Relationship between Mechanical Absorption and Birefringence of Regenerated Cellulose Solid in Solvent

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ABSTRACT: This study correlates the temperature dependence of birefringence Δn of a regenerated cellulose solid in a solvent with thermal chain motion evaluated from mechanical loss tangent $\tan \delta$. Two regenerated cellulose hollow fibers composed of fine spherical particles (primary particles) from 10 to 20 nm in size were used. Solvents as immersing media were methanol, ethanol, *n*-propanol, and ethylene glycol. The temperature dependence of Δn in the solvent was measured by the freezing method and the equilibrium method proposed by us. [*Bull. Fac. Human Environ. Sci., Fukuoka Women's Univ.*, **28**, 37 (1997)] ① Δn vs. temperature curves by the freezing method showed a few peaks at the temperature region where $\tan \delta$ vs. temperature curve showed peaks or a shoulder. ② Peak value varied with immersing media and freezing conditions. ③ For the sample having anisotropic orientation of the working direction of the intermolecular hydrogen bond, a few peaks were observed in the case of the freezing method at β_a absorption due to a local twisting motion of a main chain. ④ In the lower temperature region between β_a absorption and α_a absorption, due to a micro-Brownian motion of a main chain, Δn was reflected in molecular interactions between the medium and cellulose molecules. In the temperature region of α_a absorption, a few peaks of Δn appears in both methods. Δn peaks thus correlate closely with the onsets of mechanical absorption.

KEY WORDS Regenerated Cellulose / Solvent / Birefringence / Diffusion / Freezing Method / Equilibrium Method / Mechanical Absorption /

The higher order structure of a polymer solid influences significantly diffusion. The region into which a particle and a molecule diffuse should be discussed from two standpoints: (1) whether the geometrical size of the space is enough or not for the diffusion and (2) whether the micro-Brownian motion of a cellulose chain is activated sufficiently or not. This region is referred to as the diffusible region. It is important in studying the particle diffusion to know higher order structures of polymer solids and thermal molecular motion of the polymer chains.

The thermal molecular motion may be influenced by the particle diffused. In spite of the necessity of these investigations as for the diffusible region and the thermal molecular motion activated by the particle diffused, few investigations have been carried out so far.¹ This is because there is no way for measurement of the effect of particles on motion and evaluation of the diffusible region.

We proposed in the previous paper² a viscoelastic method for evaluation of the diffusible region and change in the thermal molecular motion of a polymer solid due to the diffusion of the particle. The diffusible region and solvent content in a given amorphous region are evaluated through the method.³

To evaluate thermal molecular motion of the chain in the medium containing a particle and the diffusional behavior of the particle, recently we proposed the method for the measurement of the temperature dependence of birefringence Δn in a liquid medium.^{4,5} We proved the possibility of evaluating the thermal molecular motions and the diffusion of a solvent by the following three procedures: ① freezing of thermal molecular motions (referred to as freezing method), ② diffusional equilibrium (equilibrium method), ③ step-wise excita-

tion (transitional method). Through these methods, we evaluate intermolecular interactions between particle and polymer chain.

The theoretical background of Δn proposed so far is not enough for explanation of the temperature dependence of Δn observed in a solvent. Δn has been regarded as the sum⁶ of ④ Δn due to the orientation of the molecular chains along a fiber axis in a crystalline and a non crystalline regions and ⑤structural birefringence. Experimental Δn taught us that the influence of the plane orientation and thermal molecular motions on Δn should be added to the contributions of ④ and ⑤.^{7,8}

This paper shows the temperature dependence of Δn and dynamic viscoelasticities in a medium for two typical regenerated cellulose hollow fibers whose higher order structure has been well-investigated. We establish the relationship between the curves of Δn vs. temperature and thermal molecular motion for a regenerated cellulose solid in a medium containing a particle, and finally show the validity of the measurement of the curves of Δn vs. temperature in the medium containing the particle.

EXPERIMENTAL

Sample Preparation

Regenerated Cellulose Fiber.^{2,9} (1) Porous Cuprammonium Regenerated Cellulose Hollow Fiber (BMM40): BMM40 was prepared as reported previously.² Mean pore size was 40 nm.⁹ The higher order structure of BMM40 was represented by a stack structure of the secondary particle of *ca.* 75 nm in size. The secondary particle was composed of aggregates of primary particles of *ca.* 15 nm in size. BMM40 was almost non crystalline and showed little orientation of molecular chains along

Figure 1. Schematic representation of change in temperature of a sample (polymer solid) and an immersing solvent with time: (1) Freezing method: Arrows indicate the direction of the temperature change. ●, sample (polymer solid); ○, solvent; ⊙, sample in an immersing solvent at equilibrium; ○●, sample in the neighborhood of a solvent; T_s , temperature of holding a sample and/or a solvent before measurement; T_f , temperature of freezing of thermal molecular motion of a polymer chain; T_b , bottom temperature of cooling a sample and/or solvent. $T_{\max}(\beta_a)$, peak temperature of β_a absorption. (1) freezing method; (2) equilibrium method.

a fiber axis⁹ (this orientation is referred to as chain orientation). The crystal plane (110) in a crystalline region and/or the working direction of the intermolecular hydrogen bond in a non crystalline region were oriented in the circumferential direction of the hollow fiber in the case of BMM40.¹⁰ Increase in the crystallinity with storage time for BMM40 was observed.¹¹ We distinguished BMM40 as BMM40(1) and BMM40(2). BMM40(2) indicated that about 180 days passed at $RH=0\%$ and free of tension after BMM40(1) was used. (2)Virus Removal Hollow Fiber (BMM35): BMM35 was prepared by the similar procedure of BMM40 and was provided from Asahi Chemical Ind. Co., Ltd., Japan. Mean pore size was 35 nm. The higher order structure of BMM35 was similar to BMM40. BMM35 had a higher degree of chain orientation than that of BMM40, and the plane orientation of BMM35 held at a slightly lower level than that of BMM40. These two samples were kept in a desiccator packed with dry silicagel before use for more than a week.

Solvent as a Particle. The following solvents were used as immersing media during measurement of the Δn and dynamic viscoelasticity: methanol, ethanol, *n*-propanol, ethylene glycol. These were guaranteed reagent grade manufactured by Wako Pure Chemical Ind. Ltd. (Japan).

Measurements

Temperature Dependence of Δn in Solvent. Δn vs. temperature curves were measured with heating/cool-

Table I. T_s and T_f used in the freezing method

Solvent	Sample	T_s /K	T_f /K
Methanol	BMM40	296	173
	BMM35	296, 493, 543	173
Ethanol	BMM40	296	163
<i>n</i> -Propanol	BMM40	296	163

T_s , temperature of holding a sample and/or a solvent before measurement; T_f , temperature of freezing thermal molecular motion of a polymer chain.

Table II. T_s and T_b used in the equilibrium method

Solvent	Sample	T_s /K	T_b /K
Methanol	BMM40	296	173
Ethanol	BMM40	296	163
<i>n</i> -Propanol	BMM40	296	163
Ethylene Glycol	BMM35	253, 296, 373	250

T_s , temperature of starting a sample and/or solvent; T_b , bottom temperature of cooling a sample and/or solvent.

ing equipment⁴ installed with a polarized microscope. Two typical methods of the freezing method⁵ and the equilibrium method⁵ were used. The thermal histories employed in both methods are shown in Figure 1. Δn was measured by Berek's compensator. (1) Freezing method⁵: The sample was kept at the temperature T_s for 10 min, and then was quenched into the solvent kept for 10 min at temperature T_f where most thermal molecular motion of polymer chains was frozen. Changes in Δn were measured as a function of temperature under heating rate of 5 K min^{-1} . All samples, and solvents, T_s , and T_f are summarized in Table I. (2) Equilibrium method⁵: After a sample was kept at T_s for 10 min in a solvent to attain diffusional equilibrium, it was cooled to T_b in the solvent at 5 K min^{-1} , and then were kept at T_b for 10 min. The temperature dependence of Δn was measured at 5 K min^{-1} . All samples and solvents, and the T_s and T_f are summarized in Table II.

Dynamic Viscoelasticities in a Solvent. Storage modulus E' and loss tangent $\tan \delta$ were measured with Rheovibron DDV-IIc (Toyo-Boldwin Co., Ltd., Japan) by the previous method² at 110 Hz, and heating rate of 3 K min^{-1} .

RESULTS AND DISCUSSION

General Views of Δn vs. Temperature Curve

Figure 2 shows the temperature dependence of Δn of BMM40(1) in methanol by the freezing and the equilibrium methods. T_s was fixed at 296 K. We observe a few peaks in the case of the freezing method. In the freezing method, it should be noted that, Δn was measured under the condition that solvent molecules cannot diffuse into the fine space among primary particles at the start and then diffusion proceeds with increasing temperature. In the case of the equilibrium method there were no obvious peaks until near T_s , although there was

one peak below T_s . There has been no report on peaks of Δn lower than T_s . The appearance of peaks above T_s was related to the measuring method and solvent, and the peak location corresponded to the mechanical absorptions of β_a .³ β_a absorption was due to local twisting motion of the main chain.

Figure 2. Temperature dependence of Δn of BMM40(1) in methanol at $T_s = 296$ K: Open circle, by the freezing method; filled circle, by the equilibrium method. Arrows indicate Δn peak positions.

Figure 3. Temperature dependence of E' and $\tan \delta$ for BMM40(1) in methanol: Absorptions of β_{a2} , β_{a1} , α_{sh} , α_{22} , and α_{21} locate at the temperature indicated in the figure.

Relationship between Thermal Molecular Motion and Appearance of a Peak in Δn vs. Temperature Curve

Figure 3 shows the temperature dependence of dynamic viscoelasticity for BMM40(1) in methanol. The conditions of the measurement correspond to the equilibrium method in measurement of Δn . Five absorption peaks are observed in the curve of $\tan \delta$ vs. temperature between melting and boiling temperatures of methanol: β_{a2} , β_{a1} , α_{sh} , α_{22} , and α_{21} absorptions⁹ from lower temperature side, whose peaks were 193–213, 228–237, 236–243, 268, and 288 K, respectively. The mechanism of absorption is summarized in Table III based on the published literatures.^{2,9} β_a absorption was used as a general term of β_{a1} and β_{a2} absorptions. By application of the theoretical equation to give peak temperature of the dynamic viscoelasticities,³ methanol molecules can diffuse into the region which gives the α_2 absorption.

Figures 4(1) and 4(2) show the temperature dependence of Δn of BMM40(1) and BMM40(2), respectively. Methanol was used as the immersing medium. Temperature between 170 and 240 K correspond to the range of β_a and α_{sh} absorption in methanol. There can be observed three or more peaks in the case of the freezing method. The corresponding peaks are not observed in the case of the equilibrium one. The peak temperatures were located at β_{a2} , β_{a1} , and α_{sh} absorption. We can conclude that mechanical absorption of β_{a2} , β_{a1} , and α_{sh} gives the peak in Δn vs. temperature curve obtained by the freezing method by the use of methanol.

A comparison with BMM40(1) of Figure 4(1) and BMM40(2) of Figure 4(2), shows differences in the number of peaks of Δn and levels of Δn . It is probable that structural change such as crystallinity changes with storage time cause the differences. The number of peaks depends on the number of distinguishable mechanical absorptions, such as the separation from β_a absorption into β_{a2} and β_{a1} , and separation between β_{a1} and α_{sh} . In this way, the peak number of Δn for BMM40 is sensitively reflected to the fine structural change during storage.¹⁰

Figures 5(1) and 5(2) show the temperature dependence of Δn for BMM40(1) and BMM40(2) between 240–340 K, respectively. This range corresponds to the range of α_{sh} , α_{22} , and α_{21} absorptions in methanol. There can be observed a few peaks of Δn in the case of freezing and equilibrium. Δn peaks are closely related to α_a adsorption.

Table III. Mechanism of mechanical absorption of a regenerated cellulose solid

Absorptions	$T_{\max}/K^a$	$\Delta H_a/kJ\ mol^{-1}\ ^b$	Mechanism	Region ^c
α_a {	α_1 558–578	1200	Micro-Brownian motion of main chain	Intra-primary particle
	α_{21} 488–563	290	Ditto	Ditto
	α_{22} 413–563	210	Ditto	Ditto
	α_{sh} 413–513	— ^d	Ditto	Interface of a primary particle
α_{H_2O}	303–323	— ^d	Co-operative motion of H_2O and main chain	Intra-primary particle
m	273	∞	Melting of water adsorbed	Space among primary particles
β_a {	β_{a1} 225	170	Local twisting motion of main chain	Interface of a primary particle
	β_{a2} 210	280	Ditto	Intra-primary particle

^a Peak temperature of $\tan \delta$ under dry air at 110 Hz. ^b Apparent activation energy. ^c Region in which the polymer chains gives absorption. ^d Not decided.

Figure 4. Temperature dependence of Δn of BMM40 in methanol at $T_s = 296$ K: Open circle, by the freezing method; filled circle, by the equilibrium method. (1) BMM40(1); (2) BMM40(2). BMM40(2) indicates sample obtained by storing BMM40(1) in air of RH of 0% at 25°C for six months under free of tension. Arrows indicate Δn peak positions.

Occurrence of Δn Peak

Δn Peak in the Range of β_a Absorption. In the case of the equilibrium method, no Δn peak was observed or only small peaks were observed in the temperature range of β_a absorption. The temperature dependence of Δn , $d\Delta n/dT$ (T ; temperature) evaluated by this method in methanol for BMM40 and 35 was 6.3×10^{-7} and $4.6 \times 10^{-6} \text{ K}^{-1}$, respectively. β_a absorption gives this increase in Δn .

The Δn peak in the case of the freezing method was always larger than that of the equilibrium method. The appearance of Δn peak is considered to be related to non-equilibrium of the absorption of the solvent.

Judging from the principle of the freezing method,⁵ it is reasonable to assume that the above thermal molecular motion of cellulose chains is frozen at T_f of 173 K. Methanol molecules do not yet diffuse into the inside of primary particles at T_f , although they diffuse into voids among secondary particles. This diffusion was confirmed through the increase in the transparency of the sample. With increasing temperature, the thermal molecular motion of β_a absorption is released. Activated thermal motion may give rise to the diffusion of methanol molecules into the interface and then inside the primary particles. The diffusion of methanol on to the surface of the primary particle may give additional increase in Δn since Δn peak was larger than the case of the equilibrium method. This additional increase will be given in the forth-coming paper.¹²

In the case of the equilibrium method, the additional

Figure 5. Temperature dependence of Δn of BMM40 in methanol at $T_s = 296$ K: Open circle, by the freezing method; filled circle, by the equilibrium method. (1) BMM40(1); (2) BMM40(2). Arrows indicate Δn peak positions.

diffusion of methanol into the cellulose solid may not occur at lower temperature than T_s ($= 296$ K). Because of completion of the diffusion into the interface of the primary particle, abrupt increase in Δn with increasing temperature cannot be expected. Consequently, there are not observed any obvious peaks but a monotonous increase in Δn .

The appearance of peaks of Δn obtained through the freezing method may be due to two opposite effects on Δn : increase in Δn with temperature mentioned above and the opposite. Δn decreases toward values obtained by the equilibrium method at above temperature of β_a because of the concentration equilibrium of a methanol.

Δn Peak in the Range of α_a Absorption. The peak temperature and value changed with T_s in the equilibrium method and T_f in the freezing method. Δn of the sample, obtained by cooling down to the room temperature after elevating above the peak temperature, did not coincide with the value before elevation. This indicates the Δn peak is strongly related to irreversible change in the higher order structure.

Above T_s , structural change due to the thermal molecular motion located at higher temperature than T_s may occur with increasing temperature. The appearance of peaks of Δn may be due to the two opposite effects of positive temperature dependence of Δn and a negative dependence. The positive dependence is caused by anisotropy of thermal expansion and anisotropic diffusion of a methanol molecule along a polymer chain axis. The negative dependence is caused by irreversible decrease in the chain orientation due to the segmental micro-Brownian motion. The micro-Brownian motion,

Figure 6. Temperature dependence of Δn of BMM40(2) in ethanol by the freezing method: The arrows indicate the Δn peak position.

Figure 7. Temperature dependence of Δn of BMM40(2) in *n*-propanol by the freezing method: Arrows with open mark indicate Δn peak positions and one with closed mark indicates the Δn minimum position.

Table IV. Peak temperatures of $\tan \delta$ ($T_{\max}$) in various solvents for BMM40

Solvent	$T_{\max}/K$				
	β_{a2}	β_{a1}	α_{sh}	α_{22}	α_{21}
Dry air	200	230	378—473	413—513	488—563
Methanol	193—213	228—237	236—243	268	288
Ethanol	ca. 210	ca. 260	ca. 290	ca. 340	
<i>n</i> -Propanol		223 ^a	268—306	338—343	355
Ethylene glycol			< 300	308	350

^a Not separated into two absorptions of β_{a1} and β_{a2} .

activated by diffusion of a methanol molecule, gives rise to acceleration of the diffusion of methanol. A few peaks due to the combination of the positive and the negative dependence of Δn were thus seen.

Applications to Other Solvents

Figure 6 shows the temperature dependence of Δn of BMM40(2) in ethanol by the freezing method between 170 and 340 K. There can be observed a few peaks in this temperature range. Table IV summarizes peak temperature $T_{\max}$ of $\tan \delta$ for BMM40 in several solvents. A broad and gentle peak of β_a absorption was not separated into two peaks, β_{a1} and β_{a2} . For the curve of Δn vs. temperature by the freezing method, the peaks corresponding to β_a adsorption are observed separately. The peaks of Δn may always be expected whenever the onset of the thermal molecular motion with increasing temperature is realized.

Figure 8. Temperature dependence of Δn of BMM35 in ethylene glycol by the freezing method: $\bullet$, $T_s = 253$ K; $\blacksquare$, 296 K; $\blacktriangle$, 373 K. Arrows indicate Δn peak positions.

Figure 9. Temperature dependence of Δn for BMM35 in methanol at $T_s = 543$, 493, and 296 K by the freezing method: $\square$, $T_s = 543$ K; $\triangle$, 493 K; $\circ$, 296 K. Arrows indicate Δn peak positions.

Figure 7 shows the temperature dependence of Δn of BMM40(2) in *n*-propanol by the freezing method between 170 and 340 K. A few peaks are observed. It is difficult to separate β_a absorption into two peaks, β_{a1} and β_{a2} , in the case of $\tan \delta$ as shown in Table IV. By referring to Figures 4, 5, 6, and 7, we can conclude the value of Δn peaks and their temperature location by the freezing method varied with the solvent.

Figure 8 shows the temperature dependence of Δn of BMM35 in ethylene glycol by the equilibrium method. T_s are 253, 296, and 373 K. The peak, located near 250 K in the case of $T_s = 253$ K, shifts to higher temperature side and the peak value falls with increasing T_s . The temperature range of this peak corresponds to the range between α_{22} and α_{21} absorptions in ethylene glycol. In the case of T_s of 373 K, no peaks were observed. Δn above the peak temperature increased with T_s . when BMM35 attains diffusional equilibrium in ethylene glycol above 250 K, the chain orientation is relaxed by activated thermal molecular motion resulting in decrease in Δn near 250 K. Change in Δn above T_s is due to relaxation of the remaining chain orientation. The peak of Δn is observed on the temperature of a few degrees higher than T_s . The thermal molecular motion related to α_{22} absorption was completely activated in ethylene glycol at $T_s = 373$ K. Thus decrease in Δn does not take place in the temperature range of α_{22} absorption. From the experimental fact that Δn after the peak increase with increasing T_s , we can conclude that the heat treatment

above T_s in ethylene glycol makes the chain orientation high.

Figure 9 shows the temperature dependence of Δn for BMM35 in methanol at $T_s = 543$, 493, and 296 K by the freezing method. With increasing T_s , Δn below α_a absorption increased greatly, and Δn value above α_a absorption increased slightly. The Δn peak located near 250 K becomes greater and clear with an increase in T_s . This temperature range of the peak covers the temperature range of α_{sh} and α_{22} absorption. Thus, we can evaluate quantitatively changes in the higher order structure, such as the plane orientation originated by the solvent in freezing, and additional increase in Δn due to the diffusion of solvents as showing quantitative analysis of the Δn vs. temperature curve.

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