Stress Relaxation in Short Jute Fiber-Reinforced Nitrile Rubber Composites

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Synopsis

Stress relaxation measurements in tension have been made on nitrile rubber vulcanizates containing short jute fibers. The effects of strain level, bonding system (silica-resorcinol-hexa), fiber orientation, fiber content, temperature, and prestraining on the rate of stress relaxation have been investigated. Existence of a relaxation mechanism within the first 200 s is reported.

INTRODUCTION

In recent years short fiber-reinforced elastomer composites have gained importance because of their advantages in processing, anisotropy in properties, easy dispersion, and improved adhesion to the rubber using bonding agents. Earlier work on short fiber-rubber composites was confined to studies on mechanical properties and the effect of fiber orientation on ultimate properties.[1-3] De and coworkers studied various technical properties, including dynamic mechanical properties of short jute and short silk fiber-reinforced elastomer composites.[4-8] However, it appears that no systematic studies have been reported on the stress relaxation of short fiber-rubber composites. Stress relaxation properties assume importance in view of the increasing use of short fiber-reinforced composites in such products as hoses, belts, tires, and gaskets. In this paper, the results of our studies on the stress relaxation of short jute fiber-nitrile rubber (NBR) composites are reported. The effect of strain level, bonding agent, fiber content and orientation, temperature, and prestrain on the relaxation behavior have been studied.

EXPERIMENTAL

Materials

Jute fiber (Grade TDI) as supplied by Indian Jute Industries Research Association, Calcutta, was chopped to 6 mm length using a fiber-cutting machine and predried at 100°C before use. Nitrile rubber (Perbunan N 3307), supplied by Bayer Ltd., West Germany, with an acrylonitrile content of 33%, was used.

Sample Preparation

Formulations of the mixes are shown in Table I. Mixes were done on a 150 × 330 mm open roll mill. Nip gap and number of passes were maintained for

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TABLE I
Formulations of Mixes

Ingredients	Mix A	Mix B	Mix C	Mix D	Mix E
Nitrile rubber	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Jute fiber	—	—	20	20	10
Silica[a]	—	5	—	5	5
Resorcinol	—	5	—	5	5
Hexa[b]	—	5	—	3.2	3.2
Sulfur	2.0	2.0	2.0	2.0	2.0
CBS[c]	0.8	0.8	0.8	0.8	0.8
Optimum cure time at 150°C (min)	12	8.5	12.5	8.5	8

[a] Vulcasil-S obtained from Bata India Ltd., Calcutta.
[b] Hexamethylenetetramine supplied by Bengal Waterproof Ltd., Panihati, West Bengal.
[c] N-cyclohexyl benzothiazole sulfenamide, manufactured by Indian Explosives Ltd., Rishra.

all mixes and care was taken to orient the fiber maximum in the mill direction. For better dispersion, molten resorcinol[9] and finely powdered hexamethylenetetramine were used. The mixes were vulcanized to their optimum cure times, as determined by Monsanto Rheometer R-100. Sheets 2 mm thick were molded at 150°C and 4.5 MPa pressure in an electrically heated press. Dumbbell specimens (ASTM D 412; type C) were punched out of these sheets.

The effects of strain level, fiber content, temperature, and prestrain have been studied on samples containing fibers oriented in the longitudinal direction.

Apparatus

An Instron model 1195 universal testing machine was used for stress relaxation measurements. The samples were pulled to the desired strain level at a strain rate of approximately 0.061 s^{-1}, and the decay of stress as a function of time was recorded on a chart paper initially at a high chart speed and later at a slow speed.

RESULTS AND DISCUSSION

Effect of Strain Level

Linear plots were obtained when σ/σ_0 is plotted against $\log t$ (Fig. 1) for gum samples at four strain levels (σ_0 is obtained from the maximum load at $t = 0$ when the desired strain is reached; σ is the stress at subsequent times t). The slopes and intercepts vary little with strain level (see Table II). These results are in agreement with those reported by Gent[10] for natural rubber and by Voet et al.[11] for styrene-butadiene (SBR), butyl, and polybutadiene rubbers.

The results of fiber-loaded samples (mixes C and D) are shown in Figures 2 and 3, respectively. Unlike in the case of gum vulcanizate, experimental points for these systems appear to lie on two straight lines; the first line is of greater slope and applies for short times (< 200 s) and the second line for longer
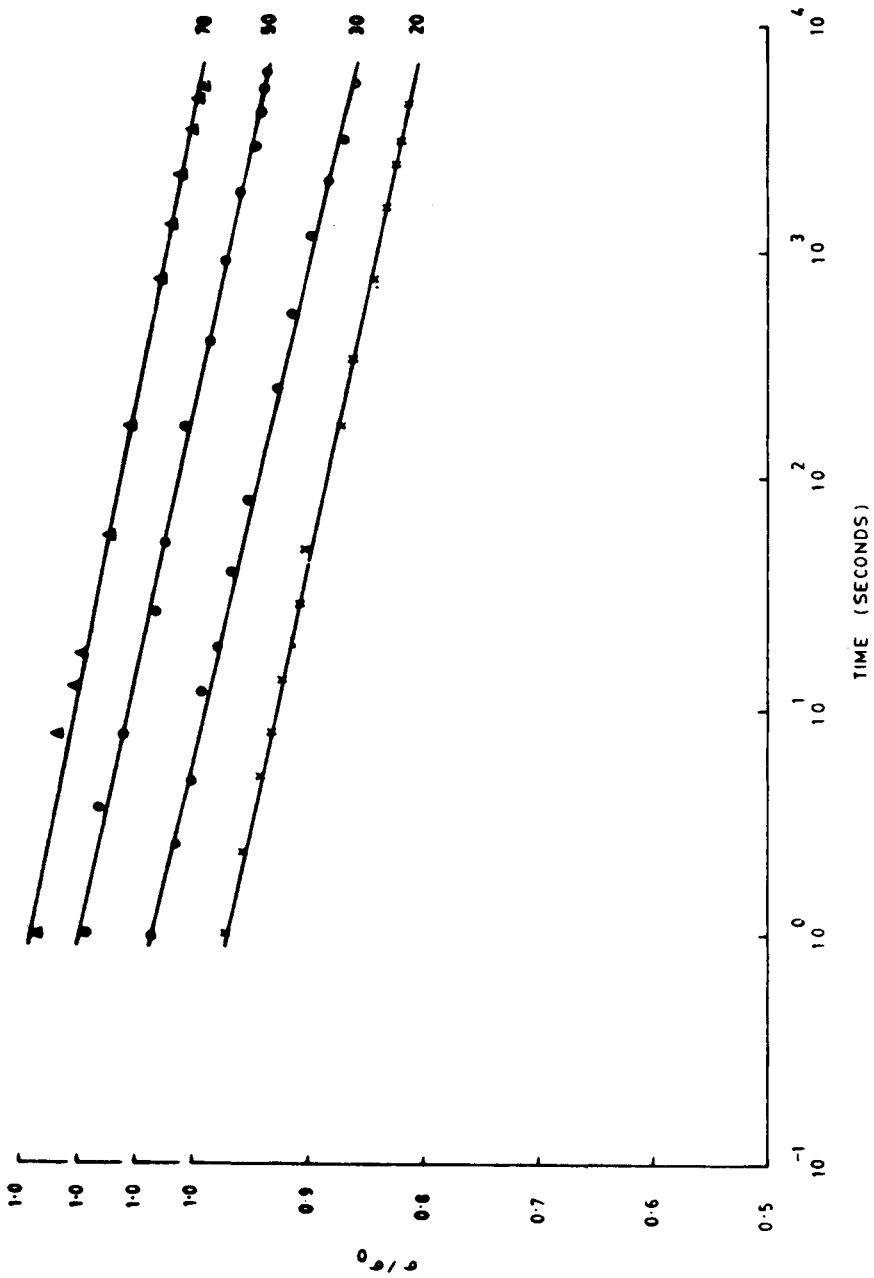
Fig. 1. Stress relaxation curves of NBR gum vulcanizate (mix A). Successive graphs are displaced upward by 0.05 for clarity. Figures against lines indicate elongation.

TABLE II
Results of Stress Relaxation Measurements

Strain (%)	Slope (negative)			Intercept at 1 s			Contribution of early process (%)	Intersection point on time axis (s)
	Early	Later	Difference	Early	Later	Difference		
Mix A (NBR gum)								
20	0.043	—	—	0.968	—	—	—	—
30	0.044	—	—	0.985	—	—	—	—
50	0.042	—	—	0.992	—	—	—	—
70	0.032	—	—	0.966	—	—	—	—
Mix C (NBR-jute fiber)								
20	0.101	0.079	0.022	0.906	0.857	0.049	5.5	178
30	0.117	0.076	0.041	0.916	0.834	0.082	9.0	100
50	0.136	0.069	0.067	0.921	0.782	0.139	15.1	117
70	0.138	0.071	0.067	0.916	0.793	0.123	13.4	112
Mix D (NBR-jute fiber-bonding agent)								
20	0.085	0.062	0.023	0.885	0.843	0.042	4.8	67
30	0.084	0.055	0.029	0.885	0.823	0.062	7.0	137
50	0.088	0.065	0.023	0.886	0.841	0.045	5.1	91
70	0.083	0.066	0.019	0.879	0.841	0.038	4.3	108

times. Similar results were obtained by Mackenzie and Scanlan[12] for carbon black-filled vulcanizates, in which the earlier process was assigned to the breakdown of the carbon black structure.

In the present case, incorporation of fiber (mix C) results in two relaxation processes that persist even in the presence of the bonding system (silica-resorcinol-hexa system). Thus, the initial relaxation may arise from a rearrangement or reorientation at the fiber/rubber interface.

The experimental data of the fiber-filled vulcanizates may be characterized by four parameters: two slopes and corresponding intercepts on the ordinate at 1 s. These values are shown in Table II for different strain levels for mixes C and D. They were obtained by fitting the data using the method of least squares. It is seen that in all cases the earlier slope is greater than the later. In the case of mix C, the rate of stress relaxation (as indicated by the slope) due to the earlier process increases with strain level. However, it becomes independent of strain when bonding agent is added (mix D). Owing to bonding, there is improved adhesion between fiber and rubber resulting in a strong interface. Therefore, relaxation at the interface is not affected by strain level. However, a weak interface, as in mix C, would lead to faster relaxation of the stress as the strain level is increased.

A method[12] of estimating the contribution of the early mechanism to the relaxation in the system is to divide the difference of intercepts of the two lines by the intercept of the first line at $t = 1$ s. This fraction, expressed as a percentage, is also shown in Table II. From the table it is seen that the contribution of the early process increases with strain level from 5 to 15% in the case of mix C. However, in the case of mix D, which contains bonding system, the contribution is nearly constant and independent of strain level, because of better bonding at the fiber/rubber interface.

It may also be noted that the time of intersection of the two lines is approximately constant (about 100 s) and independent of strain level and
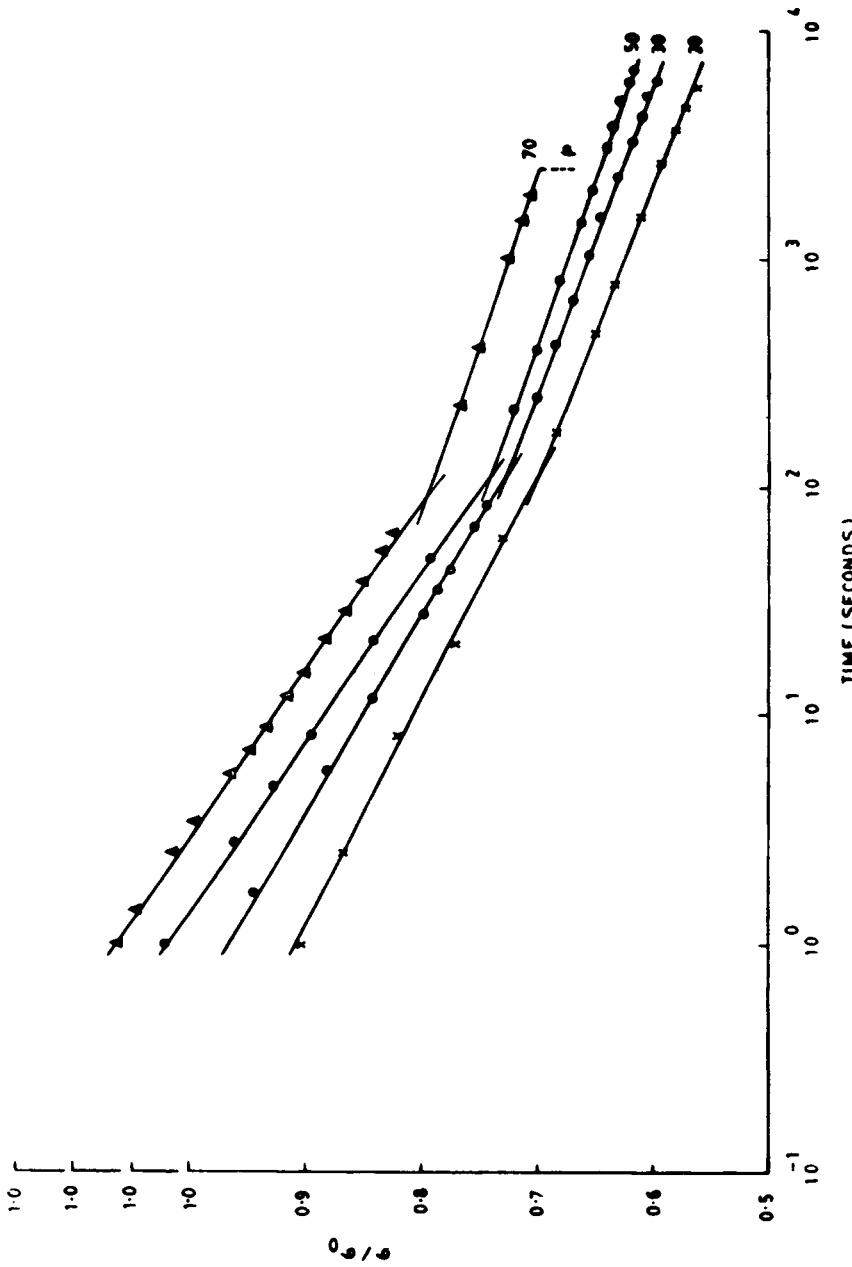
Fig. 2.   Relaxation results for mix C. Successive graphs are displaced upward by 0.05. Figures against curves indicate elongation. At P, sample broke.
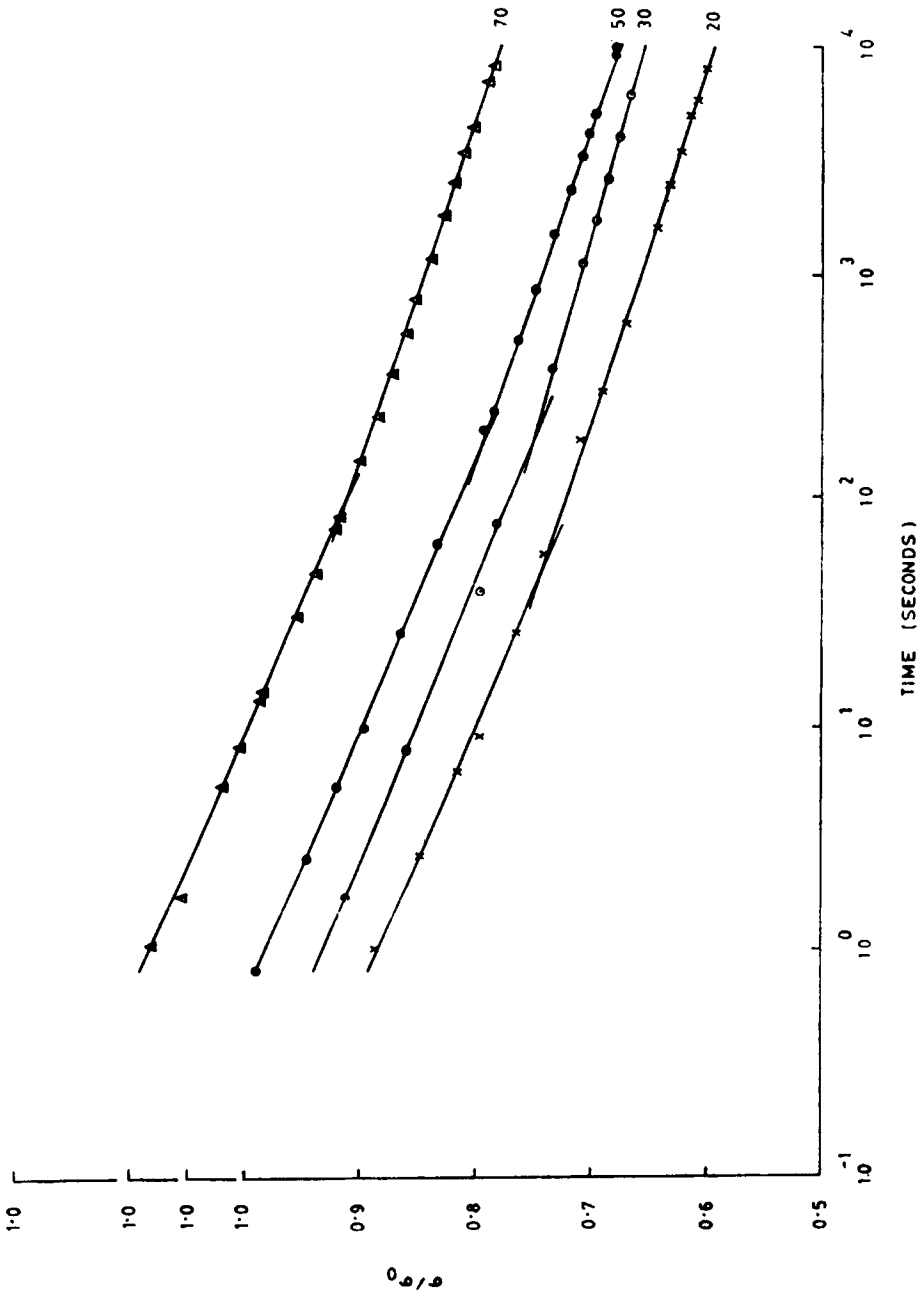
Fig. 3. Relaxation results for mix D. Successive graphs are displaced upward by 0.05, 0.10, and 0.20, respectively. Figures against lines indicate elongation.
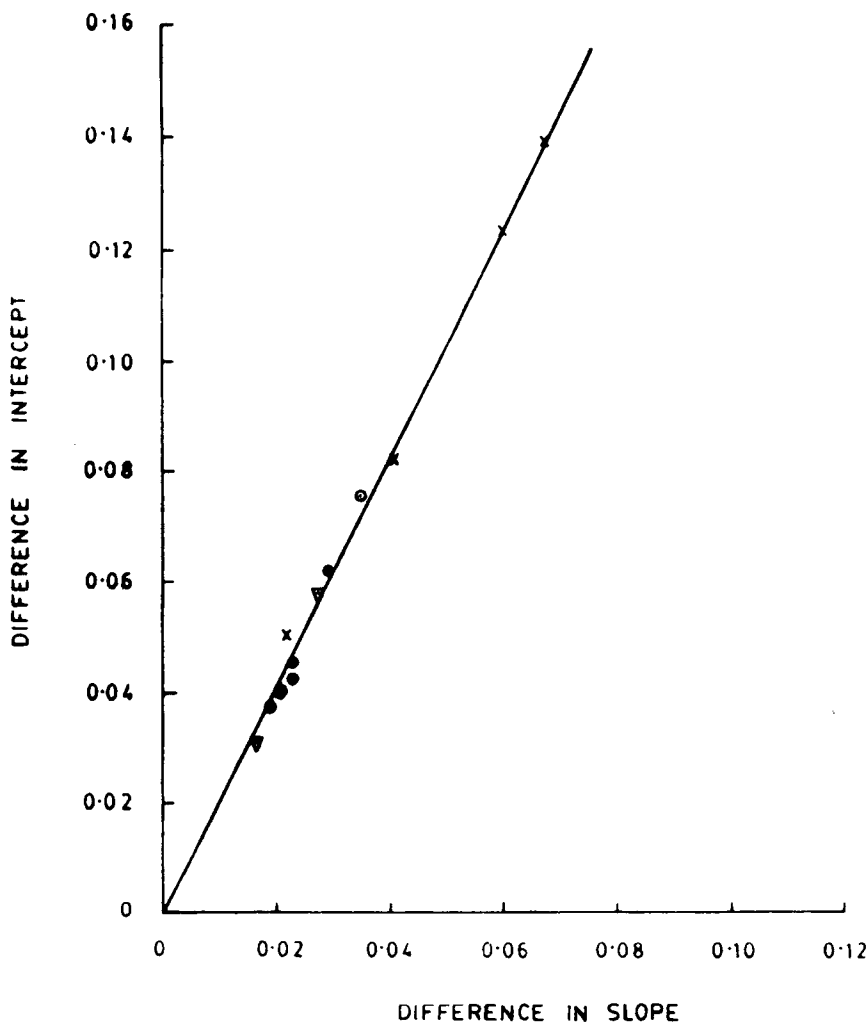
Fig. 4. Relation between intercept differences and slope differences for relaxation at 25°C in vulcanizates containing 20 phr jute fiber: (●) mix D, (×) mix C, (⊙) transversely oriented samples, (▲) prestrained samples.

presence of bonding agent. This time of intersection, which is obtained analytically and is shown in Table II, represents the change over time at which the mechanism operating at short times becomes exhausted.

An interesting relationship is shown in Figure 4, which is a plot of the difference in intercepts of the two lines versus the difference in their slopes. The points lie more or less on a single line through the origin, regardless of the strain level, orientation of fibers, prestraining, and presence of bonding agent. The slope is a measure of the rate of stress relaxation, whereas the intercept on the ordinate (σ/σ_0) represents the fraction of stress that has relaxed at time $t = 1$ s. Thus Figure 4 indicates that a linear relation exists between the stress relaxed at a given time and the rate of stress relaxation.
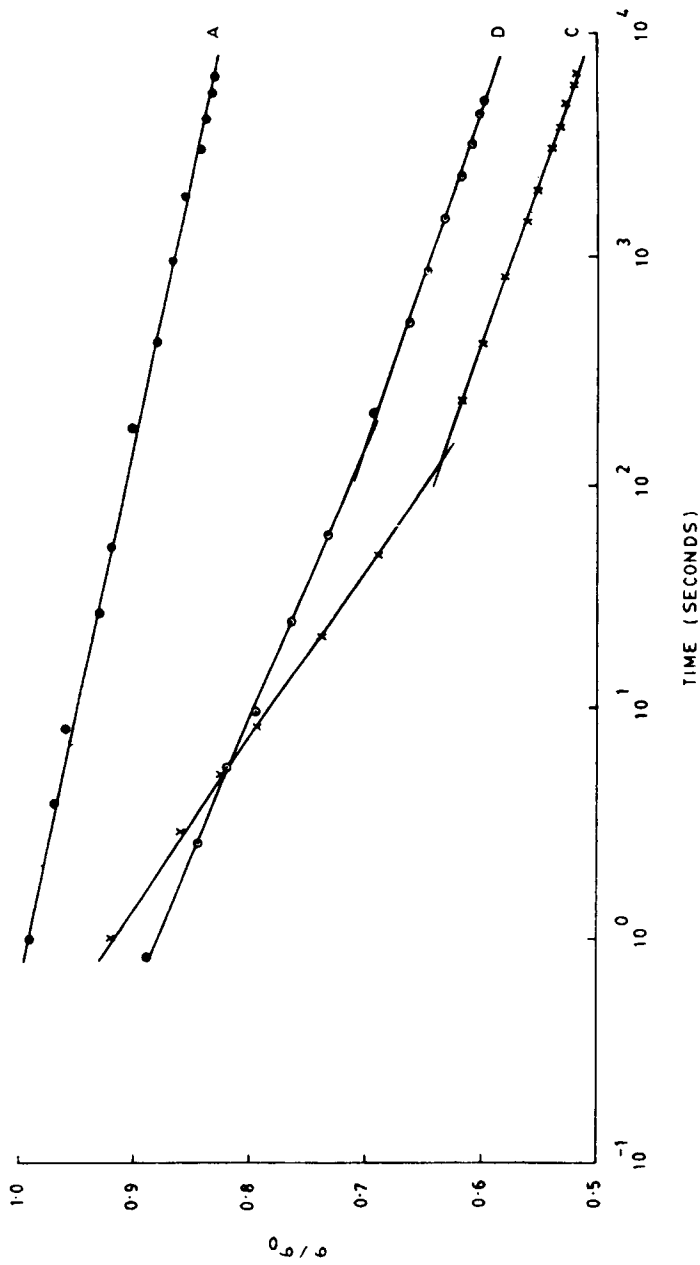
Fig. 5. Comparison of stress relaxation results for mix A, mix C, and mix D at 30% elongation.

Effect of Bonding Agent

It is found that sample from mix C is swollen by 90% but mix D shows 36% swelling when swelling is carried out in chloroform for 24 h at 25°C. This clearly indicates the improved adhesion between fiber and rubber in mix D. This effect is also shown in their stress relaxation behavior.

In Figure 5, the stress relaxation curves of mixes A, C, and D are compared. The gum compound has the lowest rate of relaxation, and mix C has the highest rate at all strain levels. Addition of bonding agent (mix D compared to mix C) lowers the relaxation rate to some extent.

The increase in relaxation rate due to fiber addition could be attributed to stress softening and strain amplification.[13]

However, it may be noted that, at 70% elongation, the sample from mix C was found broken after about 1 h (denoted by P in Fig. 2). This indicates that a very high rate of relaxation is not desirable beyond a certain strain level.

Effect of Fiber Content

Figure 6 illustrates the effect of fiber concentration (mixes B, D, and E) on the stress relaxation curves. The rate of relaxation and contribution of the early process increase with fiber content, and the time at which the earlier relaxation mechanism is exhausted shifts to higher values. This is shown in Table III. According to the theory of strain amplification,[13] owing to the inextensibility of the filler, the strain in the elastomer matrix is greater than the overall strain, resulting in the rubber phase having an instantaneous modulus higher than for a gum rubber at an equivalent extension. Relating strain amplification to stress relaxation, Derham[14] showed that the stress relaxation rate increases with carbon black loading. Similar results are obtained in short fiber-NBR composites, as shown in Figure 6.

Influence of Temperature

Stress relaxation measurements have been made at different temperatures. Figure 7 shows the relaxation curves obtained for mixes C and D at 25, 50, and 75°C by attaching the Instron temperature cabinet. The results for these vulcanizates are summarized in Table III.

Temperature produces interesting effects on the stress relaxation of fiber-rubber composites. The rate of relaxation and the importance of the short time relaxation process are decreased at higher temperatures. As shown in Table III, the initial slope falls with temperature; the contribution of the short-time relaxation mechanism is reduced and exhausted at shorter times. Similar results were observed for carbon black-SBR vulcanizates.[12] The variation of initial slope with temperature is gradual in the case of mix C and rapid in the case of mix D, which contains bonding system.

Effect of Fiber Orientation

The effect of fiber orientation on stress relaxation behavior was investigated for mixes C and D at 30% strain. The results are shown in Figure 8. In the case of mix D, samples containing fibers oriented longitudinally and transversely have the same rate of relaxation for the initial process. However, the contribu-
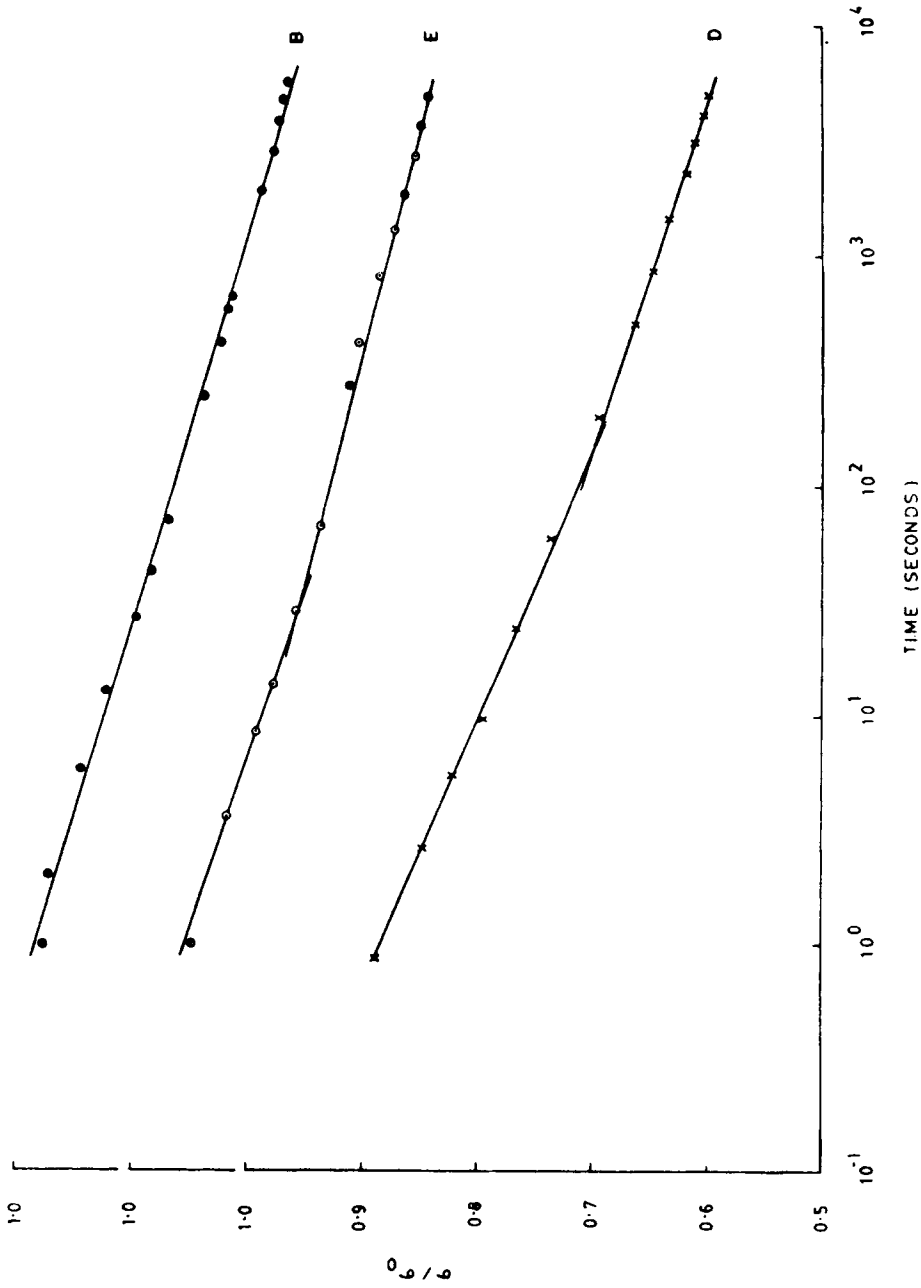
Fig. 6. Effect of fiber content on stress relaxation mix B, mix D, and mix E at 50% elongation. Successive graphs are displaced upward by 0.10.

TABLE III
Effect of Fiber Concentration and Temperature on Stress Relaxation Properties

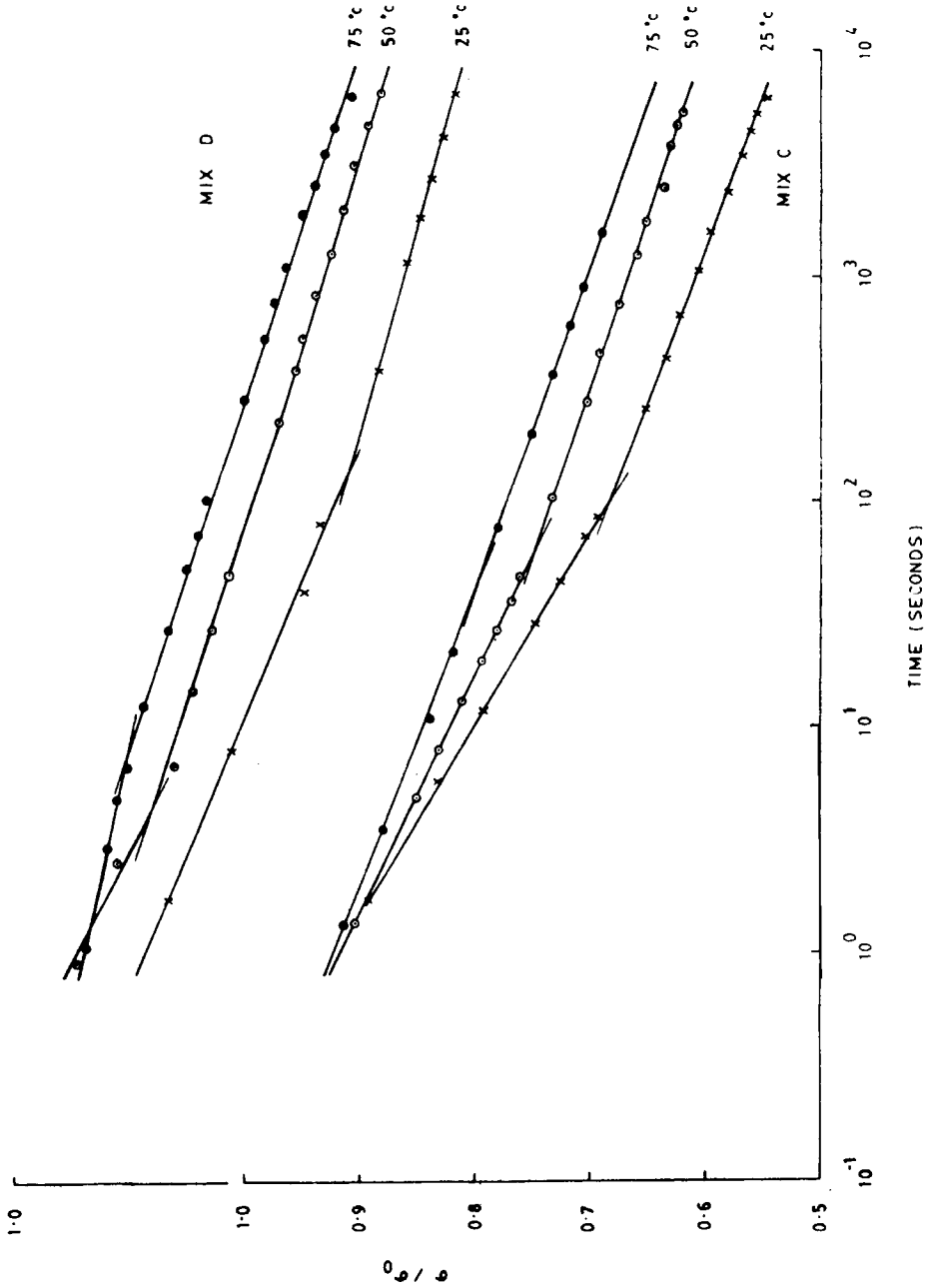|	Strain (%)	Slope (negative)			Intercept at 1 s			Contribution of early process (%)	Intersection point (s)
		Early	Later	Difference	Early	Later	Difference		
Effect of fiber content									
Mix B (no fiber)	50	0.059	—	—	0.981	—	—	—	—
Mix E (10 phr)	50	0.060	0.053	0.007	0.946	0.935	0.011	1.2	37
Mix D (20 phr)	50	0.088	0.065	0.023	0.886	0.841	0.045	5.1	91
Effect of temperature									
Mix A: 25°C	30	0.044	—	—	0.985	—	—	—	—
50°C	30	0.035	—	—	0.994	—	—	—	—
Mix C: 25°C	30	0.117	0.076	0.041	0.916	0.834	0.082	9.0	100
50°C	30	0.101	0.067	0.034	0.925	0.864	0.061	6.6	62
75°C	30	0.076	0.067	0.009	0.918	0.903	0.015	1.6	46
Mix D: 25°C	30	0.084	0.055	0.029	0.885	0.823	0.062	7.0	137
50°C	30	0.076	0.065	0.011	0.933	0.926	0.007	0.8	4
75°C	30	0.042	0.067	-0.025	0.934	0.963	-0.029	—	15

Fig. 7.　Effect of temperature on relaxation results for mix C and mix D at 30% elongation. Plots for mix D are shifted upward by 0.2.
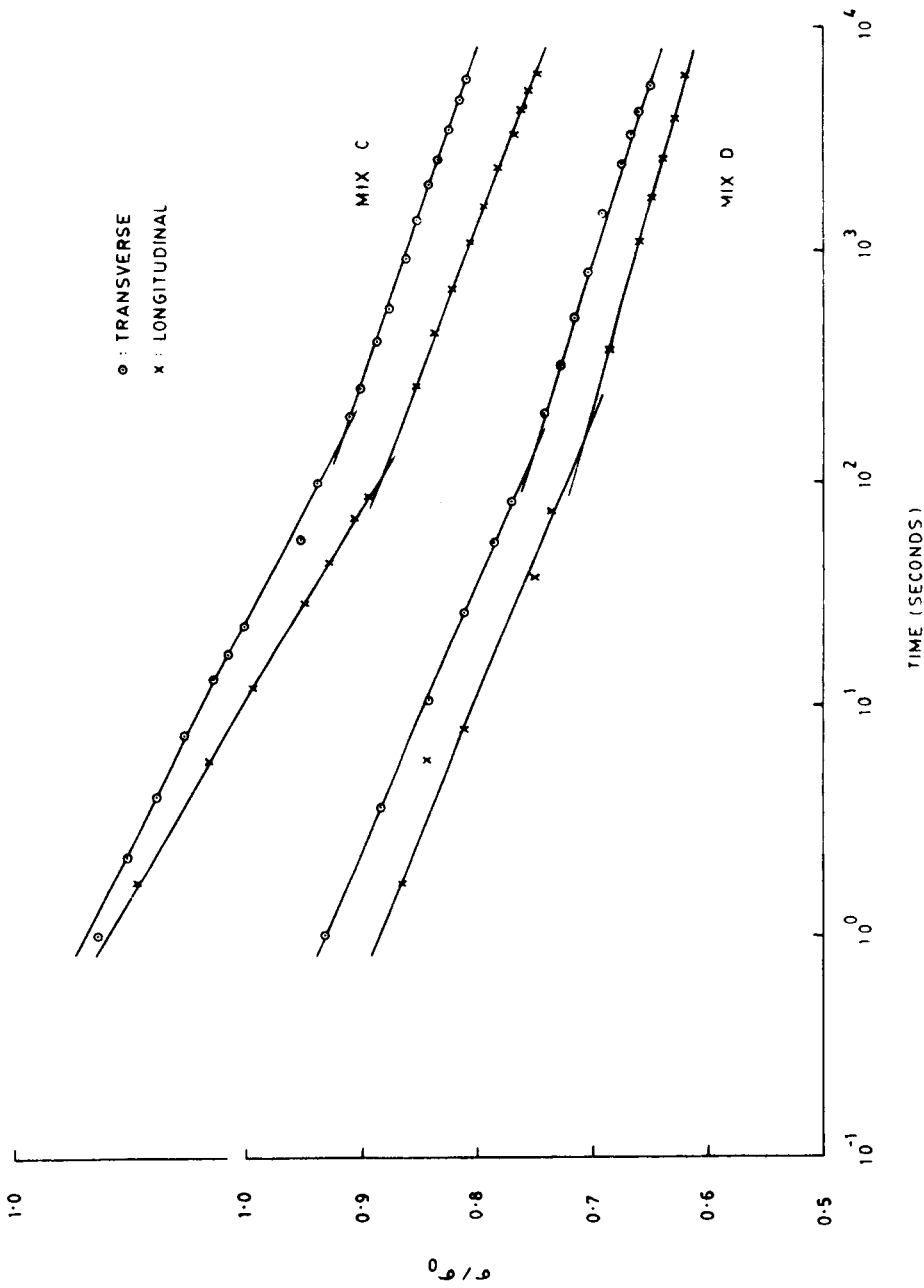
Fig. 8.   Effect of fiber orientation on relaxation for mix C and mix D at 30% elongation. Plots for mix C are displaced upward by 0.2.

TABLE IV
Dependence of Stress Relaxation on Fiber Orientation and Prestrain for NBR-jute Fiber Vulcanizates at 30% Elongation

|	Slope (negative)			Intercept at 1 s			Contribution of early process (%)	Intersection point (s)
	Early	Later	Difference	Early	Later	Difference		
Effect of orientation								
Mix C: Longitudinal	0.117	0.076	0.041	0.916	0.834	0.082	9.0	100
Transverse	0.102	0.067	0.035	0.936	0.861	0.075	8.0	139
Mix D: Longitudinal	0.084	0.055	0.029	0.885	0.823	0.062	7.0	137
Transverse	0.085	0.064	0.021	0.930	0.890	0.040	4.2	80
Effect of prestrain								
Mix C: no prestrain	0.117	0.076	0.041	0.916	0.834	0.082	9.0	100
prestrain (100%)	0.061	0.033	0.028	0.924	0.867	0.057	6.2	103
Mix D: no prestrain	0.084	0.055	0.029	0.885	0.823	0.062	7.0	137
prestrain (100%)	0.076	0.059	0.017	0.924	0.893	0.031	7.0	67
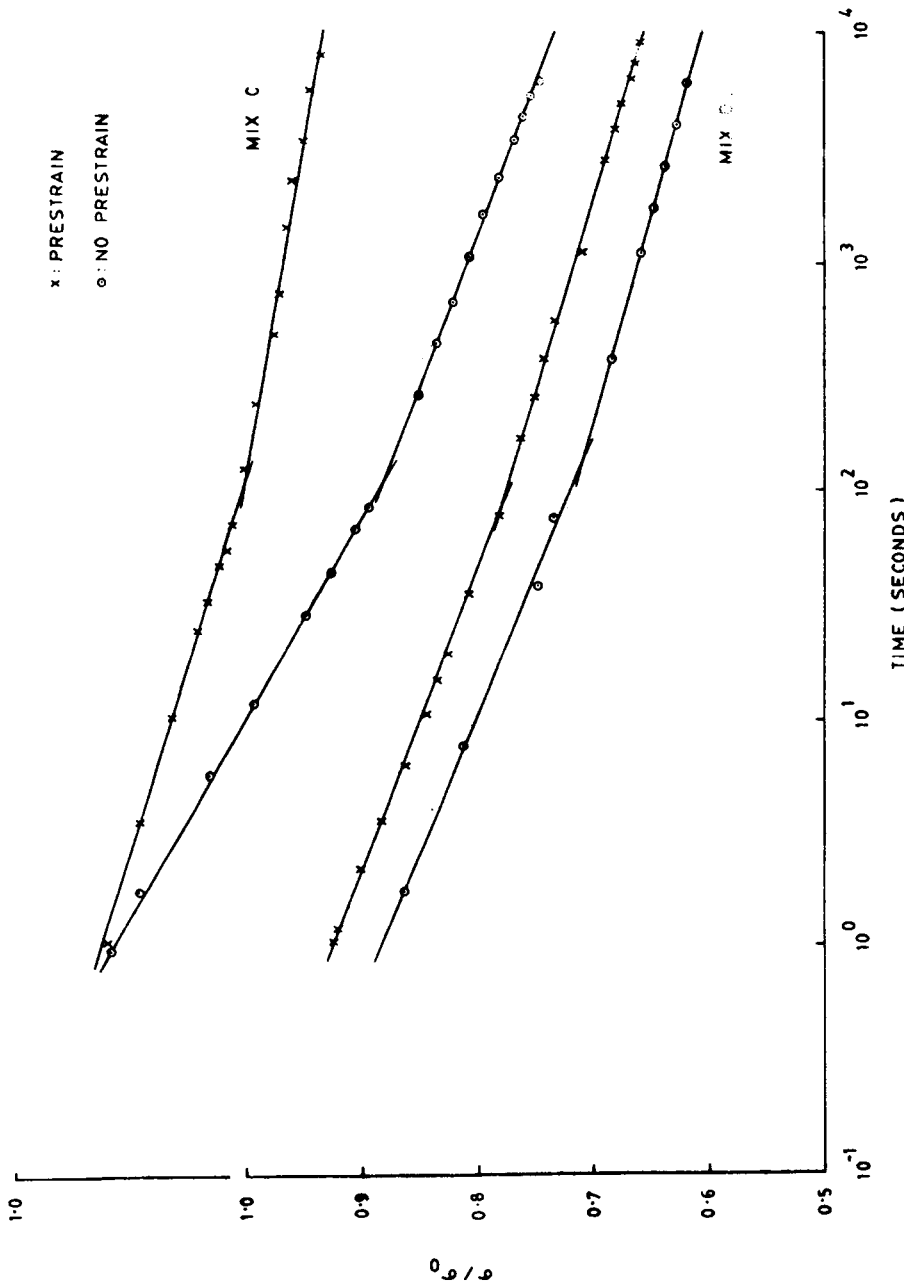
Fig. 9.   Effect of prestrain on relaxation for mix C and mix D at 30% elongation. Plots for mix C are shifted upward by 0.2.

tion of this relaxation mechanism is slightly decreased when the fibers are transversely oriented (see Table IV).

In the case of mix C, which does not contain bonding agent, the rate of relaxation is somewhat higher when the fibers are longitudinally oriented. However, as shown in Table IV, the contribution of the earlier relaxation process is nearly the same.

Effect of Prestrain

The effect of prestraining on stress relaxation properties was investigated. The sample was stretched to 100% extension, the strain was released, and the sample was allowed to recover for 5 min. It was then subjected to a constant strain of 30% and the decay of load with time was recorded. The stress relaxation of samples from mixes C and D with and without prestrain is compared in Figure 9. Prestraining produces a profound effect on the relaxation rate in the case of mix C, which has no bonding agent. The slopes of the earlier and later lines drastically decrease, but the relative contribution of the early process and the transition time remain unchanged (Table IV). One way in which the stress relaxation rate increases owing to the addition of fillers is stress softening, in which filler-filler bonds and filler-rubber bonds are broken. It is reported[14] that the contribution of stress softening can be minimized by prestraining. The decreased rate of relaxation in prestrained fiber-rubber composites can thus be explained.

However, this type of behavior is different from that observed in carbon black-rubber vulcanizates,[12] in which the slopes of the earlier and later lines remain unaffected because of different relaxation mechanisms. In the case of mix D, prestraining produces only a small reduction in the slopes (as shown in Table IV) and the contribution of earlier relaxation process is essentially same. It is possible that bonding agent has a restraining effect on the interface and prevents complete debonding at fiber/elastomer interface.

CONCLUSIONS

The results indicate the existence of a relaxation mechanism at very short times (< 200 s) in short jute fiber-NBR composites. This is evident from the following:

1. Existence of two linear sections in the plot of stress versus logarithmic time
2. Variation of the initial slope when strain level is increased, bonding agent is added, orientation of the fibers is changed, temperature is raised, or samples are prestrained.

The nature of the relaxation is to some extent a matter of speculation. That the relaxation behavior is influenced by bonding agent indicates that the process involves the fiber/rubber interface.

In general, short fibers increase the rate of stress relaxation over the corresponding unfilled vulcanizates. Composites containing bonding agent exhibit slower relaxation than those without bonding system. When bonding agent is absent, the rate of stress relaxation is dependent on strain level. The rate of stress relaxation and the importance of the earlier relaxation process

diminish as temperature increases. These effects are more pronounced in composites that do not contain bonding agent.

The effect of orientation on the relaxation behavior appears to be marginal. Prestraining decreases the stress relaxation rate considerably, particularly for composites without bonding agent, and is ascribed to stress softening. On the whole, fiber in the presence of a bonding system imparts optimum stress relaxation behavior to the composites.

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