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Effects of Cyclic Loading on the Dynamic Viscoelastic Properties of Crosslinked Polymers Reinforced with Randomly Distributed Short Glass Fiber

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Synopsis

This study describes the effects of the application of cyclic uniaxial loading on the viscoelastic response properties of two crosslinked copolymers which contain short, randomly distributed glass fibers as reinforcing agents. The additional viscoelastic dispersion, observed with unstressed glass-filled polymers and which occurs somewhat above the primary glass transition temperature of the matrix resin, disappeared as a result of the applied cyclic loading. A concurrent lowering of the rubbery modulus of the composite was observed.

INTRODUCTION

It has been reported in the previous paper[1] that an additional dispersion appears at the higher-temperature side of the primary dispersion for crosslinked polymers reinforced with randomly distributed short glass fiber and that the additional dispersion is obscured or disappears by the application of cyclic tensile loading less than 1/10 of the static tensile strength. This fact suggests that the interaction between polymer matrix and reinforcing material in composites can be delicately affected by a relatively small stimulus.

The purpose of this work is to obtain fundamental information concerning the change in internal structure of composite accompanied with cyclic loading. The samples used in this work are crosslinked polystyrene and poly(methyl methacrylate) reinforced with randomly distributed short glass fiber. The change in internal structure was deduced from the change in the dynamic viscoelastic properties of the composite subjected to cyclic tensile loading at various temperatures.

EXPERIMENTAL

Samples

The samples used in this work are listed in Table I. Because the presence of reinforcing material in relatively large concentrations could considerably obscure the effect of the matrix–reinforcing material interface, composites reinforced with relatively small concentrations of fiber were used in this work.

TABLE I
Sample Characteristics

Symbol	Composition of matrix resin, weight ratio			Content of glass fiber,[d] vol-%	Cure condition
	MMA[a]	St[b]	EGDM[c]		
MM	95	0	5	0	benzoyl peroxide was used as catalyst (0.2 phr)
MC				4.6	
SM	0	95	5	0	gelled at 100 °C and postcured at 140°C for 4 hr
SC				4.6	

[a] Methyl methacrylate.
[b] Styrene.
[c] Ethylene glycol dimethacrylate.
[d] E glass fiber, length 10 mm, diameter 9 μ.

Ethylene glycol dimethacrylate was used as crosslinking agent. Styrene, methyl methacrylate, and ethylene glycol dimethacrylate were purified as usual. The composites were prepared by impregnating the random-planar fiber mat with the mixture of ingredients of the polymer matrix and then by curing according to the specified cure condition. The random-planar fiber mat was obtained by uniformly and randomly dispersing 10-mm-long glass fiber in a large volume of water, in which poly(vinyl alcohol) was dissolved as binder of the fibers at a concentration of 1%, then scooping the dispersed fibers on wire netting, and finally drying the scooped fibers at 100°C between glass plates under a slightly compressed state.

Cyclic tensile loading was applied at a mean stress of 0.6 kg/mm^2, a stress amplitude of 0.5 kg/mm^2, and a cycling rate of 6000 rpm (100 Hz) using a Viscoelastic Spectrometer (Iwamoto Seisakusho Co.). A total of 3.5×10^5 cycles was applied. The temperatures at which the cyclic loading was applied were 15°, 45°, and 70°C for M samples and 15°, 45°, and 65°C for S samples. The specimens subjected to the cyclic tensile loading at 15°, 45°, 65°, and 70°C were designated F_{15}, F_{45}, F_{65}, and F_{70}, respectively.

Measurements

Dynamic viscoelastic properties were measured using a Viscoelastic Spectrometer. The temperature dependence of the complex dynamic tensile modulus was obtained at frequencies of 10 and 100 Hz. Tensile strength and elongation were measured at 15°, 45°, 65°, and 70°C using the Instron tensile tester. The strain rate was 10 mm/min.

RESULTS

Tensile Strength and Elongation. The tensile strength and elongation of each sample are listed in Table II. The cyclic mean stress applied to the sample as mentioned in the above section was about 1/10 to 1/7 of the tensile strength listed in Table II.

Effect of Cyclic Loading on Dynamic Viscoelastic Properties of Unreinforced Samples. The secondary dispersion of MM shows a peak around 45°C on the loss modulus E''-versus-temperature curve at a frequen-

TABLE II
Tensile Strength (S) and Elongation (γ) at Various Temperatures

	15 °C		45 °C		65 °C		70 °C	
Symbol	S, kg/mm²	γ, %	S, kg/mm²	γ, %	S, kg/mm²	γ, %	S, kg/mm²	γ, %
MM	6.1	6.4	5.8	8.0	—	—	5.1	12.0
SM	5.4	9.5	5.0	11.0	4.3	12.5	—	—
MC	6.4	6.3	6.2	7.5	—	—	5.9	10.4
SC	5.6	9.0	5.5	10.5	5.2	11.8	—	—

cy of 100 Hz, as shown in Figure 1. The dynamic viscoelastic properties of the fatigued samples (MM-F_{15}, MM-F_{45}, and MM-F_{70}) are compared with those of the unfatigued sample (MM) at a frequency of 10 Hz in Figure 1. The change in the viscoelastic properties accompanying the fatigue can hardly be noticed.

The E'' of SM at a frequency of 100 Hz increases with temperature below the primary dispersion, as shown in Figure 2. The dynamic viscoelastic properties of the fatigued samples (SM-F_{15}, SM-F_{45}, and SM-F_{65}) are compared with those of the unfatigued sample (SM) at a frequency of 10 Hz. The change in the viscoelastic properties accompanying the fatigue can hardly be noticed in this case, too.

Effect of Cyclic Loading on Dynamic Viscoelastic Properties of Composites. The dynamic viscoelastic properties of MC composites are shown in Figure 3. The temperatures of primary and secondary dispersions of MC are almost the same as those of MM. The additional dispersion appears as a hump at the higher-temperature side of the primary dispersion (α) for MC, as reported in a previous paper.[1] The obscuring or disappearance of the addi-

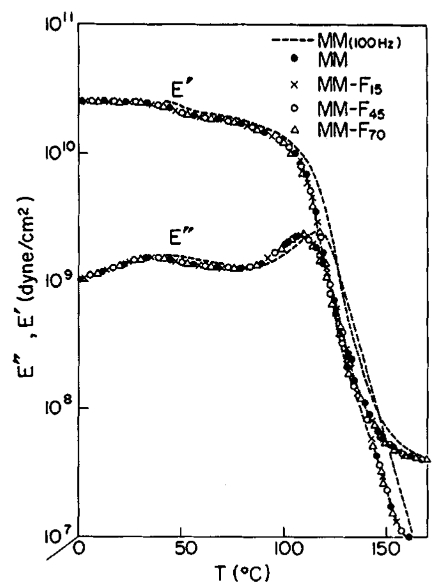

Fig. 1. Effects of cyclic loading on viscoelastic properties of MM.

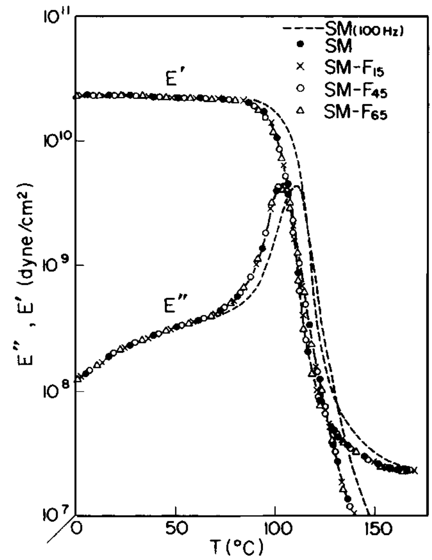

Fig. 2. Effects of cyclic loading on viscoelastic properties of SM.

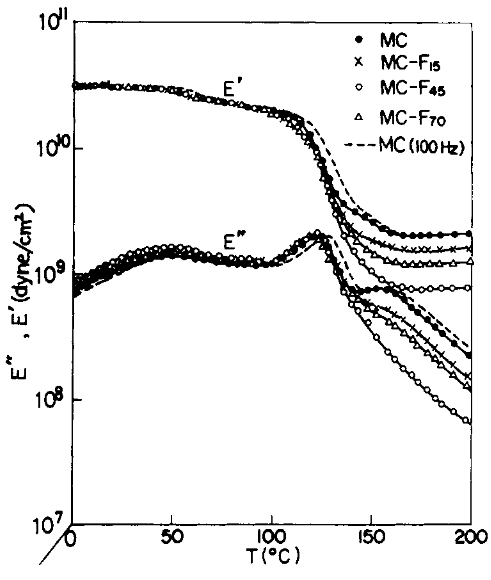

Fig. 3. Effects of cyclic loading on viscoelastic properties of MC.

tional dispersion and the decrease in rubbery modulus are the most prominent changes accompanying fatigue, as shown in Figure 3. The degrees of these changes increase in the order of MC-F_{45}, MC-F_{70}, MC-F_{15}.

The dynamic viscoelastic properties of SC composites are shown in Figure 4. The E'' of SC at a frequency of 100 Hz increases with temperature below the primary dispersion temperature, as in the case of SM. The additional dispersion appears as a shoulder above the temperature of the primary dispersion (α). The obscuring or disappearance of the additional dispersion and the decrease in rubbery modulus are also seen in the case of SC as the most

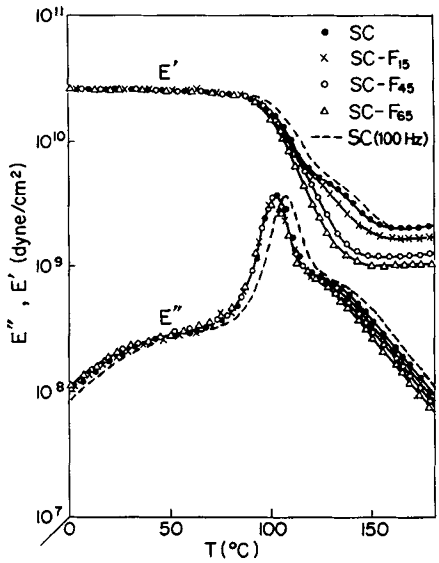

Fig. 4. Effects of cyclic loading on viscoelastic properties of SC.

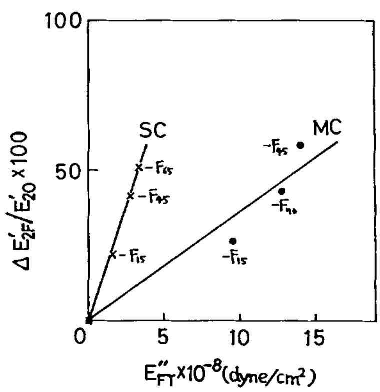

Fig. 5. Relation between loss modulus corresponding to the temperature at which fatigue was induced (E''_{FT}) and ratio of decrease in rubbery modulus with fatigue ($\Delta E'_{2F}/E'_{20}$).

prominent changes associated with fatigue. The degrees of these changes increase with the temperature at which the stress is applied, contrary to the case of MC.

DISCUSSION

As mentioned above, though the viscoelastic properties of the unreinforced samples were hardly affected by the fatigue, those of the composites were predominantly affected as to the rubbery modulus and the additional dispersion. It is considered from these facts that the changes in the viscoelastic properties of composites associated with fatigue are caused by changes in the interaction between resin matrix and reinforcing fiber. Furthermore, from the facts that the changes in viscoelastic properties are most pronounced when the temperature at which the cyclic loading is applied is near the secon-

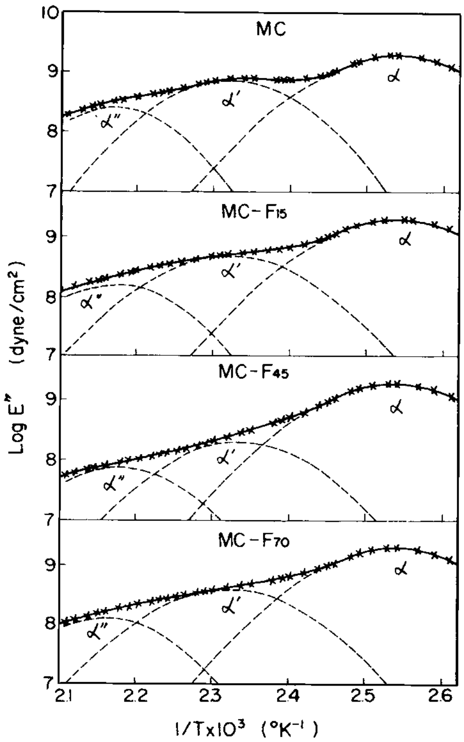

Fig. 6. Separation of relaxation mechanisms via plot of log E'' vs. $1/T$ for MC composites. Broken curves are a Gaussian function to hit each mechanism.

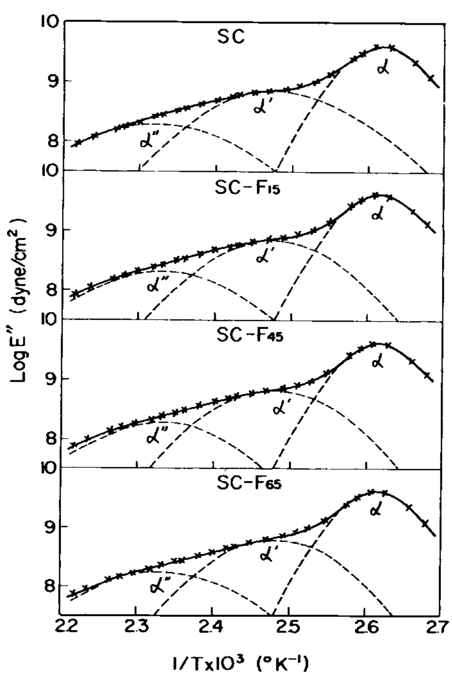

Fig. 7. Separation of relaxation mechanisms via plot of log E'' vs. $1/T$ for SC composites. Broken curves are a Gaussian function to hit each mechanism.

TABLE III
Constants Characterizing the Gaussian Functional Form of Each Mechanism

Symbol	Mechanism	A	$C \times 10^8$	$(1/T_0) \times 10^3$
	α	9.26	0.039	2.54
MC	α'	8.85	0.053	2.32
	α''	8.39	0.074	2.17
	α	9.26	0.039	2.54
MC-F_{15}	α'	8.64	0.045	2.32
	α''	8.18	0.064	2.17
	α	9.26	0.039	2.54
MC-F_{45}	α'	8.30	0.053	2.34
	α''	7.85	0.066	2.18
	α	9.26	0.039	2.54
MC-F_{70}	α'	8.57	0.045	2.32
	α''	8.09	0.067	2.16
	α	9.57	0.127	2.62
SC	α'	8.83	0.057	2.47
	α''	8.31	0.038	2.32
	α	9.57	0.127	2.62
SC-F_{15}	α'	8.83	0.061	2.48
	α''	8.31	0.048	2.33
	α	9.57	0.127	2.62
SC-F_{45}	α'	8.81	0.060	2.48
	α''	8.27	0.052	2.33
	α	9.57	0.127	2.62
SC-F_{65}	α'	8.80	0.064	2.48
	α''	8.25	0.043	2.33

dary dispersion temperature of the resin matrix for the case of MC, and that these changes become more pronounced with increase in the temperature at which the stress is applied in the case of SC, the changes in the interaction between resin matrix and reinforcing fiber associated with fatigue are considered to be closely related to the absorbing capacity of mechanical energy of the resin matrix. It has been reported[2] that the fatigue behavior of unreinforced thermoplastic resin is related to its damping capacity.

It is well known that the capacity of mechanical energy absorption or that of energy dissipation in the viscoelastic material subjected to forced vibration can be related to the loss modulus of the material. Thus, the dissipated energy during fatigue can be roughly considered to be proportional to the loss modulus corresponding to each temperature at which the fatigue was given at a frequency of 100 Hz, E''_{FT}. In Figure 5, the ratio of the decrease in rubbery modulus by fatigue, $\Delta E'_{2F}/E'_{20}$, which is represented by eq. (1), was plotted as a function of E''_{FT}:

$$\Delta E'_{2F}/E'_{20} = 1 - \frac{E'_{2f}}{E'_{20}} \tag{1}$$

where E'_{20} and E'_{2f} are the rubbery modulus of unfatigued and fatigued samples, respectively.

For the unreinforced sample, which has the same composition as the resin matrix of the composite, the value of $\Delta E'_{2F}/E'_{20}$ is zero. As seen in Figure 5, the nonzero value of $\Delta E'_{2F}/E'_{20}$ for composite means that the interaction between resin matrix and reinforcing fiber is affected by the fatigue. The lin-

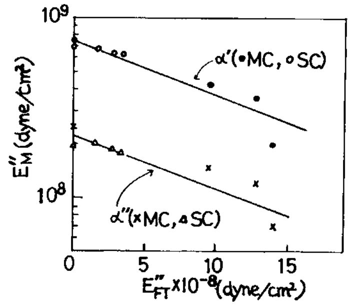

Fig. 8. Relation between E''_{FT} and relaxation strength of α' and α'' mechanisms (E''_M).

ear relationship between $\Delta E'_{2F}/E'_{20}$ and E''_{FT} means that the absorbing capacity of mechanical energy of the composite has a direct bearing on the changes in the interaction between resin matrix and reinforcing fiber accompanying the fatigue.

The ratio $E''_{FT}/(\Delta E'_{2F}/E'_{20})$, which is obtained from the slope of the straight lines in Figure 5 and is larger for MC than for SC, can be considered to be a measure of the relative strength of the interaction between resin matrix and reinforcing fiber in the composite.

The additional dispersion was separated from the primary dispersion (α) according to the method of Kawai.[3] The procedure is based on the following three assumptions: (1) additivity for assessing the contribution of each relaxation mechanism to the viscoelastic functions, (2) validity of the time–temperature superposition hypothesis within each mechanism independently of other mechanisms, and (3) a Gaussian-type symmetric function with respect to the plot of logarithm of loss modulus versus reciprocal absolute temperature for each mechanism, i.e.,

$$\log E'' = A \exp\left[-C\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{2}$$

where A, C, and $1/T_0$ are constants to characterize the Gaussian-type function, i.e., the logarithmic value of the maximum loss modulus, the parameter representing the sharpness of the dispersion, and the reciprocal absolute tem-

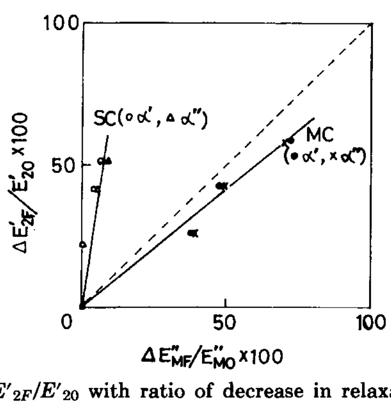

Fig. 9. Correlation of $\Delta E'_{2F}/E'_{20}$ with ratio of decrease in relaxation strength with fatigue ($\Delta E''_{MF}/E''_{MO}$).

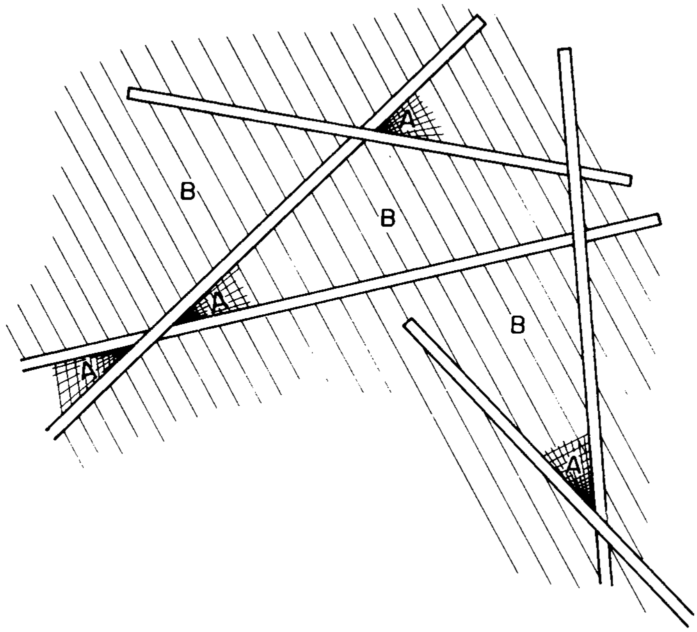

Fig. 10. Schematic representation of intersection of glass fibers in the composite (see text).

perature at which the loss modulus reaches a maximum value. The results are shown in Figures 6 and 7. As reported in the previous paper,[4] the additional dispersion is further decomposed into two mechanisms (α' and α''). The constants characterizing the Gaussian functional form of each mechanism are listed in Table III. Although the α dispersion is not affected by the fatigue, the values of A for the α' and α'' mechanisms generally decrease with fatigue. The real value of A, E''_M, by which the relaxation strength of each mechanism can be roughly estimated, is plotted as a function of E''_{FT} in Figure 8. As seen in the figure, E''_M of both mechanisms decreases with increase in E''_{FT}, and the plots of MC and SC for each mechanism fall around the same line. The correlation of the ratio of decrease in the rubbery modulus with fatigue, $\Delta E'_{2F}/E'_{20}$, with that in the relaxation strength, $\Delta E''_{MF}/E''_{M0}$, is shown in Figure 9. The ratio of decrease in the relaxation strength is represented by eq. (3):

$$\Delta E''_{MF}/E''_{M0} = 1 - \frac{E''_{Mf}}{E''_{M0}} \tag{3}$$

where subscripts 0 and f mean the original and fatigued samples, respectively. As seen in Figure 9, the correlation is relative good for MC. For SC, the ratio of decrease in the rubbery modulus by fatigue is far greater than that in the relaxation strength.

An assignment was proposed for the α' and α'' mechanisms in the previous paper[4] as follows: Figure 10 shows schematically the intersection of glass fibers in the composite. The resin matrix penetrated in such a region as A, which is part of the space partitioned by the intersected fibers at an acute angle, is considered to be strongly constrained as to mobility compared with the resin matrix penetrated in such an extensive space as region B. Therefore, the solid structure of decreased mobility or higher transition temperature is considered to be possibly formed in region A accompanying the curing. The structure of region A seems to be responsible for the α' mechanism. The α'' mechanism is considered to arise from the friction or slippage between the glass fiber and the resin matrix of region A because of increased mobility of the resin matrix accompanying further temperature rise. Thus, the change in the fraction of the structure responsible for the α' mechanism by the fatigue ought to directly affect the rubbery modulus, and the relaxation strength of the α'' mechanism is also considered to be affected in the same way as that of the α' mechanism by the fatigue.

As mentioned above, the relative strength of the interaction between the resin matrix and glass fiber is larger for MC than for SC. Therefore, the stress induced in the resin matrix around the fiber during the curing, especially that induced in region A of Figure 10, possibly becomes larger for MC than for SC. Consequently, for the case of MC, it is considered that the structure of region A is predominantly affected by the fatigue, and the correlation of $\Delta E'_{2F}/E'_{20}$ with $\Delta E''_{MF}/E''_{M0}$ becomes good. On the other hand, for the case of SC, it is considered that fatigue damage occurs at random position because of the smaller induced stress in region A compared with MC, and the correlation of $\Delta E'_{2F}/E'_{20}$ with $\Delta E''_{MF}/E''_{M0}$ becomes poor.

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