Coconut-Fiber-Reinforced Rubber Composites

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Synopsis

Different formulations of rubber with chopped coconut fiber (treated and untreated) as reinforcing agent were prepared. These reinforced systems were vulcanized at 153°C and the properties of the vulcanizates were studied by stress–strain, shore A hardness, and abrasion loss measurements. The bonding between the rubber and fillers were improved by the addition of bonding agents. The bonding effect of different bonding agents were compared. The reinforcing property of the treated fiber was compared with the untreated one. Aging resistance of the composites were studied. The fracture surfaces have been studied by scanning electronmicroscopy (SEM) and the failure mechanism has been explained.

INTRODUCTION

The reinforcement of rubber with short fibers imparts good strength and stiffness to the soft as well as tough rubber matrices.[1] Recently,[2-8] short fiber reinforcement of rubber matrices has gained importance due to processing advantages and improvements in mechanical properties like damping. Various fibers like glass, rayon, nylon, aramid (KEVLAR), asbestos, and cellulose have been studied as reinforcements in both natural and synthetic rubber matrices by many workers.[4-8] The use of jute fiber and waste silk fiber as reinforcing fillers for natural rubber and oil-extended carboxylated rubber has been investigated by De et al.[9-11] The use of coconut fiber as a reinforcing filler for plastics has also been reported recently. [12] However, no attempt seems to have been made so far to evaluate the use of coconut fiber as a reinforcing fill for rubber matrices. In this paper report the results of our studies in this area in natural rubber matrices with the following objectives:

1. modification of fiber surface;
2. effect of fiber concentration on the physical properties of the rubber composites;
3. effect of different bonding agents on the physical properties of the rubber composites;
4. aging resistance of the composites;
5. failure mechanism.

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TABLE I
Formulation of Mixes

Mix composition (phr)	A, without fiber	B		C		D	
		U	T	U	T	U	T
NR[a]	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Coconut fiber[b]	—	10	10	30	30	60	60
Calcium carbonate	—	—	—	—	—	—	—
Carbon black	—	—	—	—	—	—	—
CBS	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur[c]	2.5	2.5	2.5	2.5	2.5	2.5	2.5

[a] Natural rubber RMAIX, supplied by Pioneer Rubber Company, Madras. U = untreated fiber; T = treated fiber.

[b] Coconut fiber, origin of Pondicherry. Fiber length 10–20 mm; fiber diameter 0.28 ± 0.17 mm; fiber tensile strength 160 ± 80 NM/m^2; modulus of elasticity 2.4 ± 0.62 GN/m^2.

[c] Sulfur, supplied by E. Merck, A. G.

EXPERIMENTAL

Formulations of the rubber mixes are given in Tables I and II. Coconut fiber from Pondicherry, South India, chopped to a length of 8 mm, was used as the untreated (U) reinforcing filler. Treated (T) reinforcing filler was prepared from the raw coconut fiber by imersing it in 10% aqueous alkali (NaOH) heating for 3–4 h at 100–150°C, washing with water several times and drying. The fiber was then chopped to 8 mm length and used for reinforcement. Mixing was done in a 150 ×330 mm open mixing mill with a nip gap of 0.25

TABLE II
Formulation of Mixes[a]

Max composition (phr)	E		F		G		H
	U	T	U	T	U	T	T
NR	100	100	100	100	100	100	
SBR	—	—	—	—	—	—	—
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Phenol–formaldehyde resin[b]	10	10	—	—	—	—	—
Resorcinol–formaldehyde resin[c]	—	—	5	5	5	5	10
Precipitated silica[d]	—	—	2	2	2	2	5
Coconut fiber	30	30	30	30	30	30	30
CBS	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Hexa[e]	—	—	—	—	5	5	10

[a] U = untreated fiber; T = treated fiber.

[b] Phenol–formaldehyde resin (E. Merck, A. G.), donated by Madras Rubber Factory, Madras.

[c] Resorcinol–formaldehyde resin (E. Merck, A. G.), donated by Madras Rubber Factory, Madras.

[d] Silica, donated by Madras Rubber Factory, Madras.

[e] Hexamethylenetetraamine (E. Merck, A. G.), donated by Madras Rubber Factory, Madras.
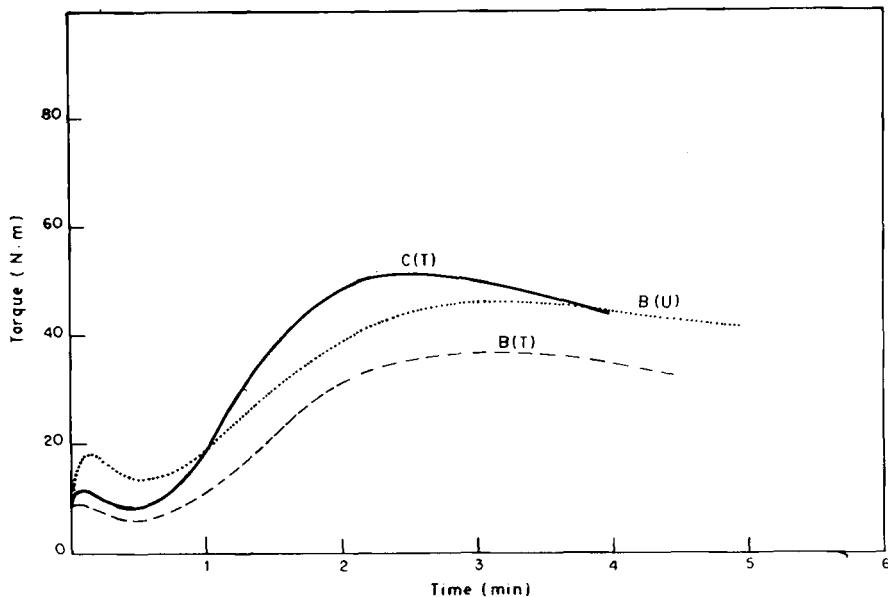
Fig. 1.   Rheographs of mixes B(U), B(T), C(T), and F(T) obtained from Monsanto Rheometer R-100 150°C.

mm. Care was taken to ensure that, in all mixes, the fiber orientation was the same as indicated by the grain direction. Fiber breakage invariable occurred during mixing due to the viscosity and high modulus of the stocks and the low extensibility of the coconut fiber. The mixes were vulcanized at 153°C at their respective optimum cure times as obtained from the rheographs of a few samples measured in a Monsanto R-100 rheometer (Fig. 1).

The properties of the vulcanizates were measured by the standard procedures. Stress–strain data were obtained with an Instron 1193 at a crosshead speed of 500 mm/min. Tensile testing were done according to ASTM methods 412–517. Shore A hardness was measured according to ASTM D 676–527. Abrasion loss was measured in a cryodon Akron Abrader, the samples being abraded for 500 revolutions. The dumbbell-shaped specimens were allowed to age for 48 and 168 h at 70°C in the oven to determine their aging resistance. The scanning electron microscopy (SEM) studies were carried out using an S-150 Stereoscan model.

RESULTS AND DISCUSSION

Modification of the Fiber Surface

The most important factor for obtaining good fiber reinforcement in the product is the strength of adhesion between the rubber and the fiber. The extent of adhesion between them depends upon the structure and polarity of these materials. Though coconut fiber is a natural fiber with hydroxyl groups on its surface, its high tenacity (modulus of elasticity) and low cohesive strength leads to poor adhesion to rubber. Hence, to achieve a better coupling between the fiber and the rubber, some pretreatment has to be given to the

TABLE III
Properties of Volcanizates[a]

Properties	Fiber orientation[b]	Mix A, without fiber	Mix B		Mix C		Mix D	
			U	T	U	T	U	T
Hardness (A)								
(i) After aging for 48 h at 70°C		30	32	35	50	60	65	70
(ii) After aging for 168 h at 70°C		42	32	35	50	60	70	70
		45	35	40	60	65	72	75
Tensile strength (MP2)	L	16.3	6.2	4.0	3.3	2.9	1.8	1.4
	T		6.0	3.8	3.1	3.1		1.7
(i) After aging for 48 h at 70°C	L	24.0	8.2	5.7	5.1	3.2	1.8	2.3
	T		6.9	4.3	5.0	3.9	1.7	2.8
(ii) After aging for 168 h at 70°C	L	5.9	7.8	3.4	2.1	2.8	1.5	3.0
	T		3.0	1.1	1.0	1.2	0.9	1.0
Elongation at break (%)	L	770	570	520	500	480	410	230
	T		760	710	620	540	520	380
(i) After aging for 48 h at 70°C	L	680	550	510	500	460	400	250
	T		720	710	610	500	510	530
(ii) After aging for 168 h at 70°C	L	450	250	220	200	190	210	200
	T		690	580	590	460	370	530
Abrasion (%) Loss in weight percentage		—	49.2	46.1	42.3	37.0	40.0	28.8

[a] U = untreated fiber; T = treated fiber.
[b] L denotes longitudinal and T denotes transverse orientation.

fiber prior to its application. As reported earlier by Czuikovszky and his co-workers,[12] the surface of this fiber can be modified by aqueous alkali treatment at elevated temperatures, and this was found to improve its adhesion properties significantly.

Effect of Fiber Concentration on the Physical Properties of the Vulcanizates

Table III gives the characterization of the vulcanizates corresponding to the formulations of mixes A, B, C, and D. The effect of fiber concentration on the physical properties of the composites with both treated and untreated types of fiber was investigated. The rheographs (Fig. 1) show a gradual increase in the maximum torque values with an increase in the fiber loading. The curves in the rheographs cross each other because of differences in their scorch times and cure tests. The variation of tensile strength and elongation at break with fiber content is given in Table III and Figure 2. It can be seen that the influence of the rubber matrix on the stress–strain relationship of the vulcanizate is gradually replaced by the influence of the fiber with increasing loading. Depending upon the fiber type and the extent of loading on a particular rubber stock, it is usually not difficult to achieve a fair degree of orientation[13] of the fibers within the mixes.

In general, tensile strength of the reinforced vulcanizates decreases abruptly to a value which is about 2.5 times less than that of the reinforce vulcanizate
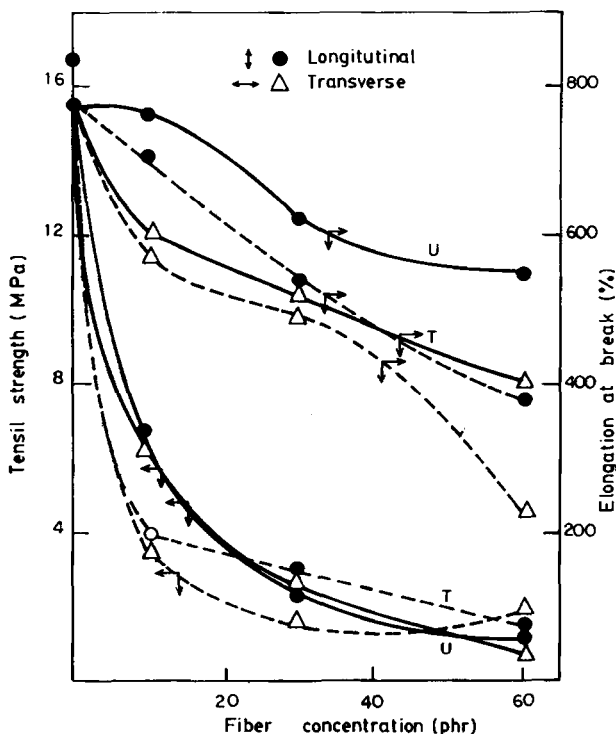

Fig. 2. Variation of tensile strength and elongation at break with volume loading of fiber: ($\updownarrow$,●) longitudinal; (↔ , ○) transverse.

even with a fiber loading of just 10 vol %. However, further decrease in tensile strength with increasing fiber loading was only gradual. This is in contrast to the earlier reports[3,4,11] of increased tensile strength with increased fiber loading. Many workers[1,9-11] reported a detailed study on the anisotropy in physical properties. Tensile strength in the longitudinal direction decreases up to a loading of 10 vol % and then increases gradually. Similarly, in the case of the transverse direction, the values of tensile strength drop with fiber content upto 10 vol %. Hence, in this investigation, we studied the effect of fiber content from 10 to 60 vol %. The value of tensile strength in the transverse direction remains independent of the fiber content. This is due to the weakening of rubber matrix by the presence of transversely oriented fibers. As compared to the treated fiber, untreated fiber gives better tensile strength values.

Regarding hardness, an increase in hardness was observed with increased fiber loading, the treated fibers giving better hardness values than the untreated fibers (Fig. 3). However, there was a corresponding steady decrease in the elongation of the fiber-loaded samples, with increased loading, the treated fibers again giving lower elongation values than the untreated fibers for a particular fiber loading. The elongation at break in the transverse direction also registers the same trend but with consistently higher values. With increasing fiber loading, the hardness values increased gradually, with an associated decrease in the elongation at break in the case of both treated and untreated fiber composites. Figure 4 is the SEM photomicrograph of a tensile fractured surface at mix C with longitudinally oriented treated fibers. It shows matrix deformation and inhibition of the propagating fracture path by
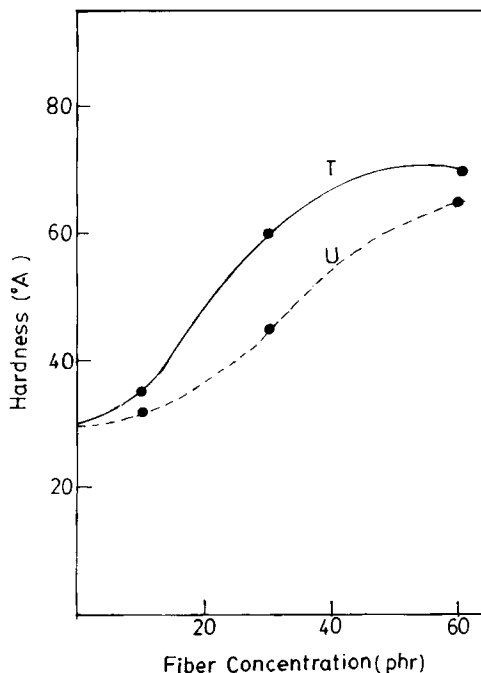

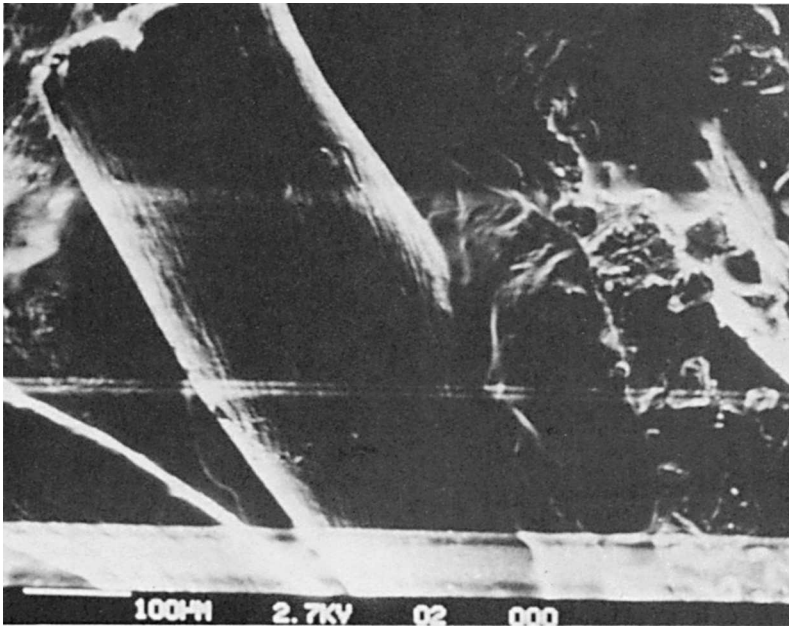Fig. 3. Variation of hardness with volume loading of fiber.

Fig. 4. SEM photomicrograph of the tensile fractured surface of mix C (treated) (fibers oriented longitudinally).
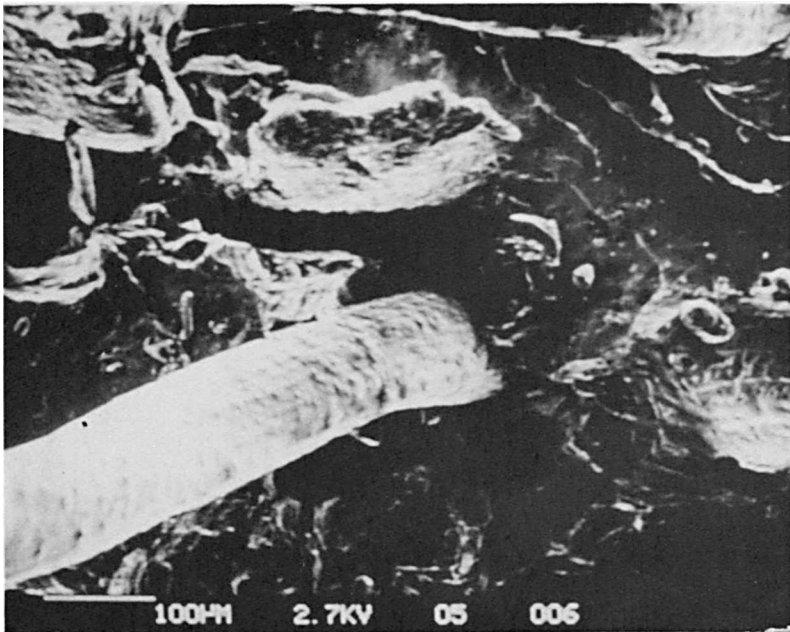

Fig. 5. SEM photomicrograph of the tensile fractured surface of mix C (treated) (fibers oriented transversely).

TABLE IV
Properties of Vulcanizates[a]

Properties	Fiber orientation	Mix E		Mix F		Mix G		Mix H
		U	T	U	T	U	T	T
Hardness (A)		60	70	70	70	70	70	75
(i) After aging for 48 h at 70°C		60	70	70	70	70	75	75
(ii) After aging for 168 h at 70°C		65	70	75	75	73	83	85
Tensile strength (MPa)	L	1.9	4.0	5.7	6.2	5.3	1.8	4.8
	T	1.2	3.1	3.9	4.1	4.8	1.6	3.9
(i) After aging for 48 h at 70°C	L	2.2	3.7	5.4	5.2	3.7	1.7	4.9
	T	0.8	1.2	2.1	2.0	1.9	0.9	2.2
(ii) After aging for 168 h at 70°C	L	1.6	2.6	2.2	2.4	2.8	1.7	2.4
	T	0.4	1.1	1.3	1.5	1.1	1.2	1.0
Elongation at break (%)	L	320	480	310	320	280	260	300
	T	510	590	480	550	450	230	350
(i) After aging for 48 h at 70°C	L	280	420	280	290	240	220	180
	T	400	490	460	440	370	160	190
(ii) After aging for 168 h at 2°C	L	160	240	140	150	140	80	60
	T	270	460	220	280	300	100	110
Abrasion (%)								
Loss in weight percentage		34.7	31.0	17.3	6.2	12.8	9.3	15.0

[a] U = untreated fiber; T = treated fiber.
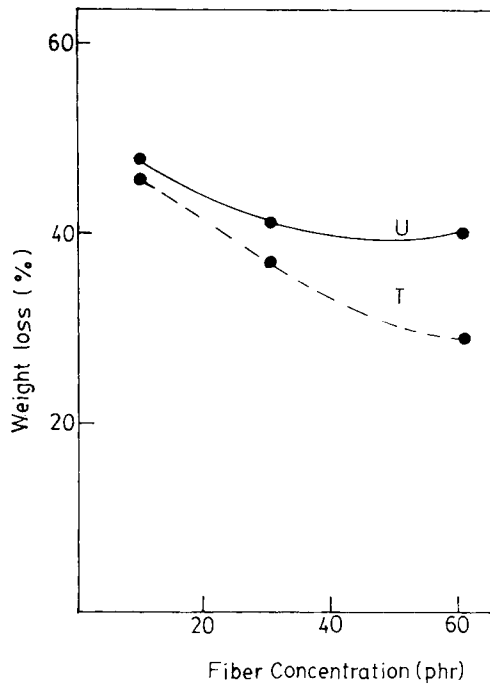[b] L denotes longitudinal and T denotes transverse direction

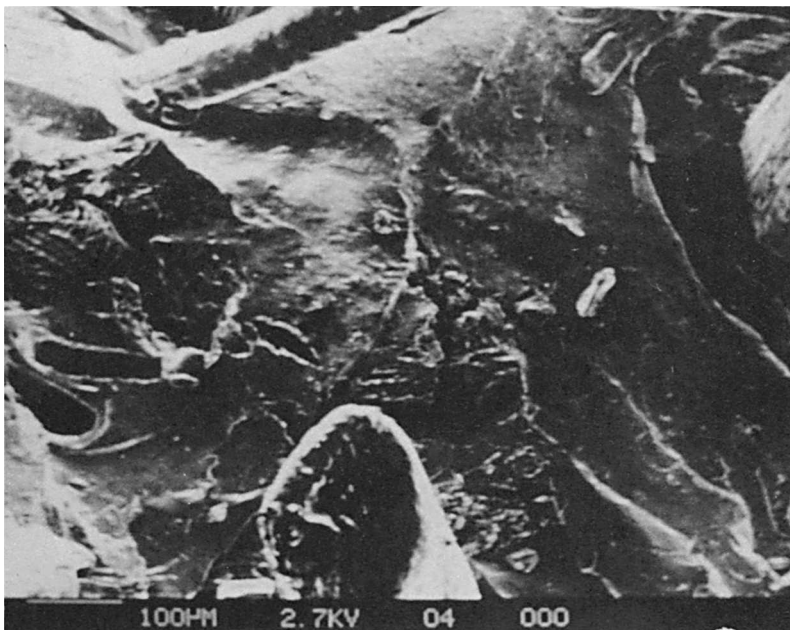Fig. 6. Variation of abrasion loss in volume loading of fiber.

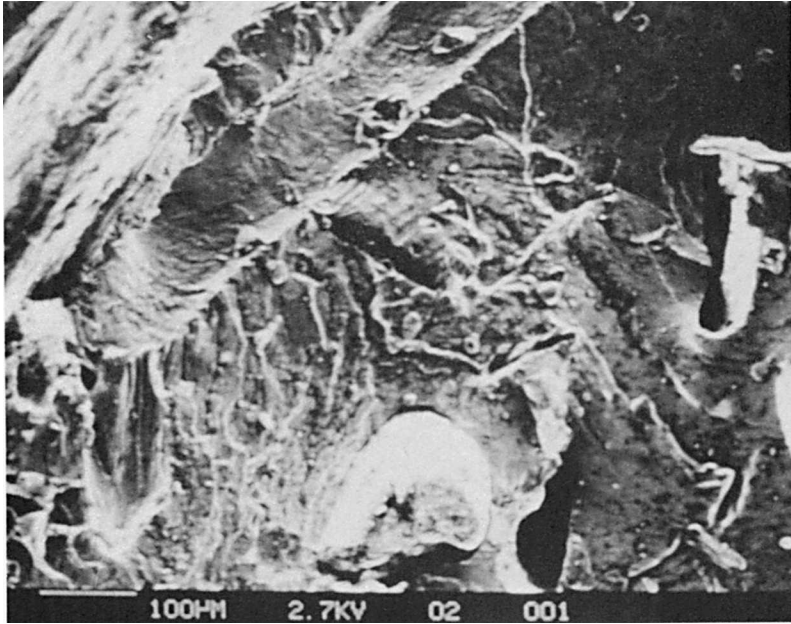Fig. 7. SEM photomicrograph of abraded fracture surface of mix C (untreated).

Fig. 8.   SEM photomicrograph of abraded fracture surface of mix C (treated).
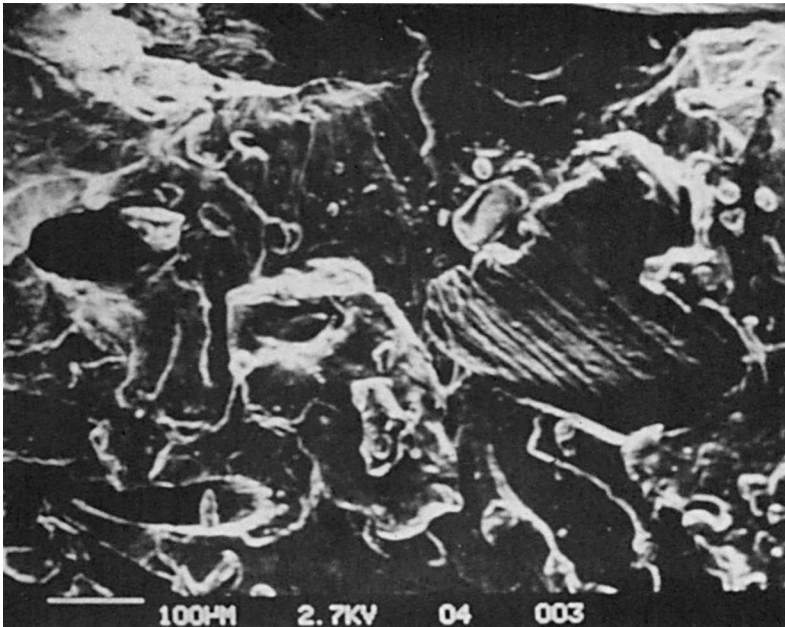

Fig. 9.   SEM photomicrograph of abraded fracture surface of mix F (treated).

the bonded fibers. Figure 5 shows a typical SEM photomicrograph of the tensile fractured surface of mix C with transverse orientation of fibers. In the case of transversely oriented fibers, the crack progress in the direction of fiber alignment and tensile strength in this direction is less compared to strength in longitudinally oriented fibers, where crack progresses perpendicularly to the orientation direction as reported.[11]

Again, in contrast to the earlier report[9] on other natural fibers, the abrasion resistance registered an improvement with increasing loading of fiber (Tables III and IV; Fig. 6), which may be attributed to the high tenacity (160 ± 80 NM/m^2.) of coconut fiber.[12] Abrasion loss in general, which is mainly due to the repeated mechanical scrapping away of surface grains, depends on the hysterisis properties of the vulcanizate. Abrasion resistance is proportional to the product of the specific mechanical loss in elementary cycle and the fatigue resistance of rubber. The abrasion loss in fiber composited may also be due to the loss of fiber, which is evident by the presence of short broken fibers on the surface. The SEM studies (Fig. 7 and 8) also reveal that the abrasion loss of fiber composites is mainly due to the loss of fiber. The resistance to the abrasion loss in treated fiber-loaded samples is higher than in the samples with untreated fiber. The lowest values of abrasion loss were observed in those vulcanizates containing resorcinol–formaldehyde and precipitated silica with the treated fiber reinforcement. In the case of mix F, the abraded fracture surface shows holes and cracks on the surface. Here the silica aggregates are responsible for failure (Fig. 9).

Effect of the Bonding Agent on the Composite

The effects of a few bonding agents, viz.:

1. phenol–formaldehyde (10),
2. resorcinol–formaldehyde : Precipitated silica (5 : 2),
3. resorcinol–formaldehyde : Precipitated Silica : Hexa (5 : 2 : 5),
4. resorcinol–formaldehyde : Precipitated silica : Hexa (10 : 5 : 10),

on the properties of the rubber mixes were also studied. In general, physical properties of the mixed were found to change favorably with the addition of (1) (mix E) as well as (2) (mix F) binders applied with both untreated and treated fibers. This improvement is, however, higher in the treated fibers than in the untreated fibers. Addition of hexa (3) has an effect only in untreated fiber (mix G). Enhancing its ratio to 10 phr (4) (mix H) binding strength improved significantly. The above studies have revealed that the use of the bonding agent (2) for the reinforcement of rubber by treated coconut fibers resulted in vulcanizates with very good physical properties (Table IV). SEM photomicrograph (Fig. 10) of mix H (without adhesion) shows very short segment of fibers and holes left after the fibers are pulled out from the matrix. This is due to poor bonding agents, and the adhesion between the fiber and rubber matrix is evident. The voids may be caused by shear deformation and not from debonding fibers. Figures 11 and 12 are the SEM photomicrographs of mixes F and G, which contain bonding agents 2 and 3. The improved adhesion between the fiber and rubber matrix is evident. The role of silica in
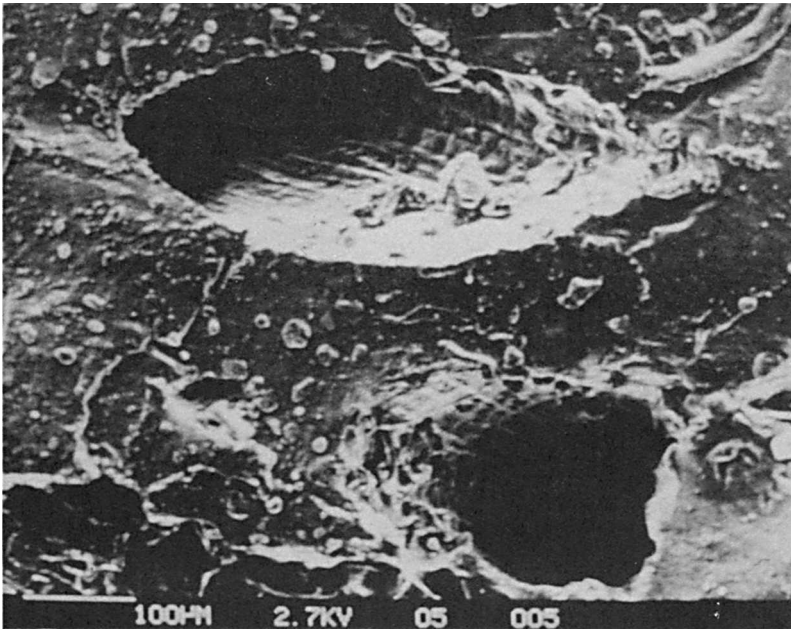
Fig. 10.   SEM photomicrograph of tensile fractured surface of mix B (untreated) (without adhesion).
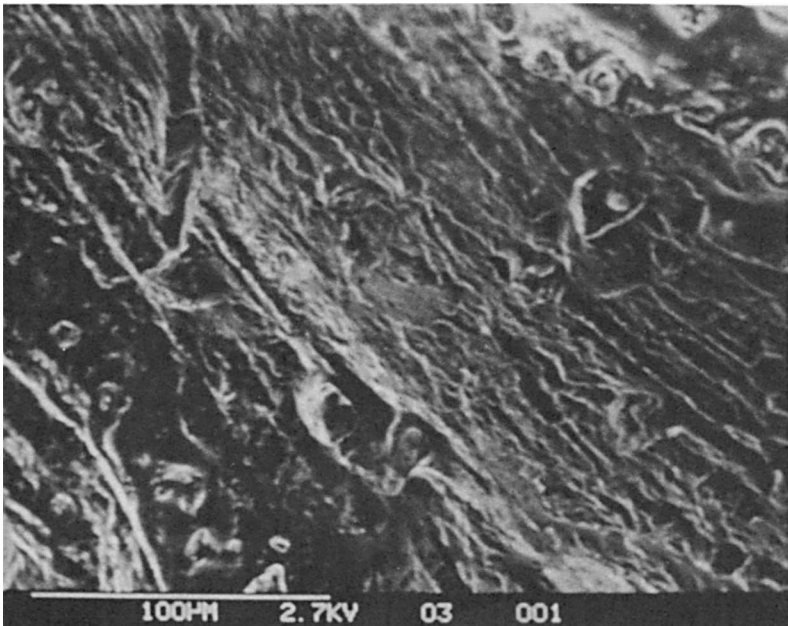

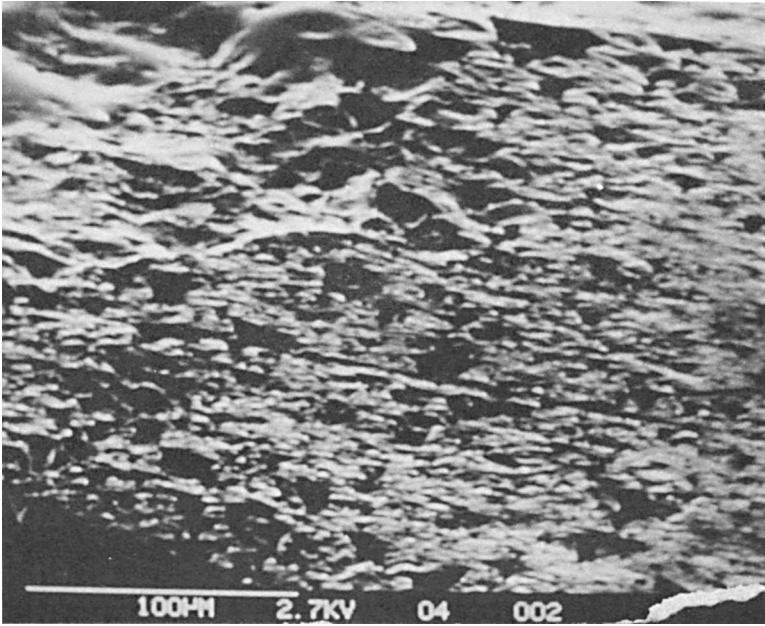Fig. 11.   SEM photomicrograph of mix F.

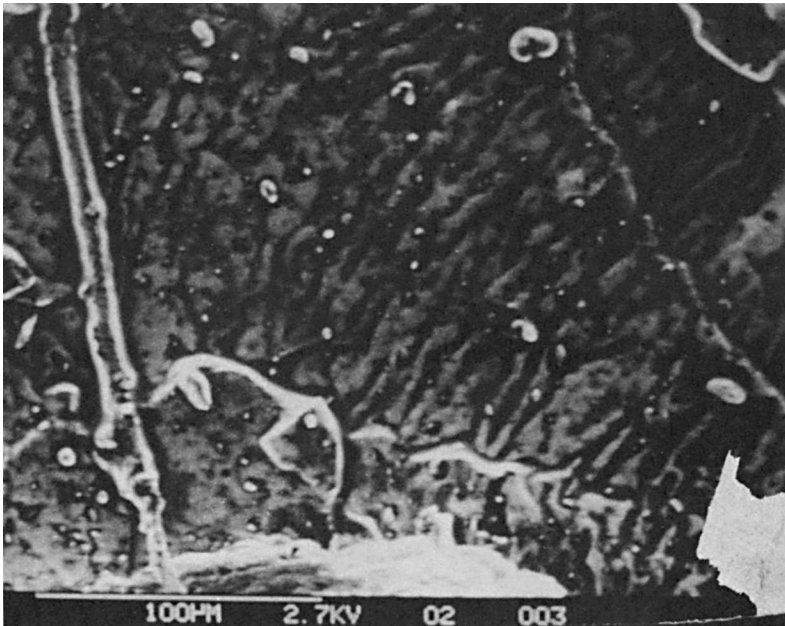Fig. 12.   SEM photomicrograph of mix G.
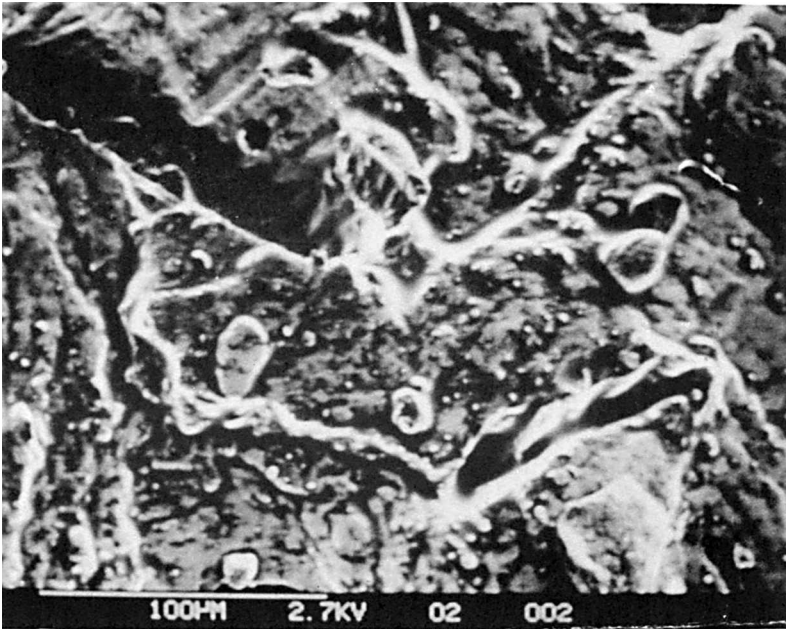

Fig. 13.   SEM photomicrograph of mix H.

Fig. 14.   SEM photomicrograph of tensile fractured surface of mix G after aging (treated).

the improvement of adhesion was also confirmed[9,11] in the presence of Hexa by the SEM (Fig. 13).

Aging Resistance of the Rubber Composites

Aging resistance of all mixes were studied, and the percentage retention of properties after aging for 48 h and 168 h is given in Tables III and IV. Retention of tensile strength after aging was found to be independent of fiber loading. It can also be seen that the strength of bonding between the fiber and the rubber matrix depends remarkably on aging i.e., aging for 48 h improves the properties of the composites since the fibers do not deteriorate by aging, and they carry maximum load when bonded properly to the matrix. But there is actually a small reversal in these properties: If the aging time is extended to 168 h, the retention of properties after aging is low and becomes dependent on the matrix. The SEM study (Fig. 14) of the failure surface (mix G) after aging, indicating an interesting change. The rough surface is caused by the network of silica aggregates in the matrix and not by the fibers.

CONCLUSIONS

The following conclusions can be drawn from this investigation:

1. In general, the alkali-treated fiber imparts better physical properties to the rubber mixes than the untreated fiber.
2. Coconut fiber acts as a reinforcing agent only when added above a volume loading of 10 phr.

3. The bonding between coconut fiber and rubber matrix is generally poor and can be enhanced by the use of a suitable bonding agent. In this study, resorcinol–formaldehyde : precipitated silica (5 : 2) bonding agent promoted sufficient adhesion.
4. The aging resistance of the coconut-fiber-reinforced rubber composites is excellent for a fiber loading of 30 phr with bonding agents.
5. Mechanical anisotropy is observable at the higher fiber loadings (10–60 phr).

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