Stress Relaxation Behavior of Short Kevlar Fiber-Reinforced Thermoplastic Polyurethane

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SYNOPSIS

Stress relaxation behavior of short Kevlar fiber-reinforced thermoplastic polyurethane (TPU) is studied with respect to strain level, strain rate, fiber loading, and fiber orientation and temperature. The existence of a two-step relaxation mechanism for unfilled stock and a three-stage relaxation mechanism for the fiber-filled stock is reported.

INTRODUCTION

The importance of short-fiber elastomer composites basically arises from their advantages in processing, anisotropy in properties, design flexibility, and low cost. The mechanical and rheological properties of the short-fiber elastomer composites have been investigated extensively,[1-7] whereas short-fiber thermoplastic elastomer composites remain comparatively less explored. Mechanical properties, effect of fiber orientation on the ultimate properties, and processability of short silk-fiber-reinforced natural rubber–polyethylene blends were studied earlier.[8] However, no systematic work has been undertaken on the stress relaxation behavior of short-fiber thermoplastic elastomer composites.

Stress relaxation emerges as an important property because of the increasing use of short-fiber composites in static and dynamic applications under stress, for instance, in hoses, V belts, tubes, and cables. Bhagawan et al.[9] have studied the stress relaxation behavior of short Jute fiber–Nitrile rubber composites with respect to the effect of strain level, bonding agent, and prestrain. Flink and Stenberg analyzed the stress relaxation of short cellulose fiber–natural rubber composite through procedure X and continuous relaxation spectra and by plots of $E(t)/E_{(t=0)}$ vs. log t.[10]

In the present work the stress relaxation behavior of short Kevlar fiber–TPU composite is investigated. The effect of fiber loading, fiber orientation, strain level, strain rate, and temperature on stress relaxation is studied.

EXPERIMENTAL

Materials

Ether-based thermoplastic polyurethane, Estane-58311 ($M_w = 1.5 \times 10^5$; T_g determined by dynamic mechanical analysis at $-21°C$), was procured from B. F. Goodrich Co. and Kevlar staple fiber (T-970) approximately 6 mm in length (L/D 500) was obtained from Du Pont De Nemours.

Procedure

Formulation of the mixes are given in Table I. The mixes were prepared in a Brabender plasticorder PLE 330 fitted with a cam-type mixing head. The ingredients were dried at 120°C for 2 h to remove moisture. The mixing was carried out at 180°C at a rotor speed of 60 rpm for 6 min after which the stock was sheeted out on a laboratory size (330 × 250 mm) mixing mill at tight nip. Tensile sheets were molded at 180°C on a Labo press provided with a water-cooling facility. Dumbbell specimens (ASTM D-412, type C) were punched out of the sheet along and across the grain direction. A schematic representation of the orientation of fibers in different test specimens is shown in Figure 1. The length distribution of the extracted fibers after dissolving the matrix in tetrahydrofuran solvent is shown in Figure

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Table I Composition and Densities of Mixes

Ingredient	*A*	*B*	*C*	*D*	*E*
	phr[a]				
TPU	100	100	100	100	100
Kevlar	0	10	20	30	40
Density, g/cm^3 (theoretical)	1.12	1.14	1.17	1.19	1.21
Density g/cm^3 (calculated)	1.12	1.14	1.17	1.19	1.20

[a] Parts per hundred rubber.

2. The theoretical and experimentally determined densities of the mixes are given in Table I.

The stress relaxation measurements were carried out in an Instron Universal Testing Machine model 1195. The test specimen was pulled to desired strain levels (10–500%) at fixed and different strain rates (0.016–0.400 s^{-1}). The test was carried out at four different temperatures (25–100°C) using an Instron high-temperature cabinet. Samples were conditioned at the test temperature for about 15 min before testing. The stress was recorded as a function of time on a chart paper initially at a higher speed and later at a lower speed. The ratio $\sigma_{(t)}/\sigma_{(0)}$ is plotted vs. the logarithm of time, $\sigma_{(t)}$ and $\sigma_{(0)}$ being stress at time t and that at zero time, respectively.

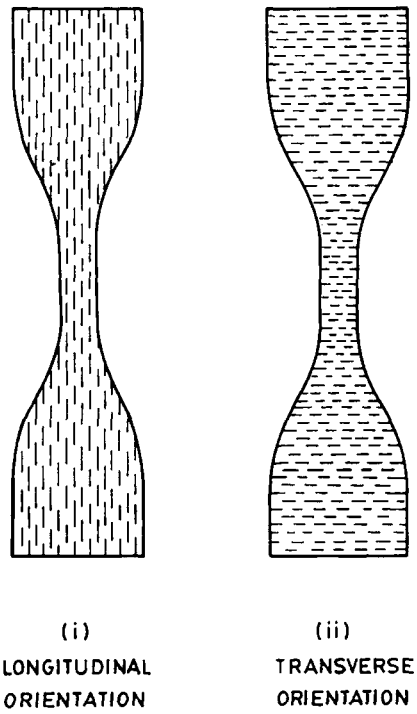
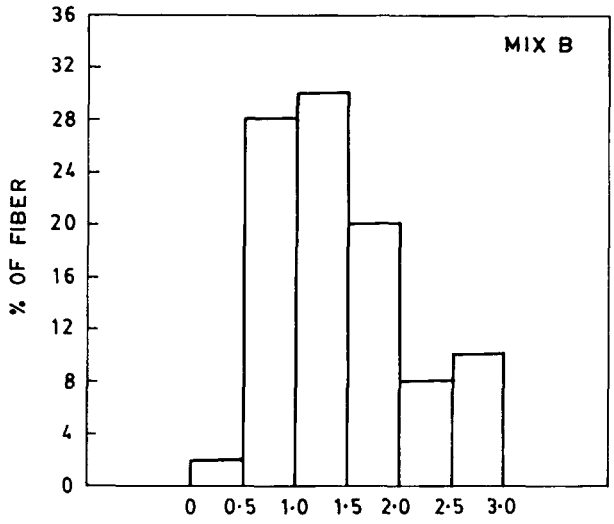


Figure 1 Schematic representation of orientation of fibers in relaxation test specimen.



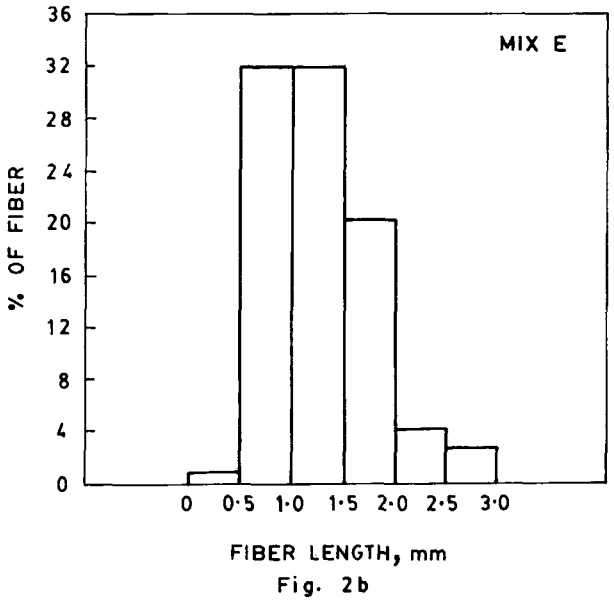


Figure 2 (a) Distribution of fiber length after mixing (mix *B*). (b) Distribution of fiber length after mixing (mix *E*).

RESULTS AND DISCUSSION

Effect of Strain Level

Figure 3 gives the stress relaxation plot ($\sigma_{(t)}/\sigma_{(0)}$ vs. log t) of the gum compound (mix A) at different initial strain levels. The rate at which the initial strain is attained is kept constant (0.160 s^{-1}) in all the runs. It is interesting to note that in all the cases the points fall on two intersecting straight lines, unlike the behavior reported for elastomer gum compounds.[10] The stress relaxation plot consisting of two straight lines of unequal slopes indicates a different mechanism of relaxation operating—one that operates at shorter times (< 200 s) and another that is prominent at the later stages of relaxation.[11] The point of intersection of these two straight lines is the time at which a changeover takes place from one mechanism of relaxation to the other. The features that characterize the two lines are their slopes and intercepts. These are given in Table II. The slopes were calculated using a linear regression method. The contribution of the early process of relaxation was calculated, as suggested by Mackenzie and Scanlan,[11] by dividing the difference of the two intercepts by the intercept of the first line at t = 1 s. These, expressed as percentages, are also given in Table II.

The rate of relaxation at shorter times, as indicated by the slopes, are found to be independent of the strain levels up to 100% extension. The independence of relaxation on strain at lower strain levels has been reported earlier in the case of natural rubber,[12,13] styrene butadiene, and butyl and butadiene rubber vulcanizates.[14] However, at the higher extension (500%) the rate of relaxation is increased by 65%. This may be attributed to progressive build-up of the crystalline phase in the stretched state. Crystallization under high deformation and the resulting proportionate relaxation of stress have been established[15] in the case of natural rubber vulcanizates. The second slope is found to increase with strain level. The crossover point is shifted to shorter times at higher strains levels, indicating that the initial mechanism of relaxation is exhausted at the shorter period under higher deformations.

Effect of Strain Rate

The effect of strain rate on the stress relaxation of unfilled TPU has been studied at two different strain

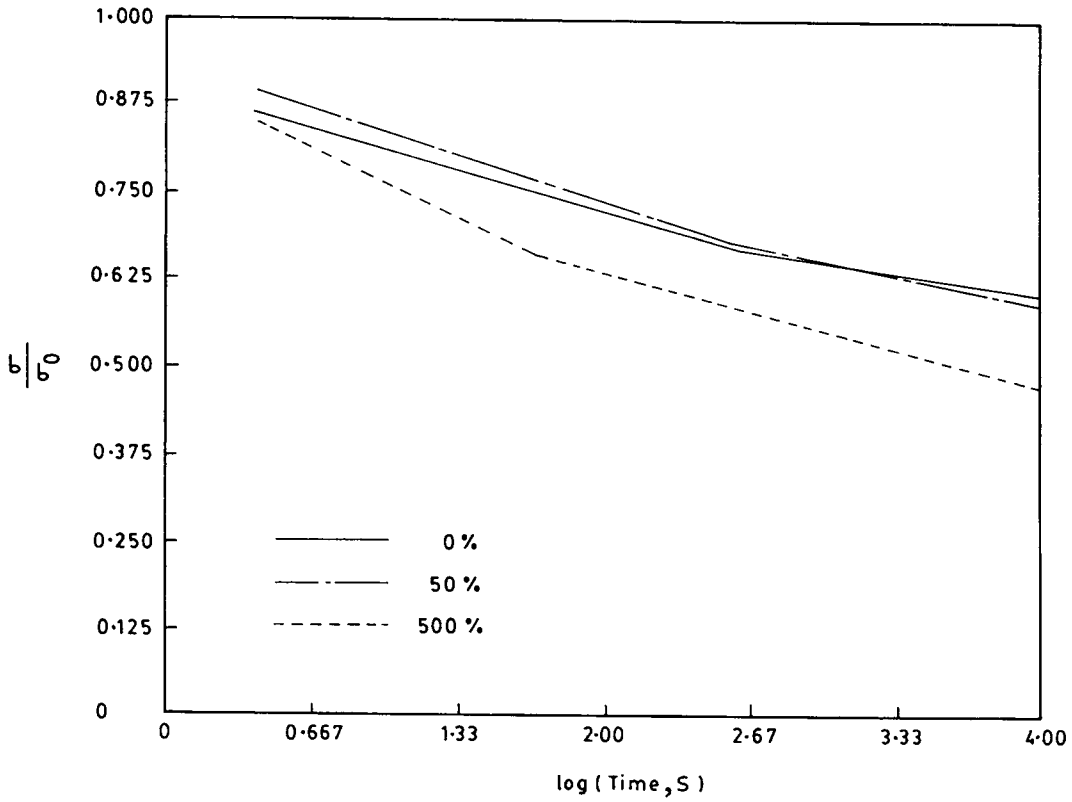


Figure 3 Effect of strain level on stress relaxation of mix A (strain rate, 0.16 s^{-1}).

Table II Effect of Strain Level on Stress Relaxation of Mix *A*

Strain (%)	Slope I, $\times 10^2$	Slope II, $\times 10^2$	Intercept I	Intercept II	Contribution of Initial Mechanism (%)	Crossover Time (s)
10	9.0035	4.2526	0.8999	0.7761	13.73	423
50	9.7555	6.5373	0.9298	0.8503	8.54	384
500	15.2117	8.0421	0.9086	0.7945	12.55	49

levels, viz., 100 and 500%, and the corresponding stress relaxation plots are given in Figures 4 and 5, respectively. The slopes and intercepts are given in Table III. At the low strain rate (0.016 s^{-1}) the stress relaxation plots show three distinct modes of relaxation at the two strain levels studied. In both cases the initial slope increases with the strain rate whereas the second slope decreases with an increase in strain rate. However, at 500% strain the initial slope shows a fall at 0.4 s^{-1} strain rate. This discrepancy at higher elongation may be due to the crystallization effect as explained earlier. At low strain rates part of the crystallization and the corresponding relaxation of stress takes place as the sample is being deformed. Since the force is recorded after attaining the desired strain level, the initial part of the relaxation that takes place during deformation is not recorded. This is not applicable fully at higher strain rates.

Effect of Fiber Loading

The variation of the relaxation behavior with fiber loading is shown in Figure 6, and the corresponding slope values are given in Table IV.

The fiber-filled stocks show three-step relaxation as indicated by three straight lines of different slopes in Figure 6. The initial rate of relaxation is reduced

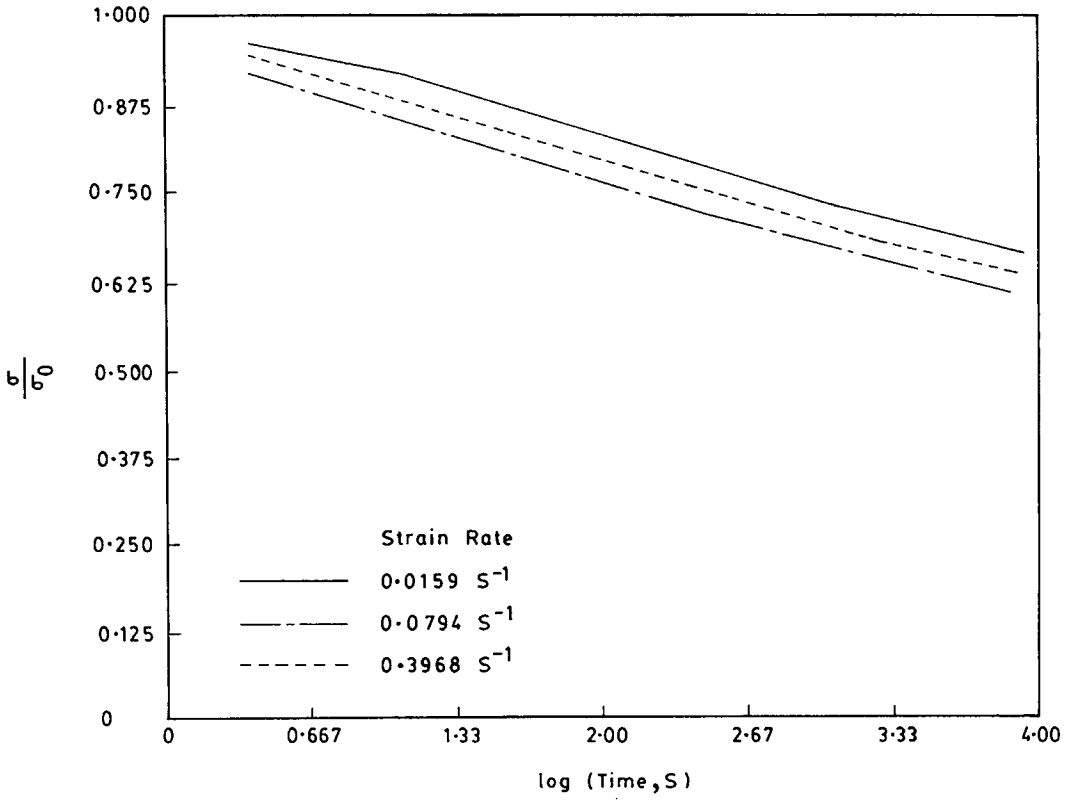


Figure 4 Effect of strain rate on stress relaxation of mix *A* at 100% strain.

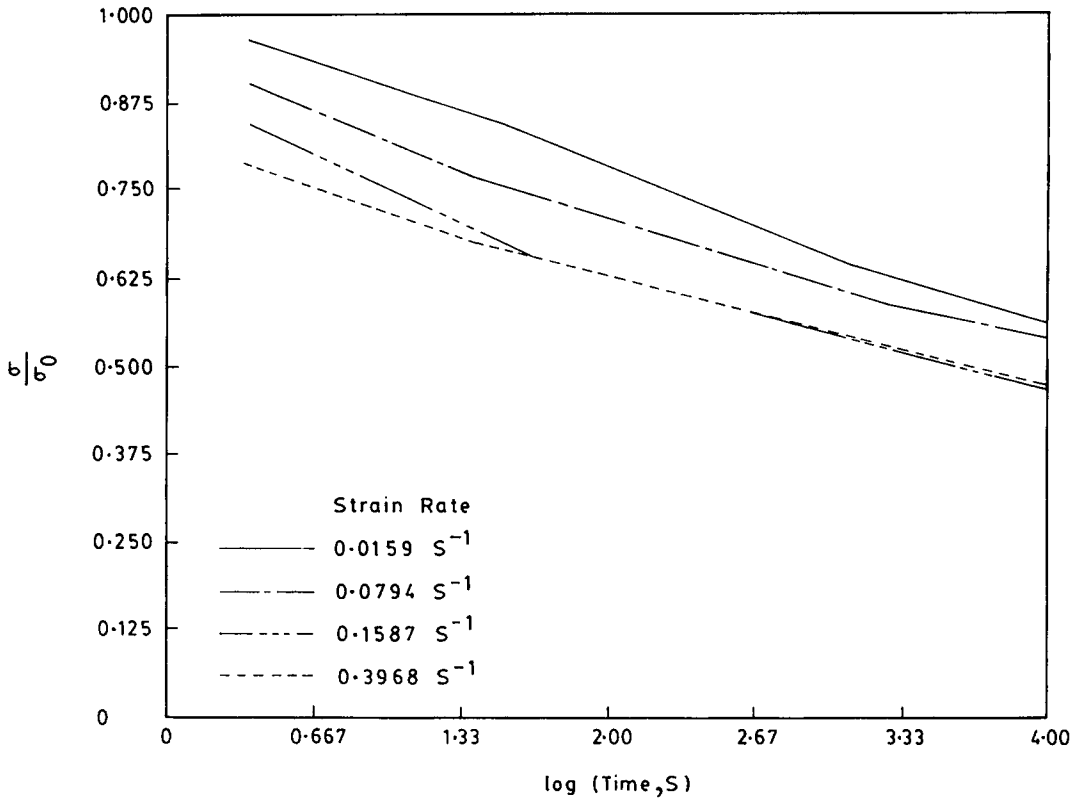


Figure 5 Effect of strain rate on stress relaxation of mix *A* at 500% strain.

by about 60% in the presence of 10–30 phr of fiber, after which further addition of fibers does not change this rate of relaxation significantly. At 40 phr fiber loading the initial rate of relaxation shows approximately 100% increment. The second slope is found to be higher in the case of fiber-filled stocks and the third slope increases with fiber loading. This indicates that the mechanism that operates initially as well as at later stages of relaxation are functions of fiber loading. According to Bhagawan et al.,[9] the first part of the relaxation in a fiber–rubber composite can be attributed to orientation at the fiber–matrix interface. As the fiber content increases, the fiber–matrix interface also increases, which should give rise to a higher initial rate of relaxation. However, in the case of unfilled TPU, two distinct modes of relaxation are observed, which indicates the involvement of other factors in addition to that previously given. Since the TPU consists of hard segments that act as "virtual physical crosslinks" in

Table III Effect of Strain Rate on Stress Relaxation on Mix *A*

Strain (%)	Strain Rate (s^{-1})	Slope, × 10^2			Intercept			Crossover Time	
		I	II	III	I	II	III	I	II
100	0.0159	6.39	9.34	8.33	0.99	1.00	0.99	12	1283
	0.0397	9.00	—	8.48	0.98	0.97	0.96	—	1893
	0.0794	10.12	8.39	8.39	0.96	0.94	0.94	320	—
500	0.0159	10.50	11.22	9.5	1.00	1.00	0.94	35	1135
	0.0794	13.93	9.07	5.45	0.96	0.88	9.77	25	200
	0.1587	15.24	8.04	—	0.90	0.79	—	44	—
	0.3968	12.20	8.74	—	0.84	0.79	—	26	—

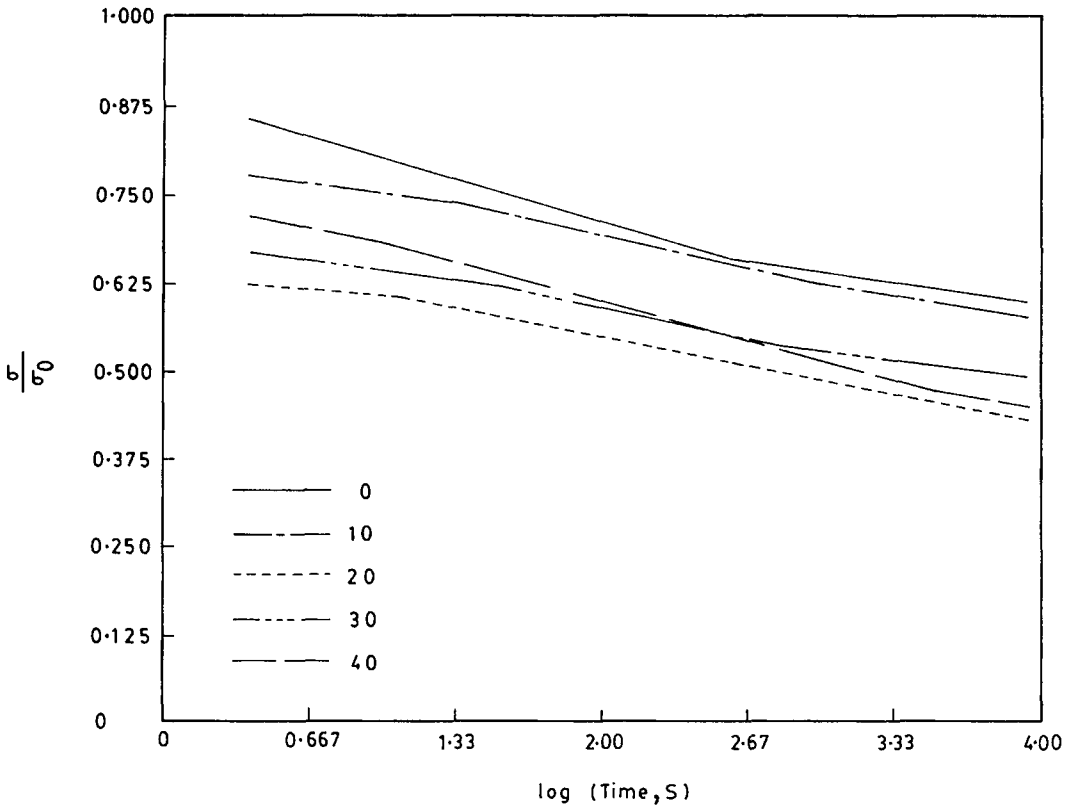


Figure 6 Effect of fiber loading on stress relaxation.

the soft matrix in which they are dispersed,[17] the initial relaxation may be arising out of the combined effect of the orientation at the hard–soft and fiber–matrix interfaces, whereas the second one may be due to the flow of soft matrix under tension at longer times. At lower fiber content, even though fiber–matrix interface is higher compared to unfilled stock, the matrix gets diluted, resulting in less reinforcement, whereas at higher fiber loading the matrix is restrained sufficiently to give a net reinforcement effect, which results in higher relaxation. Similar observations have been reported earlier[10] for highly reinforced rubber composites.

The rate of relaxation at longer times is found to increase with fiber loading. According to Mullins and Tobin,[16] the overall extension of a composite is due to local deformation, which may be on the order of the breaking elongation of the "soft regions" in the composite. The fibers restrain the soft regions, thereby reducing the amount of soft regions available for deformation and resulting in higher relaxation. The third slope also is found to increase with fiber loading. However, the values are less than that of the second slope at all fiber loadings.

The time of first transition is shifted to shorter times on incorporation of the fiber and remains more

Table IV Effect of Fiber Loading on Stress Relaxation

Fiber (phr)	Slope, $\times 10^2$			Intercept			Crossover Time	
	I	II	III	I	II	III	I	II
0	9.0031	4.2526	—	0.8999	0.7761	—	423	—
10	3.5112	6.7749	2.9612	0.7886	0.8301	0.7071	25	1000
20	3.4984	5.887	5.8932	0.6414	0.6644	0.6414	12	—
30	3.5300	5.9026	4.4856	0.6800	0.7100	0.6686	26	1028
40	6.5786	8.6423	6.7921	0.7495	0.7740	0.7121	35	3297

Table V Effect of Fiber Orientation on Stress Relaxation

Mix	Orientation	Slope, $\times 10^2$			Intercept			Crossover Time	
		I	II	III	I	II	III	I	II
A	L	9.00	4.25	—	0.90	0.78	—	423	—
	T	10.85	5.46	—	0.86	0.73	—	400	—
B	L	3.51	6.78	2.96	0.79	0.83	0.71	25	1000
	T	6.78	10.22	4.15	0.76	0.80	0.57	20	500
C	L	3.50	5.89	—	0.64	0.66	0.70	12	—
	T	7.15	9.92	8.35	0.81	0.85	0.81	24	528
D	L	3.53	5.91	4.48	0.68	0.71	0.67	26	1028
	T	6.13	8.19	6.0	0.77	0.80	0.91	17	174
E	L	6.57	8.65	6.79	0.75	0.77	0.71	35	3297
	T	3.51	7.30	5.98	0.65	0.70	0.67	29	447

or less independent of fiber loading, whereas the second transition time is shifted to longer times with fiber loading.

Effect of Fiber Orientation

Table V gives the slopes and intercepts of stress relaxation plots in the orientation of fibers at various loading rates ranging from 10 to 40 phr, and Figure 7 gives the corresponding plots of mixes *A* to *E*. In all cases it is observed that the initial rate of relaxation in the transverse direction is about 100% higher than that in the longitudinal direction, except at 40 phr, which shows a higher rate in the longitudinal direction. The second and third slopes are also found to be higher in the transverse direction.

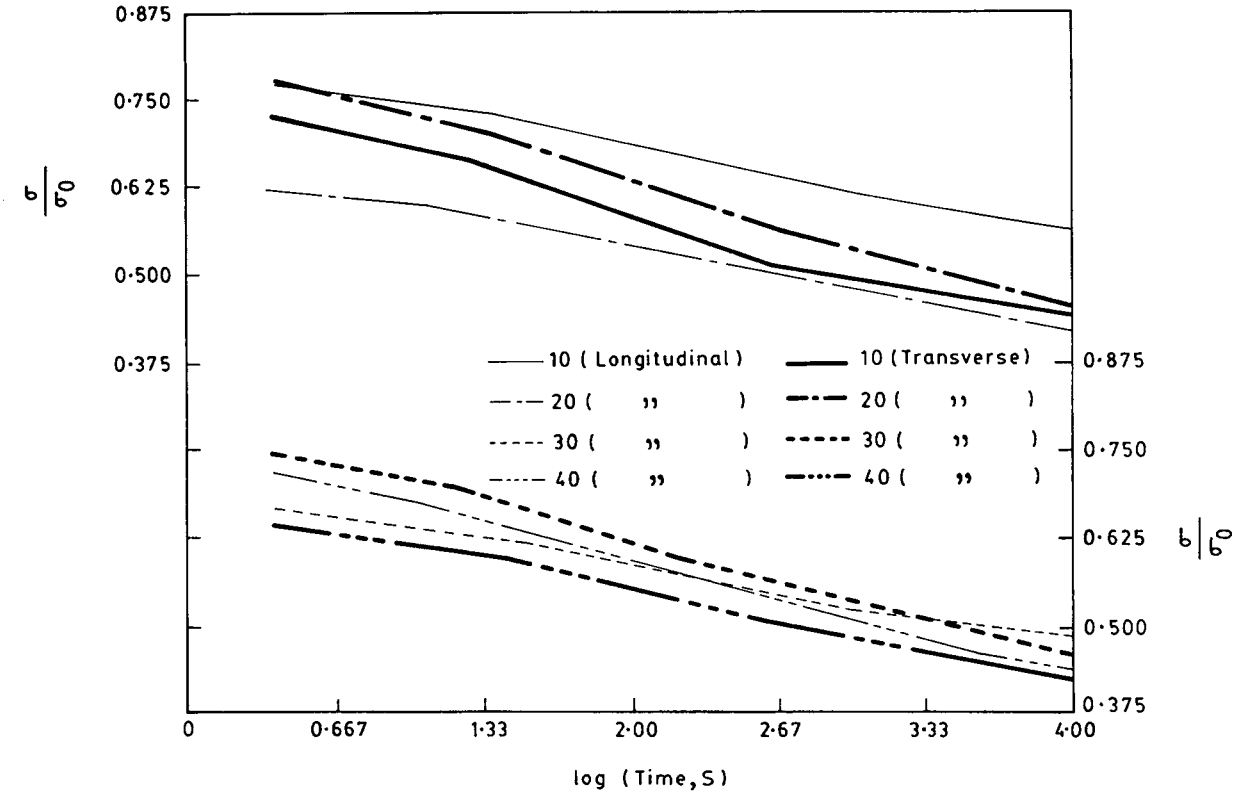


Figure 7 Effect of fiber orientation on stress relaxation of mixes *B*, *C*, *D*, and *E*.

The effect of fiber loading on the transverse orientation of fibers is similar to that in the longitudinal direction. The initial rate of relaxation is reduced by 66% on incorporation of 10 phr of fibers, beyond which an increase in fiber content does not significantly influence the rate of relaxation.

Effect of Temperature

The relaxation studies were carried out at three temperatures in addition to room temperature. The stress relaxation plots at 25, 50, 75, and 100°C are given in Figures 8, 9, and 10 for mixes *A*, *D*, and *E*, respectively, and the corresponding slopes and intercepts are shown in Table VI. In the case of the unfilled stock (mix *A*) it is observed that the initial slope decreases first with temperature, in agreement with the observation reported earlier.[9,10] However, at 100°C, the rate increases slightly. The second slope increases with temperature, and at a higher temperature a third slope becomes apparent.

In the case of fiber-filled stocks (30 and 40 phr), the short- and long-term relaxation rates increase marginally with temperature up to 50°C and shoot up at higher temperatures. The relaxation at longer times is predominantly due to chemical relaxation. Chemical relaxation being a function of temperature, the second slope increases with temperature. The rate of the third mode of relaxation increases only marginally with temperature. The activation energy, calculated for the second mode of relaxation from the plots of log(slope) vs. inverse temperature, is given in Table VI. The activation energy is found to decrease with increasing fiber content. This indicates a reduced temperature sensitivity of relaxation in the presence of fibers.

CONCLUSIONS

From this study the following conclusions may be drawn:

1. Stress relaxation of ether-based thermoplastic polyurethane takes place in two stages in the unfilled state and in three stages in presence of short Kevlar fibers.
2. On increasing the strain level from 10 to 500%, the first mode of relaxation increases by 66% whereas the second mode of relaxa-

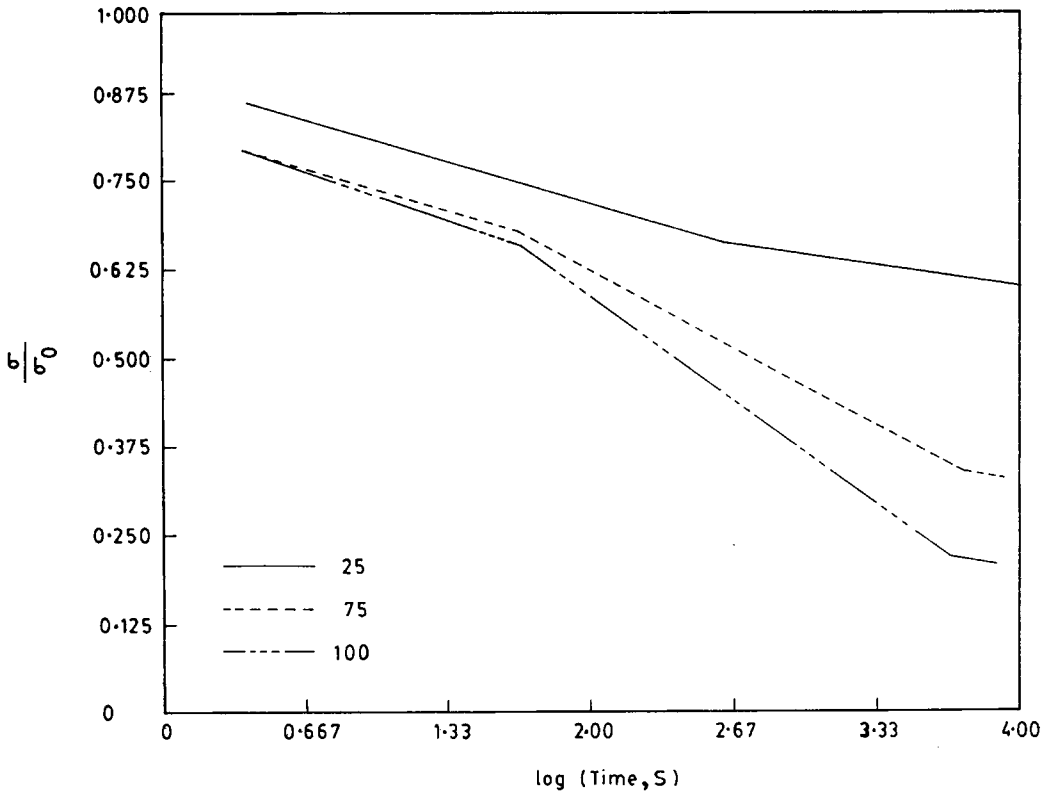


Figure 8 Effect of temperature on stress relaxation of mix *A*.

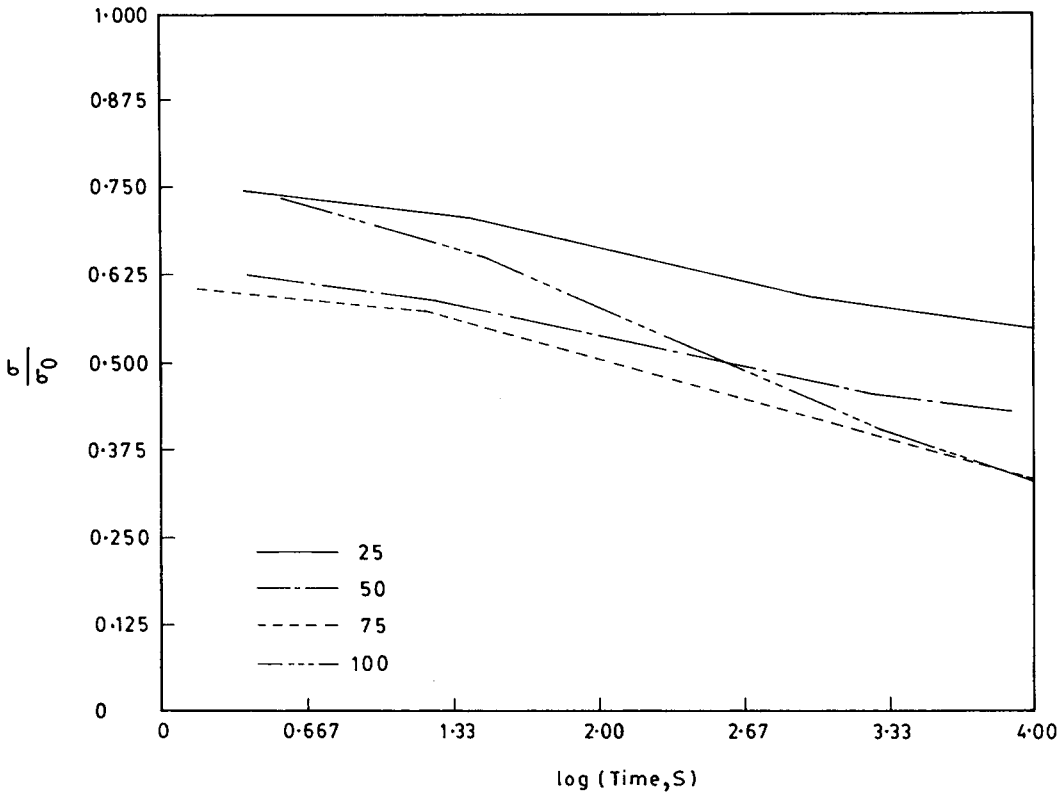


Figure 9 Effect of temperature on stress relaxation of mix *D*.

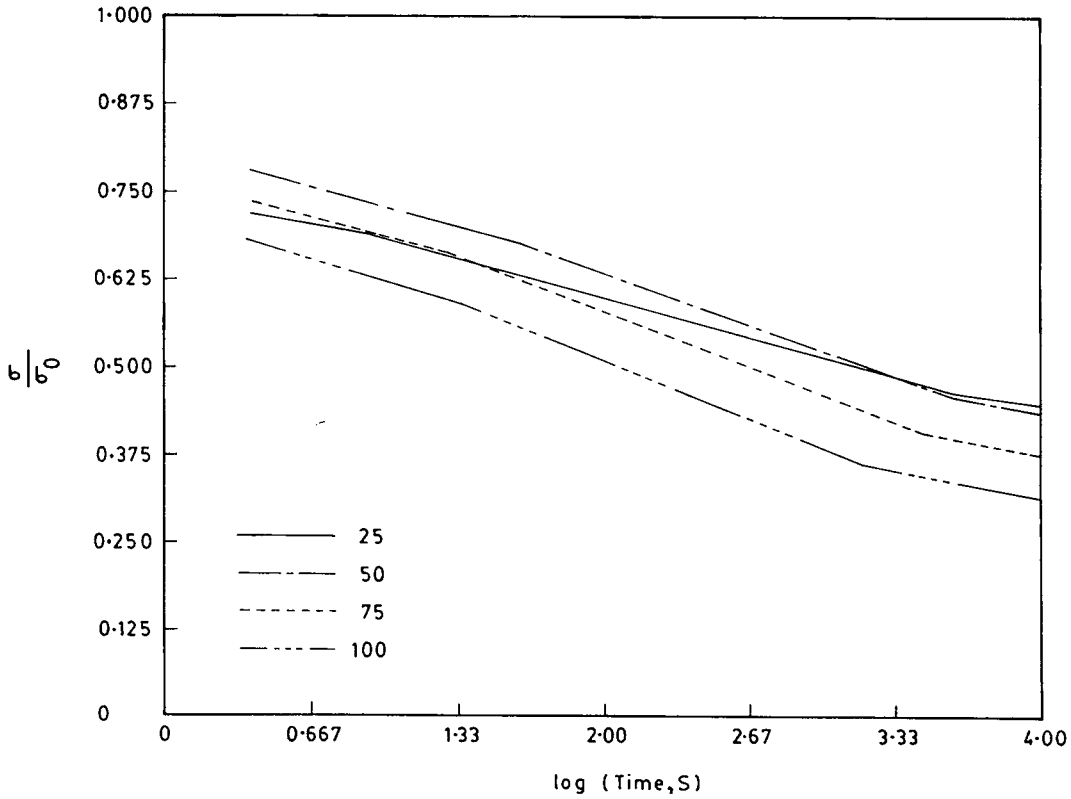


Figure 10 Effect of temperature on stress relaxation of mix *E*.

Table VI Effect of Temperature on Stress Relaxation

Mix	Temperature (°C)	Slope, $\times 10^2$			Intercept			Crossover Time (s)		Activation Energy (kcal/mol)
		I	II	III	I	II	III	I	II	
A	25	9.00	4.25	—	0.90	0.78	—	423	—	—
	75	7.82	14.66	6.72	0.82	0.91	0.61	46	6069	2.04
	100	10.62	21.35	6.82	0.84	1.00	0.55	45	4998	—
D	25	3.53	5.90	4.48	0.68	0.71	0.67	26	1028	—
	50	3.22	6.67	4.61	0.63	0.66	0.59	17	2125	1.01
	75	4.51	9.14	—	0.62	0.69	—	16	—	—
	100	7.96	12.94	9.59	0.78	0.84	0.63	28	1893	—
E	25	6.56	8.65	6.79	0.75	0.77	0.71	35	3297	—
	50	6.27	8.53	6.39	0.71	0.74	0.67	41	2963	0.71
	75	7.52	11.62	7.13	0.76	0.81	0.69	21	2791	—
	100	9.51	12.14	7.82	0.72	0.75	0.60	24	1516	—

tion increases by 100% in the case of unfilled TPU.

3. On changing the strain rate from 0.016 to 0.16 s^{-1} at 500% strain level, the first-stage relaxation increases by 50% and the second stage decreases by 25%.
4. Fiber loading in the range 10–30 phr decreases the first mode of relaxation by about 60%. When fibers are oriented in the direction perpendicular to the applied force, the initial rate of relaxation increases by 100% at 10–30 phr fiber loading.
5. In general, the temperature sensitivity of relaxation is reduced in the presence of fibers.

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