Effect of Particulate Fillers on Short Jute Fiber-Reinforced Natural Rubber Composites

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Synopsis

The effect of carbon black on the processing characteristics and physical properties of jute fiber-reinforced composites and the role of silica and carbon black in promoting the adhesion between jute fiber and natural rubber have been studied. It was found that presence of silica is not essential to develop adhesion between fiber and rubber in the presence of carbon black. However, silica and carbon black can improve adhesion by minimizing the resin formation and controlling it to a low molecular weight species. Processing properties like green strength and mill shrinkage are improved by the addition of fiber. Carbon black does not affect mill shrinkage, but improves the green strength. Breakage of jute fiber during mixing is severe, but the extent of breakage is not affected by the presence of carbon black. The minimum loading of fiber to achieve reinforcement is reduced in the presence of carbon black. It was also found that the presence of clay in jute fiber rubber composites impairs the properties. Scanning electron microscopy (SEM) has been used to assess the failure criteria.

INTRODUCTION

Recently short fiber-reinforced rubber composites have gained importance due to their processing advantages and good mechanical properties like damping.[1-8] Murty and De have reported results of their studies on short jute fiber-reinforced natural rubber composites.[9] Foldi[10] has reported the processing advantages obtainable with short fiber–rubber composites. The presence of particulate fillers such as carbon black in short fiber-reinforced composites is expected to produce a good combination of processing and technical properties. With this objective in mind, the present work has been undertaken.

Silica has been found to be essential for developing the adhesion between rubber and fiber.[9] The role of silica in promoting adhesion had been studied earlier by Creasy et al.[11] Recently, Morita[12] has reported the relative effects of resorcinol and hexamethylene tetramine (hexa) on the rate of resin formation, but the effect of silica was not studied. It had been shown that carbon black can also promote adhesion in the absence of silica.[13] It is important, therefore, to study how silica or carbon black affects the dry bonding system.

We report in this paper the results of our work on jute fiber-reinforced natural rubber composites filled with particulate fillers such as carbon black and clay. Attempts have been made to assess the roles of silica and carbon black in adhesion and to study the failure criteria with scanning electron microscopy (SEM).

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EXPERIMENTAL

Jute fiber (Grade TD1) as supplied by the Indian Jute Industries Research Association, chopped to 6 mm length, was used as the reinforcing fiber. Mixing was done on a 150 mm × 330 mm open mixing mill. Nip gap, mill roll speed ratio, and the number of passes were kept the same in all the mixes. During mixing, care was taken to ensure fiber orientation in the grain direction in all the mixes. During mixing, fiber breakage occurred and the mean aspect ratio of fibers decreased from 130 to 15. Distribution of fiber length after breakage was obtained by dissolution of the compounds in benzene, followed by extraction of fibers and measurement with an optical microscope, and the results are shown in Figure 1. There was, however, no change in the average diameter (0.05 mm) during mixing. The fiber length distribution was studied both in the presence and absence of carbon black and the observed fiber breakage was almost the same.

The green strength of the compound was determined by the method given by Foldi.[10] The compound was heated for 2 min at 121°C to remove tack, and green strength was taken to be the stress at yield point. The mill shrinkage was determined according to ASTM D 1917-62T.

Mixes were vulcanized at 150°C to their respective optimum cure times as obtained from Monsanto R-100 rheometer. The method of preparation of the vulcanizates was the same as reported earlier.[14] Stress–strain data were obtained by using an Instron 1193 at a crosshead speed of 500 mm/min. Tensile strength and tear strength were measured according to ASTM methods D 412-51T and

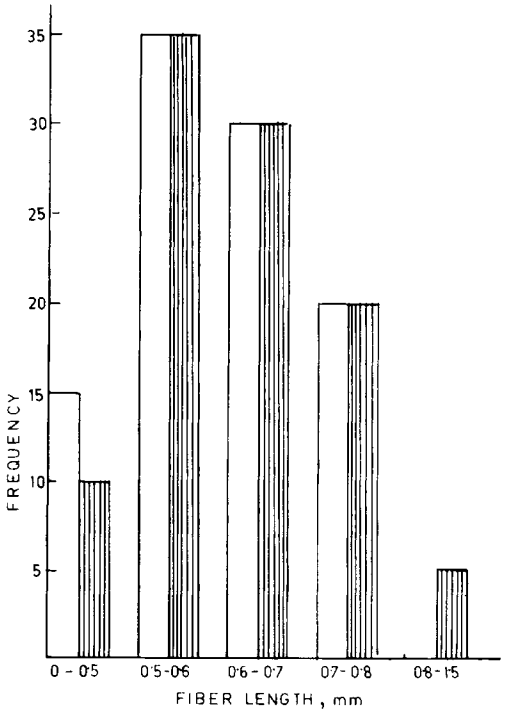


Fig. 1. Histogram showing the distribution of fiber lengths: (▥) In the presence of carbon black; (▭) in the absence of carbon black. Average diam = 0.05 mm.

D 624-54, respectively. Heat buildup measurements were done with a Goodrich Flexometer according to ASTM D 623-67 method A. Compression set measurements were done according to ASTM D 395-61, method B. Shore A hardness was determined according to ASTM D 676-52T. Resilience was measured at 35°C with a Dunlop tripsometer according to BS 903 Pt. 2, 1950. Abrasion loss was measured with a Croydon Akron abrader, and the samples were abraded for 500 revolutions. The orientation of the fibers was maximum along the grain direction. All the tests except abrasion, resilience, and hardness were carried out both along and across the grain direction. The orientation of fibers for abrasion test samples was considered random. Test specimens for resilience and hardness measurements were cut from rectangular sheets. The orientation of fibers was normal to the application of load in these cases.

The dumbell shaped specimens were aged for 24 h at 100°C in a Blue M, FC 712 air aging oven to determine aging resistance.

The tensile and tear fracture surfaces were sputter-coated with gold within 72 h of testing. The fracture surfaces and the scan area are given in Figure 2. The SEM studies were carried out with a Philips 500 model scanning electron microscope.

RESULTS AND DISCUSSION

Role of Silica and Carbon Black in Adhesion

Earlier[9] we reported that bonding between jute fiber and natural rubber can be obtained by the addition of 5 phr silica, 5 phr resorcinol, and 3.2 phr hexa. To study whether addition of silica is essential in a carbon black loaded system, we have chosen mixes A–D as given in Table I. Stress–strain data of the mixes are

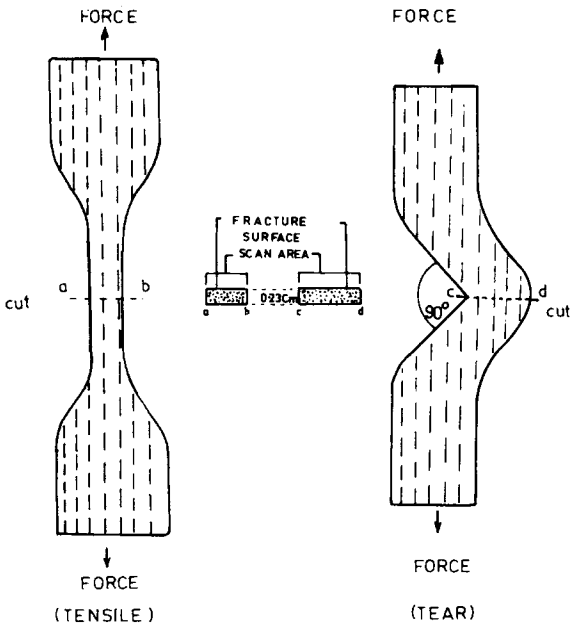


Fig. 2. Fracture surfaces and scan areas.

TABLE I
Formulations of Mixes

Mix	A	B	C	D
Natural rubber[a]	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Resorcinol	0	0	5	5
GPF black[b]	20	20	20	20
Processing oil	2	2	2	2
Silica[c]	0	5	0	5
Jute fiber[d]	25	25	25	25
CBS[e]	0.8	0.8	0.8	0.8
Sulfur	2	2	2	2
Hexa[f]	0	0	3.2	3.2

[a] Crumb rubber, ISNR Grade 5, supplied by the Rubber Research Institute of India, Kottayyam.

[b] Vulcan XC-72, GP 1206, supplied by Cabot Corporation, Billerica, MA.

[c] Vulcasil-S, supplied by Bayer (India) Ltd., Bombay.

[d] Jute fiber, TD1, supplied by the Indian Jute Industries Research Association, Calcutta.

[e] N-Cyclohexyl-2-Benzothiazylsulfenamide, supplied by Alkali and Chemical Corporation of India, Rishra.

[f] Hexamethylene tetramine, supplied by E. Merck, A. G. Germany.

given in Figure 3. From the stress–strain data it can be seen that in mixes A and B adhesion between fiber and matrix is poor when no bonding agent is present. The curves for mixes C and D are similar and indicate no additional improvement in adhesion by the addition of silica in the carbon black loaded system. The same conclusion can be drawn from physical properties of composites, as reported in Table II. Strength values are similar in mixes C and D. It is concluded from

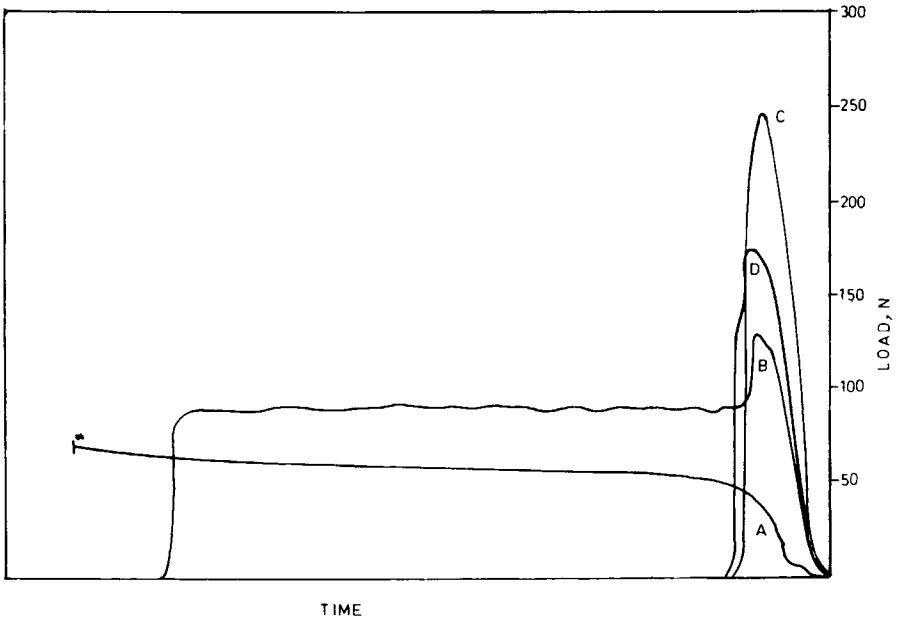


Fig. 3. Stress–strain data of mixes A–D: crosshead speed = 500 mm/min; chart speed = 1000 mm/min; (*) load at break = 140 N.

TABLE II
Physical Properties of Vulcanizates

Property	Orientation[a]	A	B	C	D
Tensile strength (MPa)	L	5.5	6.3	10.6	9.4
	T	5.0	4.9	6.1	6.7
Tear strength (kN/m)	L	24.2	40.0	46.9	55.8
	T	23.4	36.0	38.1	42.7
Elongation at break (%)	L	410	60	10	10
	T	420	400	190	190
Aging retention of tensile strength (%)	L	78	100	112	150

[a] L denotes longitudinal and T denotes transverse orientation.

the combination of both the present work and the earlier work of the authors[9] that addition of either carbon black alone or both silica and carbon black to a rubber compound containing resorcinol and hexa is essential to achieve good adhesion between the fiber and the rubber matrix. We have chosen mix C for our subsequent studies.

Morita[12] has recently suggested that increase in viscosity in mixes containing only resorcinol and hexa but no curatives can be attributed to resin formation. We have taken the mixes E–I as reported in Table III in order to study the roles of silica and carbon black in promoting adhesion. The rheographs of mixes E–I are given in Figure 4. From the rheometric data (Table III) it can be seen that torque increment, presumably due to resin formation, is affected considerably by silica. The presence of silica in the mix appears to control the resin formation to low molecular weight species. These low molecular weight species can diffuse easily and help in adhesion. It is also evident from the values of torque increment for mix G containing only fiber that fiber does not affect resin formation, and accordingly no adhesion was developed in that case.[9] It is also interesting to note that resin crosslinking, as shown by the V_r values (Table III), is also affected by the presence of fillers. Mix E containing no filler shows some restriction to swelling due to crosslinking of rubber by resin. The other mixes disintegrated when kept in benzene, thereby indicating no crosslinking of rubber. V_r may also indicate restriction of swelling due to resin formation. Since V_r values in mixes

TABLE III
Formulations of Mixes and Results of Rheometric and Swelling Studies

Mix	E	F	G	H	I
Natural rubber	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Resorcinol	5	5	5	5	5
GPF black	—	—	—	—	20
Oil	—	—	—	—	2
Silica	—	5	—	5	—
Jute fiber	—	—	15	15	—
Hexa	3.2	3.2	3.2	3.2	3.2
Torque increment (N.m)	1.1	0.7	1.1	0.6	0.9
Maximum torque (N.m)	1.7	1.4	1.8	1.2	1.6
V_r[a]	0.038	0	0	0	0

[a] Volume fraction of rubber in swollen vulcanizate (swollen in benzene for 36 h at 35 ± 1°C).

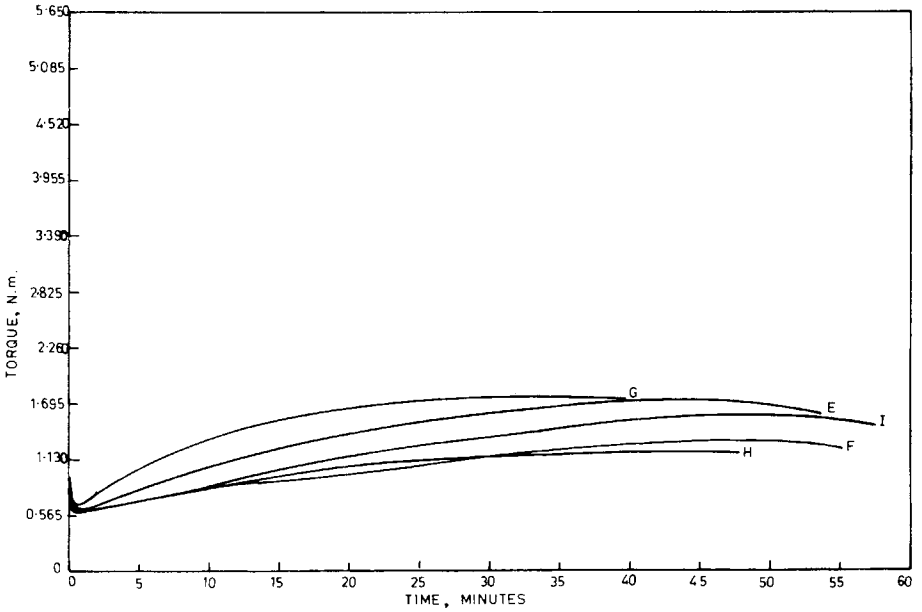


Fig. 4. Rheographs of mixes E–I.

containing silica and carbon black are nil, it can be assumed that resin formation is restricted in the presence of silica and/or carbon black. The decrease in torque increment in the case of mix I containing carbon black is not considerable. This may be due to the presence of carbon black which, by itself, increases torque. From this we may conclude that both silica and carbon black promote adhesion by restricting the resin formation. Our observations give a direct evidence to the mechanism proposed by Creasy et al.[11] However, the role of silica in increasing the wettability cannot be ruled out.[11]

Processing Characteristics

Processing characteristics are reported in Table IV. Fiber reinforced composites exhibit considerable green strength at a loading of 25 phr fiber. In the presence of carbon black the green strength increases. It is quite interesting to note that mill shrinkage is reduced considerably in the presence of jute fiber. Carbon black has no marked effect on mill shrinkage of short fiber-reinforced rubber compounds.

TABLE IV
Processing Characteristics of Mixes[a]

Carbon black loading (phr)	0	0	0	20	20	20
Jute fiber loading (phr)	0	5	25	0	5	25
Silica loading (phr)	5	5	5	0	0	0
Green strength (MPa)	0	0	1.2	0	0.5	2.0
Mill shrinkage (%)	57	36	3	52	21	4

[a] Base recipe: natural rubber 100, ZnO 5, stearic acid 2, resorcinol 5, CBS 0.8, sulfur 2, hexa 3.2.

Physical Properties

Table V shows the formulations of the mixes J–N. Their physical properties are reported in Table VI. Comparison of the values of tensile strength in the longitudinal direction indicates that the nature of variation of tensile strength with volume loading of fiber is not affected by the presence of carbon black. When the fibers are not sufficient to restrain the matrix, large stresses will be developed at low strains and the distribution of stress will not be uniform. But when the fibers are sufficient to restrain the matrix, the stress distribution will be uniform, and the effective function of fibers as reinforcing agents can be observed. Similar observations have been made by previous workers.[5,15] A close study of the variation of tensile strength values reveals that the minimum loading of fiber necessary to act as reinforcing agent shifts to lower values in the presence of carbon black. Dzyura[16] had reported earlier that if the matrix strength is higher, the minimum amount of fiber required to restrain the matrix shifts to a lower value. We have reported[17] that the presence of carbon black restricts the flow of the matrix and thereby restrains it. It can be argued that carbon black restricts the matrix to some extent, and further restriction of matrix flow can be achieved with the addition of a low amount of fiber.

Values of elongation at break drop down drastically from 500% to 260% by the addition of only 5 phr jute fiber in carbon black loaded composites. In the absence of carbon black the drop in the value of elongation at break is gradual up to 10 phr jute fiber. This again confirms that the minimum amount of fiber necessary for observable reinforcement is lower in the presence of carbon black. Further addition of carbon black does not produce much changes.

Tear strength increases in the presence of fibers. Addition of carbon black does not have much effect on tear strength values. Carbon black filled composites yield a rough fracture surface typical of knotty type tear.[9] It has been reported that both carbon black and short jute fiber increase the tear strength by obstructing the tear paths proceeding straight.[18,9]

Carbon black filled composites register higher heat buildup even at lower loadings of jute fiber. Further addition of carbon black results in higher values of heat buildup. This is because both carbon black and jute fiber make the compounds stiffer, and stiffer composites, as explained earlier, experience higher stress for a given strain generating more heat. The stiffness of composites with longitudinally aligned fibers is higher in the direction of application of stress than that for the composites with fibers aligned transversely. Thus the composites with longitudinally oriented fibers show higher heat buildup values than those with transversely oriented fibers. The variation of hardness with fiber loading is similar to the variation of heat buildup with fiber loading, confirming the above explanation.

Compression set does not change much with fiber loading. However, it increases with increase in carbon black content. Higher values of compression set in the case of samples with longitudinally aligned fibers may be due to the buckling of fibers when stressed in the direction of alignment. Resilience drops down with increase in fiber loading. The black filled composites exhibit lower values of resilience.

Flex resistance is poor for all the fiber-reinforced composites, and carbon black reduces it further. As both carbon black and jute fiber make the vulcanizate stiffer, it is likely that flex resistance decreases with the increase in the loading

TABLE V
Formulations of Mixes

Mixes	J_1	J_2	J_3	K_1	K_2	K_3	L_2	L_3	M_1	M_2	M_3	N_1	N_2	N_3
Natural rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Resorcinol	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Carbon black	0	20	30	0	20	30	20	30	0	20	30	0	20	30
Oil	0	2	3	0	2	3	2	3	0	2	3	0	2	3
Silica	5	—	—	5	—	—	—	—	5	—	—	5	—	—
Jute fiber	0	0	0	5	5	5	10	10	15	15	15	25	25	25
CBS	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Hexa	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2	3.2
Optimum cure time at 150°C (min)	12	11.5	13	10	10.5	11.75	10	10.5	8	9.5	10.75	8	9.25	10.5

TABLE VI
Physical Properties of Vulcanizates[a]

Property		J_1	J_2	J_3	K_1	K_2	K_3
Tensile strength (MPa)	L	12.8	14.3	10.8	7.7	11.3	9.3
	T	11.9	14.8	11.8	10.1	12.2	8.5
Tear strength (kN/m)	L	15.5	17.7	24.5	24.3	36.7	27.8
	T	21.0	21.3	27.3	34.4	30.0	28.6
Elongation at break (%)	L	630	400	350	430	250	250
	T	600	450	300	500	260	300
Flexing resistance to failure (kilocycles)	L	44	40	20	10	3	4
	T	44	44	10	10	10	3
Heat buildup (ΔT) (°C)	L	19	18	33	18	33	58
	T	19	23	31	11	30	40
Compression set (%)	L	33	38	52	36	49	62
	T	32	35	—	51	51	61
Resilience (%)		73	67	51	71	65	54
Hardness (shore A)		39	35	60	55	74	70
Abrasion loss (cc/500 rev)		0.49	0.48	0.47	1.26	1.01	0.85
Tensile strength retained after aging (%)		—	41	47	—	51	65

Property		L_2	L_3	M_1	M_2	M_3	N_1	N_2	N_3
Tensile strength (MPa)	L	6.2	7.6	6.1	7.9	8.7	8.8	13.0	12.5
	T	6.5	6.7	5.0	8.6	7.9	5.6	7.7	7.7
Tear strength (kN/m)	L	36.1	30.0	46.0	42.1	33.8	43.6	50.9	40.9
	T	40.6	41.3	56.9	47.2	38.5	40.3	34.3	34.8
Elongation at break (%)	L	250	150	60	70	100	20	10	20
	T	300	260	200	250	200	150	150	120
Flexing resistance to failure (kilocycles)	L	2.5	2	5	1	1	1	3.5	0.5
	T	3	3	8	—	1	2	6	1
Heat buildup (ΔT) (°C)	L	36	43	27	43	42	37	37	50
	T	38	43	27	41	59	35	38	42
Compression set (%)	L	44	49	34	50	51	38	48	55
	T	46	57	34	48	55	47	48	63
Resilience (%)		58	51	65	61	53	60	60	49
Hardness (shore A)		75	80	75	85	82	85	90	90
Abrasion loss (cc/500 rev)		1.17	0.86	1.54	1.16	1.15	1.49	1.26	1.27
Tensile strength retained after aging (%)		79	80	—	100	95	—	96	97

[a] Results of mixes J_1, K_1, M_1, and N_1 have been taken from the authors' earlier work.[9]

of carbon black and jute fiber. The failure in the case of fiber-reinforced composite begins with local buckling of fiber, which breaks on subsequent flexing leading to crack formation. Propagation of crack results in failure.

The abrasion loss increases with the increase in fiber content. But the presence of carbon black decreases the abrasion loss, and the property is improved further at a higher loading of carbon black. It is known that, in natural rubber vulcanizates, abrasion resistance is increased by the reinforcing carbon black. The presence of fiber decreases the abrasion resistances, while carbon black functions in the opposite direction.

Aging resistance values reflect the earlier conclusion that the amount of fiber necessary for showing the reinforcing characteristics is less in the presence of carbon black. When fibers act as reinforcing filler, the load is carried mainly

TABLE VII
Formulations and Physical Properties of Clay Filled Mixes

Mix		O	P	Q	R	S	T
Natural rubber		100	100	100	100	100	100
Zinc oxide		5	5	5	5	5	5
Stearic acid		2	2	2	2	2	2
Resorcinol		5	5	5	5	5	5
Clay[a]		40	40	40	40	40	40
Silica		15	15	15	15	15	15
Fiber		0	2	10	15	25	35
CBS		0.8	0.8	0.8	0.8	0.8	0.8
Sulfur		2	2	2	2	2	2
Hexa		3.2	3.2	3.2	3.2	3.2	3.2
Optimum cure time at 150°C (min)		14.5	14	13.5	12.75	10.25	11.5
Tensile strength (MPa)	L	6.7	5.0	5.1	7.0	7.1	11.0
	T	7.2	4.0	4.9	5.9	5.5	5.7
Elongation at break (%)	L	400	300	200	90	20	10
	T	350	330	330	270	130	90
Tear strength (kN/m)	L	24.4	17.6	31.2	30.2	39.1	42.5
	T	18.0	20.2	32.9	36.2	38.4	35.2
Aging retention of tensile strength (%)	L	—	90	92	93	100	100

[a] Hindustan Clay supplied by Bata (India) Ltd., Batanagar, Calcutta.

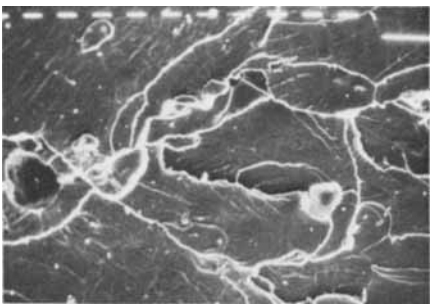
by the fibers. Since they do not deteriorate with aging, the properties are retained at the same level even after aging.

Effect of Clay

Formulations and physical properties of clay-filled jute fiber-reinforced composites are given in Table VII. Variations of tensile strength and elongation at break with fiber loading are not affected much by the presence of clay. Values of tensile strength in the presence of clay are lower than those obtained in the absence of clay. Tear strength increases with fiber content as in the other cases. In general, the strength values are lower in clay-filled mixes.

SEM Studies

Tensile and tear fracture surfaces of mixes J_2, N_2, O, and S were examined with SEM to study their failure criteria. Figure 5(a) shows the SEM photomicrograph of the tensile fracture surface of mix J_2 containing carbon black, resin, and no fiber. The general surface shows slip lines between holes formed by the separation of aggregates. These holes act as nuclei for crack propagation. One such hole, when examined under high magnification, reveals interesting features. There are parabolic cracks radiating from the nuclei indicating a brittle type of failure [Fig. 5(b)]. The clay-filled composite without fiber (mix O) undergoes tensile rupture by layer delamination [Fig. 6(c)]. This type of failure was observed earlier[17] for the tensile fracture of carbon black–silica blend filler system. The nature of fracture surface of jute fiber-reinforced composites is not affected by the presence of fillers. In the presence of carbon black [mix N_2, Fig. 5(d)], orientation and dispersion of fibers are better than those observed in the presence



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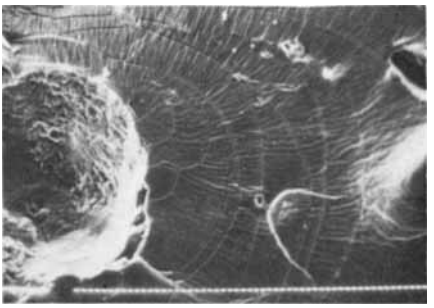

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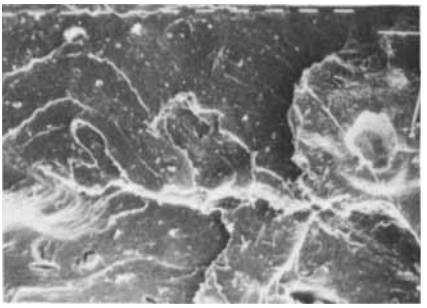

(c)

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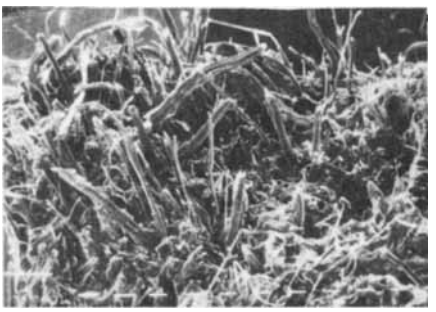

(e)

Fig. 5. Photomicrographs of tensile fracture: (a) tensile fracture surface of mix J_2 (50 ×) (tilt 0°); (b) parabolic slip lines generating from one hole (100 ×) (tilt 0°); (c) tensile fracture surface of mix O (50 ×) (tilt 0°); (d) tensile fracture surface of mix N_2 (50 ×) (tilt 0°); (e) tensile fracture surface of mix S (50 ×) (tilt 35°).

of clay [mix S, Fig. 5(e)]. There is evidence for the tensile fracture through fiber pullout [Fig. 5(e)] in composites loaded with clay and jute fiber.

Tear fracture surface in the case of mix J_2 shows branched tear lines [Fig. 6(a)]. The tear paths are obstructed from proceeding straight and thus giving high tear strength. The tear fracture surface of mix O, as in the case of tensile fracture, is similar to that observed for carbon black–silica system[17] [Fig. 6(b)]. The nature of fracture surface of fiber-reinforced composites is not affected by the presence of fillers. Figure 6(c) shows the general surface of tear fracture of mix N_2, and Figure 6(d) shows the general surface of the tear fracture of mix S. There is some debonding in the case of mix S containing clay and jute fiber. In the presence of fibers there are no tear paths to be seen. The increase in tear

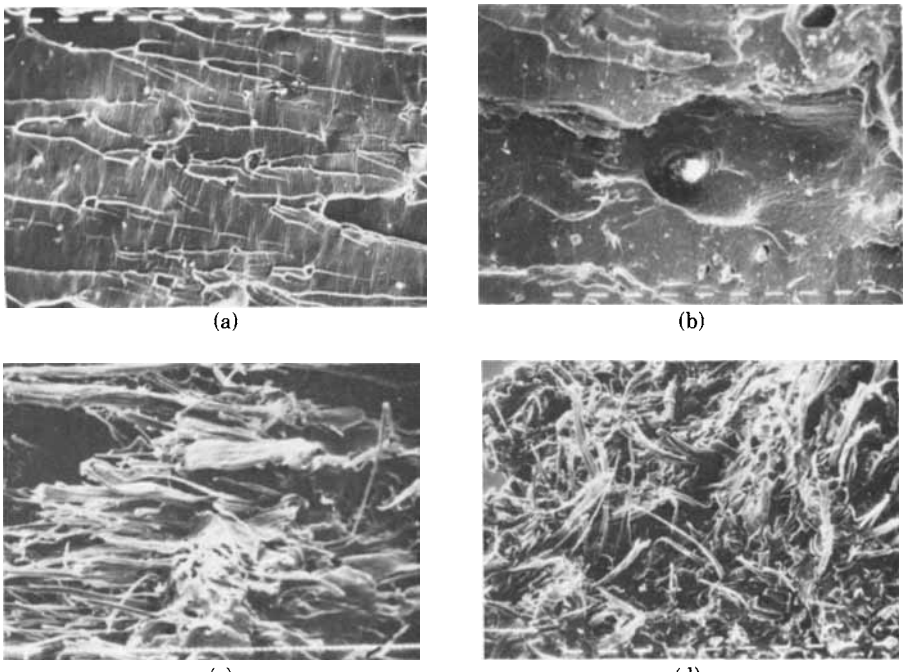

Fig. 6. Photomicrographs of tear fracture: (a) Tear fracture surface of mix J_2 (50 ×) (tilt 0°); (b) Tear fracture surface of mix N_2 (100 ×) (tilt 0°); (c) Tear fracture surface of mix O (50 ×) (tilt 0°); (d) Tear fracture surface of mix S (50 ×) (tilt 35°).

strength of jute fiber-reinforced composites may be due to the role played by fibers in obstructing the tear paths.

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