

# Dynamic Viscoelasticity of Isoprene Rubber Reinforced with Short Cellulose Fibers

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## Synopsis

The dynamic viscoelasticity was investigated for isoprene rubber (IR) composites filled with untreated and chemically treated cellulose fibers. Mercerization and benzylolation were employed as chemical treatments. Bleached kraft pulp and cellulose powder were used as cellulose fillers. By mixing cellulose fillers, the dynamic modulus  $E'$  of IR composites was improved, especially above the glass transition temperature. Benzylolation of cellulose fibers reduced  $E'$  of IR composite, while mercerization increased it. A  $\tan \delta$  peak was observed at about  $-33^\circ\text{C}$  at 110 Hz along with a shoulder peak at about  $-16^\circ\text{C}$  for the IR composites. The intensity of the  $\tan \delta$  peak decreased when mixed with cellulose fillers. The shoulder peak next to the main peak could be separated assuming a Gaussian type equation;  $\log E'' = D \exp\{-C[(1/T) - (1/T_0)]^2\}$ , where  $D$  is the maximum value of  $\log E''$  vs.  $1/T$  curve,  $T_0$  is the maximum temperature, and  $C$  is a parameter to determine the width of the Gaussian function. From the Arrhenius plot of the frequencies against  $1/T_0$ , the apparent activation energies were calculated as 220–235 kJ/mol for the shoulder peak ( $\alpha_1$  process) and ca. 180 kJ/mol for the main peak ( $\alpha_2$  process). The  $\alpha_2$  process is caused by the glass transition of the rubber matrix. The  $\alpha_1$  process is assigned as the molecular motion of the rubber matrix strongly restricted by the fiber element.

## INTRODUCTION

Short-fiber-reinforced rubber has the combined characteristics of flexibility of rubber matrix and stiffness of fibers.<sup>1</sup> Recently short-fiber-reinforced rubber composites have been studied extensively, because short fibers as reinforcing elements have the advantages of mechanical properties, dispersion, adhesion with rubber matrix, and so on.<sup>1–4</sup>

Cellulose short fibers are considered to be especially suitable short-fiber reinforcing elements, since cellulose has high modulus (20–70 GPa), high tensile strength (ca. 1 GPa), a suitable aspect ratio for processing (50–200), low cost, and low density (ca. 1.6 g/cm<sup>3</sup>). Furthermore, cellulose fibers are not as brittle as glass fibers and are effective in processing.<sup>5</sup> Another advantage of cellulose fibers is that the mechanical properties can be changed by chemical treatment. It is known that the mechanical properties of rubber composites depend on the properties of the added reinforcing elements.

In a previous paper,<sup>6</sup> isoprene rubber (IR) composites filled with cellulose fibers were prepared, and the effect of chemical treatments of cellulose fibers on the mechanical properties of the composites were investigated. As chemical treatments, mercerization and benzylolation were employed. It was found that

benzylation of cellulose fibers reduced the modulus and the tensile strength of the rubber composites, but mercerization significantly improved both of them.

In this study, the dynamic viscoelasticity of the IR composites filled with treated and untreated cellulose fibers is investigated. We have paid particular attention to the effect of filled fibers on the dynamic modulus and the loss factor in the primary dispersion region.

## EXPERIMENTAL

### Materials

Table I shows recipes for the rubber composites. IR (Nippol IR 2200, Nippon Zeon Co. Ltd.) was used as matrix rubber. In this study, two types of cellulose fillers were used; bleached kraft pulp (Stora Kopparberg, Sweden) and cellulose powder (KC flock, Kokusaku Pulp Co. Ltd.). Cellulose fibers were mercerized and benzylation in the same way as described in the previous paper.<sup>6</sup> The fiber content in IR was kept at 40 phr.

The vulcanization time of the composites was determined at 150°C by using an oscillating rheometer (Toyoseiki Co. Ltd.) and was found to be 11 min for kraft pulp fiber reinforced rubber, 8 min for mercerized kraft fiber containing rubber, 7 min for benzylation kraft fiber reinforced rubber, and 16 min when cellulose powder was used. Details of the vulcanization have been reported elsewhere.<sup>6</sup> Five kinds of rubber samples were prepared: unfilled IR vulcanizate, IR filled with cellulose powder (CP-IR), IR filled with kraft fibers (KP-IR), IR filled with mercerized kraft pulp fibers (MKP-IR), and IR filled with benzylation kraft pulp fibers (BKP-IR).

### Measurements

The dynamic viscoelasticity of rubber composites was measured by using a Rheovibron DDV-IIC (Orientec Co. Ltd.). The dynamic modulus  $E'$ , loss modulus  $E''$ , and  $\tan \delta$  were measured as a function of temperature at frequencies of 3.5, 11, 35, and 110 Hz. The heating rate was 2°C/min. Rectangular specimens with a width of 5 mm and a thickness of 1 mm were used. The length between the clamps was 20 mm for IR and CP-IR, and 50 mm for KP-IR, MKP-IR, and BKP-IR.

TABLE I  
Recipes for Rubber Composites

Isoprene rubber	100.00 g
ZnO	5.00
Stearic acid	2.00
Sulfur	2.00
Dibenzothiazyl disulfide	1.25
Tetramethylthiuram disulfide	0.15
Cellulose fibres	40.00

## RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the dynamic modulus  $E'$  for KP-IR and CP-IR compared with IR vulcanizate. When cellulose fibers are mixed with IR, the dynamic modulus of the rubber composites is improved. The reinforcing effect of filled fibers above the glass transition temperature ( $T_g$ ) is higher than that below  $T_g$ .  $E'$  of CP-IR is lower than that of KP-IR over the temperature range from  $-100$  to  $30^\circ\text{C}$ . According to Halpin's relation,<sup>7</sup> the modulus of the composites increases with increasing values in the aspect ratio of filled fibers.

Figure 2 shows the temperature dependence of  $\tan \delta$  for IR, CP-IR, and KP-IR at 110 Hz. IR has a sharp peak at about  $-33^\circ\text{C}$ , which is caused by micro-Brownian motion in molecular chains. The rubber composites filled with cellulose fibers have a broad peak in the primary dispersion region. This broad peak seems to be superposition of two peaks, i.e., a main peak at about  $-33^\circ\text{C}$  and a shoulder peak at about  $-16^\circ\text{C}$  in the  $\tan \delta$  curve. As will be discussed later, this peak can be separated into two peaks. The intensity of the main peak is lowered by mixing the cellulose fillers into the rubber. In the case of  $\tan \delta (= E''/E')$ , the mixing law, eq. (1), can also be applicable for this rubber composite system<sup>8</sup>:

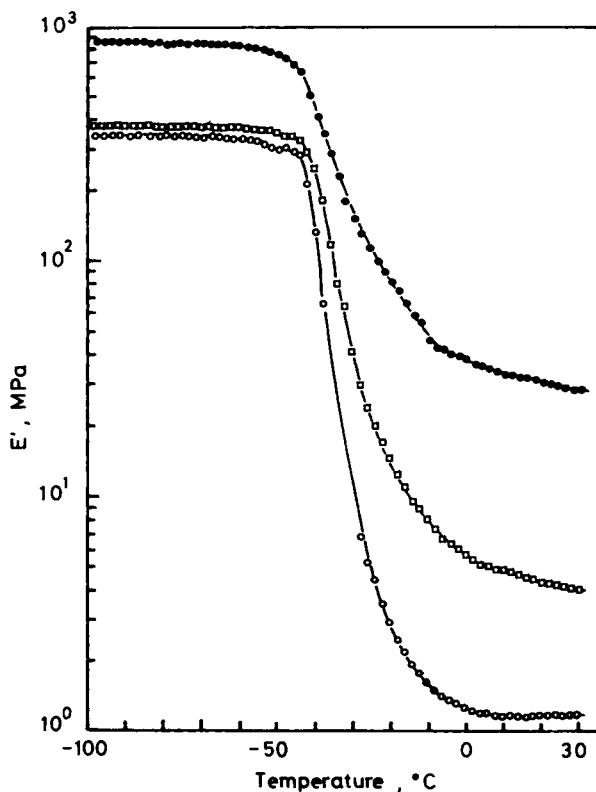


Fig. 1. The temperature dependence of the dynamic modulus at 110 Hz for KP-IR (●), CP-IR (□), and IR (○).

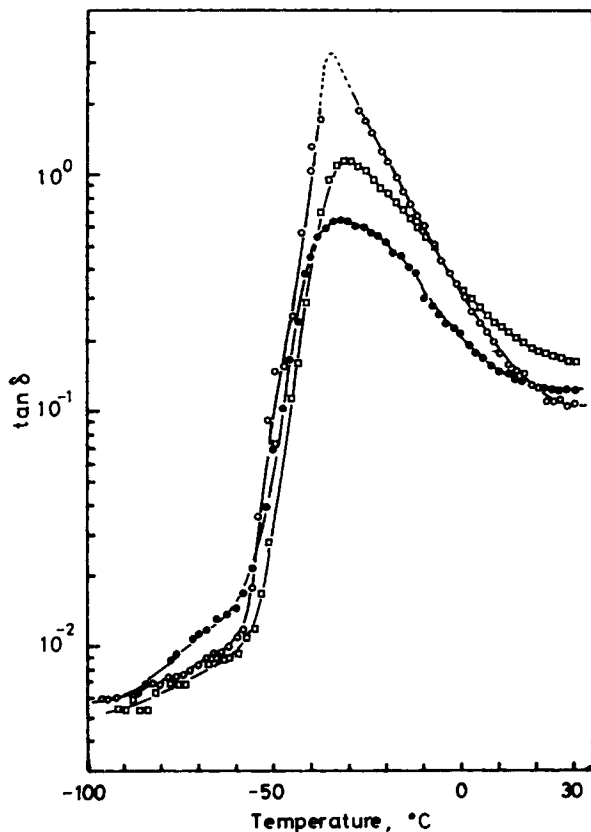


Fig. 2. The temperature dependence of  $\tan \delta$  at 110 Hz for KP-IR ( $\bullet$ ), CP-IR ( $\square$ ), and IR ( $\circ$ ).

$$(\tan \delta)_c = (\tan \delta)_1 \cdot \phi_1 + (\tan \delta)_2 \cdot \phi_2 \quad (1)$$

where  $(\tan \delta)_c$ ,  $(\tan \delta)_1$ , and  $(\tan \delta)_2$  are  $\tan \delta$  of the composite, matrix, and fibers, respectively. Usually  $(\tan \delta)_1 \gg (\tan \delta)_2 \approx 0$ , then eq. (1) is approximated as eq. (2)<sup>9</sup>:

$$(\tan \delta)_c \approx (\tan \delta)_1 \cdot \phi_1 \quad (2)$$

Therefore, the  $\tan \delta$  peak of filled polymer is lower than that of unfilled polymer.

Figure 3 shows the temperature dependence of  $E'$  for the rubber composites filled with chemically treated fibers (MKP-IR and BKP-IR) and untreated kraft pulp (KP-IR) compared with that for IR vulcanizate. The fiber content of each rubber composite is kept at 40 phr. Above  $T_g$  the reinforcing effect of filled fibers on  $E'$  of the rubber composites depends on the chemical treatments of fibers. Mercerization increases the modulus of cellulose fibers,<sup>9</sup> while benzoylation plasticizes cellulose fibers and reduces the modulus.<sup>10</sup> Accordingly, MKP-IR has the highest  $E'$  and BKP-IR has the lowest  $E'$ .

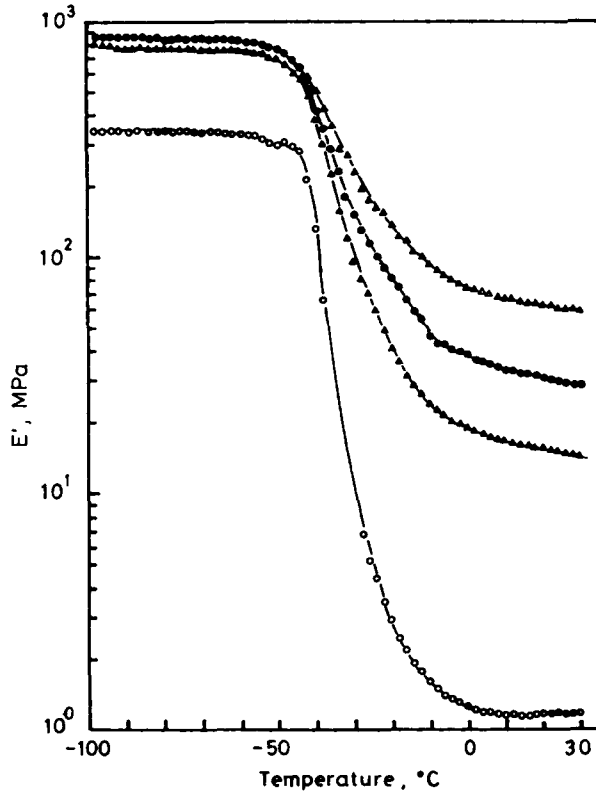


Fig. 3. Effect of chemical treatment of cellulose fibers on the dynamic modulus at 110 Hz: ( $\Delta$ ) MKP-IR; ( $\blacktriangle$ ) BKP-IR; ( $\bullet$ ) KP-IR; ( $\circ$ ) IR.

Figure 4 shows the changes in the  $\tan \delta$  curves for MKP-IR, KP-IR, BKP-IR, and IR as a function of temperature. The main peak appears at about  $-33^\circ\text{C}$  and the shoulder peak can be also observed at about  $-16^\circ\text{C}$ . The intensity of the  $\tan \delta$  peak depends on the magnitude of  $E'$  for each composite. Namely, the rubber composite having higher  $E'$  value has lower intensity of  $\tan \delta$ . This can be explained from the definition of  $\tan \delta$ , i.e.,  $\tan \delta = E''/E'$ .

The shoulder peak in the  $\tan \delta$  curve was observed at about  $-16^\circ\text{C}$  at 110 Hz for the rubber composite filled with cellulose fibers as shown in Figures 2 and 4. Multiple relaxation mechanisms can be separated on the following assumptions<sup>11</sup>:

1. Additivity can be applied for assessing the contribution of each relaxation mechanism to the viscoelastic functions.
2. The time-temperature superposition hypothesis is valid for each relaxation mechanism.
3. The loss modulus of each relaxation mechanism has a symmetric function and a Gaussian type equation such as eq. (3) can be applied for temperature dispersion:

$$\log E'' = D \exp \left\{ -C \left[ \left( \frac{1}{T} \right) - \left( \frac{1}{T_0} \right) \right]^2 \right\} \quad (3)$$

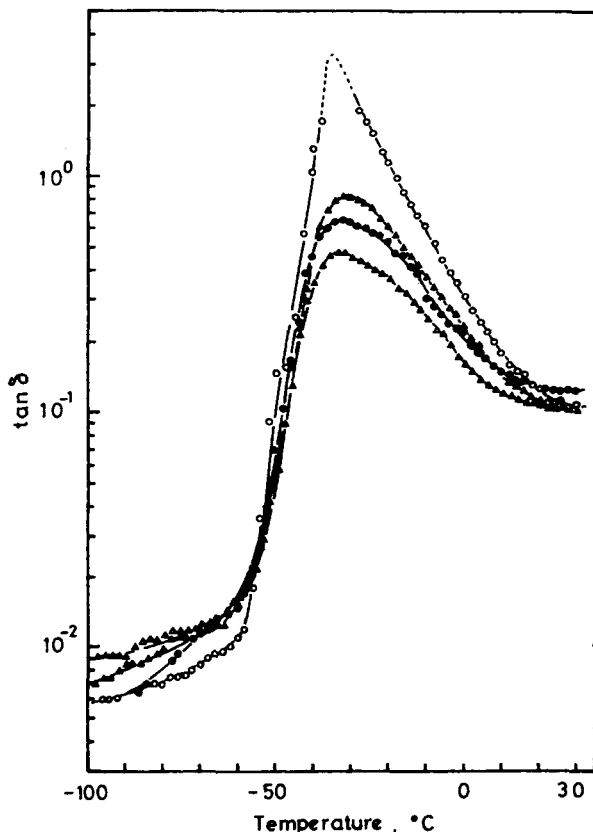


Fig. 4. Effect of chemical treatment of cellulose fibers on the  $\tan \delta$  at 110 Hz: ( $\Delta$ ) MKP-IR; ( $\blacktriangle$ ) BKP-IR; ( $\bullet$ ) KP-IR; ( $\circ$ ) IR.

where  $D$  is the maximum value of the logarithmic loss modulus,  $T_0$  is the absolute temperature at which the loss modulus takes the maximum value, and  $C$  is a parameter to determine the width of the Gaussian function. At first the parameter  $C$  is determined using the trial and error method in order to match eq. (3) with the experimental values of  $\log E''$  around the maximum. Then one can subtract the calculated values from the experimental values, and the other peaks can be separated.

Figure 5 shows an example of the separation of the relaxation mechanisms superposed in the primary dispersion region of IR. In this case a small peak can be separated from the main peak at a higher temperature. This separated peak is very small and the mechanism of the peak is different from the peak separated from the  $E''$  peak having a shoulder peak for rubber composites mixed with fibers. In general, several peaks can be separated from an  $E''$  primary peak using eq. (3) even if the main original peak does not have the shoulder.<sup>11</sup> This means that the  $E''$  primary peak corresponds to the distribution of the relaxation time and usually polymers have some wide distribution. However, a large peak could be separated from the  $E''$  peak having a shoulder peak at a higher tem-

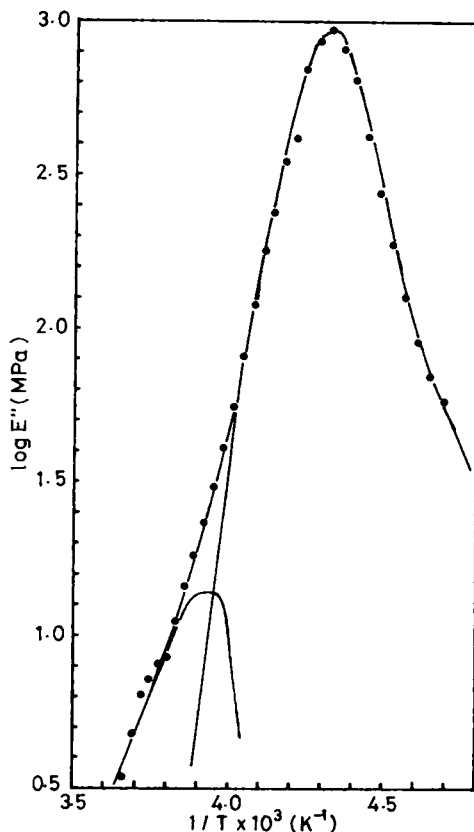


Fig. 5. Separation of the peak according to eq. (3) for IR.

perature, as shown in Figure 6. The mechanism of this large separated peak may be different from that of the small peak from the  $E''$  peak without the shoulder peak in question for unfilled rubber, as can be seen in Figure 5. The separation analysis shown in Figure 6 is an example of the rubber composite KP-IR. The peak located at the higher temperature is called the  $\alpha_1$  process and that at the lower temperature is the  $\alpha_2$  process. The primary dispersion region for other composites, i.e., MKP-IR, BKP-IR, and CP-IR could be also separated into two relaxation processes as well as for KP-IR.

Figure 7 shows a typical example of the temperature dependence of the dynamic viscoelasticity for KP-IR as a parameter of frequency. The  $\tan \delta$  peak and  $E'$  curve at the lower frequencies shift to lower temperatures. In the  $\tan \delta$  curve, the shoulder peak is observed besides the main peak at each frequency. The temperature dispersion for MKP-IR, BKP-IR, and IR was also measured as a parameter of frequency. Each shoulder peak for the rubber composites was separated using the technique described above. Apparent activation energies for  $\alpha_1$  and  $\alpha_2$  processes can be approximated by the following Arrhenius relationship:

$$f = f_0 \exp(-E_a/RT_0) \quad (4)$$

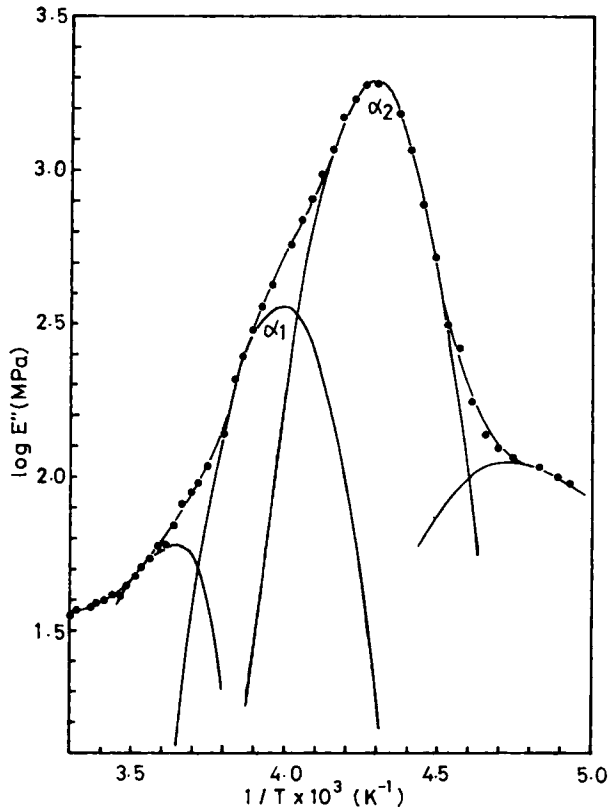


Fig. 6. Separation of the shoulder peak by eq. (3) for KP-IR.

where  $f$  is the measuring frequency,  $f_0$  is a constant,  $E_a$  is the apparent activation energy,  $T_0$  is the absolute temperature at which the maximum of  $\log E''$  occurs, and  $R$  is the gas constant.

Figure 8 shows the typical Arrhenius plots for KP-IR. Straight lines are obtained for  $\alpha_1$ - and  $\alpha_2$ -relaxation processes. From the slope of these straight lines, the apparent activation energies are calculated as 219.0 kJ/mol for  $\alpha_1$ -relaxation and 178 kJ/mol for  $\alpha_2$ -relaxation. Analogous straight lines could be obtained for MKP-IR, BKP-IR, CP-IR, and IR. The activation energies were calculated as listed in Table II along with the peak temperatures at 110 Hz. This kind of the shoulder peak has not been paid attention to in rubber composites. However, the double loss peaks have sometimes been observed in epoxy resin composites<sup>12,13</sup> or filled polydimethylsiloxane.<sup>14</sup> In the case of epoxy resin,<sup>13</sup> the activation energies have been reported as 250–270 kJ/mol for the  $\alpha_1$  process and 502 kJ/mol for the  $\alpha_2$  process. The activation energy for epoxy resin is higher than that of rubbers because of strong intermolecular interaction.

The activation energy for the  $\alpha_2$ -relaxation process which is caused by onset of the micro-Brownian motion in the chain molecules of rubber matrix is ca 180 kJ/mol except for CP-IR, and agrees with that for chloroprene rubber, EPDM, or polyurethane.<sup>1</sup> The activation energy for CP-IR is a little higher than that of other composites. This may be caused by increase in  $T_g$ . As can



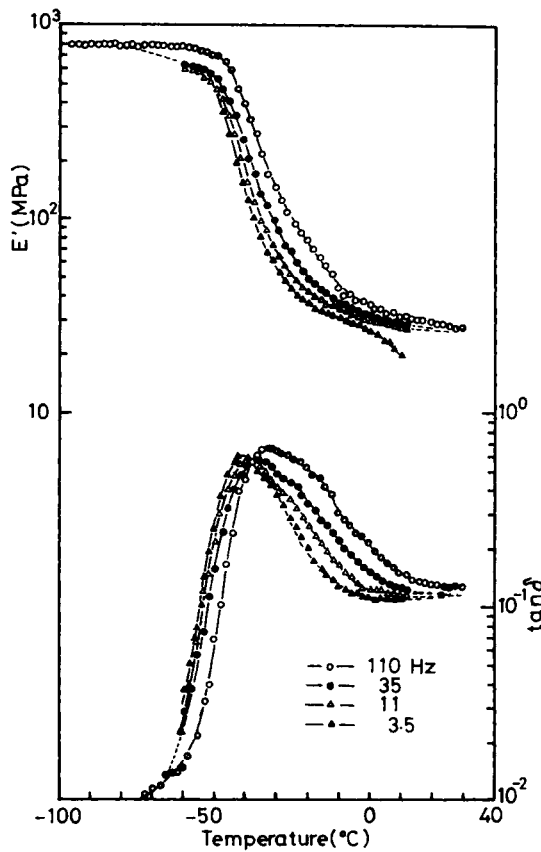


Fig. 7. The temperature dependence of the dynamic viscoelasticity of KP-IR as a function of frequency.

be seen in Table II, the location of the main peak (the  $\alpha_2$  process) is  $-39$ – $-40^\circ\text{C}$  at 110 Hz for IR and the IR composites filled with cellulose fibers, but in the case of CP-IR it appears at  $-37.7^\circ\text{C}$ . Cellulose powder has a large surface area than cellulose fibers such as kraft pulp, and it may increase the glass transition temperature in the same way as observed in the case of polymers mixed with fine powder.<sup>15</sup> The activation energy for the  $\alpha_1$  process is 220–230 kJ/mol and higher than that for the  $\alpha_2$  process. The location of the  $\alpha_1$  process is  $-22$ – $-23^\circ\text{C}$  at 110 Hz for every type of rubber.

The  $\alpha_1$  process may be caused by the interaction between rubber matrix and fibers, and has the higher activation energy than the  $\alpha_2$  process. For example, molecular motions of rubber matrix which is in contact with fibers, interposed between fibers, and/or located in cross parts of fibers, should be strongly restricted by fiber element, and thus the activation energy for such molecular motions is higher than that for unrestricted rubber matrix. When cellulose fibers such as KP, MKP, and BKP are mixed with rubber, entanglements are formed between fibers, and fiber blocks can be developed in the rubber matrix. Molecular motion of the rubber which is included in the fiber blocks is naturally restricted strongly by fibers and may occur as the  $\alpha_1$  process.

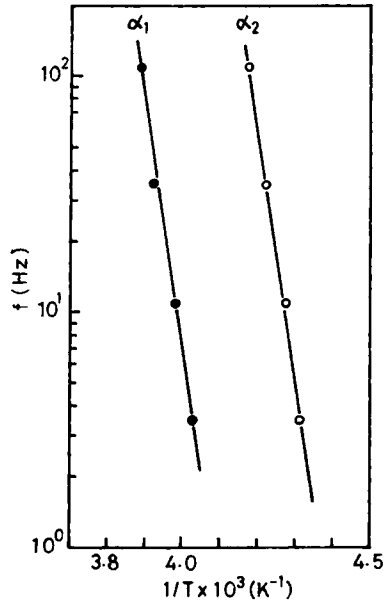


Fig. 8. The Arrhenius plots for KP-IR.

## CONCLUSIONS

The dynamic viscoelastic properties of IR composites filled with untreated and chemically treated cellulose fibers were investigated and the following results were obtained:

1. The dynamic modulus  $E'$  of IR composites was improved above the glass transition temperature. Benzylation of cellulose fibers reduced  $E'$  of the IR composite, while mercerization increased it.
2. An  $E''$  peak having a shoulder peak was observed for the IR composites.
3. The shoulder peak located at a higher temperature could be separated from the main peak using a Gaussian type equation,  $\log E'' = D \times \exp\{-C[(1/T) - (1/T_0)]^2\}$ .
4. From the Arrhenius plots of the frequency against  $1/T_0$ , the apparent activation energies were calculated as 220-235 kJ/mol for the shoulder

TABLE II  
Apparent Activation Energies and Peak Temperatures at 110 Hz

		IR	KP-IR	MKP-IR	BKP-IR	CP-IR
$\alpha_1$	$E_a$ (kJ/mol)	—	219.0	221.5	235.3	235.8
	$T_{max}$ (°C)	—	-22.0	-21.7	-23.9	-23.0
$\alpha_2$	$E_a$ (kJ/mol)	191.0	178.0	183.9	171.4	214.9
	$T_{max}$ (°C)	-40.4	-40.4	-38.8	-39.1	-37.7

peak (named the  $\alpha_1$  process), and 180 kJ/mol for the main peak (named the  $\alpha_2$  process).

5. The  $\alpha_2$  process is caused by the glass transition of the rubber matrix. On the other hand, the  $\alpha_1$  process is assigned as the molecular motion of the rubber matrix strongly restricted by the fiber element.

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