensile strength, tear strength and abrasion resistance increase with fiber concentration and are higher in the longitudinal direction. An increase in fiber concentration decreases the resilience and compression set.

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REFERENCES

1. Coran, A.Y., Hamed, P. and Goettler, L.A. (1976). *Rubber Chem. Technol.*, **49**: 1167.
2. Boustany, K. and Arnold, R.L. (1976). *J. Elastoplast.*, **8**: 160.
3. Brokenbrow, B.E., Simens, D. and Stokoe, A.G. (1969). *Rubber J.*, **151**: 51.
4. Derringer, G.C. (1971). *J. Elastoplast.*, **3**: 230.
5. O' Connor, J.E. (1977). *Rubber Chem. Technol.*, **50**: 945.
6. Coran, A.Y., Boustany, K. and Hamed, P. (1974). *Rubber Chem. Technol.*, **47**: 396.

7. Coran, A.Y., Boustany, K. and Hamed, P. (1975). *J. Appl. Polym. Sci.*, **15**: 2471.
8. Chakraborty, S.K., Setua, D.K. and De, S.K. (1982). *Rubber Chem. Technol.*, **55**: 1286.
9. Murty, V.M. and De, S.K. (1982). *Rubber Chem. Technol.*, **55**: 287.
10. Murty, V.M. and De, S.K. (1982). *J. Appl. Polym. Sci.*, **27**: 4611-4622.
11. Akthar, S., De, P.P. and De, S.K. (1986). *J. Appl. Polym. Sci.*, **32**: 5123-5146.
12. Roy, R., Bhowmick, A.K. and De, S.K. (1993). *J. Appl. Polym. Sci.*, **49**: 263.
13. Derringer, G.C. (1971). *Rubber World*, **165**: 45.
14. Ibarra, L. (1993). *J. Appl. Polym. Sci.*, **49**(9): 1595-1600.
15. Guo, W. and Ashida, M. (1993). *J. Appl. Polym. Sci.*, **49**(6): 1081-1091.
16. Ibarra, L., Maciass, A. and Palma, E. (1995). *Kautsch. Gummi Kunstst.*, **48**(3): 180-184.
17. Miwa, M. and Heriba, N. (1994). *J. Maier. Sci.*, **29**(4): 973-977.
18. Pegorano, M. and Dilandro, L. (1992). *34th International Seminar on Macromolecules*. 193.
19. Setua, D.K. and Dutta, B. (1984). *Rubber Chem. Technol.*, **29**: 3097-3114.
20. Setua, D.K. and Dutta, B. (1983). *Rubber Chem. Technol.*, **56**: 808.
21. Senapati, A.K., Kutty, S.K.N., Pradhans, B. and Nando, G.B. (1989). *Inter. J. Polymeric Mater.*, **12**: 203.
22. Furukawa, Masatsugu, Walanabo, Hirotsuke, Takada and Tadahiko (October 1996). *Jpn. Kokai Tokkyo Koho* 28 April. 1998. Appl. 96/264,269.4, p. 8.