

# Static Tensile and Dynamic Mechanical Properties of Hydroxypropylcellulose Films Prepared under Various Conditions

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## Synopsis

The films of hydroxypropyl cellulose (HPC), which is a lyotropic and thermotropic liquid crystal, were cast under various conditions of temperature and concentration. The effects of the casting conditions on the static tensile and dynamic mechanical properties of the cast films were determined, and the results were compared with those of films prepared by means of hot compression. The tensile properties of the films prepared by both processes (cast and hot compression) were unsatisfactory in comparison with other liquid crystalline polymers, and this was partly due to water absorbed during the test. In dynamic properties, two distinct transitions were detected. The higher one, around 110°C, was associated with the rotation of an unhydroglucose ring and the lower one, around 25°C, was associated with the  $T_g$ . There were no marked differences in the properties between cast films and hot-compressed films, except the disappearance of the  $T_g$  for hot-compressed film prepared at a relatively higher temperature. The basis for defining the liquid crystalline structure in cast and hot-compressed films are not directly given in this preliminary paper. However, judging from the dynamic mechanical properties and refractive index data for films prepared by both processes, it appears that dimethylacetamide-cast films and films compressed at 180 and 200° C may have some structures related to liquid crystalline phase and that inter- and intramolecular hydrogen bonding play an important role in lyotropic and thermotropic liquid crystalline behavior for HPC.

## INTRODUCTION

Hydroxypropylcellulose (HPC) is a water-soluble cellulose derivative. Its basic properties have been characterized by the Hercules researchers,<sup>1-4</sup> and because of its utility HPC has been applied in many fields, especially in food and drug industries.

In 1976, when Werbowyj and Gray discovered that the concentrated solutions of HPC in water form a liquid crystalline phase,<sup>5</sup> HPC appeared before the footlights again. Since then, a great many researchers have reported the rheological and optical properties of concentrated solutions of HPC in various solvents from different points of view.<sup>6-17</sup>

The properties mentioned above are very important because a proper interpretation of the properties made in the appropriate conditions provides important information about applications in spinning. Since the duPont fiber Kevlar was successfully formed by wet spinning of a liquid crystalline solution of a p-linked aromatic polyamide,<sup>8</sup> it has been well known that fibers made from liquid crystalline dopes have superior mechanical properties. Some researchers have already determined the qualities of fiber spun from the isotropic and anisotropic dopes of cellulose derivatives.<sup>19,20</sup>

Although the fiber with specific properties has been one of the major applications of liquid crystal-forming cellulose derivatives, fiber applications seem to be less likely for cellulose derivatives because cellulose derivatives are regarded as semiflexible polymers and have a limit in tensile properties compared with rigid main-chain polymers. However, the limitation in fiber application does not necessarily reduce the possibility of film application. If the cholesteric structure in liquid crystalline solution of the cellulose derivative remains unchanged during casting, the film prepared from such a solution should have specific characteristics and can be applied to for new end uses. It is interesting to develop the casting techniques, to control the structures of films beneficially, and to investigate how the structure in a concentrated solution of cellulose derivative is reflected in the solid film of cellulose derivative. HPC may be a convenient model to investigate the problems noted above because HPC can be dissolved in a relatively wide range of solvents and the structure in the liquid crystalline state may be readily altered by changing concentration, solvent polarity, and temperature.<sup>21</sup> These are the reasons for HPC to be given priority in preference to the other cellulose derivatives. Furthermore, HPC can also form thermotropic liquid crystal,<sup>22-24</sup> and structures in both lyotropic liquid crystalline phase and thermotropic phase can be compared. However, little is known concerning the mechanical and dynamic properties of HPC solid films in spite of their essential importance, partly due to a serious drawback of picking up the water from the atmosphere.

In this article, as a preliminary stage, HPC films were cast under various conditions of temperature and concentration. The effects of solvent casting conditions on the static tensile properties and dynamic viscoelasticities of HPC films were determined, and we compared the results of casting films with those of films prepared by means of hot compression. In addition, the possible presence of ordered phases in the films prepared by different processes was also briefly discussed.

## EXPERIMENTAL

### Materials

Hydroxypropylcellulose (HPC) was of commercial reagent grade supplied by Tokyo Kasei Kogyo Co. Ltd. The weight-average molecular weight of the HPC was  $9.3 \times 10^4$ , as determined by intrinsic viscosity in ethanol at 25°C and the relation:<sup>3</sup>

$$[\eta] = 2.6 \times 10^{-5} M_w^{0.915}$$

Before use, HPC powder was vacuum dried at 70°C for about 24h.

*N,N*-Dimethylacetamide (DMA) was commercial reagent grade (Wako Pure Chemical Ind. Ltd.) and purified by distillation prior to use.

### Preparation of Films

The preparation of HPC films in this paper are classified into two groups, that is, casting and hot-compression processes. They are abbreviated as C and H processes, respectively. In the C process, films from six different

processes are examined. Hereinafter, the procedures of each process are outlined.

### *Casting*

In the first process (C-1), HPC was dissolved in DMA at room temperature and the 20 wt% solution was prepared by magnetically mixing for about 24 h. The solution was spread slowly with a glass rod on a 17 x 12 cm glass plate, which was framed with a 2-mm thick glass plate on the edges with a built-in cavity 2 mm thick. The framed glass plate containing the solution was kept in a mercury bath, and solvent was allowed to evaporate for about a week in the laboratory's atmosphere. The resulting film was peeled from the plate and was dried again in vacuum at 40° C for 24h, and then it was stored in a desiccator over P<sub>2</sub>O<sub>5</sub>.

In the second process (C-2), the framed glass plate containing the 20 wt% solution was kept in a mercury bath, in which a thermostat was located, at 40° C for a couple of days. The resulting film was colorless and unfortunately could not be peeled from the plate.

In the third process (C-3), the framed glass plate containing the 20 wt% solution was kept in a mercury bath with a thermostat at room temperature for about 4 days, whereupon iridescent color was partly visualized on the surface of the solution. Then, the plate containing the solution was transferred into a thermostat-equipped vacuum and dried at 40° C in a vacuum for about 30 min. The surface of the resulting film was slightly colored blue. After the film was peeled from the plate, it was dried at 40°C in a vacuum for 24 h and then stored in a desiccator.

For the fourth process (C-4), the 20 wt% solution on the framed glass plate was dried in a thermostat at room temperature for about 4 days. The procedure was the same as C-3, and film was iridescent. Then the plate was dried at 60°C in a vacuum for about 30 min. The film was still iridescent and at a different point from the film prepared according to C-3. The film peeled from the plate was dried again at 40° C in a vacuum for 24 h and stored in a desiccator.

In the fifth process (C-5), the iridescent film on the glass plate was prepared in the same manner as C-3. The plate was transferred into a desiccator, and the desiccator was evacuated with a vacuum pump. Then the desiccator was kept in a refrigerator at -18°C for about 3 weeks. Once a day, we introduced air into the desiccator by opening a cock and made the desiccator vacuum again. The film changed from iridescent to colorless. The peeled film was stored in a desiccator after vacuum drying at 40° C for 24h.

In the sixth process (C-6), the 55 wt% solution was prepared by magnetically mixing at room temperature for about 2 months. The solution showed the typical cholesteric color. The critical concentration for onset of the liquid crystalline phase in this system was 45 wt% at room temperature, and at over 50 wt% the solutions were pure liquid crystalline.<sup>25</sup> The degassed solution was run on a glass slide and was forced to spread by stroking with a spatula. Then the solution on the slide glass was kept in a mercury bath equipped with a thermostat at room temperature for 2 days. The cholesteric color disappeared from the film. The colorless film peeled from

the glass slide was dried at 40° C in a vacuum for 24 h and stored in a desiccator.

The conditions of each process described above are summarized in Table I.

### *Hot Compression*

In the H process, films from three different processes, depending on the compression temperature, are examined here.

For the first process, (H-1), dried HPC powder was placed between two aluminum foil sheets and positioned between the platens of a simple hydraulic press. The assembly was heated to a given temperature, 180°C. The pressure was then brought to about 8 kg/cm<sup>2</sup>, resulting in some flow of HPC between the aluminum foil sheets. After 5 min the compressed HPC between the foil sheets was quenched in the refrigerator at -18°C. The resulting film was then peeled from the aluminum foil sheets and stored in a desiccator.

Other films were prepared by means of the same procedures as H-1 except at the compression temperature. The compression temperatures were 200 and 220°C, and the processes were abbreviated H-2 and H-3, respectively. In this hot compression, film thickness was controlled with spacers located on a hot plate. The conditions of the H series are summarized in Table II.

Three different types of specimen for static tensile and dynamic mechanical tests were examined in this work and are schematically illustrated in Figure 1. Specimen A was cut along a line parallel to a long side of the cast film, which was similar to the spread direction of the concentrated solution. Specimen B was cut from the short side of the cast film. Finally, specimen C was cut diagonally at a 45° direction to a long side of the cast film. In the H processes, specimens were cut radially from the center of the film, and the direction seemed to correspond to the spread direction of C-6 film.

### **Thermogravimetry (TG)**

Thermal stability and the content of absorbed water of the films were evaluated by TG at a heating rate of 5°C/min. Typical thermograms are given in Figure 2. The curves changed at about 100°C, because of the evaporation of the absorbed moisture.

TABLE I  
Conditions for Casting Processes

Process	Initial concentration (wt%)	Temperature (°C)	Vacuum
C-1	20	RT <sup>a</sup> → RT	No
C-2	20	40 → 40	No
C-3	20	RT → 40	Yes
C-4	20	RT → 60	Yes
C-5	20	RT → -18	Yes
C-6	55	RT → RT	No

<sup>a</sup> Room temperature.

TABLE II  
Conditions for Hot-Compression Processes

Process	Temperature (°C)	Heating time (min)	Pressing time (min)
H-1	180	5	5
H-2	200	5	5
H-3	220	5	5

### Static Tensile Properties

Static tensile properties for film specimens (0.08 mm thickness  $\times$  1 cm wide  $\times$  5 cm long) were determined by using a Tensilon (Toyo Baldwin Co. Ltd.) at room temperature (20°C). The relative humidity in the laboratory was 55–60%. An interval between chucks of 2 cm was chosen. The tests were performed at a crosshead speed of 5 mm/min. Each film was tested at least 10 times, and the mean value was reported. Each reproducibility of Young's modulus, tensile strength, and elongation was found to be within 3, 5, and 12%, respectively. Engineering stress was considered. During the test, about 4 wt% water seemed to be absorbed in the test specimen. The content of water was estimated from Figure 2.

### Dynamic Mechanical Properties

Dynamic mechanical properties for the film specimen were determined by using a Rheovibron DDV-11-C (Toyo Baldwin Co. Ltd.) in the temperature range from 10 to about 130°C at a heating rate of 0.5°C/min and a constant frequency of 110 Hz. The size of specimen was 0.08 mm thick  $\times$  1.7 mm wide  $\times$  3 cm long for measurements in C-series films and 0.1 mm thick  $\times$  1.7 mm wide  $\times$  3 cm long in H-series films. Cooling of the specimen in the instrument with liquid nitrogen was attempted; however, film was dissolved and melt broken within 5 min at  $-150^{\circ}\text{C}$ . No matter what the cooling rate or predrying conditions of the specimen, no reliable data in the temperature range below 0°C could be obtained. All data in this article were determined in the winter season (room temperature of around 5°C at 3:00 A.M.).

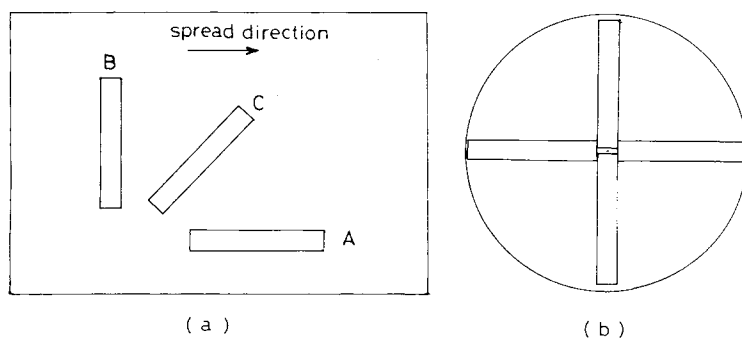


Fig. 1. Schematic representation of the specimens for tensile and dynamic mechanical tests: (a) cast film, (b) hot-compressed film.

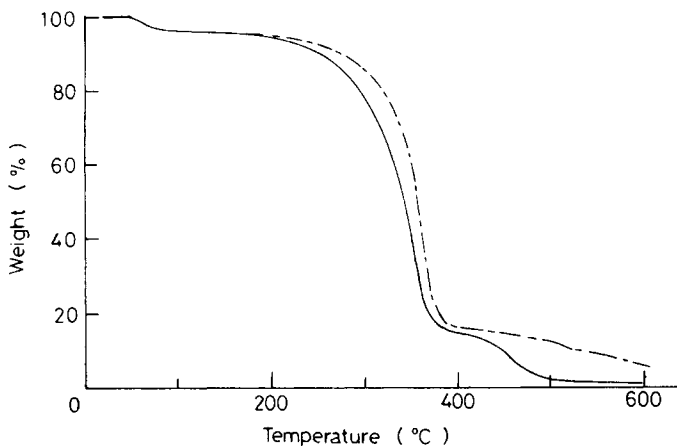


Fig. 2. Thermogravimetric curves for films at a heating rate of 5°C/min; (XXX) C-1, C-5, and H-1 films in air, (XXX): C-1 film in N<sub>2</sub>.

### Refractive Index Temperature Measurement

An Abbé refractometer (Shimazu Seisakusho Ltd.) with a rotatable polarizer mounted on the eyepiece was used to measure the two principal refractive indices of film starting at 13°C and then the temperature at intervals of 5°C up to 40°C. The temperature was controlled to  $\pm 0.1^\circ\text{C}$ . At all temperatures, the refractive index equilibrium was established in about 20 min. To get close contact between the film and the prisms, we used silicone oil as immersion fluid. All measurements were made using the sodium D line.

## RESULTS AND DISCUSSION

### Static Tensile Properties

First, the effect of the direction of cutting specimen from cast film on the tensile properties was investigated for the films of C-1 and C-3. Three types of specimen are schematically shown in Figure 1. The results of each specimen are summarized in Table III. Specimen A had relatively higher Young's modulus and lower elongation than specimens B and C and the subsequent experiments were carried out for only specimen A.

Tensile properties for films of the C-series are shown in Table IV. C-1, C-3, and C-4 films did not show marked differences in properties, and the values of Young's modulus were from  $1.8$  to  $2.1 \times 10^9$  dyn/cm<sup>2</sup> and of tensile strength were  $1.18$ – $1.33 \times 10^8$  dyn/cm<sup>2</sup>. On the other hand, C-6 film cast from the anisotropic solution had a somewhat higher Young's modulus and tensile strength and a little lower elongation than C-1, C-3, and C-4 films even taking experimental error into account.

One of the authors, (Suto) determined the tensile properties of HPC film from hot compression and described that Young's modulus was  $3.4 \times 10^9$

TABLE III  
Effect of the Direction of Cutting Specimen from Cast Film on Tensile Properties for C-1 and C-3 Films<sup>a</sup>

	C-1			C-3		
	Young's modulus (dyn/cm <sup>2</sup> , × 10 <sup>9</sup> )	Tensile strength (dyn/cm <sup>2</sup> , × 10 <sup>8</sup> )	Elongation (%)	Young's modulus (dyn/cm <sup>2</sup> , × 10 <sup>9</sup> )	Tensile strength (dyn/cm <sup>2</sup> , × 10 <sup>8</sup> )	Elongation (%)
A	2.14	1.18	41.2	2.12	1.31	53.1
B	1.91	1.00	40.9	2.09	1.21	57.0
C	—	—	—	1.42	0.90	63.2

<sup>a</sup> For A, B, and C, see text and Fig. 1a.

TABLE IV  
Tensile Properties for Each C-series Film

Process	Young's modulus (dyn/cm <sup>2</sup> , × 10 <sup>9</sup> )	Tensile strength (dyn/cm <sup>2</sup> , × 10 <sup>8</sup> )	Elongation (%)
C-1	2.14	1.18	41.2
C-3	2.12	1.31	53.1
C-4	1.84	1.33	51.4
C-6	2.52	1.50	39.3

dyn/cm<sup>2</sup> and elongation to break was 20%.<sup>26</sup> By comparing the results from C-series films with those from H-series films, the latter should show better tensile properties. However, the values attained in this study were considerably smaller than those of fibers spun from anisotropic solution.<sup>19</sup> The inferior tensile properties should be partly due to the absorbed water acting as plasticizer. HPC film is so hygroscopic that it seems to take up water during the test, as suggested in Figure 2. It is evident that the tensile properties of cast film strongly depend on the surface and internal structures of the film, and the structures are affected by drying rate and surface tension. Therefore, the small difference in the properties should also be due to little difference in casting conditions. Consequently, to get a more serious difference in properties, the film should be prepared in drastic casting conditions and tested in an atmosphere of no moisture. Casting from a non-liquid crystalline system should also be tried for comparison.

As described above, the tensile properties were unsatisfactory in comparison with other liquid crystalline polymers. Although the difference observed in the tensile properties of films prepared by various conditions was not so marked as expected, it was meaningful. Then, the properties still serve as a measure of relatively estimating an ordered phase.

### Dynamic Mechanical Properties

Temperature dependencies of dynamic modulus  $E'$ , loss modulus  $E''$ , and loss tangent  $\tan \delta$  at 110 Hz for C-series films are presented in Figure 3. With respect to  $\tan \delta$ , two transitions were apparent within the experimental temperature range, labeled  $\alpha$  and  $\beta$  in order of decreasing temperature at which they were detected. The transition temperatures are summarized in Table V. The basic molecular mechanism underlying the higher temperature transition ( $\alpha$ ), which occurred around 110°C, is known to be a rotational, translational motion of the chain along the main chain. In our case, the  $\alpha$  transition is suggested to be associated with the rotation of unhydroglucose ring. The next transition ( $\beta$ ), around 25°C, can then be associated with the onset of large-scale motion of molecular chain segments, that is the glass-rubber transition ( $T_g$ ). In fact, Aspler and Gray reported the  $T_g$  for HPC between 10 and 30°C in measurements by gas chromatography.<sup>27</sup> Other evidence for the  $T_g$  around 25°C are discussed below.

It is well known that the  $T_g$  can be determined by refractive index of variation with temperature.<sup>28</sup> For comparison with the mechanical data,



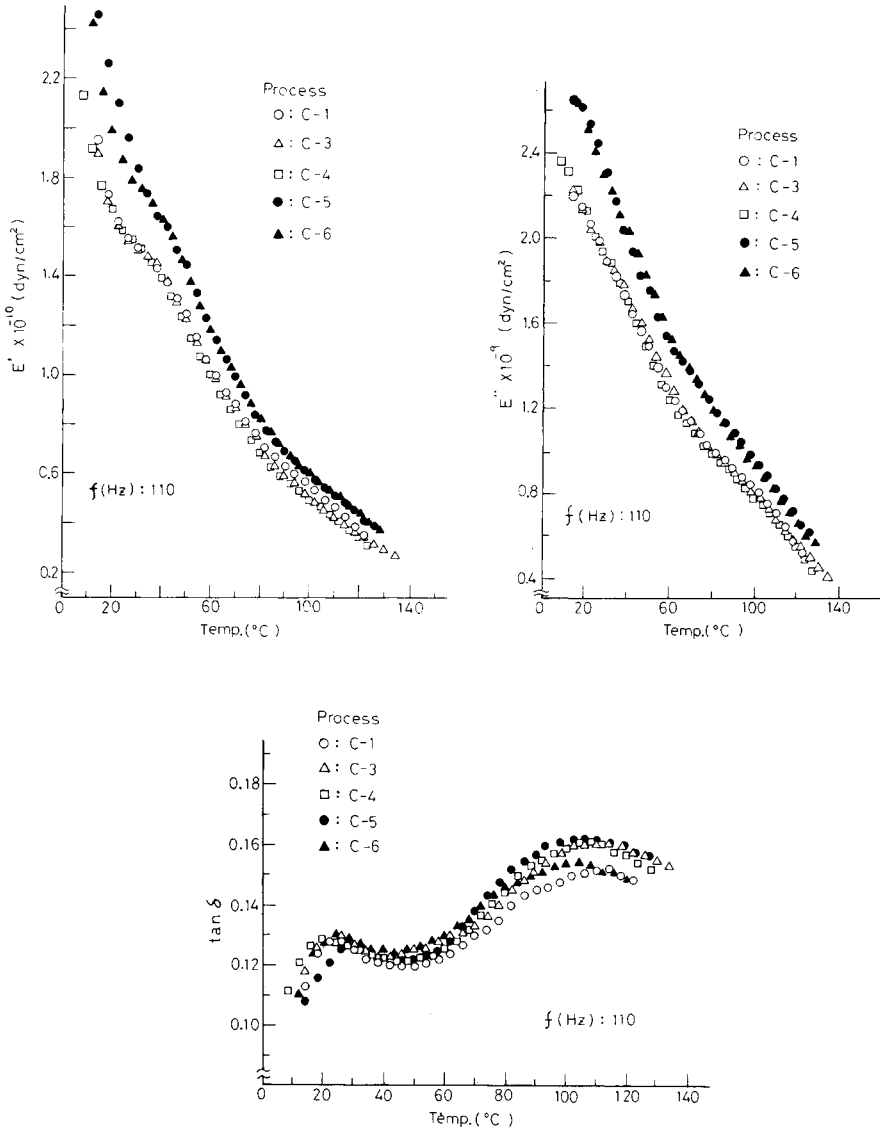


Fig. 3. Temperature dependence of dynamic mechanical properties at 110 Hz for C-series films: (a) dynamic modulus, (b) loss modulus, (c) loss tangent.

temperature dependence of refractive index for C-1 film shown in Figure 4.  $n_{\parallel}$  and  $n_{\perp}$  are the principal refractive indices parallel and perpendicular to the plane of the measuring prism, respectively. The intersecting lines drawn on the refractive index-temperature plot imply that the change in slope occurs sharply at a specific temperature, indicating a transition of the second-order type. Heating up to 120°C was attempted; however, it was not possible to determine any transition owing to the scattering of the refractive index data at higher temperatures. The temperature at which the change in slope occurred was the same for other C-series films within the experimental error.

TABLE V  
Transition Temperatures at 110 Hz for Each C- and H-series Film

Process	$\beta$ (°C)	$\alpha$ (°C)
C-1	24	110
C-3	22	114
C-4	20	104
C-5	30	110
C-6	30	112
H-1	30	106
H-2	32	124
H-3	—	122

There is also a simple empirical relationship between  $T_g$  and melting temperature ( $T_m$ ) for crystalline polymers.<sup>29</sup>

$$\frac{T_g}{T_m} = 0.67 \text{ epep for unsymmetrical polymers}$$

$$\frac{T_g}{T_m} = 0.50 \text{ for symmetrical polymers}$$

The  $T_m$  for HPC has been reported to be around 190°C by differential scanning calorimetry (DSC).<sup>23</sup> In accordance with the above relationship for unsymmetrical polymers, we can predict a  $T_g$  of about 35°C for HPC.

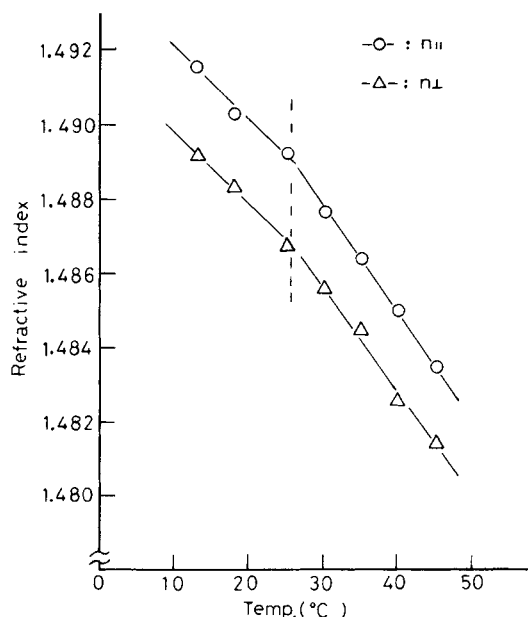


Fig. 4. Temperature dependence of two principal refractive indices for C-1 film. For  $n_{||}$  and  $n_{\perp}$ , see text.

In general, the  $E'$  of solid polymer is of the order of  $10^{10}$  dyn/cm<sup>2</sup> in a glass state. In this study, the  $E'$  values below the transition temperature were from 1.5 to  $2.5 \times 10^{10}$  dyn/cm<sup>2</sup>, typical values for the polymer in a glassy state.

On the basis of the evidences described above, we speculated that the transition corresponded to the  $T_g$ .

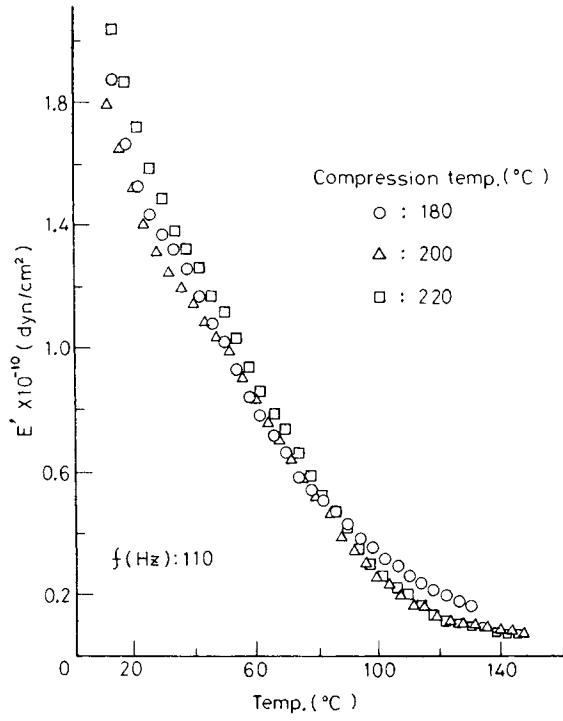
With regard to  $E'$  and  $E''$ , the  $\alpha$  and  $\beta$  transitions were too small in magnitude to be detected. In the temperature range slightly below the  $T_g$ , the difference in  $E'$  and  $E''$  for each C-series film could be regarded as significant and the  $E'$  and  $E''$  for C-5 and C-6 films were larger than those for other films. However, the difference decreased with rising temperature.

For H-series films,  $E'$ ,  $E''$  and  $\tan \delta$  are shown in Figure 5 (a), (b), and (c), respectively. A marked effect of compression temperature on  $\tan \delta$  was found. At  $\beta$  transition,  $\tan \delta$  decreased in magnitude with rising compression temperature, and for H-3 film (compression temperature, 220°C), the  $\beta$ -transition peak tended to be indistinct. In contrast to the  $\beta$  transition, at  $\alpha$  transition  $\tan \delta$  in magnitude increased with rising compression temperature. The specific temperatures at which  $\alpha$  and  $\beta$  transitions occurred were slightly shifted to higher temperature as the compression temperature rose.

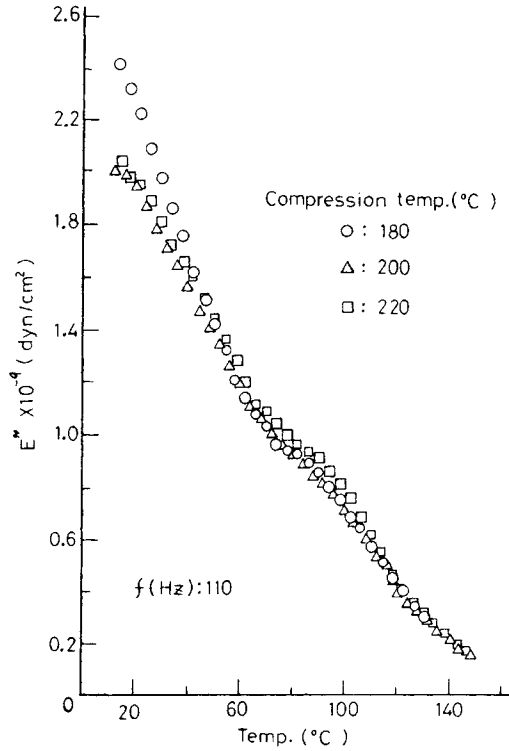
In general, extensive thermal decomposition takes place below the  $T_m$  for cellulose derivatives,<sup>30</sup> which renders the elucidation of the transition temperatures difficult. Actually, HPC films for the H series were slightly brown, and the color was deeper as the compression temperature rose. Therefore, it is necessary to verify whether decomposition took place during preparation of the H-series films. Thermal stability of the HPC film was evaluated by thermogravimetry, and the typical thermograms are given in Figure 2. Figure 2 shows that the HPC films exhibit good resistance to thermal decomposition up to 240°C, at which 5% weight loss occurred in air. Consequently, the onset of thermal decomposition is not useful for interpretation of the transition behaviors observed in H-series films.

Samuels has noted from infrared spectroscopic observations of water-cast HPC films that inter- and intramolecular hydrogen bonding persists up to 260°C although weakened by thermal agitation.<sup>1</sup> His observations suggest that the hydrogen bonding appears to play an important role in the transition behaviors of the bulk HPC. The rotation of unhydrogrucose ring is seriously restricted by hydrogen bonding. As the temperature rises, the hydrogen bond is weakened and the chain mobility is induced. Therefore, the effect of compression temperature on  $\alpha$  and  $\beta$  transitions for H-series films can be reasonably explained by the decrease in hydrogen bond, and  $\beta$  transition appears to reflect the hydrogen bonding.

White and coworkers found that the bulk HPC was a thermotropic liquid crystal at 200–210°C using a hot-stage polarized light microscopy.<sup>22,23</sup> Suto determined the effect of hot-compression temperature on the tensile properties of HPC sheet and showed that over 200°C the elongation to break increased rapidly and a yield point appeared in the stress-strain diagram.<sup>26</sup> The phase transition temperature of 220°C agreed qualitatively with the temperature at which  $\beta$  transition disappeared in this study. The phase transformation from thermotropic liquid crystal to isotropic melt can also



A



B

Fig. 5. Temperature dependence of dynamic mechanical properties at 110 Hz for H-series films: (a) dynamic modulus, (b) loss modulus, (c) loss tangent

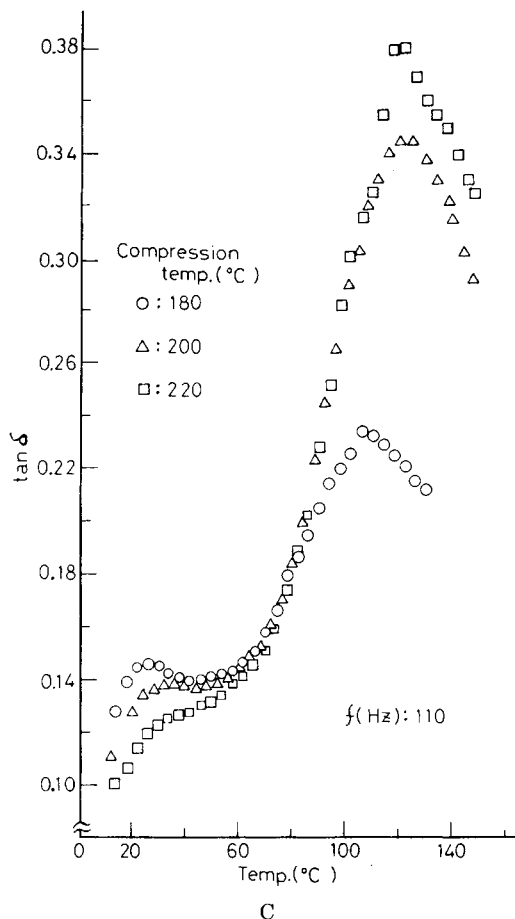


Fig. 5. (continued from previous page)

be discussed in terms of the decrease in hydrogen bond. Kamide and Saito have pointed out that a cellulose chain with no hydrogen bond is intrinsically very flexible.<sup>31</sup> Then, when the hydrogen bond is weakened by thermal agitation, the molecular chain of HPC should transfer from an apparent semiflexible conformation (liquid crystal) to an inherent flexible one (isotropic melt).

As previously described, there were no marked differences in properties between C- and H-series films, except the disappearance of the  $\beta$  transition for H-series film prepared at a relatively higher compression temperature. The reason for this difference is not clear now, but possibly a change in the numbers of inter- and intramolecular hydrogen bonding may contribute to the different behavior between C- and H-series films. We need the other observations, for example, IR investigation, in order to determine the quantity of hydrogen bonding.

From the industrial viewpoint, the H process is preferable to the C process, because the H process can be developed as a continuous processes (i.e., T-die extrusion or calendering), by which higher productivity of film can be achieved. The H process is based on the postulated formation of a ther-

motropic liquid crystalline phase. Most lyotropic liquid crystalline cellulose derivatives also form thermotropic mesophases, hence, the H process is not specific if thermal decomposition is kept in mind.

Finally, we consider the problem whether the films prepared by the C and H processes have any structure originated from the liquid crystalline phase. For C-series films that are not stretched, the refractive index  $n_{\parallel}$  did not equal  $n_{\perp}$  at each temperature, as shown in Figure 4. This result means that the HPC molecules in C-series films are oriented. Moreover, the  $\beta$  transition occurred around 25°C and seems to be associated with the hydrogen bonding and to be more or less correlated with the formation of the liquid crystalline phase.

In conclusion, the basis for defining the liquid crystalline structure in C- and H-series films is not directly given in this preliminary paper. However, judging from the dynamic mechanical properties and refractive index data for each series film, it appears that C-series and H-1 films may have some structures related to the liquid crystalline phase, and that inter- and intramolecular hydrogen bonding play an important role in lyotropic and thermotropic liquid crystalline behaviors for HPC.

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