Fluorinated thermoset polyurethane elastomers prepared from polyether coprepolymers formed from mono-substituted fluorinated oxetane monomers and tetrahydrofuran

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This application is directed to novel fluorinated polymers and prepolymers derived from mono-substituted oxetane monomers having fluorinated alkoxymethylene side-chains and the method of making these compositions. The mono-substituted fluorinated oxetane monomers having fluorinated alkoxymethylene side-chains are prepared in high yield by the reaction of a fluorinated alkoxides with either 3-halomethyl-3-methyloxetane premonomers or aryl sulfonate derivative of 3-hydroxymethyl-3-methyloxetane premonomers. Preparation of a mono-substituted 3-bromoethyl-3-methyl- oxetane premonomer via a simple, high yield process amenable to commercial scaleup is also disclosed.

The fluorinated oxetane monomers of this invention can be readily homo/co-polymerized in the presence of a Lewis acid and polyhydroxy compounds to obtain hydroxy-terminated polyether prepolymers having fluorinated alkoxymethylene side chains. Additionally, the fluorinated oxetane monomers can be copolymerized with non-fluorinated monomers such as tetrahydrofuran to give polyether prepolymers with improved hydrocarbon compatibility. These prepolymers are polydisperse and exhibit number average molecular weights from 5,000 to about 50,000. These prepolymers are amorphous oils with primary hydroxy end-groups and thus function efficiently as the soft block for the synthesis of a variety of thermoset/thermoplastic elastomers and plastics having the characteristics of very low surface energy, high hydrophobicity, low glass transition temperature and low coefficient of friction. The polyurethanes derived from the prepolymers of this invention are elastomeric and, in addition to the above characteristics, exhibit high moisture resistance, high tear strength and excellent adhesion to a variety of substrates.

Stress Relaxation of Polyester Fiber-Polyurethane Elastomer Composite with Different Interfacial Bonding Agents

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ABSTRACT: The stress relaxation behavior of polyurethane elastomer and short polyester fiber filled elastomer composites with and without bonding agents at different strain levels and strain rates was studied. It was found that these compounds exhibit a multistage relaxation mechanism and that the rate of relaxation and cross-over time depend on the strain level and strain rate. The incorporation of fibers reduced the stage-I relaxation rate and increased the cross-over time of the gum vulcanisate. A higher rate of relaxation (first stage) was shown by the composites with longitudinal fiber orientation and composites with bonding agents.

INTRODUCTION

RECENTLY, SHORT FIBER reinforced rubbers have been used in a large number of applications such as V-belts, hoses, tubes, cables, etc. The attractive characteristics of these composites are their anisotropic

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properties, design flexibility, advantages in processing and low cost. Earlier works on short fiber reinforced rubber composite were confined to the mechanical, dynamic mechanical, rheological properties and the effect of fiber characteristics, orientation and adhesion between the fiber and the matrix etc. on the above properties [1–12].

Stress relaxation, the gradual reduction of stress with time under constant strain, has been studied by many workers in elastomeric matrices [13–16]. The effect of carbon black reinforcement on the stress relaxation has also been studied by some workers [15–18]. The influence of reinforcement with short fibers on the stress relaxation behavior of the matrix has not been studied systematically, although some details are available [19–21]. Because of the increasing use of short fiber reinforced rubber composites in both dynamic and static applications studies on stress relaxation behavior become important. This paper presents the result of our studies on stress relaxation of short polyester fiber reinforced polyurethane composite. The effect of strain level and strain rate on the gum vulcanisate, effect of fiber loading, effect of fiber orientation and effect of bonding agent on the stress relaxation behavior are investigated.

EXPERIMENTAL

Materials

Ether-based polyurethane, Adiprene CM (Mooney viscosity at 100°C–60) was obtained from Uniroyal Chemical Co. Inc., USA, and polyester staple fiber (approximately 4 mm length and 21 μ diameter), was procured from Madura Coats, India Ltd. Zinc-stearate, LR grade, product was obtained from Reidel (India) Chemicals. Caytur-4, a zincchloride—MBTS complex, used as a catalyst for polyurethane vulcanisation, was procured from Uniroyal Chemical Co., USA. MBTS (Dibenzothiazyldisulphide), was supplied by Bayer India Ltd. MBT (Mercaptobenzothiazole) was obtained from E. Merck India. Sulphur used was of commercial grade and was provided by Sameera Chemicals, Bombay, India. Polypropylene glycol with a molecular weight of 2000, was obtained from Fluka Chemie, India. Glycerol was supplied by BDH, Bombay, India. MDI (4,4'-diphenylmethanediisocyanate) was procured from Manali Petrochemicals Ltd., India.

Procedure

Formulation of the mixes is given in Table 1. Mixes C1, C2 and C3 contain different bonding agents, MD resins, based on polypropylene

Table 1. Formulation of the mixes.

Ingredients	Mix No.						
	A	B	C	D	C1	C2	C3
Adiprene	100	100	100	100	100	100	100
PET Fiber	—	10	20	30	20	20	20
PPG	—	—	—	—	4.44	—	2.22
GL	—	—	—	—	—	0.91	0.07
MDI	—	—	—	—	0.56	4.09	0.56

Zincstearate 0.5 phr, Caytur-4 0.35 phr, Dibenzolhiazyldisulphide (MBTS) 4 phr, 2-Mercaptobenzothizole (MBT) 1 phr and Sulphur 0.75 phr are common to all mixes.

glycol (PPG), glycerol (GL) and a mixture of PPG and GL with 4,4'-diphenylmethanediisocyanate (MDI). Mixes were prepared on a laboratory size two roll mill as per ASTM D-3182 (1982). The final sheeting was carried out to orient the fiber preferentially in the mill direction. The tensile sheets were molded at 150°C on a hydraulic press to their respective cure times. Dumbbell specimens were punched out of the sheets along and across the fiber orientation.

Stress relaxation was carried out on a Zwick Universal Testing Machine Model 1445. The test specimens were pulled to desired strain levels (10–300%) at different strain rates (0.021–0.104 s^{-1}). The stress was recorded as a function of time. The ratio of σ_t/σ_0 was plotted against the logarithm of time, σ_t and σ_0 being the stress at time t and at the original applied stress respectively. The rates of relaxation were calculated from the slopes of the straight line portion of the graph.

RESULTS AND DISCUSSION

Stress Relaxation of the Gum Compound

Figure 1 shows a typical stress relaxation plot of the gum vulcanisate at 20% strain level strained at two different strain rates (0.042 s^{-1} and 0.104 s^{-1}). The figure consists of different straight lines with different slopes indicating a multistage relaxation mechanism. Slopes of these straight lines give the rate of relaxation of the compound. The point of intersection of these different straight lines indicates the cross-over time of each relaxation process. The rate of relaxation and the cross-over time of different stages of relaxation mechanism depends on the rate of straining and strain levels. It is clear from the figure that the relaxation takes place initially at a faster rate followed by a period of relatively low relaxation rate. However, beyond a time period of 240 seconds, the relaxation takes place again at a higher rate.
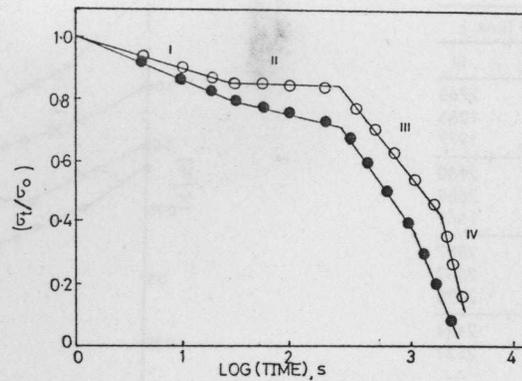
FIGURE 1. Stress relaxation plot of the gum vulcanisate at 20% strain level and at strain rates of 0.042 and 0.104 s⁻¹. ○—0.042 s⁻¹; ●—0.104 s⁻¹.
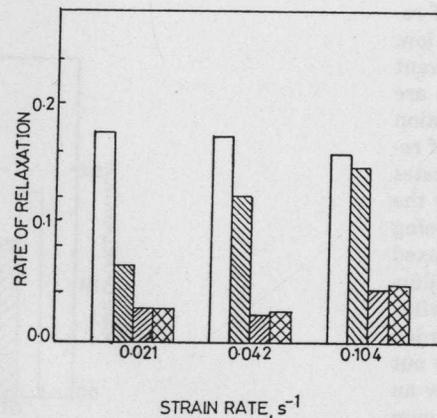

FIGURE 2. Variation of stage-I relaxation rate with strain rates and strain levels. □ 10% strain; ◺ 20% strain; ▨ 100% strain; ▩ 300% strain.
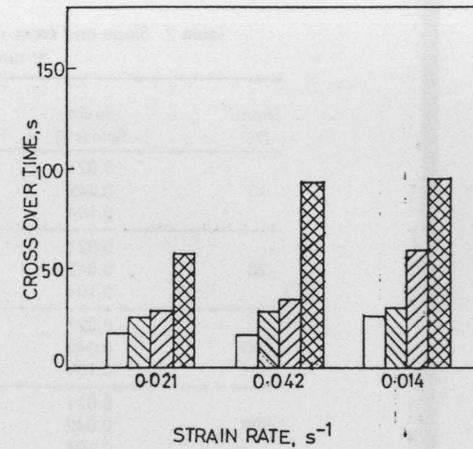

FIGURE 3. Variation of first cross-over time with strain rates and strain levels. □ 10% strain; ◺ 20% strain; ▨ 100% strain; ▩ 300% strain.

This behavior is reflected in the relaxation studies at different strain levels (10–300%) and strain rates (0.021–0.104 s⁻¹). The different rates of stage-I relaxation and the cross-over times from these plots are given in Figures 2 and 3 respectively. From the Figure 2 it is clear that at all strain rates, the stage-I relaxation rate decreases with strain level to more or less a constant value. Similar results have been reported in the case of a short Kevlar fiber reinforced composite [20]. For lower strain level the rate of relaxation is more or less independent of the strain rate but for higher strain levels the rate is increasing with the strain rate. Figure 3 shows that the cross-over time increases with increase of both strain level and strain rate.

The rate of stage-III relaxation and second and third cross-over time of the gum vulcanisate are given in Table 2. The rate of relaxation again shows a similar behavior as that of the first stage of relaxation process. However, for 300% elongation there is some deviation. The second and third cross-over times are found to be independent of strain levels as well as strain rates.

Effect of Fiber Loading

The stress relaxation pattern of the fiber filled composite at a strain

Table 2. Slope and cross-over times of the gum vulcanisate at different strain rates and strain levels.

Strain (%)	Strain Rate (s⁻¹)	III rd Slope (s⁻¹)	Cross-Over Time, s	
			II	III
10	0.021	0.456	368	2768
	0.042	0.492	258	1286
	0.104	0.153	190	1977
20	0.021	0.414	287	2950
	0.042	0.631	955	2689
	0.104	0.464	283	1562
100	0.021	0.051	219	1807
	0.042	0.039	453	2507
	0.104	0.062	244	2090
300	0.021	0.010	645	2494
	0.042	0.014	1000	2521
	0.104	0.052	502	—

FIGURE 4. Stress relaxation plot of mixes A, B, C and D at 10% strain level and at a strain rate of 0.042 s⁻¹. ○ Mix A; ● Mix B; ⊙ Mix C; ⊖ Mix D.

FIGURE 5. Effect of fiber loading on the stage-I relaxation rate of the gum vulcanisate at a strain level of 10%. ☐ Mix A; ⊠ Mix B; ▨ Mix C; ⊠ Mix D.

level of 10% and at a strain rate of 0.042 s⁻¹ is given in the Figure 4. The incorporation of fiber in the matrix does not much affect the stress relaxation pattern of the gum vulcanisate. It can be seen from the figure that though the composite exhibits a similar pattern of relaxation there is no such state where the rate of relaxation is very low. The stage-I relaxation rate of the gum vulcanisate and the different composites at a strain level of 10% and at different strain rates are shown in Figure 5. All the composites show a lower rate of relaxation than that of the gum vulcanisate and at all strain rates the rate of relaxation decreases with the increase of fiber loading. This indicates that the initial stage of relaxation process is greatly influenced by the incorporation of fibers. This is because the fiber matrix bond, being weaker in the absence of an added bonding agent, becomes relaxed during the process of straining the sample to the test strain level during which time no stress is recorded. The stress is recorded only after the sample is brought to the desired strain level. Hence, the recorded portion reflects a lower relaxation rate. This is done so as to carry out all the tests under identical conditions. Also, the composites show an increase in the rate of relaxation with strain rate as in the case of gum vulcanisate. The rate of relaxation of the other stages is also very less than that of the gum vulcanisate and are more or less independent of the fiber loading (Table 3).

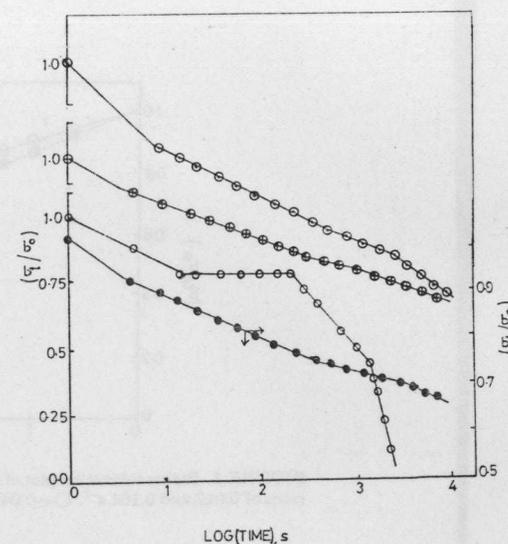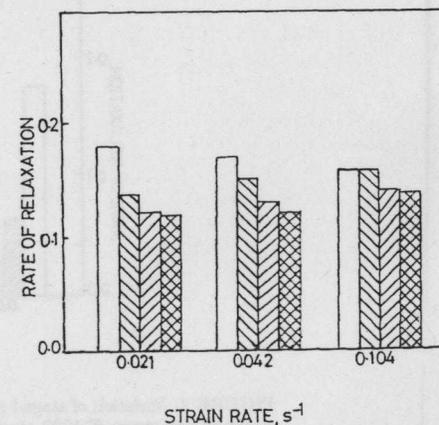The cross-over time of the first relaxation stage of the gum vulcani-

Table 3. Effect of fiber loading on the slopes and cross-over times of the composites at a strain level of 10%.

Strain Rate, s^{-1}	Fiber Loading, phr	Slopes, s^{-1}		Cross-Over Time, s	
		II	III	II	III
0.021	0	0.000	0.456	368	2768
	10	0.106	0.064	149	3727
	20	0.072	0.046	499	3104
	30	0.093	0.055	223	2493
0.042	0	0.000	0.492	258	1286
	10	0.087	0.048	401	2886
	20	0.070	0.055	499	2586
	30	0.074	0.047	303	1046
0.104	0	0.480	0.153	190	1977
	10	0.087	0.062	155	2317
	20	0.096	0.065	208	2493
	30	0.097	0.071	124	896

FIGURE 6. Effect of fiber loading on the first cross-over time of the gum vulcanisate at a strain level of 10%. □ Mix A; ◩ Mix B; ◪ Mix C; ⊠ Mix D.

sate and different composites at a strain level of 10% is shown in the Figure 6. It is clear from the figure that the cross-over time of the composites is less than that of the gum vulcanisate and the difference increases with the increase of shear rate. For the gum vulcanisate the cross-over time increases with shear rate while it decreases in the case of composites. The other cross-over times are given in the Table 3 and is evident that there is no definite trend to show any direct dependence of second cross-over time on the strain rate. However the third cross-over time decreases with the increase of strain rate.

Effect of Fiber Orientation

Figure 7 gives a typical stress relaxation plot of Mix C, with fibers oriented along and across the direction of strain. It shows that the relaxation mechanism in the transverse direction exhibits more stages than that of the relaxation in the longitudinal direction. Rate of relaxation of stage-I of the Mixes B, C and D, calculated from different plots, is shown in the Figure 8. The rate of relaxation is higher for the samples with longitudinally oriented fibers than that of the samples with transverse orientated fibers. At higher fiber loading (30 phr), however, the transverse fiber oriented samples show higher rate of relaxation. At higher fiber loadings, in the transverse direction, the contribution of the matrix to the composite stiffness becomes very limited, resulting
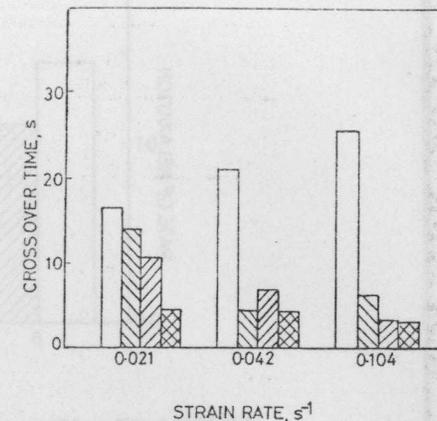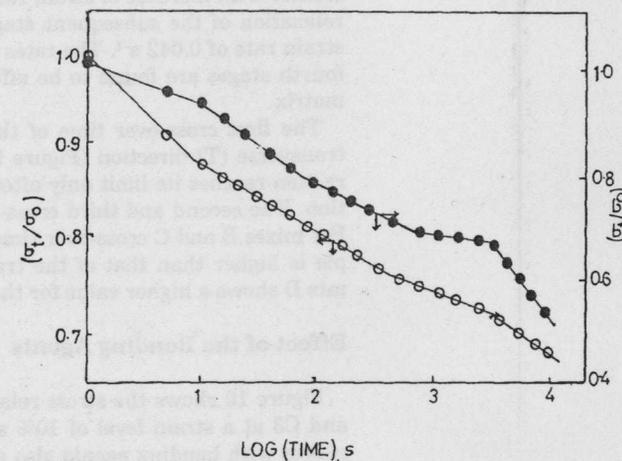

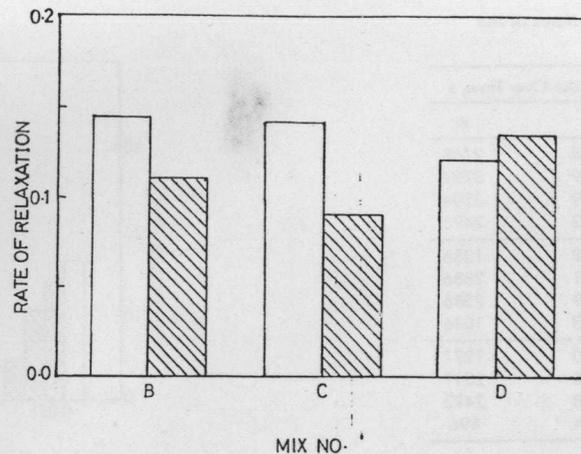FIGURE 7. Stress relaxation plot of composite with different fiber orientation. ○—Longitudinal; ●—Transverse.

FIGURE 8. Effect of fiber orientation on the stage-I relaxation rate of mixes B, C and D.
☐ Longitudinal; ▨ Transverse.

Table 4. Effect of strain rate and fiber orientation on the rate of first stage relaxation and first cross-over time of the mixes B, C and D.

Mix No.	Strain Rate (s^{-1})	Fiber Orientation	I st slope, s^{-1}	I st Cross-Over Time, s
B		L	0.138	14.9
	0.021	T	0.073	25.8
		L	0.144	4.1
	0.042	T	0.110	8.3
		L	0.160	6.4
	0.104	T	0.108	7.5
C		L	0.123	8
	0.021	T	0.081	10.1
		L	0.143	7.6
	0.042	T	0.099	16.7
		L	0.141	3.0
	0.104	T	0.134	4.3
D		L	0.120	4.6
	0.021	T	0.157	5.2
		L	0.121	3.3
	0.042	T	0.138	17.4
		L	0.139	7.2
	0.104	T	0.178	4.5

L—Longitudinal, T—Transverse.

in lower rate of relaxation. In both directions the rate of relaxation increases with increase of strain rate (Table 4). Table 5 shows the rate of relaxation of the subsequent stages at a strain level of 10% and at a strain rate of 0.042 s⁻¹. The rates of relaxation of the second, third and fourth stages are found to be affected by varying fiber content of the matrix.

The first cross-over time of the mixes in the longitudinal (L) and transverse (T) direction (Figure 9) shows that relaxation in the T direction reaches its limit only after a longer period than in the L direction. The second and third cross-over points are given in the Table 5. For mixes B and C cross-over time for the longitudinally oriented sample is higher than that of the transverse oriented samples, while the mix D shows a higher value for the transverse orientation.

Effect of the Bonding Agents

Figure 10 shows the stress relaxation curves of the Mixes C, C1, C2 and C3 at a strain level of 10% and at a strain rate of 0.021 s⁻¹. The curves with bonding agents also show a similar behavior of relaxation without bonding agents showing that the presence of bonding agents doesn't alter the relaxation pattern. However, the rate of stage-I relaxation of the composites is found to be affected by the presence of

Table 5. Effect of fiber orientation on the slopes and cross-over times at a strain rate of 0.042 s⁻¹ and at a strain level of 10%.

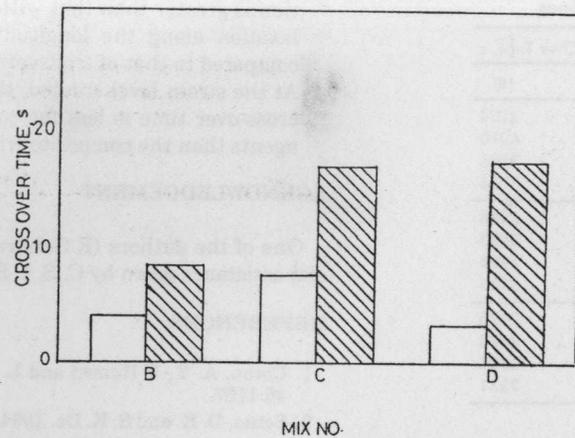| Mix No.	Fiber Orientation	Slopes, s^{-1}			Cross-Over Time, s	
		II	III	IV	II	III
B	L	0.087	0.048	0.085	401	2886
	T	0.069	0.152	0.030	75	518
C	L	0.070	0.055	0.108	499	2586
	T	0.090	0.174	0.027	54	622
D	L	0.074	0.047	0.077	303	1046
	T	0.085	0.046	0.138	1000	2725

L—Longitudinal, T—Transverse.

FIGURE 9. Effect of fiber orientation on the first cross-over time of mixes B, C, and D. □ Longitudinal; ▨ Transverse.
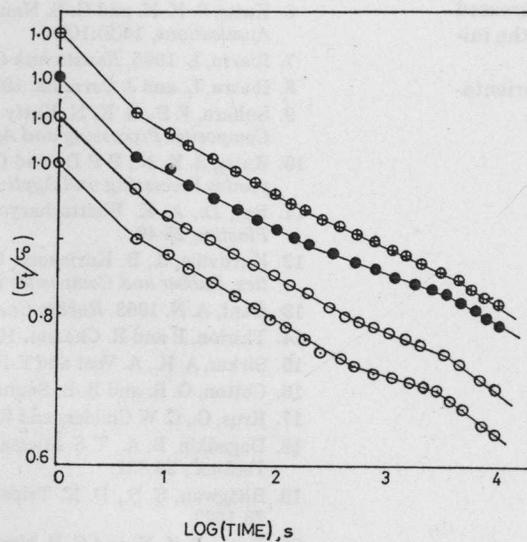

FIGURE 10. Stress relaxation curves of mixes C, C1, C2 and C3 at 10% strain level and at a strain rate of 0.021 s⁻¹. ○ Mix C; ⊕ Mix C1; ⊙ Mix C2; ● Mix C3.

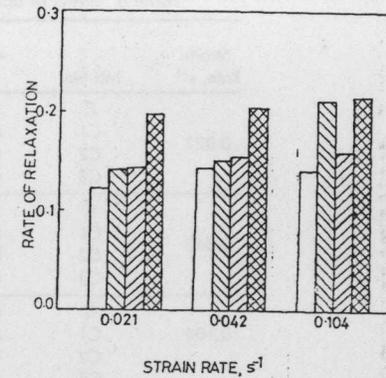
FIGURE 11. Effect of bonding agent on the stage-I relaxation rate of composite. □ Mix C; ▨ Mix C1; ▨ Mix C2; ▨ Mix C3.

bonding agents. This is because, compared to the composites without bonding agents, the fiber matrix bond in the composites with bonding agents is stronger and does not become relaxed during the straining process; rather, the relaxation takes place at a later stage which is reflected as a higher rate in the plot. Composites containing bonding agents show a higher rate of relaxation than that of the one without bonding agents (Figure 11). This is also supported by the fact that a higher relaxation rate is observed when the strain rate is high (Figures 2 and 5).

The rate of relaxation is at a maximum in the case of composites with a bonding agent based on PPG-GL mixture with MDI indicating a better bonding between fiber and matrix. Again, as in the case of composites without bonding agents, mixes C1, C2 and C3 show an increase in the rate with the increase of strain rate. The second stage of relaxation also shows a similar trend but the rate of final stages of relaxation is found to be independent of the strain rate (Table 6).

At lower strain rates the first cross-over time is less for composites containing bonding agents and it is higher at higher rates of straining (Figure 12). Second and third cross-over times do not show any linear dependence on the shear rates, as is the case with composite without bonding agents (Table 6).

CONCLUSIONS

1. The polyurethane elastomer and short polyester fiber filled elas-

Table 6. Effect of bonding agents on the slopes and cross-over times.

Strain Rate, s^{-1}	Mix No.	Slopes, s^{-1}			Cross-Over Time, s	
		II	III	IV	II	III
0.021	C	0.072	0.046	0.092	499	3104
	C1	0.076	0.058	0.089	167	4010
	C2	0.089	0.036	0.110	464	2586
	C3	0.101	0.069	0.110	167	3104
0.042	C	0.070	0.055	0.108	499	2586
	C1	0.076	0.043	0.070	373	3593
	C2	0.085	0.031	0.011	268	2994
	C3	0.110	0.071	0.117	346	3104
0.104	C	0.096	0.065	0.010	208	2493
	C1	0.062	0.023	0.069	122	2493
	C2	0.093	0.021	0.012	208	2886
	C3	0.097	0.058	0.087	136	2331

tomer composites exhibit a multistage relaxation mechanism and the rate of relaxation and cross-over time of different relaxation stages depend on the strain level and strain rate.

2. The rate of first stage relaxation of the gum vulcanisate is decreased with the incorporation of fibers showing that the fiber alters the initial mechanism of the relaxation.

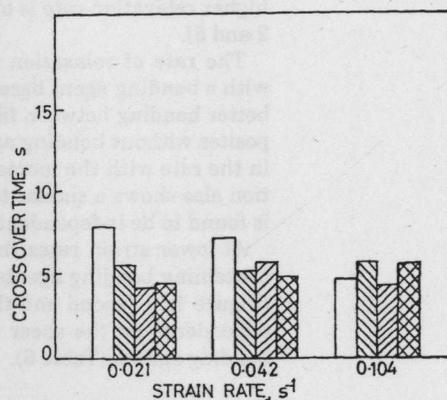3. The relaxation rate of the specimens with longitudinal fiber orienta-

FIGURE 12. Effect of bonding agent on the first cross-over time of composite. □ Mix C; ⊠ Mix C1; ▨ Mix C2; ⊠ Mix C3.

tion is greater than that with the transverse orientation and the relaxation along the longitudinal direction reaches its limit easily compared to that of transverse direction.

4. At the strain level studied, the first rate of relaxation is higher and cross-over time is less for composites containing different bonding agents than the composite without bonding agents.

ACKNOWLEDGEMENT

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