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STUDIES ON NATURAL RUBBER-SHORT SISAL FIBRE COMPOSITES

Siby Varghese, Baby Kuriakose, Sabu Thomas and Alex T. Koshy

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Effects of chemical treatment, aspect ratio and concentration of fibre and type of bonding system on the properties of natural rubber - short sisal fibre composites were evaluated. The results indicated that acetylation of sisal fibre improved the properties of the composites. Aspect ratio in the range of 20-60 was found to be sufficient for reinforcement. A minimum of 12 per cent (v/v) loading of the acetylated fibre was necessary for proper reinforcement. A two-component system consisting of resorcinol and hexamethylenetetramine was found to be better than the normal tricomponent bonding system consisting of resorcinol, hexamethylenetetramine and hydrated silica.

Key words:—Natural rubber, Sisal fibre, Short fibre, Composites, Dry bonding system, Reinforcement, Aspect ratio, Adhesion.

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INTRODUCTION

Reinforcement of elastomers with short fibres combines the rigidity of the fibre with the elasticity of rubber. The resulting composites are used in many applications, especially in hose and V-belts. They present the additional benefit that the fibre is incorporated in the compound as one of the ingredients of the receipe (Ibarra and Chamorro, 1989) and hence, they are amenable to the standard rubber processing steps of extrusion, calendering and various types of moulding. Large volume outputs of short fibre composites are thus feasible. Short fibres are also used to improve or modify certain thermodynamic properties of the matrix for specific applications, or to reduce the cost of fabricated articles (Hamed and Coran, 1978). The properties and performance of short fibre reinforced rubber composites depend mainly on: (a) concentration and type of fibre; (b) aspect ratio of fibre after mixing; (c) orientation of the fibre after mixing; and (d) degree of adhesion of the fibre to the rubber matrix. Various fibres such as glass, rayon, nylon, asbestos, aramid and cellulose have been studied as reinforcement in both natural and synthetic rubber matrices (0' Connor, 1977 and Coran *et al.*, 1976). Jute fibre and waste silk fibre as reinforcing fillers for natural rubber (NR) have also been investigated by Chakraborthy *et al.* (1982) and Setua and De (1984) respectively. The use of coconut fibre as reinforcing filler for rubber has been reported recently (Arumugam *et al.*, 1989).

Results of investigations on the cure characteristics and mechanical properties of NR reinforced with short sisal fibre are reported in this paper. The study includes effects of chemical treatment, aspect ratio and volume loading of the fibre and that of a dry bonding system, on the above properties.

EXPERIMENTAL

Materials

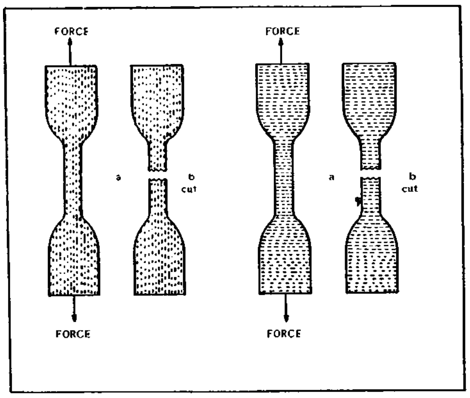
Sisal fibre is ligno-cellulosic in nature and was obtained from Tamil Nadu, South India. It is reported to contain 78 per cent cellulose, 8 per cent lignin, 10 per cent hemi cellulose, 2 per cent waxes, and 1 per cent ash (Barkakaty, 1976). It has an average diameter of 0.103 mm and a specific gravity of 1.45. NR used for the study was ISNR 3 (light colour) grade and hexamethylenetetramine and resorcinol were of laboratory reagent grade. All other ingredients were of commercial grade.

Chemical treatment of fibre

Sisal fibre was chopped to a length of 10 mm and when used as such was designated as untreated fibre. Acetylated fibre was prepared from the chopped raw sisal fibre (10 mm) as per the methods reported by Chand *et al.* (1989). The fibre was first immersed in 18 per cent aqueous sodium, hydroxide solution at 35°C for one hour washed with water several times and then dried. This fibre was soaked in glacial acetic acid for one hour at 35°C, decanted and then soaked in acetic anhydride containing two drops of concentrated sulphuric acid, for five min. The fibre was filtered through a Buchner funnel, washed with water and freed from acid and then dried in an oven at 70°C for 24 h. The treated fibre was stored in polythene bags to prevent moisture absorption.

Preparation of compounds and moulding

Formulations of the test mixes are given in Tables 1 and 2. The mixes were prepared in a laboratory model two-roll mill (150 x 330 mm) at a nip gap of 1.3 mm. The final sheeting was done by passing the compound through a tight nip having a nip gap of 0.8 mm. Blanks cut from the uncured sheet were marked with the direction of the mill grain and were vulcanized at 150°C in a hydraulic press having steam heated platens to their respective cure times, as obtained from a Monsanto rheometer. Test pieces were punched out from the moulded sheet along and across the direction of fibre orientation. The orientations of fibres along and across the grain direction are shown in Fig. 1.



LONGITUDINAL TRANSVERSE

Fig. 1. Longitudinal and transverse orientation of the fibre.

Testing of vulcanizates

Physical properties were measured as per the relevant ASTM procedures. Tests such as tensile and tear strengths were carried out along (longitudinally oriented fibre) and across (transversely oriented fibre) the grain direction. Resilience and hardness measurements were made with specimens having fibre orientation normal to the direction of application of load.

For assessing the resistance to ageing of the samples, tensile test pieces were kept in an air circulated oven, maintained at a temperature of 70°C for seven days. The

Table 1. **Formulations of mixes A to I**

	A	B	C	D	E	F	G	H	I
Natural rubber	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5	5	5	5	5
Resorcinol	0	0	8.75	8.75	8.75	8.75	8.75	8.75	8.75
Hexa*	0	0	5.6	5.6	5.6	5.6	5.6	5.6	5.6
Precipitated silica	0	0	8.75	8.75	0	5	10	0	0
Sisal fibre (untreated)	35	—	35	—	—	—	—	—	—
Sisal fibre (acetylated)	—	35	—	35	35	35	35	35	35
T D Q**	1	1	1	1	1	1	1	1	1
C B S***	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

*Hexamethylenetetramine

**2:2:4 trimethyl 1, 2 dihydroquinoline polymerised

***N–Cyclohexyl–2–benzo thiazyl sulphenamide

Table 2. **Formulations of mixes J to S**

	J	K	L	M	N	P	Q	R	S
Natural rubber	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5	5	5	5	5
Resorcinol	0	2.5	5	7.5	10	2.5	5	7.5	10
Hexa	0	1.6	3.2	4.8	6.4	1.6	3.2	4.8	6.4
Sisal fibre (untreated)	0	10	20	30	40	—	—	—	—
Sisal fibre (acetylated)	—	—	—	—	—	10	20	30	40
T D Q	1	1	1	1	1	1	1	1	1
C B S	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Optimum cure time at 150°C (min)	12.5	12.5	13.5	13.0	11.0	11.5	12.5	12.5	10.5

tensile properties of these samples were determined 24 h after the ageing period and compared with those of the original samples.

RESULTS AND DISCUSSION

Cure time

The optimum cure time of the mixes J to S and that of compounds A to I are given in Tables 2 and 3, respectively. It is clear that on increasing the fibre loading, the optimum cure time remained almost constant (J to S). This trend is observed for the mixes containing both acetylated and untreated fibre. In the presence of bonding agent optimum cure time is lower for mixes containing acetylated fibre when compared with that of compounds containing untreated fibre at the same loading. Presence of silica affects cure time. This is evident from increased optimum cure times of mixes G, D and F compared with that of E (Table 3). Silica retards cure probably by absorbing the curatives (Bachmann *et al.*, 1959).

Incorporation of resorcinol and hexamethylenetetramine as dry bonding agents also does not affect cure. This is evident from the optimum cure times of mixes E, H and I compared to that of B (Table 3). However, in the case of both acetylated and untreated fibre-filled compounds the optimum cure time is slightly lower when the fibre loading is 40 phr (Table 3).

Effect of critical fibre length

Compounds H, E and I have the same ingredients except that they contain acetylated fibre having lengths 6 mm, 10 mm and 15 mm, respectively (Table 1). Shear force during mixing orients most of the fibres along the grain direction. It also causes breakage of fibres. The extent of fibre breakage in the above mixes was determined by dissolution of the compound in benzene, followed by the extraction of fibre and examination of fibre length by a polarising microscope. The breakage analysis data of the mixes H, E and I are given in Table 4. However, no measurable change in average diameter (0.103 mm) occurred during mixing. From the data, it is seen that in mix E, majority of fibres were having an aspect ratio of 20 to 60 (2 to 6 mm length) after breakage. This mix had an original fibre length of 10 mm. Even

Table 3. **Properties of mixes A to I**

Orientation		A	B	C	D	E	F	G	H	I
Optimum cure time at 150°C (min)		10.50	11.50	15.50	13.50	11.50	13.50	13.50	11.00	12.50
Modulus at 10% elongation (MPa)	L	2.56	5.03	8.73	10.80	13.20	10.20	10.90	9.67	13.60
	T	1.02	0.93	1.78	1.90	1.84	5.32	2.51	1.25	1.11
Modulus at 20% elongation (MPa)	L	3.11	5.05	—	—	—	—	—	—	—
	T	1.36	1.62	2.80	3.15	3.10	3.60	3.90	2.02	1.81
Tensile strength (MPa)	L	4.53	5.79	8.40	11.70	14.90	11.70	10.90	10.87	14.90
	T	3.73	4.49	4.76	5.04	6.61	5.26	5.22	4.16	5.11
Tear strength (kNm^{-1})	L	47.60	47.30	66.80	86.76	87.50	85.30	86.40	62.25	82.30
	T	38.80	40.76	64.36	63.36	66.20	69.16	67.50	52.08	56.50
Elongation at break (%)	L	388.10	213.70	22.53	20.24	17.65	19.60	15.20	18.19	18.81
	T	576.70	586.60	88.20	115.60	126.75	82.20	60.40	147.06	122.60

though an aspect ratio of 100 to 200 is generally required for effective stress transfer in short fibre elastomer composites (Goettler and Shen, 1982), in the case of jute fibre-rubber composites, aspect ratio as low as 40 was reported to be sufficient for reinforcing rubber matrix, since there was very good adhesion between the fibre and rubber (Murthy and De, 1981).

In the present case it is seen that reinforcement was high for the mix which contained fibres having an original length of 10 mm, as evidenced by the higher tensile strength and modulus (Table 3) of mix E compared to those of mix H. Mix E contained a total of 65.4 per cent of the fibre in the range of 2-6 mm length after breakdown (Table 4). The tensile strength and modulus of mix I were comparable to those of mix E and not to those of mix H, even though it contained almost the same level of fibres (59.9 per cent) having length in the range 2-6 mm as that of mix H. This is likely to be due to the presence of 18.4 per cent fibres having a final length in the range of 6-10 mm. These observations indicated that an original fibre length of 10 mm is essential and sufficient for getting reinforcement in natural rubber-short sisal fibre composites. Hence further studies reported in this work were conducted using short sisal fibre having 10 mm length.

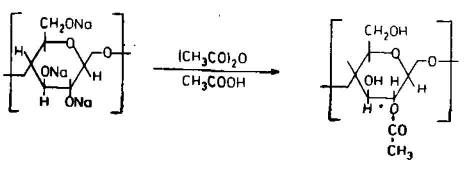
Effect of chemical treatment

One of the most important factors for obtaining good reinforcement by fibre in a rubber-fibre composite is adequate adhesion between the rubber matrix and fibre (O' Connor, 1977). Adhesion between the fibre and rubber depends upon the structure and polarity of these materials. As reported earlier by Chand *et al.* (1989), the surface of sisal fibre can be modified by aqueous alkali treatment at elevated temperature followed by acetylation and this was found to improve its adhesion to some extent.

It is possible to explain the mechanism involved. The cellulosic hydroxyl groups in the fibre are relatively unreactive, since they form strong hydrogen bonds. Alkali treatment before acetylation may destroy the hydrogen bonding in cellulosic hydroxyl groups, and cause the removal of lignin thereby making them more reactive. Considering the ring structure of cellulose, a possible route for acetylation may be as given in Scheme 1.

Table 4. **Distribution of fibre length after mixing**

Length of fibre after mixing (range in mm)	Percentage available in the mix		
	H (original length 6 mm)	E (original length 10 mm)	I (original length 15 mm)
0 - 2	40.7	19.0	21.7
2 - 4	33.9	43.0	43.3
4 - 6	25.4	22.4	16.6
6 - 8	—	12.0	11.7
8 - 10	—	3.4	6.7

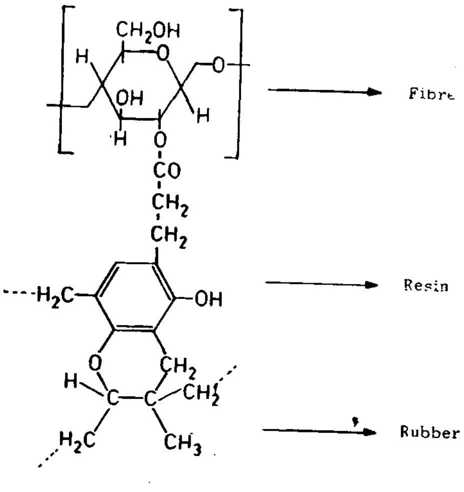


Scheme 1

The acetylation of sisal fibre supported by IR spectrum has been reported (Chand *et al.*, 1989). The hydrogen atom on the acetyl carbon atom becomes more reactive due to the presence of the carbonyl group. This may form chemical link with active sites on rubber, thereby improving adhesion. This is evident from the difference in strength of the composites containing acetylated and untreated fibres. In mixes A and C (Table 1) untreated fibre was used whereas mixes B and D contained acetylated fibres. The properties of vulcanizates given in Table 3, indicate that compound B has higher modulus and tensile strength and lower elongation at break compared with those of compound A. Similarly between compounds C and D, the latter shows higher modulus, tensile strength and tear strength and lower elongation at break. The effect of acetylation of fibre in improving the properties of the composites is also reflected in the properties of compounds P, Q, R and S compared with those of K, L, M and N respectively.

Effect of bonding agent

It has already been established that a tricomponent system consisting of hexamethylenetetramine, resorcinol and fine particle silica (HRH system) can be used as a bonding agent for most rubber and fibre combinations (Goettler and Shen, 1982). Bonding by HRH system involves a condensation reaction between resorcinol and the methylene donor (Hexa) which takes place during vulcanization and silica is reported to accelerate this reaction. The bonding resin acts as an intermediate in binding rubber and the fibre (Wootton, 1982). The bonding between rubber and acetylated fibre through the bonding resin is likely to have followed Scheme 2.



Scheme 2

Mixes A and B containing no bonding agent have very poor mechanical properties compared to mixes C and D which contained the bonding agent (Table 3). Acetylation of the fibre further enhances the effect of bonding agent as seen from the higher modulus, tensile strength and tear strength of compound D compared with those of compound C. In terms of the reactivity of the OH groups in the fibre and steric effects of the resin, acetylation of the fibre is expected to make the bonding of the resin with fibre and rubber easier.

Effect of silica

In short sisal fibre-natural rubber composites the effect of silica in the HRH dry bonding system was found to be contrary to its normal functioning in short fibre-rubber composites. Silica in the HRH system was found to decrease the mechanical properties of the composites. Compounds E, F, D and G (Table 1) contained 0, 5, 8.75 and 10 parts of hydrated silica respectively. It is observed that the tensile strength, modulus and tear strength of compounds G, D and F were lower than those of compound E. However, the decrease in these properties was not proportional to the quantity of silica. It indicated that a small quantity of silica is sufficient to influence the bonding characteristics of the RH system in this particular case. O'Connor (1977) also made similar observations with nylon and cellulosic fibres and established that the RH system is better than the HRH system. Hence in the succeeding experiments the RH system was used as the bonding agent.

Effect of fibre content

Table 2 gives formulation of mixes J to S. Here we have varied concentration of the fibre (10 mm length) from 0 to 40 phr both in the case of untreated and acetylated fibre.

In the case of untreated fibre up to 17.5 per cent volume loading tensile strength in the longitudinal direction decreased and thereafter the strength increased (Fig. 2a). For acetylated fibre upto 12 per cent volume loading tensile strength in the longitudinal direction decreased and thereafter increased. In transverse orientation of the fibre (Fig. 2b) tensile strength decreased continuously with increase in fibre concentrations, both for acetylated and untreated fibre. Greater hindrance to the progress of fracture front is experienced when fibres are oriented longitudinally (ie., perpendicular to the fracture surface). Breakage and pull out of the fibre take place mainly when fibres are oriented in the longitudinal direction, whereas for transversely oriented fibre the crack progresses in the direction of fibre alignment. Tensile strength in the longitudinal fibre orientation is, therefore,

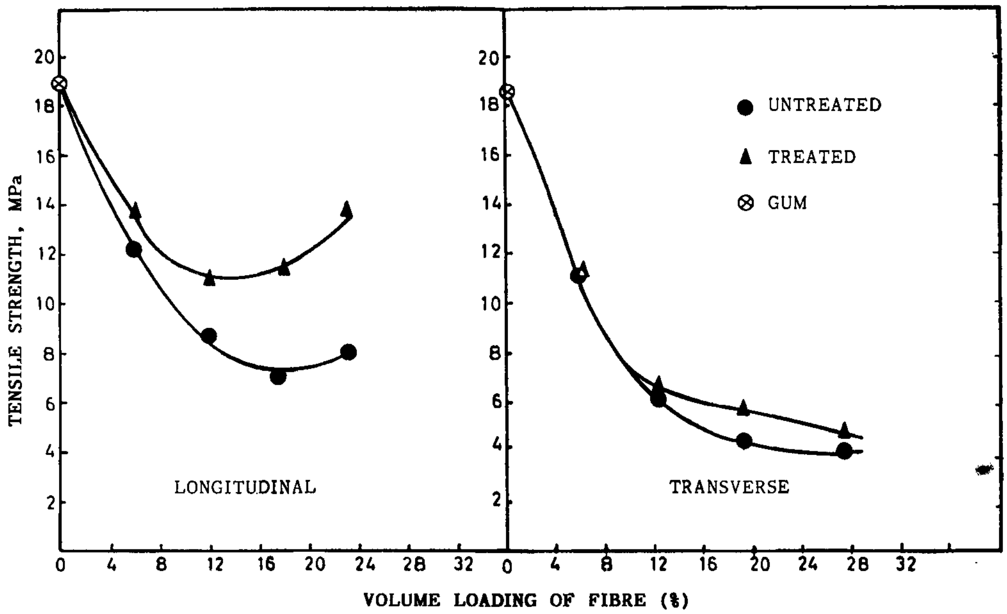


Fig. 2a. Variation of tensile strength with volume loading of fibre in the longitudinal direction.
Fig. 2b. Variation of tensile strength with volume loading of fibre in the transverse direction.

always greater than that in the transverse orientation. Lower tensile strength of mixes K to S compared with that of mix J which contained no fibre may be due to two reasons. (1) The optimum cure time of the rubber at a temperature of 150°C may not be sufficient to develop the maximum adhesive strength through resin formation. This is evidenced by better retention of tensile strength after ageing of the composites containing higher loading of fibre (Figs. 9 and 10 discussed later). (2) At low volume loadings, fibre acted as flaws rather than helping in load transfer. But at sufficiently higher loadings fibre acted as a load transfer medium and the tensile strength showed an increasing trend beyond this critical level. In the case of acetylated fibre the minimum quantity required for this was observed to be about 12 per cent (v/v) whereas for the untreated fibre the minimum value was found to be about 17 per cent (v/v). This indicated that for the treated fibre effective load transfer could take place at lower loadings because of the better bonding realized.

Both untreated and acetylated fibres were found to improve tear strength of the composite to a considerable extent (Figs. 3a and 3b). However in mixes containing untreated fibre (K to N), the increase in tear strength was less compared with the increase in compounds containing acetylated fibre (P to S). The same pattern is observed in the transverse fibre orientation also (Fig. 3b). The higher tear strength of composites having longitudinally oriented fibre is due to the obstruction of tear path by well bonded longitudinally oriented fibres, as explained earlier. This could, not take place in the case of composites having

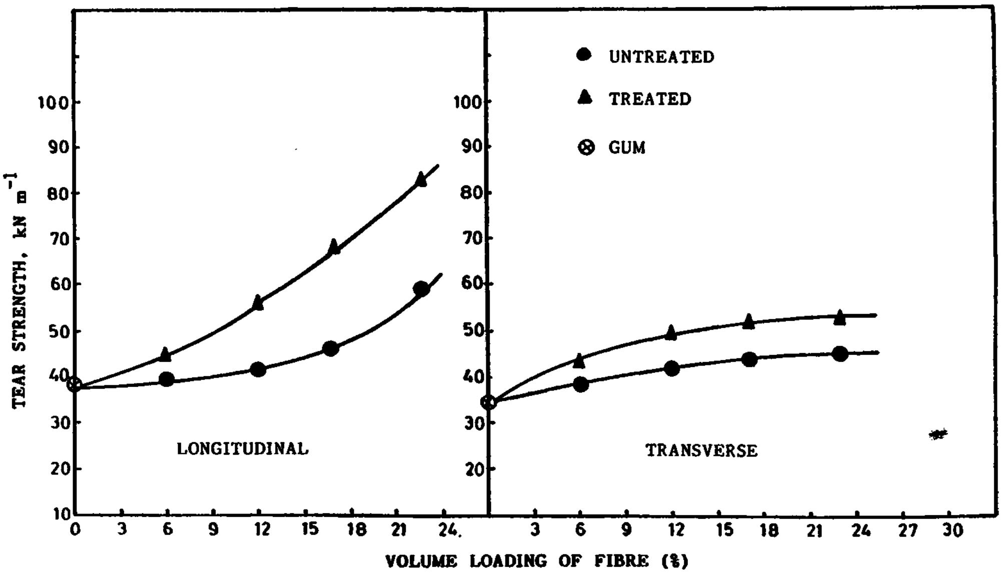


Fig. 3a. Variation of tear strength with volume loading of fibre in the longitudinal direction.
Fig. 3b. Variation of tear strength with volume loading of fibre in the transverse direction.

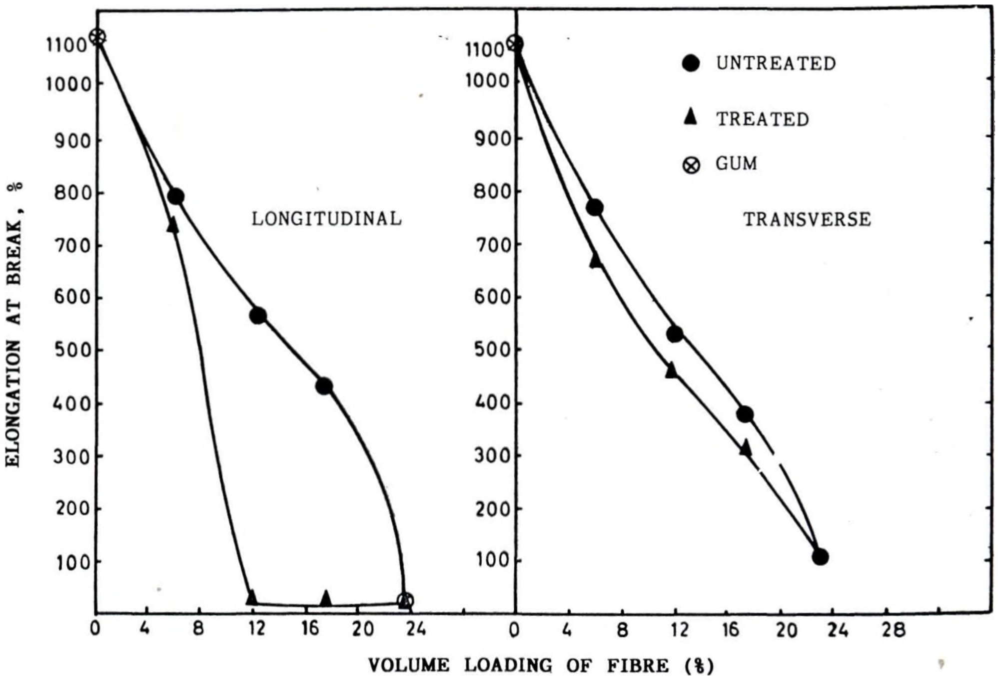


Fig. 4a. Variation of elongation at break with volume loading of fibre in the longitudinal direction.
Fig. 4b. Variation of elongation at break with volume loading of fibre in the transverse direction.

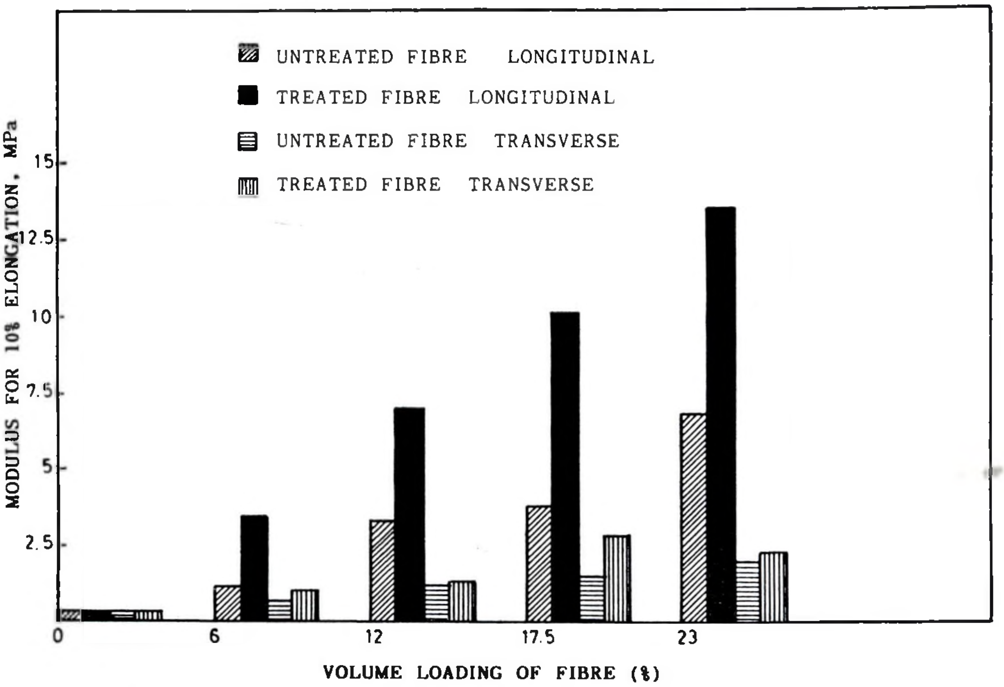


Fig. 5. Variation of modulus at 10 per cent elongation with volume loading of fibre.

transverse fibre orientation (Setua and De, 1984).

Elongation at break drops drastically with loading of fibre (Figs. 4a and 4b). In the case of composites containing the treated fibre the extent of drop is much higher than that in the untreated fibre composites. Elongation at break in the transverse direction also registered the same trend but with considerably higher values (Fig. 4b). From the variation of tensile strength and elongation at break, it can be gathered that untreated fibre is less effective in load transfer whereas acetylated fibre functions effectively as a reinforcing filler beyond a loading of 12 per cent (v/v). This is further supported by the modulus of the composites shown in Fig. 5. Modulus at 10 per cent elongation was much higher for the acetylated fibre composite compared with that containing untreated fibre at all loadings.

Compression set increased steadily with increase in volume loading of fibre. The rate of increase in set, however, decreased as the loading was increased. But set was lower for the composites having acetylated fibre (Fig. 6). It has been reported that this behaviour is due to buckling of the fibre taking place invariably when the closely packed fibres are compressed in the direction of their alignment (Murthy and De 1981). Good adhesion between the acetylated fibre and rubber reduces the extent of buckling of the fibre resulting in reduced set, for the compounds containing acetylated fibre. Hardness of the composites increased sharply with volume loading of the fibre (Fig. 7). The reinforcing effect of acetylated fibre was reflected in hardness also.

Abrasion loss decreased with increase in fibre concentration in the composite (Fig. 8). In this case also the acetylated fibre composites showed better resistance to abrasion compared with those containing the untreated fibre. Abrasion involves many basic processes such as cutting, chipping, tearing, fatigue, etc. Better abrasion resistance of the acetylated fibre composites may be resulting from the combination of higher tear strength, tensile strength and

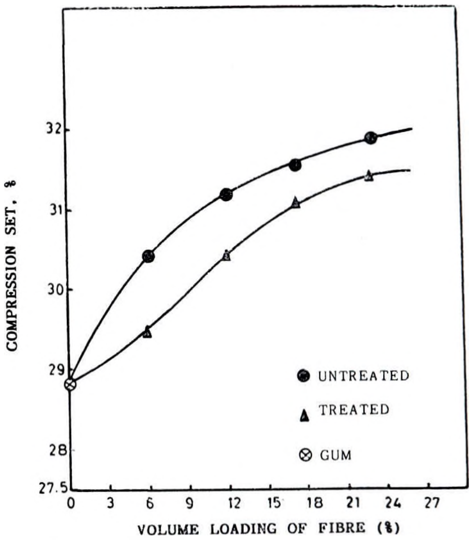


Fig. 6. Variation of compression set with volume loading of fibre.

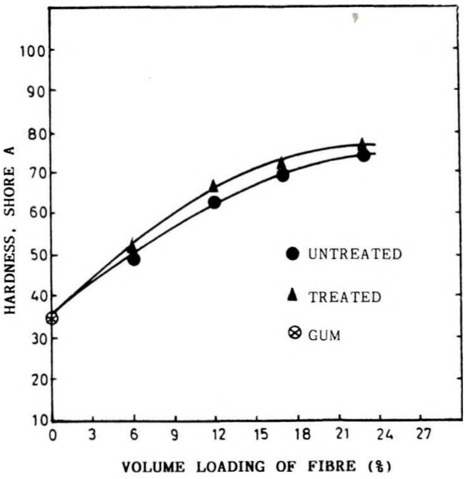


Fig. 7. Variation of hardness with volume loading of fibre.

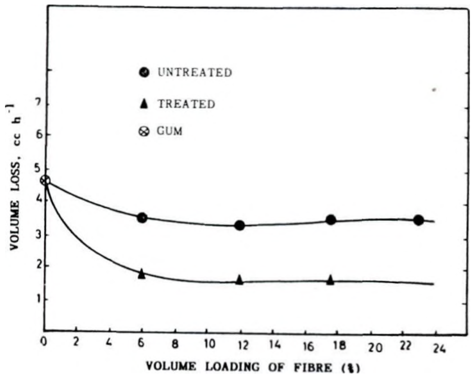


Fig. 8. Variation of abrasion loss with volume loading of fibre.

modulus achieved through better bonding with the rubber matrix.

Ageing resistance

Percentage retention of modulus and tensile strength after ageing for 7 days at 70°C for the mixes J to S is given in Figs. 9 and 10 respectively. The retention of tensile properties after ageing is found to be dependent upon fibre content. It can be seen that the retention of modulus at 10 per cent elongation increased with fibre content (Fig. 9). Since the fibres do not deteriorate much by ageing and they carry maximum load when bonded properly to rubber at optimum loading, the ageing resistance is better for compounds Q, R and S which contained sufficient fibre to offer reinforcement. The resistance of sisal fibre to ageing has been confirmed by ageing the fibre alone at 70°C for 7 days and then determining its strength. The fibre actually retained the original strength after ageing. It is also possible that full strength of the bonding resin is developed during ageing which helps in obtaining better adhesion between the fibre and the matrix. In the case of compounds P and K the retention of tensile strength after ageing is found to be more dependent on the matrix, since the fibre content in these mixes is low. It is

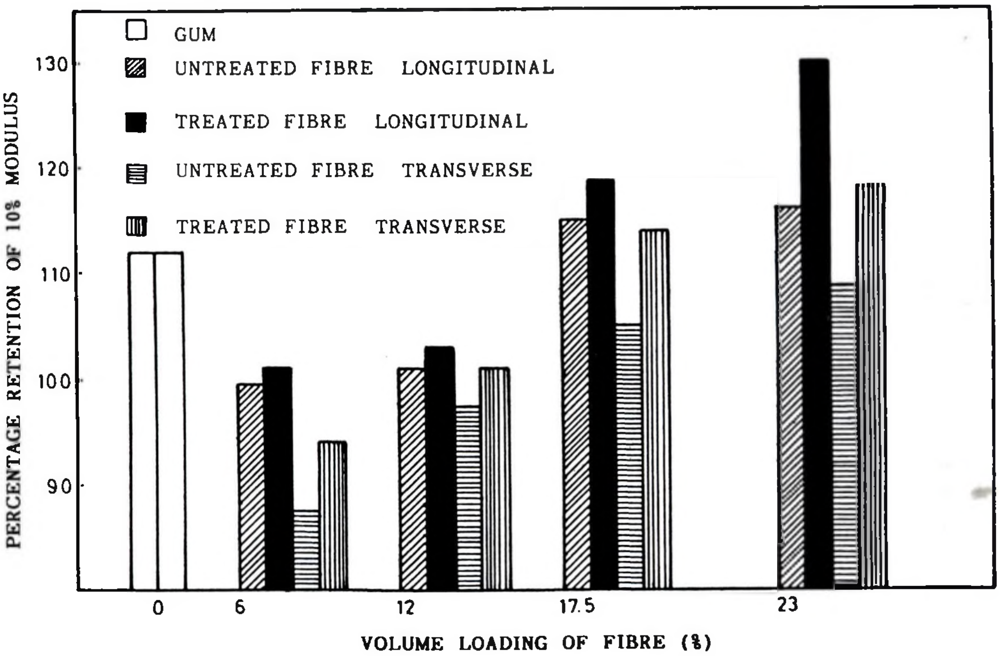


Fig. 9. Variation of modulus at 10 per cent elongation after ageing with volume loading of fibre

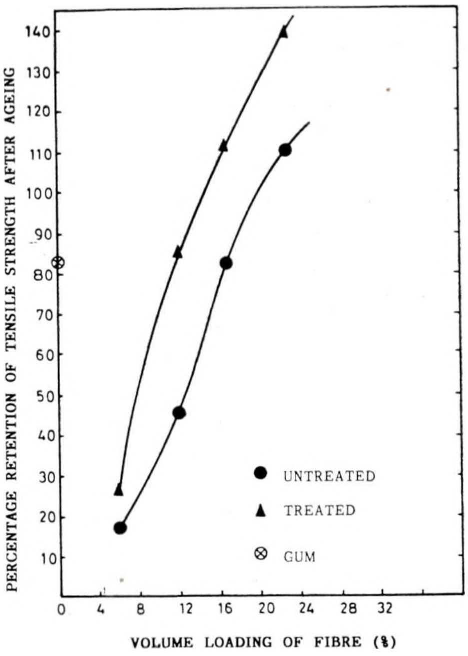


Fig. 10. Variation of tensile strength after ageing with volume loading of fibre

also observed that retention of modulus and tensile strength after ageing was better for composites containing acetylated fibre. This may be due to the better adhesion of treated sisal fibre with rubber.

CONCLUSIONS

The following conclusions emerge from the present investigations.

1. Acetylated sisal fibre imparts better physical properties to rubber than untreated fibre.

2. Bonding between sisal fibre and NR is generally poor and can be enhanced by the use of a bonding agent consisting of resorcinol and hexamethylenetetramine in the ratio 5 : 3.2. Adhesion imparted by this system is found to be better than that of the normal HRH system.

3. The minimum volume loading required for reinforcement is found to be about 12 per cent in the case of acetylated fibre.

4. The ageing resistance of the acetylated sisal fibre-reinforced rubber composites is excellent above a volume loading of 17.5 per cent in the presence of resorcinol -hexa bonding agent.

5. Mechanical anisotropy is observable at higher fibre loading.

REFERENCES

Arumugam, N., Tamareselvy, K. and Venkata Rao, K. (1989). Coconut fibre-reinforced rubber composites. *Journal of Applied Polymer Science*, **37**: 2645–2659.

Bachmann, J. H., Sellers, J. W., Wagner, M. P. and Wolf, R. F. (1959). Fine particle reinforcing silicas and silicates in elastomers. *Rubber Chemistry and Technology*, **32**: 1286–1391.

Barkakaty, B. C. (1976). Some structural aspects of sisal fibre. *Journal of Applied Polymer Science*, **20**: 2921–2940.

Chakraborthy, S. K., Setua, D. K. and De, S. K. (1982). Short jute fibre reinforced carboxylated nitrile rubber. *Rubber Chemistry and Technology*, **55**: 1286–1307.

Chand, N., Varma, S. and Khazanchi, A.C. (1989). SEM and strength characteristics of acetylated sisal fibre. *Journal of Material Science letters*, **8**: 1307–1309.

Coran, A. Y., Boustany, K. and Hamed, P. (1974). Short fibre-rubber composites. *Rubber Chemistry and Technology*, **47**: 396–410

Coran, A. Y., Hamed, P. and Goettler, L. A. (1976). The mechanical behaviour of short fibre-elastomer composites. *Rubber Chemistry and Technology*, **49**: 1167–1181.

Goettler, L. A. and Shen, K. S. (1982). Short fibre reinforced elastomers. *Rubber Chemistry and Technology*, **56**: 619–638.

Hamed, P. and Coran, A. Y. (1978). Reinforcement of polymers through short cellulose fibres. *Additives for Plastics*, **1**: 29–50.

Ibarra, L. and Chamorro, C. (1989). Reinforcement of EPDM matrices with carbon and polyester fibres-mechanical and dynamic properties. *Journal of Applied Polymer Science*, **37**: 1197–1208.

Murthy, V. M. and De, S. K. (1981). Short jute fibre reinforced rubber composites. *Rubber Chemistry and Technology*, **55**: 287–307.

O'Connor, J. E. (1977). Short fibre-reinforced elastomer composites. *Rubber Chemistry and Technology*, **50**: 945–958.

Setua, D. K. and De, S. K. (1984). Short silk fibre reinforced nitrile rubber composites. *Journal of Material Science*, **19**: 983–999.

Wootton, D. B. (1982). Heat setting and adhesive treatment. In: *Textile Reinforcement of Elastomers*. (Ed. William C. Wake and David, B. Wootton). Applied Science Publishers, London, pp 71 103.