

# Dynamic Moduli for Short Fiber-CR Composites

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## Synopsis

The dynamic moduli,  $E'$  and  $E''$ , and  $\tan \delta$  for nylon-CR and PET-CR composites with unidirectional short fibers were studied as a function of temperature by using a Rheovibron. The temperature dependence of  $\tan \delta$  showed two dispersion peaks for a nylon-CR composite. The peak at  $-28^\circ\text{C}$  corresponded to the main dispersion of CR and the peak at  $100^\circ\text{C}$  to the  $\alpha$ -dispersion of nylon 6. For a PET-CR composite, in addition to the individual dispersion of CR and PET, a small and broad peak was observed at about  $90^\circ\text{C}$ . The angular dependence of  $E'$  indicated that the short fibers assumed good orientation. The storage modulus for the composites was given by the parallel model as  $E'_c = V_f E'_f + V_m E'_m$ , where  $E'_c$ ,  $E'_f$ , and  $E'_m$  were the storage modulus for the composite, fiber, and matrix and  $V_f$  and  $V_m$  were the volume fraction of fiber and matrix, respectively. In the transverse direction of fiber, the peak values of  $\tan \delta$  at  $-28^\circ\text{C}$  were given by the following equation;  $\tan \delta_c = \tan \delta_m - \alpha V_f$ , where  $\tan \delta_c$  and  $\tan \delta_m$  are the loss tangent for the composite and matrix, respectively, and  $\alpha$  is coefficient depending on fiber type. The results indicated that a region with strong interaction was formed between fibers and CR matrix.

## INTRODUCTION

The reinforcement of rubber compounds with short fibers has become necessary in many products, especially hose and belt industries. An advantage of the short fiber-elastomer composites is that it combines the elastic behavior of the rubber with the strength and stiffness of the reinforcing fiber. The mechanical properties, such as modulus, strength, and ultimate elongation depend on fiber orientation, aspect ratio, and adhesion between fiber and matrix. During mixing, some of fibers are buckled and broken under large deformations. This results in a distribution of fiber lengths, rather than a constant length.<sup>1,2</sup> During the milling of the rubber composites, the fibers tend to orient along the flow direction; thus the mechanical properties vary in different directions. Moghe<sup>3</sup> reported on the milling parameters which cause fiber orientation and so influence the composite properties. According to Coran et al.,<sup>4</sup> the properties of cellulose fiber-elastomer composites depend on the type of elastomer used as the matrix, the fiber concentration, fiber aspect ratio, and fiber orientation. O'Connor<sup>2</sup> compared the composites reinforced with five kinds of fibers and found that their mechanical properties depend on fiber type, fiber content, fiber aspect ratio, fiber orientation, fiber dispersion, and fiber-matrix adhesion. However, most investigations of short fiber-elastomer composites have been concerned with the mechanical properties. No fundamental studies on the viscoelastic properties of short fiber filled elastomers appear to have been published.

This paper presents the results of a study on the viscoelastic properties of two kinds of short fiber-elastomer composites. The effects of fiber orientation and

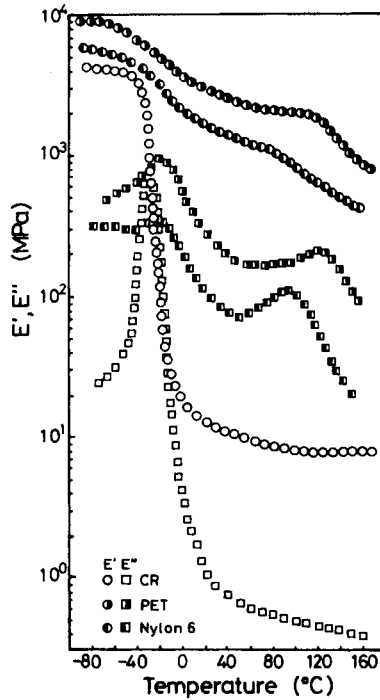


Fig. 1. Temperature dependence of storage and loss moduli for CR matrix (O, □), nylon 6 (●, ■) and PET (○, ◻) filaments: (O, ○, ●)  $E'$ ; (□, ■, ◻)  $E''$ .

volume fraction on the viscoelastic response of the composites are investigated.

## EXPERIMENTAL

**Materials.** The elastomer used was CR (Chloroprene rubber: Denka Co. Ltd.), and the short fibers used to reinforce the elastomer matrix were nylon 6 (Toray Co., Ltd.) and PET (Teijin Co., Ltd.), whose lengths were 6 mm and di-

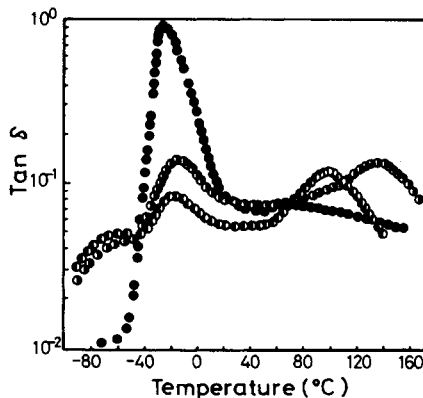


Fig. 2. Temperature dependence of  $\tan \delta$  for CR matrix (●), nylon 6 (●), and PET (○) filaments.

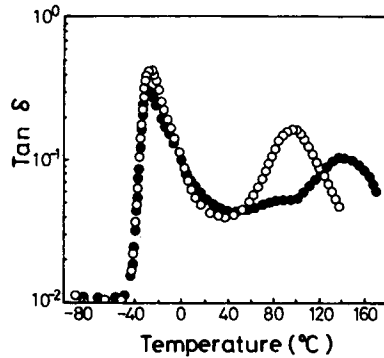


Fig. 3. Temperature dependence of  $\tan \delta$  for nylon-CR composite (O) and PET-CR composite (●);  $V_f = 10$  vol %.

ameters were  $27 \mu\text{m}$  and  $21 \mu\text{m}$ , respectively. In order to increase their adhesion to CR, nylon fibers were treated with RFL bonding agent, and PET fibers were dipped in isocyanate solution in advance and then they were treated with RFL system. The RFL dip was formulated as follows: (quantities in wt %)<sup>1</sup>; resorcinol 1.89, formaldehyde (37%) 2.77, water 48.55, aq. NaOH (1.67%) 3.06, SBR-vinylpyridine latex (41%) 41.78, concn  $\text{NH}_4\text{OH}$  (28%) 1.95. The dry add-on of adhesive was approximately 9%. The basic matrix composition is shown in Table I and remained constant throughout the experiments. However, the fiber concentration varied from 5 to 15 vol %.

**Processing.** All of the compounds and fibers were mixed in a Banbury mixer and milled for a time sufficient to disperse the fibers in the matrix at a mill opening of 2 mm. The milling direction was always kept the same in order to give a maximum amount of fiber alignment. Finally, each stock was passed

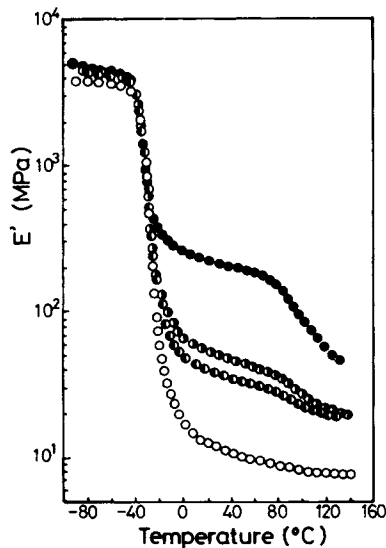


Fig. 4. Effect of fiber orientation on storage moduli for nylon-CR composite ( $V_f = 10$  vol %).  $\theta$ : (●)  $0^\circ$ ; (●)  $45^\circ$ ; (○)  $90^\circ$ ; (○) storage moduli for CR matrix.

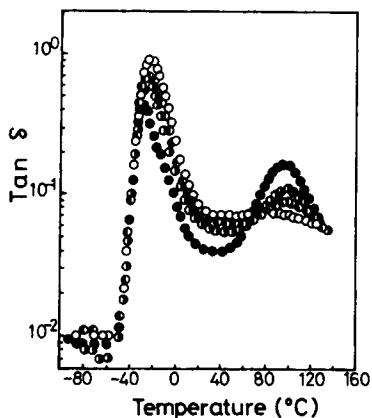


Fig. 5. Effect of fiber orientation on  $\tan \delta$  for nylon-CR composite ( $V_f = 10$  vol %).  $\theta$ : (●)  $0^\circ$ ; (◐)  $45^\circ$ ; (◑)  $90^\circ$ ; (○)  $\tan \delta$  for CR matrix.

through the mill to form a sheet in 2.0 mm thickness. All samples were cured by compression molding at  $153^\circ\text{C}$  for 20 min and were stocked in dry air. Cure must be taken to avoid flow in the mold which would disturb the mill orientation.

**Measurement of Viscoelastic Properties.** Dynamic complex modulus  $E^*$  and  $\tan \delta$  of the composites were measured by a direct reading of the dynamic viscoelastometer, Rheovibron Model DDV-III (Toyo Baldwin Co., Ltd). The Rheovibron viscoelastometer applies a sinusoidal tensile strain to the sample and uses two transducers to determine both the parameters, from which storage modulus  $E'$  and loss modulus  $E''$  can be calculated. The temperature range over which the properties were determined was  $-100$ – $150^\circ\text{C}$  at a heating rate of  $1.0^\circ\text{C}/\text{min}$ , at a frequency of 11 Hz with a strain amplitude of 0.06%, which was considered appropriate for the tests.

## RESULTS AND DISCUSSION

The storage modulus  $E'$  and loss modulus  $E''$  for nylon 6 and PET filaments and CR compound are shown as a function of temperature in Figure 1. The

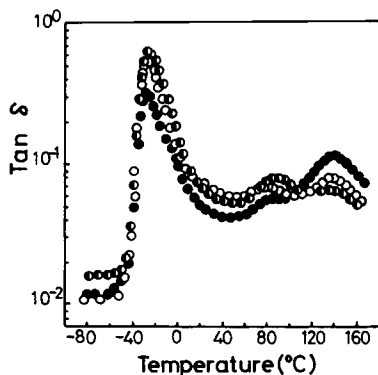


Fig. 6. Effect of fiber orientation on  $\tan \delta$  for PET-CR composite ( $V_f = 10$  vol %).  $\theta$ : (●)  $0^\circ$ ; (◐)  $45^\circ$ ; (◑)  $90^\circ$ .

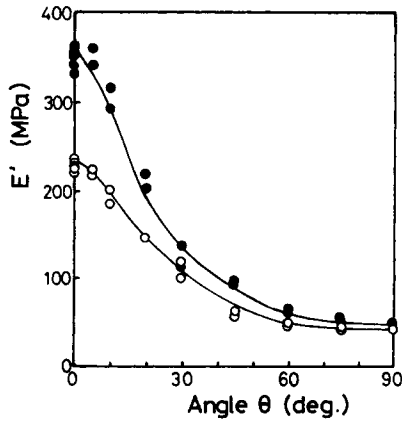


Fig. 7. Effect of fiber orientation on storage moduli for nylon-CR composite (O) and PET-CR composite (●) ( $V_f = 10$  vol %). The storage moduli calculated from eq. (1) are represented by lines.

magnitude of  $E'$  for CR compound falls sharply to the order of 10 MPa just above  $-40^\circ\text{C}$ , while the values of  $E'$  for both fibers decrease gradually with increasing temperature, and they are higher than that of CR compound by a factor of more than  $10^2$  over the whole temperature range above  $0^\circ\text{C}$ . The curve of  $E''$  for CR shows a sharp peak at  $-33^\circ\text{C}$ , whereas two peaks of  $E''$  appear at  $-20^\circ\text{C}$  and  $90^\circ\text{C}$ ,  $-20^\circ\text{C}$  and  $120^\circ\text{C}$  for nylon 6 and PET, respectively. Figure 2 shows the temperature dependence of  $\tan \delta$  for the filaments and CR compound. A large dispersion peak is observed at  $-28^\circ\text{C}$  for CR compound and two moderate peaks

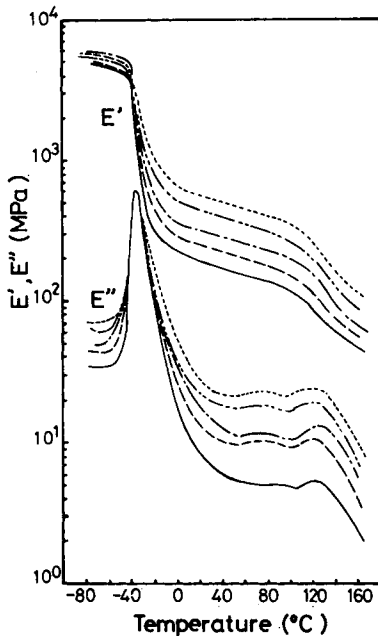


Fig. 8. Effect of fiber loading on storage and loss moduli for PET-CR composite.  $V_f$ : (—) 5%; (---) 7.5%; (-.-) 10%; (....) 12.5%; (.....) 15%.

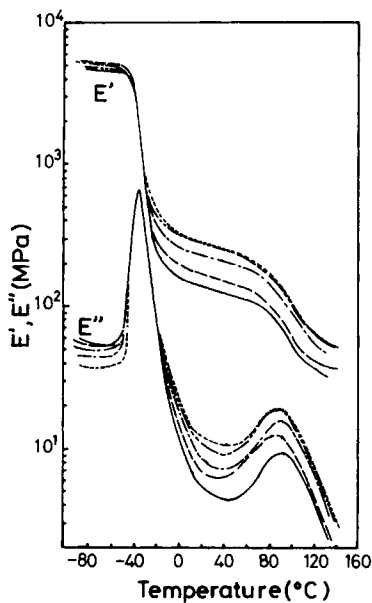


Fig. 9. Effect of fiber loading on storage and loss moduli for nylon-CR composite.  $V_f$ : (—) 5%; (--) 7.5%; (- - -) 10%; (- · - ·) 12.5%; (····) 15%.

are observed at  $-16^{\circ}\text{C}$  and  $100^{\circ}\text{C}$ ,  $-16^{\circ}\text{C}$  and  $135^{\circ}\text{C}$  for nylon 6 and PET, respectively. In the case of dynamic modulus for the fibers, the peak at the lower temperature corresponds to the  $\beta$ -dispersion, whereas the peak at the higher temperature to the  $\alpha$ -dispersion ascribed to micro-Brownian motion of amorphous chains.<sup>5</sup> Figure 3 shows the temperature dependence of  $\tan \delta$  in the longitudinal direction of fiber for nylon-CR and PET-CR composites which contain 10 vol % of the respective fibers. The  $\beta$ -dispersion peak of the fibers is weak compared to that of CR and is observed as very small shoulder at the corresponding temperature. Therefore, the peak at  $-28^{\circ}\text{C}$  corresponds to the main dispersion of CR and the peak at the higher temperature corresponds to

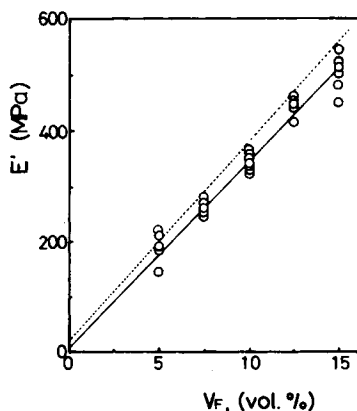


Fig. 10. Relationship between storage modulus and fiber loading at  $20^{\circ}\text{C}$  for PET-CR composite. The storage modulus calculated from eq. (2) is represented by the dashed line.

TABLE I  
Compound Recipe

Ingredients	Parts by wt
CR	100
Carbon black	36
Process oil	4
Stearic acid	2
Antioxidant	2
MgO	4
ZnO	5
Ethylene thiourea	0.5
Fibers	Variable

the  $\alpha$ -dispersion of each fiber. In addition to these two peaks, a small and broad peak is observed at about  $90^\circ\text{C}$  for the PET-CR composite. This dispersion peak will be mentioned in the latter. It is well known that the short fibers orient parallelly to the milling direction; this gives rise to anisotropy for mechanical properties of the short fiber-elastomer composites.<sup>1-4,6</sup> Figure 4 shows the effect of fiber orientation on the temperature dependence of  $E'$  for the nylon-CR composite. The curve of  $E'$  shifts to lower values as the angle ( $\theta$ ) with the fiber direction increases and becomes the lowest value in the transverse direction ( $\theta = 90^\circ$ ). The temperature dependence of  $\tan \delta$  displays more clearly the effect of the fiber orientation as is shown in Figure 5. As the angle increases, the peak at  $-28^\circ\text{C}$  rises progressively and another peak at the higher temperature falls to lower values. The temperature dependence of  $E'$  for the PET-CR composite showed the similar behavior to that for the nylon-CR composite respect to the fiber orientation. Figure 6 shows the effect of fiber orientation of  $\tan \delta$  for the PET-CR composite. The two dispersion peaks at  $-28^\circ\text{C}$  and  $135^\circ\text{C}$  display the opposite tendency with increasing of the angle similar to those for the

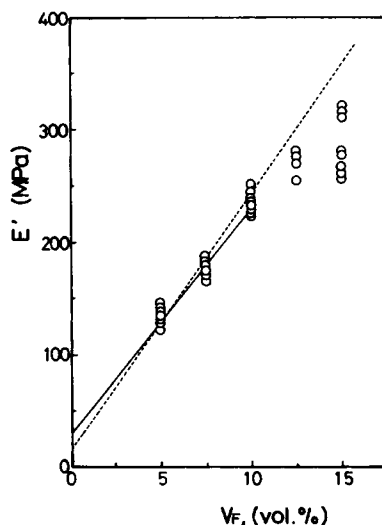


Fig. 11. Relationship between storage modulus and fiber loading at  $20^\circ\text{C}$  for nylon-CR composite. The storage modulus calculated from eq. (2) is represented by the dashed line.

TABLE II  
Factor of Fiber Loading for the Modulus of Short Fiber-CR Composites

Composite	Temp (°C)	Observed		Parallel model	
		Slope (MPa)	Intercept (MPa)	$E'_f - E'_m$ (MPa)	$E'_m$ (MPa)
Nylon 6-CR	20	2000	28.8	2150	13.8
	70	1450	15.4	1520	11.7
	100	700	12.9	940	10.8
PET-CR	20	3500	3.3	3750	13.8
	70	2600	4.0	2630	11.7
	100	2300	3.3	2500	10.8

nylon-CR composite. Furthermore, it is noted that the broad peak at 90°C protrudes with increasing of  $\theta$  and comes to be a relatively sharp peak in the transverse direction. Such dispersion peak was not observed for the nylon-CR composite, probably because the peak was shielded by the  $\alpha$ -dispersion of nylon being in this temperature range.

According to Coran et al.,<sup>7</sup> the relationship between modulus and its direction of measurement for short fiber-elastomer composites is represented as follows:

$$\frac{1}{E_\theta} = \frac{\cos^2\theta}{E_L} + \frac{\sin^2\theta}{E_T} \quad (1)$$

where  $E_\theta$  is the modulus of composite wherein the fiber axis deviates from the direction of test by the angle  $\theta$ ,  $E_L$  is the longitudinal composite modulus ( $\theta = 0^\circ$ ) and  $E_T$  is the transverse composite modulus ( $\theta = 90^\circ$ ). This relationship demonstrates considerable sensitivity to the fiber orientation. Figure 7 shows the storage moduli at 20°C against the direction of measurement for the nylon-CR and PET-CR composites. The  $E_\theta$  values calculated from eq. (1) are also plotted as the solid line curves for each composite. The obtained values agree well with respective calculated curves for both nylon-CR and PET-CR composites. This indicates that both fibers assume good orientation in the composites.

The effect of the volume fraction of fibers on  $E'$  and  $E''$  in the fiber direction are shown in Figures 8 and 9 for nylon-CR and PET-CR composites, respectively. The storage moduli  $E'$  for both composites decrease linearly with rising temperature from 0°C to 100°C. Both values of  $E'$  and  $E''$  shift to higher values with increasing fiber loading. In the case of the nylon-CR composite, however,  $E'$  for the composite containing the fiber of 15 vol % takes the same value as that containing one of 12.5 vol %. As reported previously,<sup>8</sup> nylon fibers tended to buckle during the mixing, and so a uniform dispersion of fibers in the matrix was disturbed. Therefore, the effect of increasing fiber loading dose not appear when the loading is over 12.5 vol % because of the poor dispersion.

The relationship between the storage moduli at 20°C and the volume fraction of fibers for nylon-CR and PET-CR composites displays good reproducibility as shown in Figures 10 and 11. The values of  $E'$  increase linearly with increasing fiber loading except those of nylon-CR composite containing the fiber over 12.5 vol %. From those figures, the slopes and intercepts of the solid lines drawn



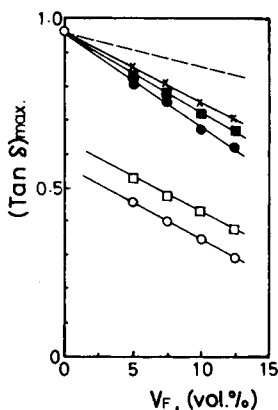


Fig. 12. Effect of fiber loading on the peak values of  $\tan \delta$  at  $-28^\circ\text{C}$ ; composites with RFL-nontreated fibers in  $\theta = 90^\circ$  (—): PET-CR composite in  $\theta = 0^\circ$  (○) and  $\theta = 90^\circ$  (●); nylon-CR composite in  $\theta = 0^\circ$  (□) and  $\theta = 90^\circ$  (■); values calculated from eq. (3) (---).

through the point of  $E'$  are given in Table II. The parallel model for modulus of composites is represented as follows

$$E'_c = V_f E'_f + V_m E'_m = (E'_f - E'_m) V_f + E'_m \quad (2)$$

where  $E'_c$ ,  $E'_f$ , and  $E'_m$  are the storage modulus for composite, fiber, and matrix and  $V_f$  and  $V_m$  are the volume fraction of fiber and matrix, respectively. The moduli at  $20^\circ\text{C}$ ,  $70^\circ\text{C}$ , and  $100^\circ\text{C}$  for the fibers and matrix are given in Table II. The values of  $E'$  calculated from the parallel model are displayed with the dashed line in the figures. It was found that the modulus in the range of  $20$ – $100^\circ\text{C}$  agreed nearly with the values calculated from the parallel model. This "parallel model" based on the assumption that matrix and fibers are strained to the same extent.<sup>9</sup> The finding suggests that the fibers are bonded strongly to the matrix so that the fiber strain equals the matrix in the range of the tensile which is applied to the composite by the viscoelastometer and that eq. (2) can be applied well to these short fiber-CR composites.

Figure 12 shows the relationship between the peak values of  $\tan \delta$  at  $-28^\circ\text{C}$  and the volume fraction of fiber for the composites. Similar to other composites,<sup>10</sup> the peak values of  $\tan \delta$  in the transverse direction of fiber decrease with increasing the volume fraction of each fiber and are displayed by the following equation:

$$\tan \delta_c = \tan \delta_m - \alpha V_f \quad (3)$$

where  $\tan \delta_c$  and  $\tan \delta_m$  are the loss tangent for composite and matrix, respectively,  $V_f$  is the volume fraction of fiber, and  $\alpha$  is coefficient depending on the fiber's type. If the mechanical damping for composites comes only from the matrix polymer, the damping ratio of composites to matrix is roughly equal to the volume fraction of polymer.<sup>11,12</sup> Namely, the peak values of  $\tan \delta$  should decrease monotonously along the dashed line shown in Figure 12. In the case of RFL-nontreated fibers, the peak values of  $\tan \delta_c$  for nylon-CR and PET-CR composites are on an identical line whose slope is steeper than that of the dashed line. Furthermore, the peak values of  $\tan \delta_c$  for the composites with RFL-treated

fibers decrease along more steeper lines depending on the fiber's type with increasing fiber loading. The results indicate that a region with strong interaction is formed between fibers and CR matrix and gives rise to decrease the apparent volume fraction of the matrix. The dispersion peak of  $\tan \delta$  appearing at 90°C for the PET-CR composite may be caused by the interface region in the composite. On the other hand, the peak values of  $\tan \delta$  at -28°C in the longitudinal direction of fiber are considerably lower than those in the transverse direction and decrease parallelly to the dashed line with increasing fiber loading as is shown in Figure 12. As described early, since the dynamic modulus in the longitudinal direction is largely affected by fiber, the peak values of  $\tan \delta$  at -28°C probably depend not only on the volume fraction of the matrix but on that of fiber.

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