

REFERENCES

- [1] Askarov, M. A., Ibragimova, G. T. and Mirkamilova, M. S. (1973). *Uzb. Khim. Zh.*, **17**, 55; *Chem. Abstr.*, **80**, 27535s (1974).
- [2] Asharov, M. A., Ibragimova, G. T. and Mirkamilova, M. S. (1973). (USSR), Deposited Doc, VINITI 7076-73, 9 p.
- [3] Hojyo, N. and Kotera, M. (1952). *J. Chem. Soc. Jpn. Ind. Chem. Sect.*, **55**, 733.
- [4] Mikamilov, M. S., Ibragimova, G. T. and Dazhalilov, A. T. (1970). *Uzb. Khim. Zh.*, **14**, 84; *Chem. Abstr.*, **74**, 76892r (1971).
- [5] Asharov, M. A., Mirkamilova, M. S. and Ibragimov, G. T., (1972). *Tr. Tashk. Politekh. Inst.*, **90**, 126; *Chem. Abstr.*, **83**, 132378c (1975).
- [6] Sumita, Y., Seko, S., Watanable, M. and Misumi, T. K. (1960). *Jpn. Pat.*, 7195, (August 23, 1958); *Chem. Abstr.*, **54**, 1770e (1960).
- [7] Lorentz, G. and Heuck, C. (1961). *Ger. Pat.*, 1,110,407; *Chem. Abstr.*, **55**, 25363c (1961).
- [8] Orobchenko, Ev., Pryanichnikova, N. Yu. and Latyshko, Tk. (1964). *USSR Pat.*, 161, 923; *Chem. Abstr.*, **61**, 10841gh (1964).
- [9] Jpn. Kokai 7460393 (1974). (to Frain Plastics Inc.); *Chem. Abstr.*, **84**, 122852j (1976).
- [10] Horosawa, F. N. (1975). U.S. Pat. 3,917,702 (to Furan Plastics Inc.); *Chem. Abstr.*, **84**, 45383c (1977).
- [11] Berlin, A. A., Liogorikii, B. I., Zapadinskii, B. I., Kazantzeva, E. A. and Stankevich, A. O. (1977). *J. Macromol. Sci. Chem.*, **A11**, 1.
- [12] Lewis, K. C. and Mulquiney, E. (1970). *Aust. J. Chem.*, **23**, 2315.
- [13] Patel, H. S. and Majmudar, G. H. (1991). *J. Appl. Polym. Sci.*, **43**, 2091.
- [14] Vogel, A. I. (1979). "A Textbook of Practical Organic Chemistry", 4th edn., Longmans, New York.
- [15] Patel, H. S. and Lad, M. J. (1995). *J. Polym. Materials*, **28**, 161.
- [16] Chatterjee, S. K. and Puchav, L. D. (1974). *J. Macromol. Sci. Chem.*, **A8**, 415.
- [17] Patel, R. N. and Patel, S. R. (1981). *Angew. Makromol. Chem.*, **96**, 85.
- [18] Stenhouse, J. (1970). *Justus Liebigs Ann. Chem.*, **156**, 199.
- [19] Belamy, L. J. (1975). "Infrared Spectra of Complex Molecules", Capman and Hall, London.
- [20] (a) Fuoss, R. M. and Strauss, U. P. (1948). *Ann. N.Y. Acad. Sci.*, **51**, 836; (b) Fuoss, R. M. and Straus, U. P. (1981). *J. Polym. Sci.*, **3**, 246.
- [21] Patel, H. S., Patel, R. N. and Patel, S. R. (1981). *Angew. Makromol. Chem.*, **99**, 125.
- [22] Malm, B. (1982). *Angew. Makromol. Chem.*, **107**, 142.
- [23] Lewis, K. G. (1957). *J. Chem. Soc.*, 531.
- [24] Yasudas, H., Hayashi, T. and Midorikawa, W. (1970). *J. Org. Chem.*, **35**, 1234.
- [25] Blatt, A. H. and Cross, N. (1964). *J. Org. Chem.*, **29**, 3306.

CURE CHARACTERISTICS AND MECHANICAL PROPERTIES OF SHORT NYLON FIBER REINFORCED ACRYLONITRILE BUTADIENE RUBBER/RECLAIMED RUBBER BLENDS

T. D. Sreeja
S. K. N. Kutty

Department of Polymer Science and Rubber Technology,
Cochin University of Science and Technology,
Cochin, India

Cure characteristics and mechanical properties of short nylon fiber reinforced acrylonitrile butadiene rubber-reclaimed rubber composites were studied. Minimum torque, (maximum-minimum) torque and cure rate increased with fiber concentration. Scorch time and cure time decreased by the addition of fibers. Properties like tensile strength, tear strength, elongation at break, abrasion loss and heat build up were studied in both orientations of fibers. Tensile and tear properties were enhanced by the addition of fibers and were higher in the longitudinal direction. Heat build up increased with fiber concentration and were higher in the longitudinal direction. Abrasion resistance was improved in presence of short fibers and was higher in the longitudinal direction. Resilience increased on the introduction of fibers. Compression set was higher for blends.

Keywords: acrylonitrile butadiene rubber, reclaimed rubber, blend, composite

INTRODUCTION

The recycling of scrap rubber and used rubber has been practiced by rubber industry by conversion to reclaimed rubber. Reclaimed rubber is a high grade compounding ingredient which is attractive in its price. Reclaimed rubber is an effective and versatile source of rubber hydrocarbon and it can be used to partly substitute virgin material in

Received 9 November 2000; in final form 13 November 2000.

T. D. Sreeja is grateful to CSIR, Government of India for financial assistance.

Address correspondence to S. K. N. Kutty, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin 682 022, India.

E-mail: sunil@cusat.ac.in

rubber compounds. One of the drawbacks of such blend is a relatively weaker matrix. One way to overcome this problem is by the use of short fibers, a waste product from textile industry. The reinforcement of rubber compounds with short fibers has become necessary in many products, especially in the tyre, hose and belt industries. Short fiber rubber composites preserve the characteristics of both the elastic behaviour of rubber and the strength and stiffness of the reinforcing fibers [1-3]. The properties of short fiber reinforced composites mainly depend on the type and concentration of fiber, the orientation and the distribution of fiber after mixing, the aspect ratio of fiber, and the degree of adhesion between the fiber and the matrix [4-14]. Polyester fibers as reinforcing agents for ethylene propylene rubber have been studied by Furukawa et al. [15]. Coir fiber reinforced NR composites have been studied by Geethamma et al. [16]. Recently mechanical properties of short polyester-polyurethane elastomer composites have been studied by Suhara et al. [17]. Varghese have studied the cure characteristics and mechanical properties of short sisal-fiber natural rubber composites [18]. In our earlier work we have found that a 90:20 blend of NBR:WTR was optimum. In the present work we report the results of our investigations on short nylon fiber reinforcement of 90:20 NBR:WTR blend. The fiber loading was varied from 0-30 phr.

EXPERIMENTAL

Materials Used

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. Reclaim (WTR) was supplied by Kerala Rubber and Reclaims, Mamala, India. The characteristics of reclaim used are given in Table 1. 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

TABLE 1 Characteristics of WTR

Parameter	Value
Acetone extract (%)	13
Carbon content (%)	39

TABLE 2 Formulation of the Mixes

Ingredient	Mix no.			
	A	B	C	D
NBR	90	90	90	90
WTR	20	20	20	20
Nylon short fibers	0	10	20	30

NBR - Acrylonitrile Butadiene rubber, WTR - Whole Tyre Reclaim (Zinc oxide - 4 phr, Stearic acid - 2 phr, HS - 1 phr, MBTS - 0.5 phr, TMTD - 1.8 phr and Sulfur - 0.3 phr are common to all mixes).

NOCIL, Bombay, India. Sulfur was supplied by Standard Chemical Company Private Ltd., Madras.

Processing

Formulation of mixes is given in Table 2. These mixes were prepared as per ASTM D 3182 (1989) on a laboratory size two roll mixing mill.

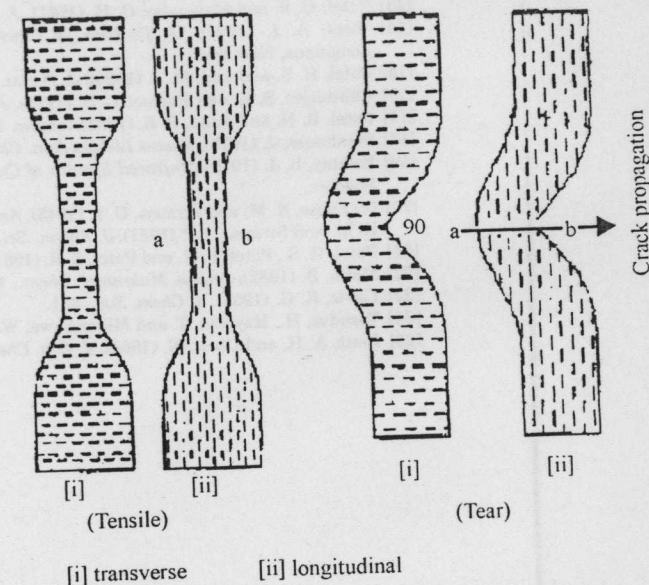


FIGURE 1 Schematic representation of fiber orientation.

Fibers were oriented preferentially in one direction by passing once through tight nip at the end of the mixing process. Schematic representation of fiber orientation in tensile and tear test samples is shown in Figure 1. Cure characteristics were determined using Goettfert Elastograph Model 67.85 at 150°C. All mixes were vulcanized in an electrically heated hydraulic press at 150°C and at a pressure of 180 kg/cm². Ageing was carried out at 70°C for 48 hour in an ageing oven. All the tests, except resilience and compression set were carried out both along and across the grain direction.

RESULTS AND DISCUSSION

Figure 2 shows the variation of minimum torque with fiber loading. The minimum torque increases from 0.021 N.m. at 0 phr to 0.08 N.m. at 30 phr fiber loading indicating the loss in processability of the composite on the introduction of fibers. Minimum torque is related to the processability of the compound. Increasing minimum torque with increasing fiber content indicates that the fiber restricts the free flow of chains.

(Maximum–minimum) torque values of the composites are given in Figure 3. (Maximum–minimum) torque values increase from 0.2057 N.m. at 0 phr to 0.42 N.m. at 30 phr fiber loading indicating a

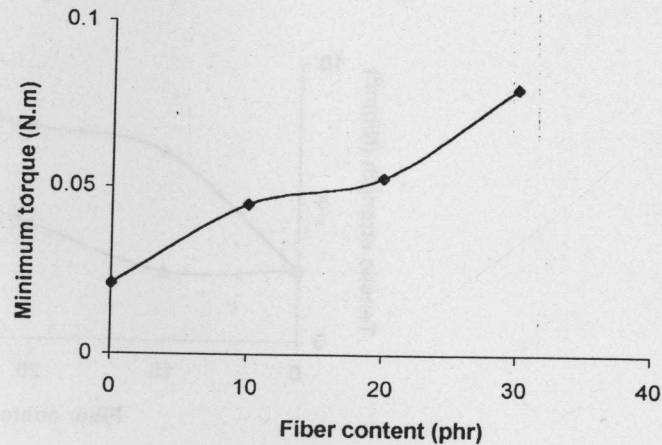


FIGURE 2 Variation of minimum torque with fiber loading.

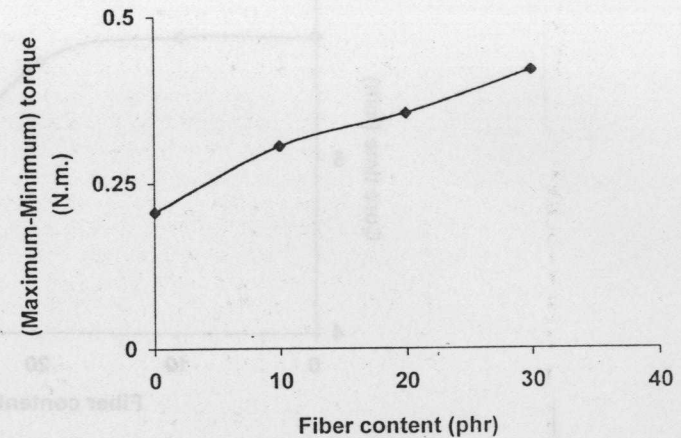


FIGURE 3 Variation of (maximum–minimum) torque with fiber loading.

more restrained matrix in the case of composites, with increase in fiber content.

Scorch time showed a reduction from 2.85 minute at 0 phr fiber to 2.4 minute at 30 phr fiber loading (Figure 4). Cure time is reduced

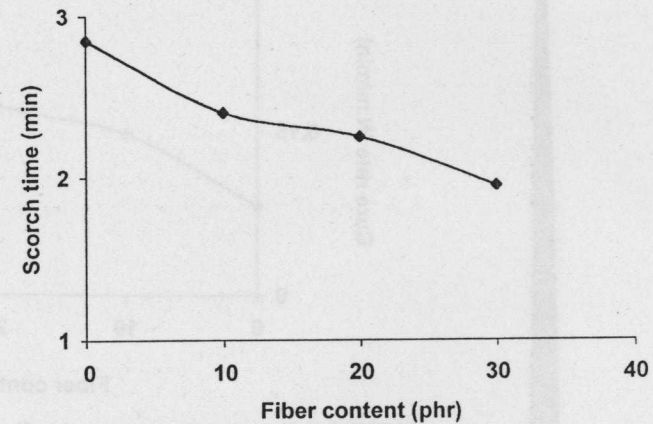


FIGURE 4 Variation of scorch time with fiber loading.

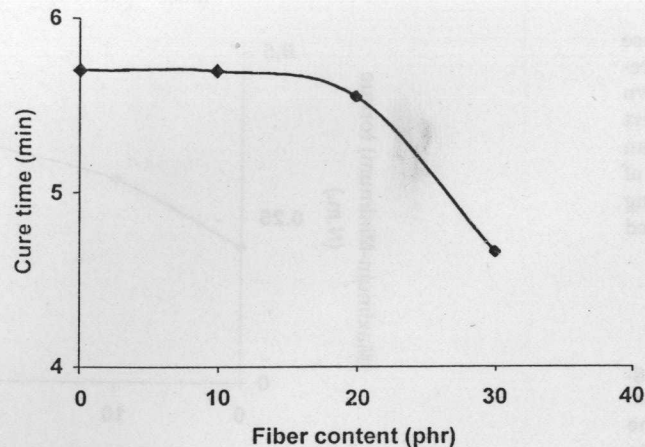


FIGURE 5 Variation of cure time with fiber loading.

from 5.75 minute at 0 phr fiber to 4.65 minute at 30 phr fiber (Figure 5). The reduced cure time is accompanied by increased cure rate values (Figure 6). The cure rate values increased from 0.0821 N.m/minute at 0 phr to 0.23 N.m/minute at 30 phr. This suggests that the cure

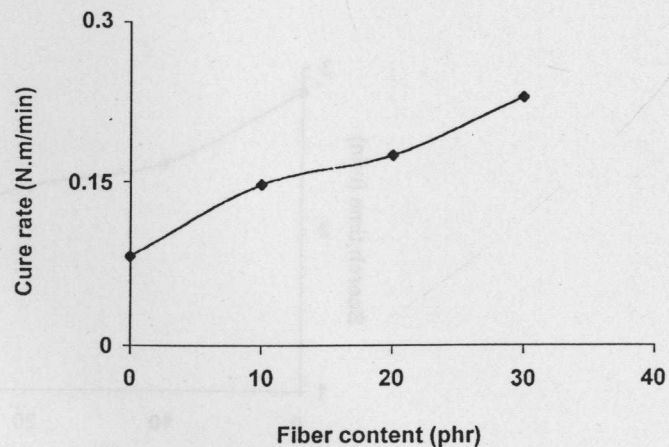


FIGURE 6 Variation of cure rate with fiber loading.

reaction is accelerated by the presence of short nylon fibers. Nylon is prone to degradation at the elevated temperature and one of the degradation product is amine and amines are known cure boosters.

MECHANICAL PROPERTIES

Figure 7 shows the variation of tensile strength of the composites with varying amounts of fiber. The tensile strength in both directions (L&T) increased with increased in fiber content. This is in contrast to the pattern reported for short Nylon fiber-NR composites, where the tensile strength-fiber relationship is non-linear with a minimum at lower fiber concentrations. This arise 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. The tensile strength in all cases was higher in the longitudinal direction. In longitudinal direction the fibers increase the overall strain resistance, and will hinder the growing crack front and hence the higher tensile strength values. As fiber concentration increases there are more and more fibers to hinder the crack front and the tensile strength increases with increase in fiber content.

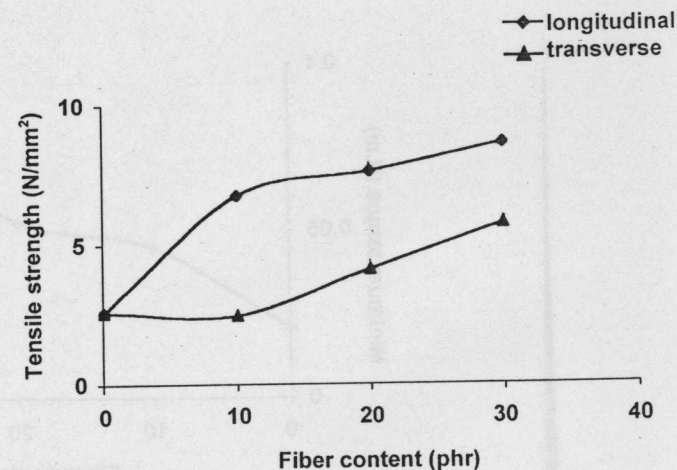


FIGURE 7 Variation of tensile strength with fiber loading.

The elongation at break values of the composites are given in Figure 8. The elongation at break values show a sharp fall on introduction of fibers but with further increase in fiber content the reduction is small. The presence of large amount of fiber tips initiate failure at low strains resulting in lower ultimate elongation values. The elongation at break values are higher in the transverse direction.

Tear strength in both direction increases with fiber content as shown in Figure 9. As fiber concentration increases there is more and more hindrance to the propagating crack front and hence the tear strength increases. The tear strength values are found to be higher in longitudinal direction. The lower values of tear strength in the transverse direction are due to the inability of fibers aligned parallel to the crack propagation to block the advancing crack front.

Resilience showed an improvement on introduction of fibers but with further fiber loading it remains unchanged (Figure 10). A lower value of resilience indicates a more viscous matrix where energy dissipation is higher by way of polymer chain slippage and interfacial bond breakage. The 20 parts of reclaimed rubber in the matrix facilitate this type of loss as they contain plasticiser and filler. The short nylon fibers are able to restrain the blend matrix, rendering it more elastic.

Variation of compression set with fiber content is shown in Figure 11. Compression set increased from 18.7 at 0 phr to 28.7 at 30 phr.

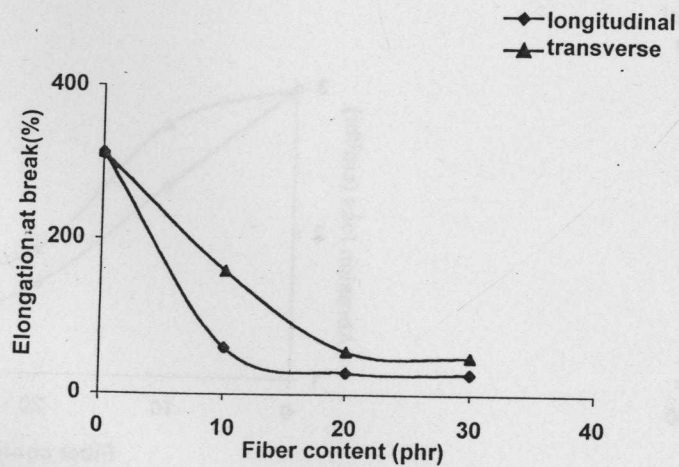


FIGURE 8 Variation of elongation at break with fiber loading.

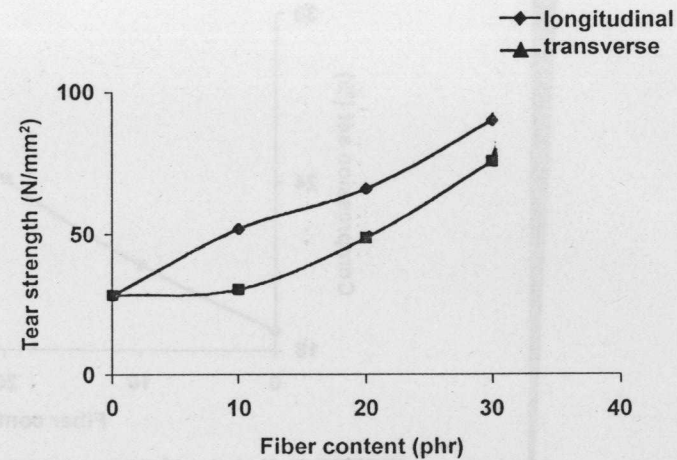


FIGURE 9 Variation of tear strength with fiber loading.

Compression set increased with increase in fiber concentration. 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.

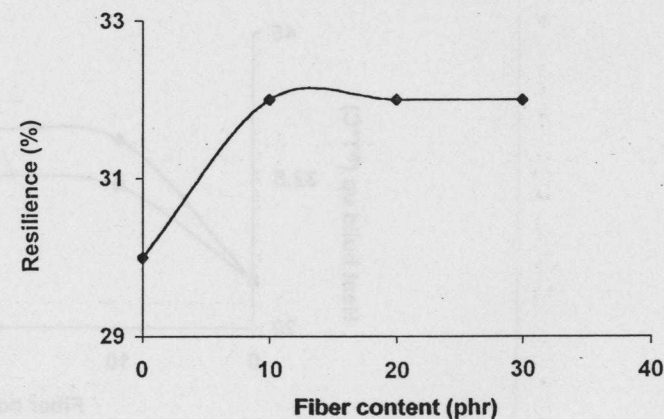


FIGURE 10 Variation of resilience with fiber loading.

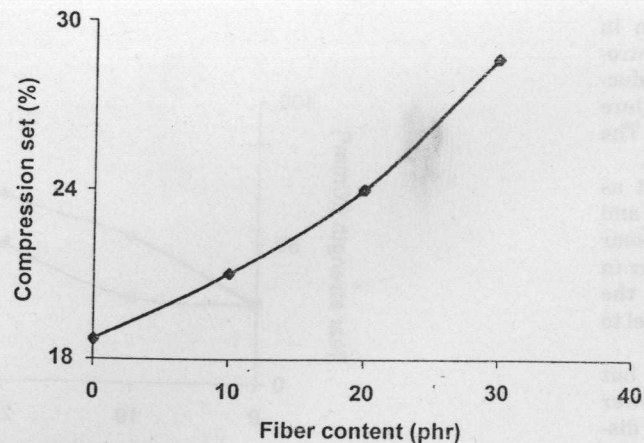


FIGURE 11 Variation of compression set with fiber loading.

The heat build up values of the composites are given in Figure 12. The heat build up increased with increase in the amount of fiber in the composite in both orientation directions of fibers. However, vulcanizates

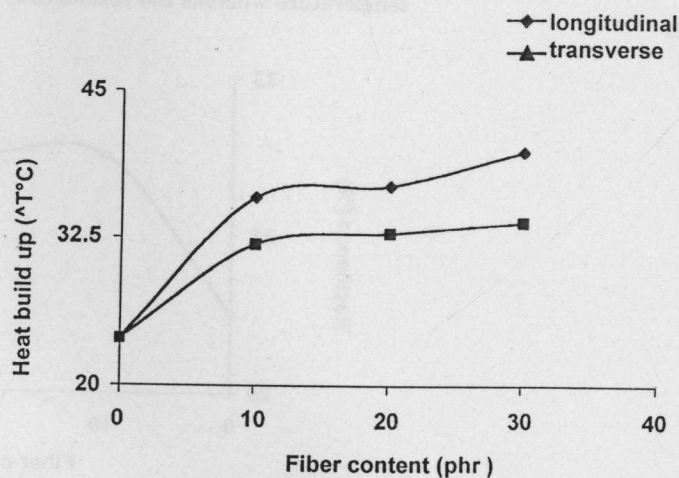


FIGURE 12 Variation of heat build up with fiber loading.

with longitudinally oriented fibers register higher hysteresis loss. Vulcanizates which are stiffer in the direction of stress, experience higher stress for a given strain and generate more heat since the dissipation of energy depends on both stress and strain amplitudes. The stiffness of the composites with longitudinally oriented fibers is higher than the stiffness of the composites with transversely oriented fibers. Thus the heat buildup is higher in the longitudinal direction.

The abrasion loss of the composites is given in Figure 13. The abrasion resistance of the composites increased with the amount of fiber in the composite, indicating a more restrained matrix with increasing fiber content. The abrasion loss in the transverse direction is higher than that in the longitudinal direction. In transverse direction the fibers get debonded and separated from the matrix more easily than in the longitudinal direction causing higher abrasion loss in that direction.

AGEING RESISTANCE

Table 3 shows the retention of tensile properties of the composites before and after ageing. In all the cases retention of tensile strength of the composites (mixes B-D) are found to be better than that of the blend (mix A). The presence of reclaim rubber in the blend makes it more prone to degradation, as it mainly consists of natural rubber.

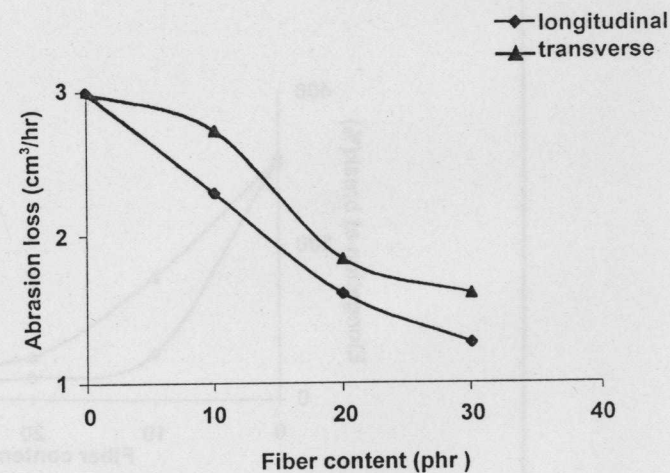


FIGURE 13 Variation of abrasion loss with fiber loading.

TABLE 3 Tensile Properties of the Mixes before and after Ageing

Mix no	Fiber orientation	Tensile strength (N/mm ²)		Percentage retention
		Before ageing	After ageing	
A		2.6	2.3	89
B	L	6.7	8	119
	T	2.8	3.6	129
C	L	7.7	8.8	115
	T	4.5	4.8	108
D	L	8.6	11.8	137
	T	5.7	6.6	116

L - Longitudinal orientation; T - Transverse orientation.

Moreover the unreacted reclaiming agents added during reclamation process also may contribute to reduced stability at elevated temperature. The presence of fibers reduces the chances of oxidative degradation reaction by making the matrix rigid and slowing the diffusion of oxygen. Hence the composites show a marginally higher tensile values after ageing. This is also supported by the lower elongation at break values of the fiber filled samples.

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

TABLE 4 Tear Properties of the Mixes before and after Ageing

Mix no	Fiber orientation	Tear strength (N/mm)		Percentage retention
		Before ageing	After ageing	
A		28.5	21	74
B	L	52.1	71.3	136.7
	T	30.7	31.6	103
C	L	66.3	87.2	132
	T	49	49.6	101
D	L	90.4	92	102
	T	76	79	104

L - Longitudinal orientation; T - Transverse orientation.

TABLE 5 Elongation at Break Values of the Mixes before and after Ageing

Mix no	Fiber orientation	Elongation at break (%)		Percentage retention
		Before ageing	After ageing	
A		312	285	91
B	L	61.4	65.3	106
	T	160.3	164.4	103
C	L	30	35.1	117
	T	57.3	95.4	166
D	L	28.8	52.2	181
	T	50.3	55.2	110

L - Longitudinal orientation; T - Transverse orientation.

compensate for such losses with interfacial bonding that is improved during ageing, the retention values are better.

The retention of elongation at break values of the composites are given in Table 5. The elongation at break values of the composites after ageing is found to be better than that of before ageing. The retention value for the blend is found to be reduced by ageing.

CONCLUSION

Introduction of short fibers to NBR - reclaimed rubber blend improves some of the mechanical properties. The tensile and tear properties improve with fiber concentration and the improvement is more effective in the longitudinal direction. The heat buildup values are higher for composites and in all cases the values are higher for samples with longitudinally oriented fibers. Resilience of the composites is higher than that of the gum compound. Compression set is higher for composites. The abrasion loss decreases with fiber concentration. Abrasion resistance is higher in longitudinal direction. The flowability of the composite is adversely affected by the fibers.

REFERENCES

- [1] Boustany K. and Hamed, P. (1974). *Rubber World*, **39**, 171.
- [2] Beatty, J. R. and Hamed, P. (1978). *Elastomers*, **27**, 110.
- [3] Rogers, J. W. (1981). *Rubber World*, **27**, 183.
- [4] Murty, V. M. and De, S. K. (1982). *J. Appl. Polym. Sci.*, **27**, 4611.
- [5] Akthar, S., De, P. P. and De, S. K. (1982). *J. Appl. Polym. Sci.*, **32**, 5123(1986).
- [6] Coran, A. Y., Boustany, K. and Hamed, P. (1986). *Rubber Chem. Technol.*, **47**, 396(1974).

- [7] O'Connor, J. E. (1977). *Rubber Chem. Technol.*, **50**, 945.
 [8] Roy, R., Bhowmick, A. K. and De, S. K. (1993) *J. Appl. Polym. Sci.*, **49**, 263(1993).
 [9] Derringer, G. C. (1971). *Rubber World*, **165**, 45.
 [10] Ibarra, L. (1993). *J. Appl. Polym. Sci.*, **49**(9), 1595.
 [11] Guo, W. and Ashida, M. (1993). *J. Appl. Polym. Sci.*, **49**(6), 1081.
 [12] Ibarra, L., Maciass, A. and Palma, E. (1994). *Kautsch. Gummi Kunstst.*, **48**(3), 180.
 [13] Miwa, M. and Heriba, N. (1994). *J. Mater. Sci.*, **29**(4), 973.
 [14] Pegorano, M. and Dilandro, L. (1992). *34th International Seminar on Macromolecules*, 193.
 [15] Furukawa, Masatsugu, Walanabo, Hirosuke, Takada and Tadahiko, (1998). *Jpn. Kokai Tokkyo Koho 28 Apr*, 8.
 [16] Geethamma, V. G., Mathew K. Thomas., Lakshminarayanan, R., Thomas, and Sabu, *Polymer*, **39**, p. 6 (1998).
 [17] Suhara, F., Kutty, S. K. N. (1998) *Polym. Plast. Technol. Eng.*, **37**(2), 241.
 [18] Siby Varghese, Baby Kuriakose, Sabu Thomas and Alex J. Koshy, (1991). *Indian J. Nat. Rubber Res.*, **4**, p. 5155.

MODIFICATION OF SAGO STARCH BY GRAFT COPOLYMERIZATION. EFFECT OF REACTION CONDITIONS ON GRAFTING PARAMETERS

M. R. Lutfor
 S. Sidik
 J. Haron
 M. Z. A. Rahman
 M. Ahmad

Department of Chemistry, Faculty of Science
 and Environmental Studies, Universiti Putra Malaysia,
 Selangor, Malaysia

Graft copolymerization of acrylonitrile onto sago starch was carried out by a free radical initiating process in which the ceric ion (Ce^{4+}) was used as an initiator. The reaction conditions significantly influence the graft copolymerization. The percentage of grafting, grafting efficiency and rate of grafting were all dependent on the concentration of ceric ammonium nitrate (CAN), acrylonitrile (AN), sago starch (AGU, anhydro glucose unit), mineral acid (H_2SO_4) and the reaction temperature and period. The optimum yield was obtained when the concentrations of CAN, AN, AGU and H_2SO_4 were used at 9.61×10^{-3} , 0.653, 0.152 and 0.187 mol L^{-1} , respectively. The optimum temperature and reaction period were 50 °C and 90 min, respectively. The rate of graft copolymerization was examined using the experimental results and the reaction mechanism. The polyacrylonitrile grafted sago starch was characterized by using FT-IR spectroscopy, DSC and SEM analysis.

Keywords: graft copolymer, sago starch, free radical, acrylonitrile, polyacrylonitrile

INTRODUCTION

Scientists are exploring ways to use starch as a replacement for petroleum-derived polymers in an effort to generate new markets for

Received 9 November 2000; in final form 25 November 2000.

Address correspondence to M. R. Lutfor, Department of Chemistry, Faculty of Science and Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia. E-mail: lutrinl@hotmail.com