

Effect of Hydrogen Bond Formation on Dynamic Mechanical Properties of Amorphous Cellulose

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Synopsis

The temperature dependence of the dynamic modulus (E') and the mechanical loss tangent ($\tan \delta$) of amorphous cellulose prepared from cellulose triacetate by saponification was measured and compared with that of cellophane, recrystallized cellulose obtained by immersing amorphous cellulose in water, and cellulose triacetate. The E' of amorphous cellulose decreased initially with increasing temperature and then began to increase at about 70°C with a maximum at 80°C, decreasing again at about 100°C. Another decrease in E' was observed at 220°C accompanied by a discontinuity at 155°C. In the $\tan \delta$ -versus-temperature curve, a medium peak at 60°C, a shoulder peak at 146°C, and a broad peak at 200°C were observed. It was found that the transition at about 60°C was related to hydrogen bond formation by free OH groups. The transition at about 150°C was attributed to a recrystallization process by heating, and the relaxation at 200°C, to the glass transition of the polymer. The decrement in E' observed at about 100°C was attributed to the cooperative motion of an individual pyranose ring in amorphous cellulose, judging from the E' and $\tan \delta$ assignment of other cellulose materials. The change in E' was also measured isothermally as a function of time in the temperature range between 40°C and 80°C, where a maximum in $\tan \delta$ and an increment in E' were observed as the temperature dependence of the dynamic viscoelasticity. The change in E' with elapsed time was analyzed kinetically, and an activation energy of 2.6 kcal/mole was calculated. This value is the expected activation energy of hydrogen bond formation.

INTRODUCTION

It is well known that amorphous cellulose is obtained by grinding cellulose in a ball mill^{1,2} or by saponification of cellulose triacetate.^{3,4} The x-ray diffractogram of amorphous cellulose shows a typical amorphous pattern. Amorphous cellulose is recrystallized to cellulose II^{3,5-8} on immersing it in water.

It has been reported that amorphous cellulose forms hydrogen bond before crystallization by heat treatment. A band at 1590 cm^{-1} in infrared spectrometry⁹ and an exothermic peak in differential scanning calorimetry¹⁰ in the temperature range of 100°C to 180°C were observed with hydrogen bond formation.

Relaxation processes with transitions in cellulose and its derivatives have been investigated by a number of investigators. However, no relaxation processes in amorphous cellulose have been reported.

In this paper, the dynamic viscoelastic properties of amorphous cellulose were measured as a function of temperature, compared with those of unplasticized cellophane, recrystallized cellulose from amorphous cellulose, and cellulose

triacetate. The effect of hydrogen bond formation on the dynamic viscoelastic behavior of amorphous cellulose was investigated.

Furthermore, the dynamic modulus during the course of hydrogen bond formation was measured isothermally, and an attempt was made to analyze it kinetically.

EXPERIMENTAL

Materials

Amorphous cellulose was prepared from cellulose triacetate film procured from Fuji Film Co., Ltd. Strips of the cellulose triacetate film was first extracted for 48 hr with an alcohol-benzene solution (1:2) in a Soxhlet extractor; then the strips, after being dried *in vacuo*, were immersed for 24 hr in a 1% sodium ethylate solution of dehydrated ethanol at room temperature. Dehydrated ethanol was prepared with the use of calcium oxide and Drierite (anhydrous calcium sulfate). The amorphous cellulose was then washed with dehydrated ethanol until the washing solution became neutral, dried *in vacuo*, and then kept in a vacuum desiccator. The x-ray diffractogram of amorphous cellulose thus obtained showed a typical amorphous pattern,¹⁰ and no acetate bands were observed in infrared spectrometry.⁹ Thus, in this work, amorphous cellulose treated with sodium ethylate was used as the specimen to measure the dynamic viscoelastic properties.

Recrystallized cellulose was obtained by immersing amorphous cellulose in distilled water at room temperature for 24 hr and drying at room temperature for a week in vacuo (10^{-5} – 10^{-6} mm Hg). Heat treatment of amorphous cellulose consisted in heating at 80°C for 1 hr and 4 hr *in vacuo*.

Procedure

The dynamic viscoelastic properties (dynamic modulus E' and mechanical loss tangent $\tan \delta$) of cellulose were measured by using the apparatus of the forced vibrational method VIBRON DDV-IIC (Toyo Baldwin Co., Ltd). Frequencies used were 3.5, 11, 35, and 110 Hz.

Measurements of the temperature dependence of E' and $\tan \delta$ were performed at a heating rate of 2°C/min and by flowing highly pure nitrogen gas (above 99.999% pure), dried through concentrated sulfuric acid and silica gel, at a rate of 100 ml/min to prevent amorphous cellulose from crystallizing by moisture.

E' at constant temperature was measured as a function of time at a frequency of 3.5 Hz in an atmosphere of highly purified nitrogen gas. In this case, the temperature errors were within $\pm 0.5^\circ\text{C}$.

Dimensions of the tested samples were 1 mm in width and 0.07 mm in thickness for amorphous cellulose and cellulose triacetate, and 2 mm in width and 0.02 mm in thickness for unplasticized cellophane. The clamp-to-clamp distance of the dynamic viscoelastic apparatus was 40 mm.

X-Ray diffractograms were obtained with a Rigaku Denki Model 3D-F x-ray diffractometer equipped with a proportional counter.

RESULTS AND DISCUSSION

X-Ray diffractograms of samples are shown in Figure 1, for cellophane (curve 1), recrystallized cellulose (curve 2), amorphous cellulose (curve 3), and amorphous cellulose heat treated at 110°C for 4 hr (curve 3'). It is clearly seen in this figure that the crystallinity of cellophane is distinctly higher than that of the recrystallized cellulose.

Figures 2 and 3 show the temperature dependence of the dynamic modulus E' and $\tan \delta$, respectively, of cellophane, recrystallized cellulose from amorphous cellulose, amorphous cellulose, and cellulose triacetate.

In order to examine the transitions of amorphous cellulose in the temperature range between room temperature and 250°C, its temperature dispersions were measured and compared with those of crystalline cellulose.

As shown in Figure 2, the dynamic modulus E' of cellophane (curve 1) decreases gradually with increasing temperature. Discontinuities are observed at about 50° and 106°C, and then E' drops significantly at 280°C. In the case of recrystallized cellulose prepared from amorphous cellulose (curve 2), E' shows discontinuities at 60°, 10°, and 174°C, then drops at 196°C, and decreases markedly up to 240°C, passing through a small maximum at 200°C. A minimum of E' is observed at 250°C, and then it begins to increase. Again, the change in E' for the recrystallized cellulose is very similar to that for cellophane in the temperature region below 200°C, but difference in behavior between the recrystallized cellulose and cellophane is observed above 200°C. The difference seems due to the different crystallinities of the crystallized cellulose and cellophane. The increase in E' from 250°C is similar to that for regenerated cellulose, amylose, and amylopectin observed by Nakamura.^{11,12} For amorphous cellulose

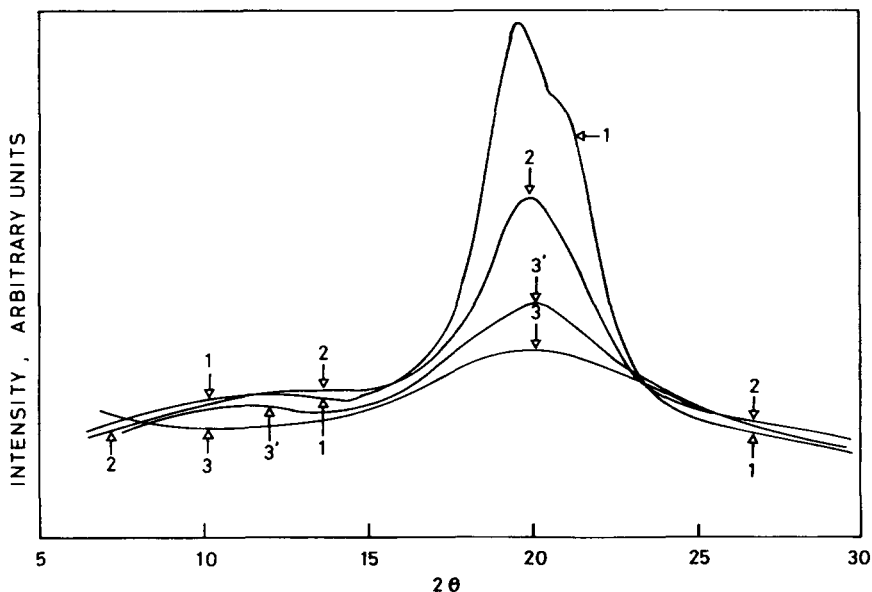


Fig. 1. X-Ray diffractograms of cellophane (curve 1), recrystallized cellulose obtained by immersing amorphous cellulose in water for 24 hr (curve 2), amorphous cellulose (curve 3), and amorphous cellulose treated at 110°C for 4 hr (curve 3').

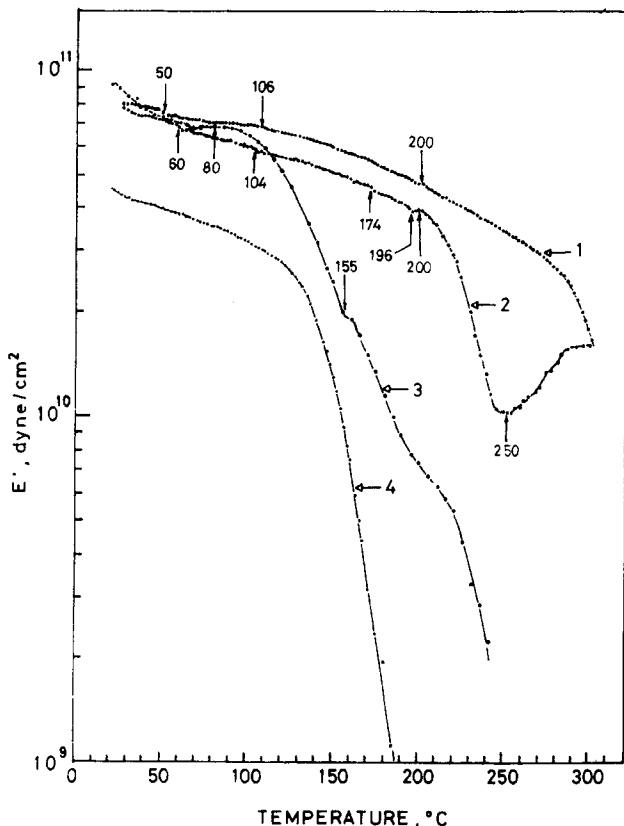


Fig. 2. Temperature dependence of dynamic modulus E' of cellophane (curve 1), recrystallized cellulose obtained by immersing amorphous cellulose in water for 24 hr (curve 2), amorphous cellulose (curve 3), and cellulose triacetate (curve 4) at 110 Hz. These were measured at $2^\circ\text{C}/\text{min}$ in dried, ultrapure nitrogen gas.

(curve 3), E' decreases initially with increasing temperature up to about 70°C , then increases with a maximum at 80°C , decreasing at about 100°C , and sharply dropping at 220°C , passing through a discontinuity at 155°C . The increase in E' at about 70°C seems related to hydrogen bond formation that restricts molecular motion; this will be discussed later. As is evident from that for crystalline cellulose. In the case of cellulose triacetate (curve 4), E' decreases gradually with increasing temperature without a significant discontinuity, markedly decreasing at 130°C .

Figure 3 shows the temperature dependence of $\tan \delta$ for the same celluloses as in Figure 2. For the purpose of comparison, $\tan \delta$ curves are displaced vertically on the logarithmic scales using arbitrary values. For cellophane (curve 1), weak peaks at 48° , 64° , 80° , and 98°C , a shoulder peak at 190°C , and a broad peak at 236°C are observed in the $\tan \delta$ -versus-temperature curve in the temperature range of 5° to 300°C . In the case of the recrystallized cellulose (curve 2), weak peaks at 60° and 80°C , a peak at 196°C , and strong peaks at 236° and 245°C are observed. A weak peak at 48°C for cellophane corresponds to the transitions which Ramiah and Goring¹³ and Kubát et al.¹⁴ have observed at

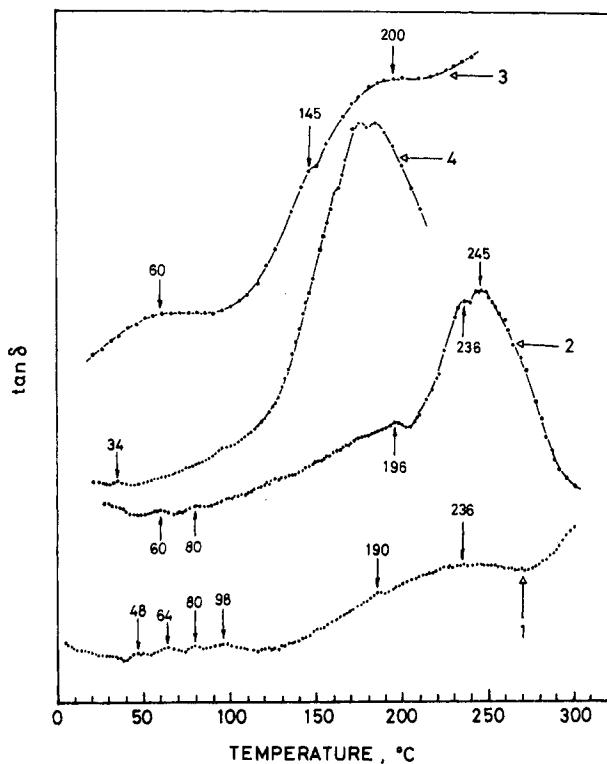


Fig. 3. Temperature dependence of $\tan \delta$ of cellophane (curve 1), recrystallized cellulose obtained by immersing amorphous cellulose in water for 24 hr (curve 2), amorphous cellulose (curve 3), and cellulose triacetate (curve 4) at 110 Hz. These were measured at $2^\circ\text{C}/\text{min}$ in dried, ultrapure nitrogen gas. The $\tan \delta$ curves are displaced vertically on the logarithmic scales for arbitrary values for convenient comparison.

19–33°C and 35–40°C, respectively, using dilatometry, and which Back and Didriksson,¹⁵ Kubát and Pattyranie,¹⁶ and Zelenev and Glazkov¹⁷ have found at 25–40°, 35°, and 20°C, respectively, using mechanical techniques. Also for cellulose triacetate (curve 3), a transition is observed at 34°C, in which range a transition has been indicated by Ueberreiter,¹⁸ Mandelkern and Flory,¹⁹ and Zelenev and Glazkov.¹⁷ The transitions at 48°C for cellophane and at 34°C for cellulose triacetate seem attributable to increased thermal motion caused by rupture of weak hydrogen bonds according to Ramiah and Goring,¹³ Back and Didriksson,¹⁵ and Zelenev and Glazkov.¹⁷ A peak at 64°C for cellophane and one at 60°C for recrystallized cellulose were equivalent to the 56–65°C transition of cellulose II pointed out by Kubát et al.¹⁴ using dilatometry. Weak peaks at 80°C and/or 98°C for cellophane and at 80°C for the recrystallized cellulose are correlated with the relaxation observed at 100°C for regenerated cellulose or at 90°C for amylose and amylopectin by torsional braid analysis performed by Nakamura.^{11,12} In this temperature range, the transition was found also by Ramiah and Goring,¹³ Back and Didriksson,¹⁵ and Zelenev and Glazkov¹⁷ at about 100°C. It has been reported that this transition may be produced by the motion of restricted segments of the main chain¹³ or by cooperative motion of individual pyranose rings in the cellulose.¹⁷

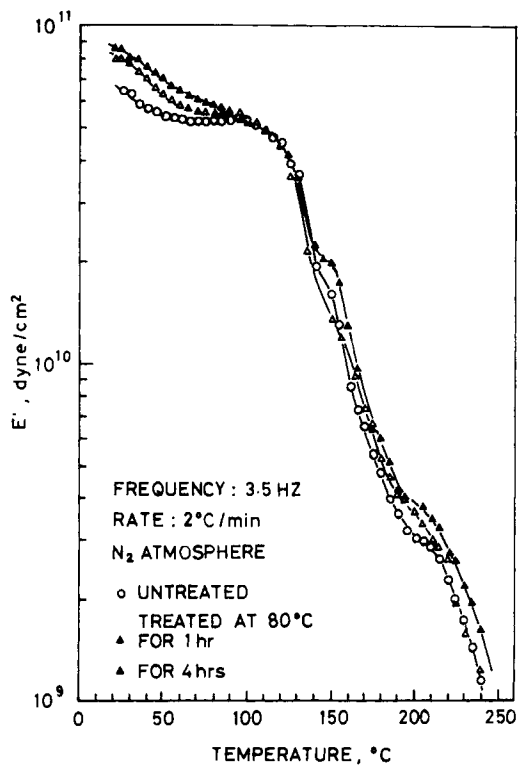


Fig. 4. Comparison of temperature dependence of dynamic modulus E' for heat treated amorphous cellulose with that for untreated amorphous cellulose.

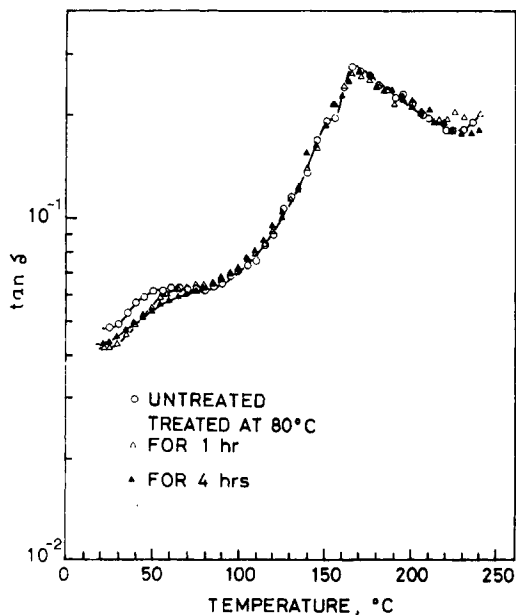


Fig. 5. Comparison of $\tan \delta$ curve for heat-treated amorphous cellulose with that for untreated amorphous cellulose.

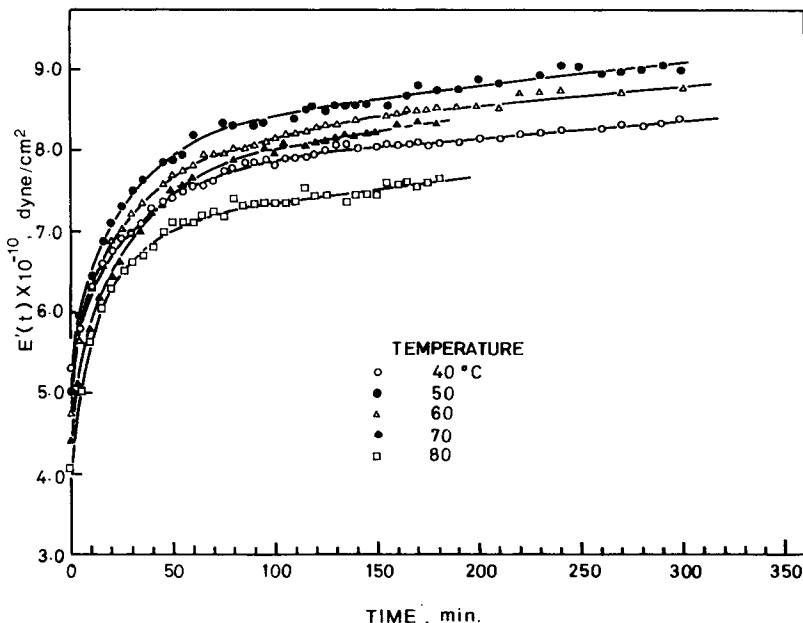


Fig. 6. Plot of E' vs. time of amorphous cellulose at constant temperature. These curves were measured isothermally at a frequency of 3.5 Hz in ultrapure, dried nitrogen gas.

In a higher temperature region, a shoulder peak at 190°C for cellophane and a small peak at 196°C for the recrystallized cellulose were observed. Simultaneously, E' of the recrystallized cellulose, as shown in Figure 2 (curve 2), increases at about 196°C. The discontinuity in E' is slight for cellophane (Fig. 2, curve 1). It has been reported that for amorphous cellulose, an exothermic peak appears in the temperature range between 100°C and 190°C (the peak temperature at 150°C) on a differential scanning calorimetry curve, and that the x-ray diffractogram shows the existence of a crystalline structure in amorphous cellulose heat treated at 130°C for 40 to 100 min.²⁰ Thus, the peak at 190°C seems to arise from the crystallization of amorphous parts in the crystalline cellulose, since a

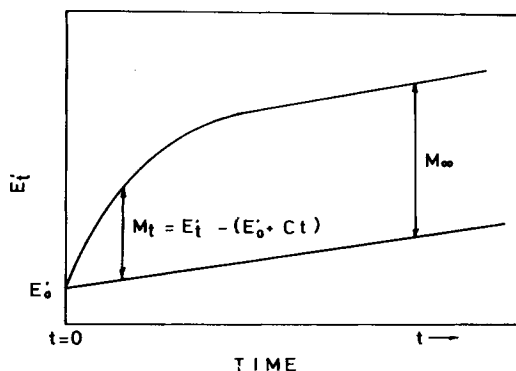


Fig. 7. Typical isotherm curve of E' as a function of time with kinetics parameters. M_t values are obtained by subtracting the straight part drawn from $t = 0$ in parallel with the straight part of E'_t in the longer time region from E'_t , and M_∞ is the value of M_t at $t = \infty$ in the longer time region.

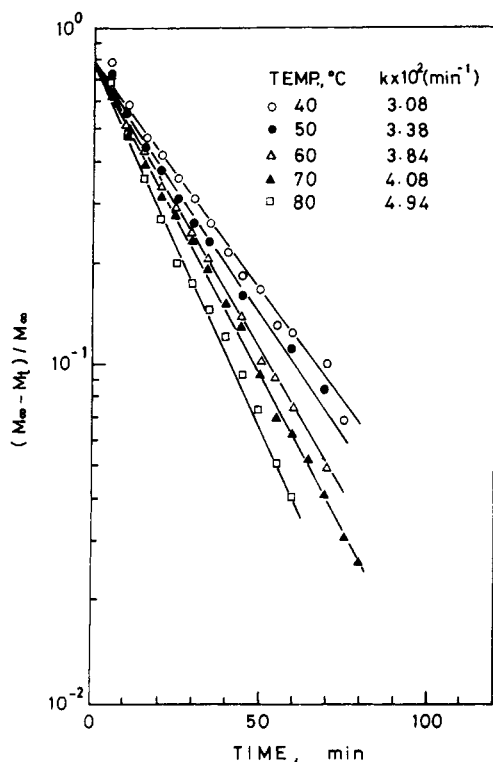


Fig. 8. Plot of $(M_\infty - M_t)/M_\infty$ vs. t .

peak in $\tan \delta$ and the increase in E' appeared more clearly in the recrystallized cellulose with greater amorphous content than in cellophane. A peak in $\tan \delta$ at 236°C for cellophane and the recrystallized cellulose might be produced by the segmental motion of amorphous molecules in the crystalline cellulose in the vicinity of glass transition temperature as reported by Nakamura^{11,12} and Back and Didriksson.¹⁵

In the case of the temperature dependence of $\tan \delta$ for amorphous cellulose, a medium peak at 60°C, a shoulder peak at 144°C, and broad peak at about 200°C can be seen in Figure 3 (curve 3). The peak at 60°C is broader and higher than that for crystalline cellulose (Fig. 3, curves 1 and 2), and E' increases in this temperature range, accompanied by a maximum peak at about 80°C. This transition seems related more to the formation of hydrogen bonds between the cellulose molecules than to the rupture of weak hydrogen bonds,^{13,15,17} or the motion of OH groups,²¹ because E' increases in this temperature range. And also, the increase in E' does not derive from the recrystallization process of amorphous cellulose, since in this temperature range it never crystallizes in a dry state.^{9,10,20}

Consequently, the mechanism for the various transition of amorphous cellulose was considered from the viewpoint of the clarified molecular assignments of transitions for the crystalline cellulose described above. The increase in E' and a maximum in $\tan \delta$ seem to occur in the temperature range between 70°C and 100°C because of the formation of hydrogen bonding which may come from the combination of free OH groups in amorphous cellulose, produced by heat

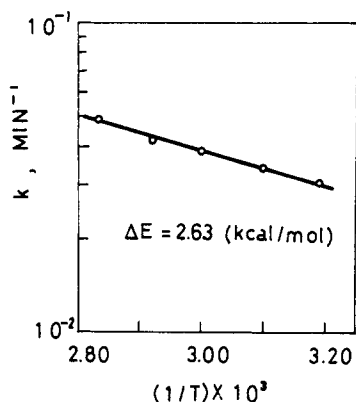


Fig. 9. Plot of $\log k$ vs. reciprocal of absolute temperature, $1/T$, according to an Arrhenius equation.

treatment or by the action of water. Subsequently, E' begins to decrease sharply at about 100°C due to the change in the conformation of individual pyranose rings in amorphous cellulose, while in the case of cellophane and the recrystallized cellulose, a slight decrease at 106°C and a discontinuity at 104°C in the E' -versus-temperature curves were observed as the motion of pyranose rings was restricted by crystals. The transition at 145°C observed as a shoulder peak in $\tan \delta$ and a discontinuity in E' seems related to the recrystallization of amorphous cellulose by heating and is consistent with the results observed by differential scanning calorimetry and infrared spectroscopy by Hatakeyama et al.²⁰ The broad peak at about 200°C may be attributable to the glass transition of amorphous cellulose. Above 230°C , another decrease in E' and an increase in $\tan \delta$ were observed, and this transition may be concerned with the thermal decomposition accompanied by the formation of low molecular substances.

The frequency dependence of the maximum temperature of $\tan \delta$ for cellophane at 236°C and for amorphous cellulose at 200°C was plotted against the reciprocal of the absolute temperature $1/T$. A linear relation was obtained, and the activation energy was calculated approximately by the Arrhenius equation. The activation energy of amorphous cellulose thus calculated (49.2 kcal/mole) agreed well with that of cellophane (46.7 kcal/mole).

For the purpose of investigating the change in the dynamic viscoelastic properties of heat treated amorphous cellulose, the temperature dependences of E' and $\tan \delta$ for amorphous cellulose treated at 80°C for 1 hr and 4 hr are shown in Figures 4 and 5. As shown in Figure 4, E' of untreated amorphous cellulose increased at a temperature of about 75°C accompanied by hydrogen bonding, while for the amorphous cellulose heat treated at 80°C before measurement of E' , no increase was observed in E' value. The E' for the amorphous cellulose heat treated at 80°C for 4 hr decreased with increasing temperature, though the values for E' were consistently high throughout the temperature range, showing the highest value, since hydrogen bonding seems to be sufficient. On the other hand, heat treatment for 1 hr may be insufficient to form hydrogen bonds and gives rise to free OH groups which form hydrogen bonds and thus cause the E' curve to become flat in that temperature range. For the amorphous cellulose heat treated at 80°C for 4 hr, a discontinuity in E' is seen clearly at 140°C , be-

cause crystallization accompanied by the reorientation of molecules is facilitated by heating even if hydrogen bonding is sufficient in cellulose.

In the curves of $\tan \delta$ (Fig. 5) for untreated amorphous cellulose, a clear peak was observed at about 50°C, indicating hydrogen bond formation, but for the heat treated amorphous cellulose, the peak was low, especially that heat treatment for 4 hr. Above 100°C, $\tan \delta$ for heat treated samples showed the same behavior as that for untreated samples.

In order to calculate the activation energy for the hydrogen bonding, E' of amorphous cellulose was measured as a function of time at a constant temperature during the course of hydrogen bond formation in the temperature range from 40° to 80°C where a maximum in $\tan \delta$ and the increase in E' were observed, as shown in Figure 2 or Figure 4. Figure 6 shows E' as a function of time within a fixed temperature range between 40° and 80°C, and this was measured at 3.5 Hz in an atmosphere of highly pure, dry nitrogen gas. E' increased exponentially in the short time region and then in a straight-line fashion in the long time region, since the motion of the molecular chain was restricted by hydrogen bonding in the same way as in a crosslinking reaction of thermosetting plastics. The time function for E' was assumed as a first-order reaction, just as in the case of thermosetting plastics,²² and analyzed kinetically.

M_t was obtained by subtracting $(E'_0 + Ct)$ from E'_t . $(E'_0 + Ct)$ was defined as the straight line drawn from $t = 0$, in parallel with the longer time region of E'_t , as shown in Figure 7. The rate constant k was calculated as follows:

$$E'_t = M_\infty\{1 - \exp(-kt)\} + \{E'_0 + Ct\} \quad (1)$$

where E'_t is the dynamic modulus at time t , M_∞ is the value arrived at by subtracting the straight part from E'_t in the longer time region; E'_0 is E' at $t = 0$, k is the rate constant, and C is a constant value. Changing eq. (1) gives

$$E'_t - \{E'_0 + Ct\} = M_\infty\{1 - \exp(-kt)\} \quad (2)$$

Substituting M_t for the left member of eq. (2), we obtain eq. (3) or eq. (4):

$$M_t = M_\infty\{1 - \exp(-kt)\} \quad (3)$$

$$\ln(M_\infty - M_t)/M_\infty = -kt \quad (4)$$

Thus, when $\log (M_\infty - M_t)/M_\infty$ was plotted against t , a linear relation was obtained for the initial state shown in Figure 8. From the slope of each straight line, the values for k in Figure 8 were obtained.

In Figure 9, plots of the rate constant k versus the reciprocal of the absolute temperature, $1/T$, were linear; and from the slope of the straight line, the apparent activation energy of 2.6 kcal/mole was calculated according to the Arrhenius relation. It is the expected value for hydrogen bond formation since, in general, the activation energy for hydrogen bonds is known to be 1–10 kcal/mole.²³

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