Thermal Molecular Motion from 150 to 350 K for Regenerated Cellulose Solids

Sei-ichi MANABE and Rumiko FUJIOKA

*Faculty of Human Environmental Science, Fukuoka Women's University,
1-1-1 Kasumigaoka, Higashi-ku, Fukuoka 813, Japan*

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ABSTRACT: We intended to clear the temperature dependence of dynamic absorption for cellulose solid in the temperature range between 150 and 350 K. Three regenerated cellulose hollow fibers whose supermolecular structures were characterized were used. Temperature dependence of dynamic viscoelasticities and birefringence in a solvent was investigated. There were three absorptions, β_a , m , α_{H_2O} at *ca.* 210, 273, *ca.* 330 K at a measuring frequency of 110 Hz, respectively. β_a absorption was separated into two absorptions, β_{a1} and β_{a2} from higher temperature side. Both originated by local twisting motion of the main chain in the amorphous region. The molecular chain to give β_{a1} may exist at an interfacial region of the primary particle and those of β_{a2} within particles. m absorption was due to the melting of H_2O adsorbed within the fine space among neighbouring primary particles. α_{H_2O} absorption originated by the cooperative motion of a main chain in the primary particle with the absorbed H_2O .

KEY WORDS Regenerated Cellulose / Mechanical Absorption / β_a Absorption / Supermolecular Structure / Viscoelasticity / Birefringence / Water / Methanol / Benzene /

The diffusion of small molecules into a polymer solid plays an important role in finishing treatments and in separation of molecules using a membrane. Diffusion is governed by the supermolecular structure of a polymer solid and thermal molecular motion of a polymer chain and small molecules. The motion is affected not only by chemical structure but supermolecular structure also.

The novel finishing treatment is for modification or design in the supermolecular structure with nanometer scale in size, especially the modification of an amorphous region, interfacial regions of polymer solids and fine particles composing the solids. Although the regenerated cellulose has been widely applied in the fields of a textiles and membranes, effective experimental techniques to investigate the supermolecular structure are very few. Since isochronal viscoelastic properties are reflected in the supermolecular structure, measurement of the temperature dependence of viscoelastic properties can give informations about the amorphous structure of the size of nm order. For example, when we use dynamic loss tangent ($\tan \delta$) vs. temperature curve for a segmental micro-Brownian movement (*i.e.*, α_a absorption), we can evaluate the heterogeneity of molecular packing in an amorphous region.¹ Judging from the size of the moving unit, we can use the absorption due to the local twisting motion of the main chain and we may evaluate the supermolecular structure having 1 nm or less in size.

As for regenerated cellulose solid, the mechanisms of the α_a absorption located between 280 and 600 K have been shown² but other absorptions located at lower temperature than room temperature have been reported by very few investigators.³ The energy loss generated by the motion of glucose ring or a side chain of $-CH_2OH$ was found at near $-55^\circ C$, though the mechanism was not well discussed. Because of the complex supermolecular structure of cellulose solid, many dynamic absorptions were observed and identification of their mechanisms was very difficult. In this study, we use the cellulose solid whose supermolecular structure is investigated rigorously in advance.

The supermolecular structure of cuprammonium regenerated cellulose hollow fiber⁴ for an artificial kidney is represented by aggregates of fine particles from 10 to 20 nm in size. These particles were named as primary particle.⁵ The mean pore size of the fiber is *ca.* 3 nm. The cuprammonium regenerated cellulose hollow fiber (BMM®) for virus elimination is also represented by aggregate of the secondary particles⁵ of *ca.* 70 nm, and the mean pore size is *ca.* 40 nm in the case of BMM 40. The secondary particle is considered composed of the primary particles from the following results: ① A transmission electron microphotograph of the surface of the secondary particle gives the uneven figure of size corresponding to that of the primary particle.⁵ ② A field emission type scanning electron microphotograph of the frozen fracture surface of BMM shows fine particles⁶ from 10 to 80 nm. ③ At the intermediate stage of the formation of BMM, the primary and secondary particles coexist.⁷

In this study, the cuprammonium regenerated cellulose hollow fiber is used and dynamic viscoelasticities are investigated in the temperature range between 150 and 350 K.

EXPERIMENTAL

Sample Preparation

(1) *Cuprammonium Regenerated Cellulose Hollow Fiber.* BMM40, BH2, and BH3 were prepared as reported previously.² The most important difference in the preparation of BMM40 comparing with other fibers is the coagulation agent, that is, acetone in the case of BMM40 and H_2O for others. All were kept in a dry air before use.

(2) *Chemical Reagents.* The following solvents were used as immersing media during measurement of the dynamic viscoelasticity and birefringence Δn : methyl alcohol, ethyl alcohol, benzene, acetone. All these were of guaranteed reagent grade manufactured by Wako Pure Chemical Ind. Ltd. (Japan). Saturated aq. solution of

NH₄Cl was used for preparing the air of relative humidity (RH) of 80% at 20°C. The environment of RH=0% at 20°C was achieved by circulating air on dry silicagel.

Measurements

(1) *Dynamic Viscoelasticities.*¹ Rheovibron DDV-IIc (Toyo-Boldwin Co., Ltd., Japan) was used. The measuring frequency was 110 Hz in the case of isochronal measurement. The heating rate was 12 K min⁻¹ in the case of a dry air (RH=0%) and 6 K min⁻¹ in the case of a solvent. The samples were kept in fluid at 293 K for more than 72 hours before measurement. For evaluating the apparent activation energy of a dynamic absorption, measuring frequencies of 110, 11, and 3.5 Hz were applied at 3 K min⁻¹ in air prepared through dry silicagel at 293 K. The cross sectional area S of the sample for BMM40 was calculated from the experimental values of the length L and weight W of the sample as follow:

$$S = \frac{W}{L\rho} \quad (1)$$

where ρ is the density of the cellulose solid and is 1.30 g ml⁻¹.

(2) *Temperature Dependence of Birefringence Δn in a Solvent.* Δn was evaluated using a compensator. The procedure of measurement and equipment with a quartz cell containing the solvent attached to a polarized microscope were developed by us.^{8,9} Two typical procedures were employed: Procedure 1: After immersing a specimen in solvent at 5 K above the melting point of the solvent followed by decreasing the temperature below the melting point, the change in Δn was measured as a function of temperature with increase in temperature up to 10 K below the boiling point of the solvent and then decreasing the temperature up to below the melting point.

Figure 1. Schematic representation of change in temperature of a specimen in an immersing liquid with time in procedures 1 and 2: bp, boiling point of the immersing liquid; mp, melting point of the immersing liquid; RT, room temperature (ca. 298 K). Procedure 1 was used to evaluate change in Δn due to the diffusion of the immersing liquid in a polymer solid and procedure 2 was used to evaluate to that due to the molecular interaction between a polymer chain and the immersing liquid at thermodynamic equilibrium.

Procedure 2: After immersing a specimen in a solvent at 10 K below the boiling point (bp) of the solvent for more than 12 hours, the specimen is quenched to 5 K above the melting point (mp) of the solvent and then the temperature dependence of Δn was measured in the temperature range between mp+5 and bp-10 under the heating and/or cooling rate of 10 K min⁻¹. These two procedures are given schematically in Figure 1.

RESULTS AND DISCUSSION

Table I summarizes structural characteristics for three cuprammonium regenerated cellulose hollow fibers, BH2, BH3, and BMM40. All of them are composed of the primary particles. The supermolecular structures of BH2 and BH3 are similar to each other without outer and inner diameters. The difference between BH3 and BMM40 is demonstrated in all characteristics cited in the table.

Figure 2 shows the temperature dependence of a dynamic modulus E' and dynamic loss tangent $\tan \delta$ for BMM40 and BH3 in a dry air on a dry silica gel. There are observed seven dynamic absorptions α_1 , α_{21} , α_{22} , α_{sh} , α_{H_2O} , m , and β_a from the higher temperature side in the temperature range between 150 and 590 K. In the previous papers,¹ five absorptions of α_1 , α_{21} , α_{22} , α_{sh} , and α_{H_2O} were reported. The four absorptions of α_1 , α_{21} , α_{22} , and α_{sh} are originated by the segmental micro-Brownian motion of the polymer chains in an amorphous region and the temperature location of these reflect the

Table I. Structural characteristics for BMM40, BH2, and BH3

Sample code	BMM40	BH2	BH3
Outer diameter/ μ m	350	420	230
Inner diameter/ μ m	280	350	200
Mean pore size/nm	40	3.5	3.0
Porosity/%	54	7	6
Particle size/nm	70 ^e	15 ^f	17 ^f
Crystallinity ^a /%	2	50	49
F_b ^b	0.0	0.34	0.33
Δn_b ^c	0.0057	0.0188	0.0280
Δn_c ^d	0.0016	0.0030	0.0050

^a Evaluated by the refractive index method.² ^b Defined as the orientation function of a molecular axis (b axis) to a fiber axis.² ^c Birefringence evaluated by Becke's line method. ^d Birefringence evaluated by the compensator method at the center of a fiber. ^e Size of the secondary particle.⁵ ^f Size of the primary particle.⁵

Figure 2. Temperature dependence of E' and $\tan \delta$ for BMM40 and BH3: Measuring conditions, heating rate of 12 K min⁻¹, frequency of 110 Hz under dry air.

density of intermolecular hydrogen bonds worked among polymer chains.² $\alpha_{\text{H}_2\text{O}}$ absorption may originate from the cooperative motion of adsorbed H_2O and polymer segment in an amorphous region. In the temperature range from 150 and 350 K, we can notice three absorptions of β_a , m , and $\alpha_{\text{H}_2\text{O}}$ for BMM40, BH2, and BH3.

Mechanism of β_a Absorption

The peak temperature of $\tan \delta$ for the β_a absorption, T_{max} , was 212 K as seen in Figure 2. We concluded that β_a absorption is related to the molecular motion of a molecular chain in an amorphous region judging from the following two evidences. That is, (1) absorption intensity increases with the content of the amorphous region as clarified by comparing with the crystallinity cited in Table I and the peak value of $\tan \delta$ for the β_a absorption in Figure 2. (2) For the sample of BMM40 with crystallinity of *ca.* 2%, the β_a absorption appears strongly.

The peak value of $\tan \delta$ for the absorption, $\tan \delta_{\text{max}}$ was about 0.060 and the value of E' after absorption was *ca.* 8 GPa for the amorphous sample of BMM40 indicating that the absorption may originate from the local twisting motion of a main chain. This assignment is supported by the apparent activation energy, temperature dependence of the birefringence, and change in the peak temperature of the β_a absorption with the coexistence of benzene, methanol, and/or water molecules.

The half value width of $\tan \delta$ -temperature curve $\Delta T_{1/2}$ for the absorption was 90 K. According to the theoretical calculation, the half value width for the absorption with a single relaxation time $\Delta T_{1/2(s)}$ is given by

$$\Delta T_{1/2(s)} = \frac{5.24 \times 10^{-3} T_{\text{max}}^2}{\Delta H_a} \quad (2)$$

where ΔH_a is apparent activation energy of the absorption in the unit of kcal mol^{-1} . Although ΔH_a of the β_a absorption is obtained experimentally below, we employ 50 kcal mol^{-1} here and get $\Delta T_{1/2(s)}$ of 4.7 degree. Consequently, the ratio of $\Delta T_{1/2}$ and $\Delta T_{1/2(s)}$ is calculated to be *ca.* 19. The values of this ratio are 6, 5.5, 6, 6.5, and 4 for the β_a absorptions of the typical solids of polyethylene, polypropylene, poly(ethylene terephthalate), poly(vinyl chloride), and poly(methyl methacrylate), respectively. The ratio of BMM40 is extremely larger than those of other polymers indicating that β_a absorption may separate into two or more absorptions with a different apparent activation energy.

Figure 3 shows the temperature dependence of $\tan \delta$ at 110, 11, and 3.5 Hz for BMM40. The β_a absorption is separated into two absorptions β_{a1} and β_{a2} . At 3.5 Hz, T_{max} of β_{a1} and β_{a2} are 224 K and 210.5 K, respectively. We conclude that the β_a absorption consists of two absorptions of β_{a1} and β_{a2} with different activation energies ΔH_{a1} and ΔH_{a2} , respectively. ΔH_a is evaluated using eq 3 from plots of $\log f$ (f , measuring frequency) vs. $1/T_{\text{max}}$.

$$\Delta H_a = -2.303R \frac{d \log f}{d(1/T_{\text{max}})} \quad (R, \text{ gas constant}) \quad (3)$$

Figure 3. Temperature dependence of $\tan \delta$ for BMM40: Filled circle, 110 Hz of measuring frequency; open circle, 11 Hz; filled triangle, 3.5 Hz.

Table II. Apparent activation energies of β_{a1} and β_{a2} absorptions for BMM40, BH2, and BH3 in kJ mol^{-1}

Sample code	Characteristics employed for evaluation	β_a Absorption	
		β_{a1}	β_{a2}
BMM40	E''^a	250	380
	$\tan \delta^b$	90	230
BH2	E''^a	130	270
	$\tan \delta^b$	140	—
BH3	E''^a	250	330
	$\tan \delta^b$	140	200
Average		170	280

^a Evaluated by plots of $\log f$ vs. reciprocal peak temperature of E'' -temperature curve. ^b Evaluated by plots of $\log f$ vs. reciprocal peak temperature of $\tan \delta$ -temperature curve.

Table II summarizes the activation energy of two β_a absorptions for BMM40, BH3, and BH2. ΔH_a for the β_{a1} absorption is about one half that of the β_{a2} absorption, that is 40 kcal mol^{-1} for the β_{a1} and 70 kcal mol^{-1} for the β_{a2} absorption. In general, ΔH_a of the absorption having T_{max} at higher temperature is larger than that at lower temperature because T_{max} is governed by an intermolecular force and the size of the moving unit. The higher T_{max} and lower ΔH_a for the β_{a1} absorption indicate that the intermolecular interaction that governs the movement of absorption is larger and the size of the moving unit of the absorption is smaller than those of β_{a2} absorption. The above difference in molecular motion of the chains of both absorptions may originate from the difference in a molecular environment of the chains. The tension worked along a chain axis of molecular chains to give the β_{a1} absorption may run more remarkably than that of the case of the β_{a2} absorption. Similar interpretation has been given to the case of α_a absorption for polyethyleneterephthalate where two α_a absorptions were observed and the α_a absorption with the higher T_{max} , α_{a1} , showed smaller ΔH_a and the molecular chains giving rise to the α_{a1} absorption were stressed.¹¹ Since the crystal region and chain orientation can be neglected, the stress on a molecular chain may

be caused by the supermolecular structure common to BH2, BH3, and BMM40. The interfacial surface of a particle is considered to be the region where stress is concentrated. Consequently, β_{a1} absorption may originate from the surface of the particle and β_{a2} is from the inside of the particle.

Figure 4 shows the temperature dependence of E' and $\tan \delta$ for BMM40 in benzene. The molecules of benzene penetrate the space of the inter-particles (in this case, the primary particle) but do not the inside of the particle because of the molecular size and hygroscopy. The temperature location of the β_{a2} absorption is not in-

Figure 4. Temperature dependence of E' and $\tan \delta$ for BMM40 in benzene: Melting point of benzene is 278.6 K. The absorption due to the melting was hidden by the α_{sh} absorption.

Figure 5. Temperature dependence of E' and $\tan \delta$ for BMM40 in methanol: Identification of the absorptions given in the figure such as β_{a2} , β_{a1} , and α_{sh} was made based on E' . The melting of methanol starts at 140 K.

fluenced by the existence of benzene but the β_{a1} absorption shifts to higher temperature and α_{sh} absorption to lower temperature. These changes indicate definitely that β_{a1} and β_{a2} absorptions originate from the interfacial region of the primary particle and from the intra-particle region, respectively.

Figure 5 shows the temperature dependence of E' and $\tan \delta$ for BMM40 in methanol. The methanol molecules penetrate the inside of the particles resulting in shift of all absorptions of β_{a2} , β_{a1} , α_{sh} , α_{22} , and α_{21} to the lower temperature side. We must note that the melting of methanol occurs in a wide temperature range from 148 to 173 K. This depression of the melting point of methanol may be due to fine spaces a few nm in size. This space corresponds to the spaces among primary particles *ca.* 20 nm in size.

Figure 6 shows the temperature dependence of Δn of BMM40 and BH3 in methanol. In Figure 6(a) is shown the case of BMM40 with increase in temperature in procedures 1 and 2, and in Figure 6(b) the case of BH3. The porosity of BMM40 is so high that methanol molecules easily penetrate the spaces of inter-primary particles in the whole area of the sample. In the case of BH3, the diffusion of molecules into spaces at the inner part of the sample needs so long period that in procedure 1, we can evaluate the diffusional behaviour of the molecules into the inter-particle space. The curve of Δn vs. temperature in Figure 6(a) shows peaks in the temperature range of β_a absorption only in the case of increasing temperature. This indicates that the diffusion of methanol molecules into the spaces among the primary particles may be accelerated through elevating temperature and diffusion into the intra-particles may be accelerated also. The diffusion of a methanol molecule to the above spaces gives rise to increase in Δn and this diffusion may occur in the temperature range of the β_a absorption in procedure 1. The diffusion of a methanol molecule into the intra-particle causes decreasing Δn

Figure 6. Temperature dependence of Δn of BMM40 and BH3 in methanol: (a), increasing temperature in procedures 1 and 2 for BMM40; (b), procedures 1 and 2 for BH3.

to the value attained after adsorption equilibrium of the solvent given in procedure 2 in Figure 2. Similar diffusional behaviour can be observed for ethanol and 1-propanol.⁹ In Figure 6(b), the temperature dependence of Δn , $d\Delta n/dT$, for BH3 is negative in procedure 1 and the gap of Δn is observed in the temperature range of β_a absorption between increasing and decreasing temperature. This may be interpreted as follow: Methanol molecules penetrate easily the intra- and inter-primary particle only above temperature of the β_a absorption. On

the other hand in the case of procedure 2, where the adsorption equilibrium is attained, $\Delta n/dT$ is positive in the range of the β_a absorption and Δn is smaller than that of procedure 1. In procedure 2 for BH3, methanol molecules adsorb in the region that gives absorptions of β_a , α_{sh} , α_{22} , and α_{21} and shift the temperature of these absorptions to the lower side as shown in Figure 5. These results indicate the molecular motion of the β_a absorption causes increase in Δn and methanol molecules within a primary particles in an equilibrium state make a decrease

Figure 7. Temperature dependence of E' and $\tan \delta$ for BMM40, BH2, and BH3 at 110, 11, and 3.5 Hz.

Figure 8. Temperature dependence of E' and E'' for BH2.

in Δn due to the activation of α_{sh} , α_{22} , and α_{21} absorptions. Consequently, we can conclude that the molecular motion to give the β_a absorption does not cause the decrease in the molecular chain orientation. This supports the assignment that local twisting motion of a molecular chain gives rise to originate the β_a absorption.

Mechanism of m Absorption

Figure 7 shows the temperature dependence of E' and $\tan \delta$ for BMM40, BH2, and BH3 at the frequencies of 110, 11, and 3.5 Hz in the temperature range of 250 and 300 K. The peak temperature of $\tan \delta$ of m absorption is located at 273 K and corresponds to the melting point of H_2O . The apparent activation energy of this absorption evaluated was infinity and this indicates the absorption is due to the molecular movement due to the melting of water molecules. E' decreases owing to the melting of the water molecules absorbed on primary particles. The decrease in E' due to the melting started at 30 K below the melting point of bulk water T_m^0 ($T_m^0 = 273$ K).

The melting point depression ΔT_m ($= T_m^0 - T_m$) is considered due to the difference in the inter-surface energy between a melt and a crystal Δa . According to the equation to give the Gibbs energy of water molecules in a fine pore, we derive the following equation for a membrane with cylindrical straight pore having radius r :

$$\Delta T_m = \frac{\Delta a T_m^0}{\Delta H_m} \frac{2}{r}, \quad \Delta T_m = T_m - T_m^0 \quad (4)$$

where, ΔH_m is the enthalpy difference between a melt and a crystal. For a water molecule, T_m^0 , ΔH_m , and Δa are 273 K, $3.35 \times 10^9 \text{ erg cm}^{-3}$, and -47 erg cm^{-3} , respectively. We can calculate r by putting T_m into eq 4. Here, T_m is determined as the temperature where E' decreases

Figure 9. Temperature dependence of E' and $\tan \delta$ for BMM40 after keeping sample in air of RH=80% for 72 hours at 293 K followed by quenching in liq. N_2 .

due to m absorption. The values of r for BMM40, BH2, and BH3 were 3.3 nm, 2.6 nm, and 2.6 nm, respectively. These values except for BMM40 are similar to the mean pore radius given in Table I, and for BMM40, r is considered the radius of the space between neighboring primary particles.

Mechanism of α_{H_2O} Absorption

The α_{H_2O} absorption could not be observed in Figures 4 and 5. This absorption could be observed distinctly for samples showing the m absorption. In the previous paper,² E' increased with temperature within the temperature range of the absorption. But this increase is not always observed. For example, Figure 1 shows E' holds constant or decreases slightly for both samples of BMM40 and BH3. Figure 8 shows the temperature dependence of E' and loss modulus E'' for BH2 in the temperature range between 300 and 340 K. The decrease in E' and increase in E'' are due to α_{H_2O} absorption. These results indicate α_{H_2O} absorption is different with from m absorption.

Figure 9 shows the temperature dependence of E' and $\tan \delta$ for BMM40 after keeping the sample in wet air of RH=80% for 72 h at 293 K followed by quenching in liq. N_2 . α_{H_2O} absorption disappeared and α_{sh} absorption separated into two of α_{sh1} and α_{sh2} . Judging from E' , α_{sh1} absorption may be consisted of α_{H_2O} and the component of α_{sh} whose T_{max} is lowered by absorbed H_2O . The disappearance of the m absorption may be due to the desorption of H_2O from a specimen during measurement without freezing H_2O on the primary particles. β_{a1} , β_{a2} , α_{sh} , α_{22} , and α_{21} absorptions shift to the lower temperature side. These results indicate water molecules exist on the intra-primary particles. The α_{H_2O} absorption originate from the segmental motion of the main chain with absorbed water molecules.

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