Viscoelastic Properties of Short-Fiber-Reinforced Rubber Composites and the Role of Adhesion

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Synopsis

Viscoelastic properties of short-fiber-reinforced natural rubber composites have been studied as a function of temperature and at different levels of adhesion. The effect of adhesion on the viscoelastic properties of the composites has been assessed, and it is found that the increase in adhesion increases the mechanical loss per cycle and modulus. With the increase in temperature the mechanical loss and modulus drop, indicating a possible deterioration of the adhesion at higher temperatures. Presence of carbon black increases the mechanical loss but does not necessarily increase the level of adhesion. The effect of overcuring has also been studied. Complex modulus of the composites displays an exponential behavior with the increase in volume fraction of fiber.

INTRODUCTION

Rubber products generally undergo dynamic stressing during service, and their resistance to the dynamic load application is important. Most rubber products are composites, reinforced with textiles. Recently, short-fiber reinforcement is found to be a suitable alternative to continuous-cord reinforcement for reasons of processing economy and design flexibility.[1] It is important, therefore, to study the response of short-fiber-reinforced composites to dynamic load application. Adhesion between the fibers and rubber matrix also plays a vital role on the success of a short-fiber-reinforced composite.[2] Earlier workers have studied the viscoelastic properties of particulate-filled rubber composites.[3] Continuous cord reinforcement such as cord rubber composites have also been studied for their resistance to dynamic load application.[4] There are conflicting views on the effect of adhesion on the viscoelastic properties of cord rubber composites.[4,5] Earlier work on short-fiber-reinforced composites is concentrated on their mechanical properties and the effect of orientation of fibers on their ultimate properties.[6–8] Recently, McLean and Read[9] have studied the storage and loss moduli of discontinuous fiber-reinforced rubber composites. But the actual effect of adhesion on the viscoelastic properties of cord rubber composites is still not clear in cord–rubber composites, let alone in case of short-fiber reinforcement.

Recently, De and co-workers[10–13] have reported the results of their studies on short-jute-fiber- and short-glass-fiber-reinforced natural rubber, styrene–butadiene rubber, and carboxylated nitrile rubber composites. In this paper we report results of our studies on the viscoelastic properties of short-jute-fiber and short-glass-fiber reinforced natural rubber and styrene–butadiene rubber composites.

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TABLE I
Formulations of the Mixes

	A	B	C	D	E	F	G	H
Mix	(NR–gum)	(NR + silica)	(NR + resin + silica)	(NR + jute—no bonding agent)	(NR + jute + resin)	(NR + jute resin + silica)	(NR + jute + black + resin)	(NR + jute + black + silica + resin)
Natural rubber[a]	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Resorcinol	—	—	5	—	5	5	5	5
Silica[b]	—	5	5	—	—	5	—	5
Jute fiber[c]	—	—	—	25	25	25	25	25
Black (GPF)[d]	—	—	—	—	—	—	40	40
Process oil	—	—	—	—	—	—	4	4
CBS[e]	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
Hexa[f]	—	—	3.2	—	3.2	3.2	3.2	3.2
Optimum cure time at 150°C (min)	14	15	17	9	7	8	10	11

[a] Crumb rubber (ISNR-5) supplied by the Rubber Research Institute of India, Kottayam (Kerala).

[b] Vulcasil-S supplied by Bata India, Ltd., Calcutta.

[c] Grade TD1 supplied by Indian Jute Industries Research Association, Calcutta.

[d] Vulcan XC 72 GP 1200, supplied by Cabot Corporation, Billerica, Mass.

[e] *N*-cyclohexyl benzothiazole sulfenamide supplied by Alkali and Chemicals Corp. of India, Rishra.

[f] Hexamethylene tetramine supplied by M and B, U.K.

The first part of the paper deals with the effect of adhesion on the viscoelastic properties of short-jute-fiber-reinforced natural rubber composites, since it was observed earlier that considerable changes in the adhesion level can be obtained by varying the composition of bonding agents.[10] In the present work, the effect of adhesion as a function of temperature has been studied, and gum vulcanizates (without fiber) have also been included for comparison. The effects of carbon black and overcuring have also been studied.

The second part of the paper deals with the effect of fiber concentration on the modulus of the composites. These studies have been done with both the jute and glass fibers and two rubbers, namely, natural rubber (NR) and styrene–butadiene rubber (SBR).

EXPERIMENTAL

Jute fiber (Grade TD1) as supplied by Indian Jute Industries Research Association, Calcutta, chopped to 6 mm length, was used. Short-treated glass fibers (length 9 mm) as supplied by Fiber-glass Pilkington, Ltd., Bombay, were used in the study.

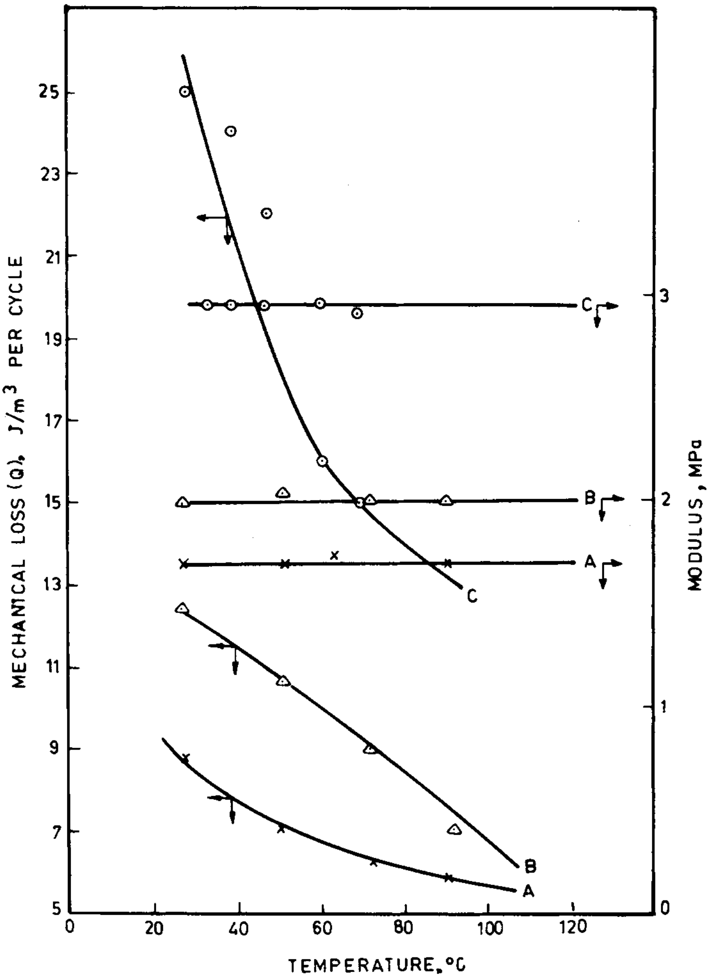

Fig. 1. Mechanical loss and modulus as a function of temperature for gum vulcanizates: (A) NR–gum; (B) NR–silica; (C) NR–silica–resin.

Mixes were done on a 15 cm × 33 cm roll mill. Nip gap and number of passes were kept the same in all the mixes. Care was taken to ensure fiber orientation maximum in the mill direction. Mixes were vulcanized at their respective optimum cure times as obtained from Monsanto Rheometer R-100. In the case of samples for overcuring, the samples were cured for an extra 15 min beyond optimum curing. The samples were molded in an electrically heated press at a temperature of 150°C under a pressure of 6.5 MPa.

Viscoelastic properties are studied with a Rheovibron DDV IIIC. The samples were tested at different temperatures between room temperature (26°C) and 100°C. All the tests were carried out at a strain amplitude of 0.0025 cm and a frequency of 35 Hz. The samples were clamped and correction for sample yielding, as suggested by Voet and Morawski,[14] was taken in consideration for calculations.

RESULTS AND DISCUSSION

Effect of Adhesion on Viscoelastic Properties

Formulations of the mixes are given in Table I. The mechanical loss and complex modulus of gum vulcanizates are given in Figure 1 as a function of temperature. It can be seen from Figure 1 that the addition of silica and/or resin increases mechanical loss. It has been reported earlier that the presence of silica increases the mechanical loss per cycle.[3] The increase in mechanical loss corresponds with the increase in modulus. This indicates that as the matrix gets stiffened by the addition of either silica and/or resin, the mechanical loss associated with the composite also increases. This confirms earlier observations on the values of heat buildup.[13] The effect of temperature on the mechanical loss is similar for the samples and in agreement with the earlier results.[4] The values of mechanical loss decrease, and the difference between different systems becomes less at higher temperature. However, the modulus does not change much with the temperature for the system without fiber.

Unlike continuous-cord reinforcement, in which case the adhesion can

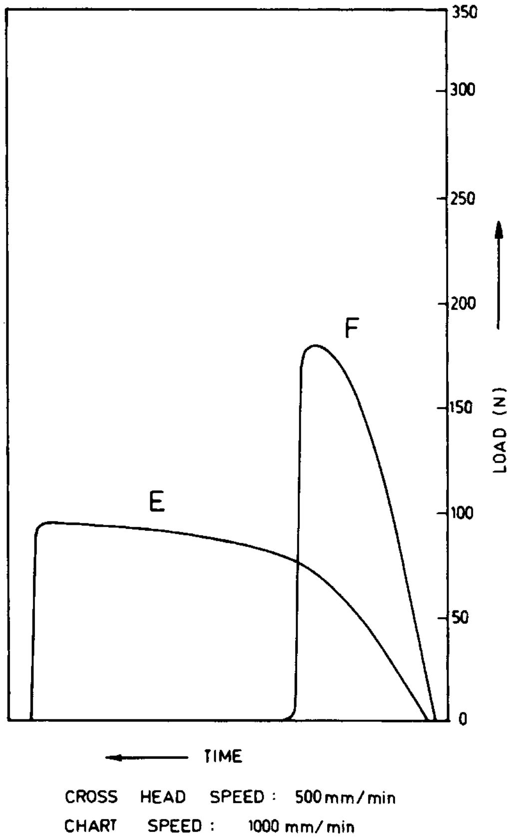

Fig. 2. Stress–strain curve for jute-fiber-reinforced natural rubber composites: (E) NR–jute fiber–resin; (F) NR–jute fiber–resin–silica.

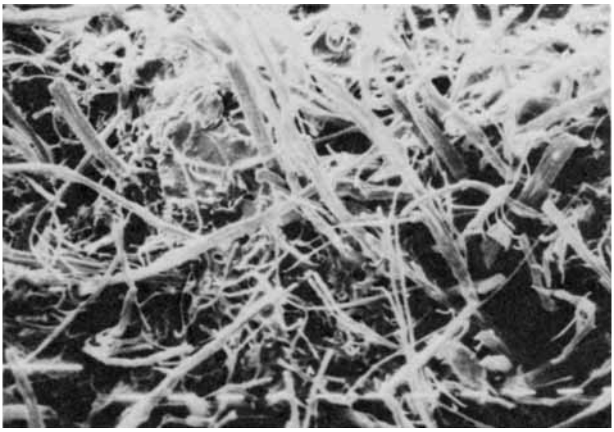

Fig. 3(a). Photomicrograph of tensile fracture surface of jute-fiber-reinforced natural rubber composites without any bonding agent (mix D).

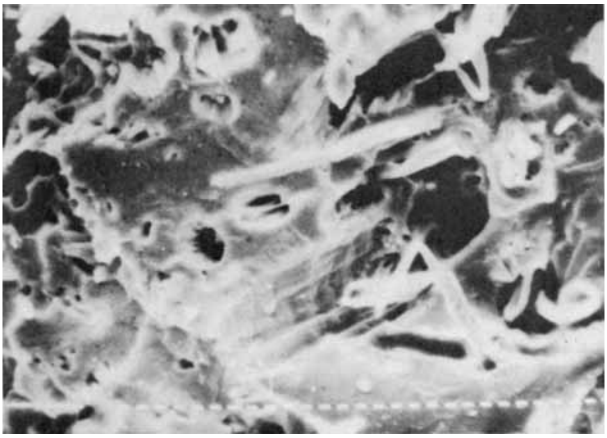

Fig. 3(b). Photomicrograph of tensile fracture surface of mix E of Figure 2.

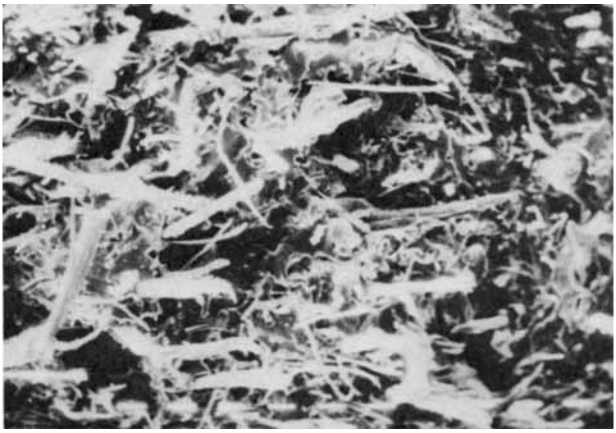

Fig. 3(c). Photomicrograph of tensile fracture surface of mix F of Figure 2.

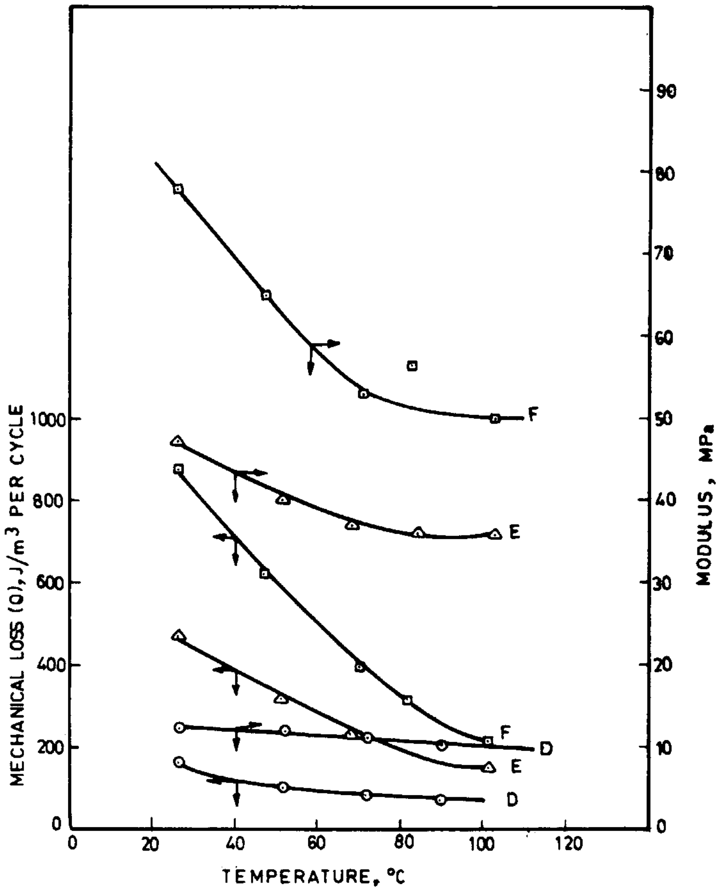

Fig. 4. Mechanical loss and modulus as a function of temperature for fiber-reinforced rubber composites: (D) NR-jute fiber; (E) NR-jute fiber-resin; (F) NR-jute fiber-silica-resin.

quantitatively be determined with the help of the H-test, the quantitative determination of adhesion is not possible in the case of short-fiber reinforcement of rubber. However, it can qualitatively be assessed either by stress-strain curves or by SEM analysis of the fracture surfaces, and a correlation between these two methods is good.[10] Figure 2 gives the stress-strain curves for mixes E and F containing 0 phr and 5 phr silica, respectively. It is quite evident from Figure 2 that the addition of 5 phr silica improves the adhesion markedly. It is further confirmed by SEM studies. Figure 3(a) gives the SEM photomicrograph of tensile fractured surface of mix D containing on bonding agent. The long stems of fibers protruding out of the rubber matrix indicate that the fibers are pulled out of the rubber matrix under tension due to poor bonding. Figures 3(b) and 3(c) give the SEM photomicrographs of tensile fracture surfaces of mixes E and F, respectively. In Figure 3(b) both debonding and fiber breakage are evident, indicating that the adhesion is improved compared to mix D but not to the desired level. The fracture through only fiber breakage is evident from Figure 3(c), which indicates that the adhesion has further improved. It is understood, therefore, that the adhesion level can be varied by varying the bonding agents.

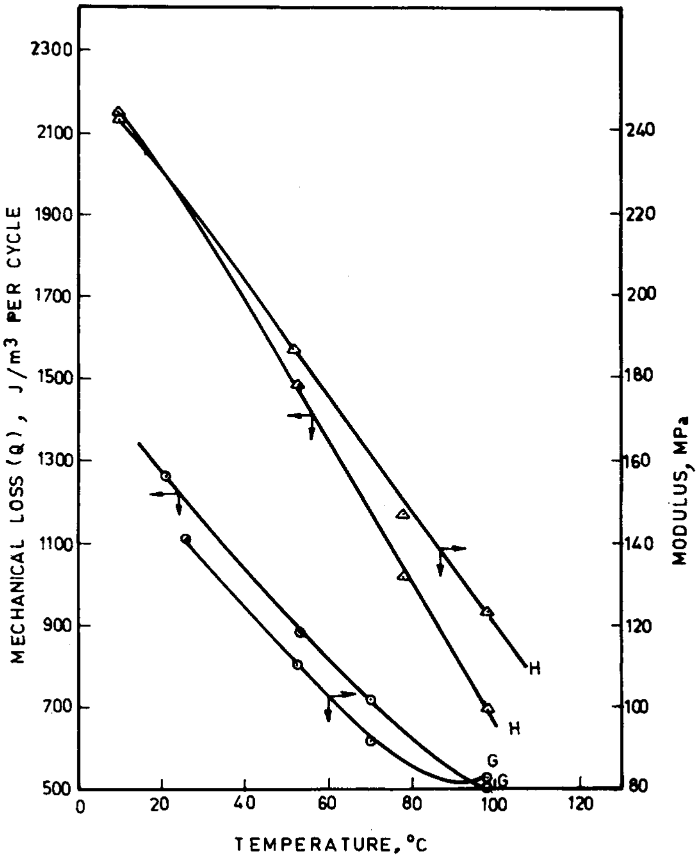

Fig. 5. Mechanical loss and modulus vs. temperature in the presence of carbon black: (G) NR–jute fiber–carbon black–resin; (H) NR–jute fiber–carbon black–silica–resin.

Figure 4 gives the mechanical loss and modulus of fiber-reinforced composites as a function of temperature. Both the mechanical loss and the modulus increase with the increase in the adhesion level, which observations similar to the observations with cord rubber composites.[4] Addition of silica, resorcinol and hexamethylenetetramine increases the value of mechanical loss by about 3 times in the absence of fiber (Fig. 1, mixes A and C) and by about 6 times in the presence of fiber (Fig. 4, mixes D and F). It can be concluded, therefore, that the adhesion is affecting the viscoelastic properties of the composites. When there is no bonding between the fiber and matrix (mix D), the fibers can slip past each other under tension, but, when there is bonding between the fibers and matrix (mixes E and F), there will be shear at the interface between matrix and fiber, which leads to increased mechanical loss. The high modulus of the well-bonded composites stems out from the fact that the load transfer between the fiber and matrix occurs through the strong matrix–fiber interface. The cords do not contribute to the mechanical loss in the cord–rubber composites in the absence of adhesion, and therefore the mechanical loss of the unbonded cord–rubber composite will be less than that of rubber.[4] But this will not be the case with short-fiber-reinforced composites. In the case of short-fiber-reinforced com-

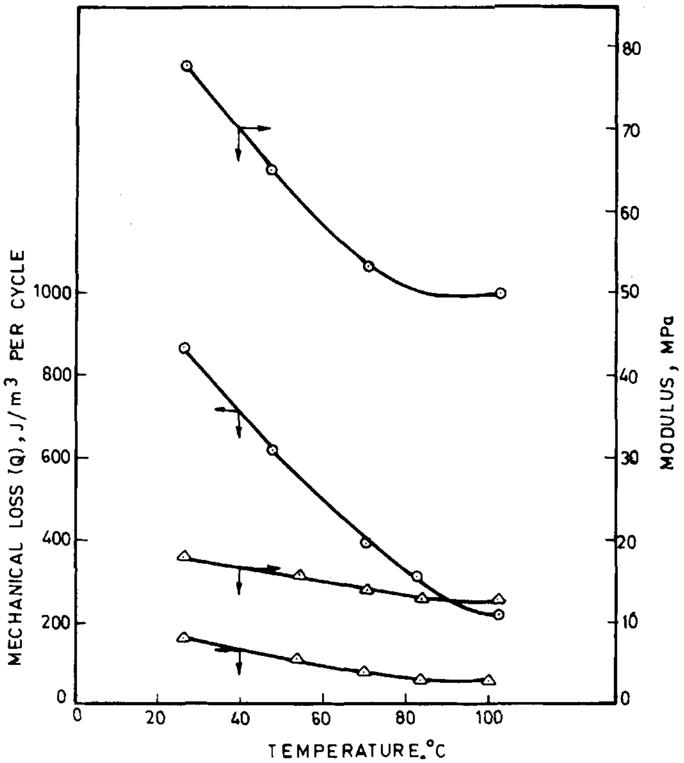

Fig. 6. Effect of orientation on the viscoelastic behavior (mix F): (⊙) longitudinal; (△) transverse.

posites when the bonding is poor, the fiber ends will be free and act as stress raisers and thus contribute to mechanical loss. However, the values of mechanical loss will increase with the increase in adhesion level, as discussed earlier.

In all the cases the effect of temperature is similar, and the modulus and mechanical loss decrease with the increase in temperature (Fig. 4). As observed for the gum stock, the difference becomes smaller as the temperature increases. This may be due to the fact that the fiber–matrix interface becomes weak as the temperature of the test is increased. The case with modulus is similar. It is interesting to note that the modulus of the composites with bonding agents (mixes E and F) has dropped and, for the composites without any bonding agents (mix D), has remained almost constant with the increase in temperature. This also confirms the above explanation that the fiber–matrix interface becomes weak at higher temperatures.

Voet and Morawski[3] have earlier reported that the addition of carbon black increases the loss modulus. Figure 5 gives the mechanical loss and modulus of the fiber–rubber composites filled with carbon black and carbon black and silica as a function of temperature. Comparison of Figures 4 and 5 reveals that the addition of carbon black increases the value of mechanical loss by about 2.5 times both in the presence and absence of silica. The effect of temperature is again

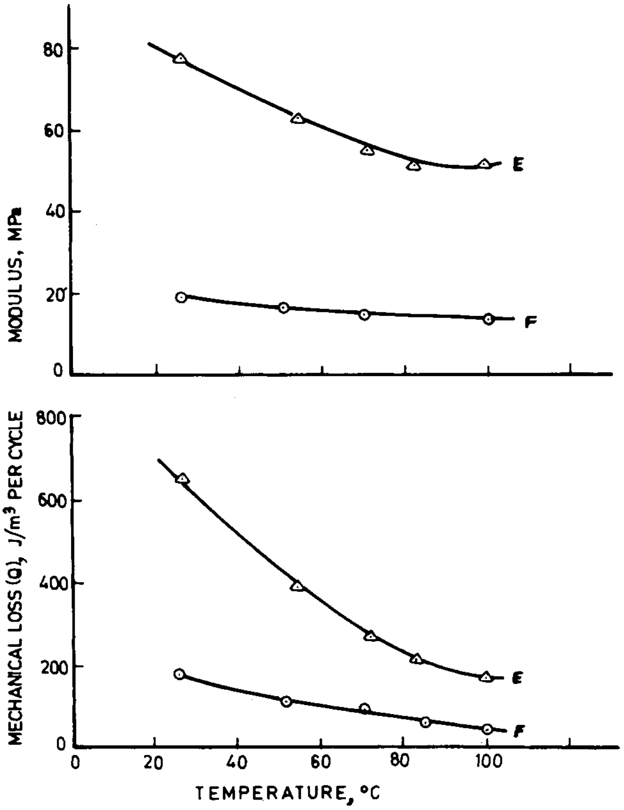

Fig. 7. Effect of overcuring on adhesion (mixes E and F).

to reduce the values of mechanical loss and modulus, indicating that the carbon black does not improve the adhesion additionally.

Figure 6 shows the effect of the direction of orientation of fibers on the viscoelastic properties. The well-bonded jute-fiber-reinforced natural rubber composites exhibits anisotropy. It was also shown earlier that the fibers present in the transverse direction contribute less to the mechanical loss and modulus of the composite.[4] When the fibers are in the direction of application of load, the load will be borne by the fibers, and they increase the modulus of the composite. Similar observations were made earlier in case of heat buildup values of the composites.[10,11]

Dunnon showed that the vulcanization time affects the adhesion considerably.[15] The rate of vulcanization is enhanced in the presence of bonding agents such as resorcinol and hexamethylenetetramine, and at optimum cure time the adhesion may not be complete, as the rates of vulcanization and adhesion are not same. Effect of overcuring was studied in order to assess the effect of vulcanization time on adhesion (Fig. 7). It is interesting to note that the adhesion as explained in terms of mechanical loss in case of the composites containing silica, resorcinol, and hexa has dropped down with overcuring. But the adhesion in the case of composite containing only resorcinol and hexa is slightly improved with overcuring. The presence of silica increases the vulcanization time (Table

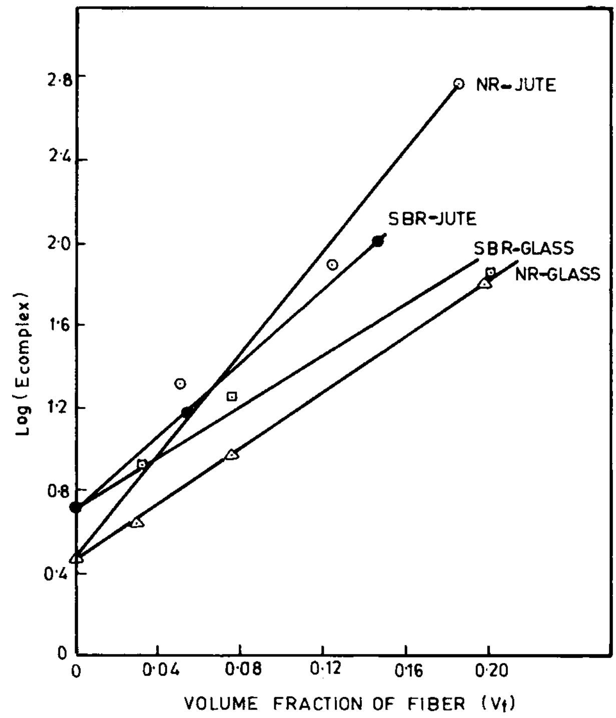

Fig. 8. Semilogarithmic plot of modulus vs. volume fraction of fiber.

I), and thus the adhesion may be complete at optimum cure time. Any further curing might deteriorate the adhesion. But, in the absence of silica, the vulcanization will be faster, giving incomplete adhesion at optimum cure time. So further curing might have enhanced the adhesion.

Effect of Fiber Concentration on the Viscoelastic Properties

Figure 8 gives the complex modulus as a function of volume fraction of fiber. The semilog plot of modulus vs. volume fraction of fiber is linear, almost in agreement with the emperical equation for Young's modulus, as proposed by Derringer[16]:

$$G = G_0 - 1 + \exp(aV^b)$$

where G = Young's modulus of the composite, G_0 = Young's modulus of the matrix, V = volume fraction of fiber, and a and b are constants. Close observation of Figure 6 reveals that jute fibers reinforce natural rubber to a higher extent than the glass fibers. In the case of glass fiber, the reinforcement of NR and SBR is almost same. In general, the reinforcement of natural rubber by short fibers is better than that of SBR. The results are in agreement with our earlier observations.[10,12,17]

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