Effect of Coagulation Conditions on Fine Structure of Regenerated Cellulosic Films Made from Cellulose/*N*-Methylmorpholine-*N*-Oxide/H$_2$O Systems

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ABSTRACT: The important properties of cellulosic fibers in the conditioned state are mainly influenced by fine structure. In particular, the development of new methods of spinning regenerated cellulosic fibers made from a cellulose/*N*-methylmorpholine-*N*-oxide (NMMO)/H$_2$O system require a better understanding of their fine structures in order to explain their special physical properties. The regenerated cellulosic films were made from cellulose/NMMO/H$_2$O according to the degree of polymerization and solution concentration (wt %) of cellulose and the concentration (wt %) of NMMO in the coagulation bath. The quantification of crystal content was carried out by the resolution of the wide angle X-ray diffraction intensity distribution on the assumption that all diffracted intensities take the form of a symmetrical Gaussian distribution centering at its Bragg angle. The X-ray diffraction patterns resolved into individual integral intensities showed that the polymorphic structure mixed with part cellulose III and II was obtained for only coagulated cellulose films. The degree of crystallinity and apparent crystalline size of regenerated cellulosic films depended on the degree of polymerization, the solution concentration of cellulose, and the concentration of NMMO. The diameter of the microfibril decreased with an increase in the concentration of NMMO. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2681–2690, 1999

Key words: new regenerated cellulose; *N*-methylmorpholine-*N*-oxide; fine structure; X-ray diffraction; symmetrical Gaussian distribution

INTRODUCTION

There are two categories for the recent research on regenerated cellulosic fiber and fabric. One is to improve wet tensile strength, which affects the dimensional stability of fabric, from the viewpoint of the improvement of their properties; another is to develop the complete recovery system of a spin-

ning solvent from the viewpoint of environmental protection and safety.

From these aspects, recent researchers focused on the preparation of cellulosic fiber under various spinning technologies from the spinning dope solution with *N*,*N*-dimethylacetamide/LiCl or *N*-methylmorpholine-*N*-oxide hydrate (NMMO).[1–5]

Regenerated cellulose fiber from the latter solvent system has been especially industrialized; typical commercialized one is a Lyocell, which has excellent wet and dry tensile strength and is highly capable of being made into mixed yarn.

Table I   Cellulose Samples and Their Properties

Sample Code	DP_w	Alpha Cellulose (%)	Solubility in 10% NaOH (%)
V60	855	94.7	7.3
V81	1180	97.0	3.7
V5	1820	97.8	2.4

Moreover, this process can remove environmental pollution by adopting the closed solvent recovery system. However, the touch and shape of the fiber may be also changed due to the fibrillation of the fiber surface from applying the mechanical actions during the dyeing and washing processes. Such fibrillation is closely related to the fine structure of the fiber. In addition, Krassig reported that cellulosic fiber properties in specific wet conditions were affected mainly by the fine structures of cellulose, such as the degree of polymerization (DP), the degree of crystallinity (DC), chain orientation, and morphology.[5] However, because Lyocell adopts a completely different process and raw cellulose from a typical viscose rayon process, we believe the fibrillation mechanisms of both processes are also different. Therefore, analysis of the fine structure is absolutely necessary to elucidate these mechanism differences.

However, recent research has been restricted to the identification of the interaction of cellulose and NMMO/H_2O solvent or investigation of the physical properties of fibers spun under various conditions in the spinning process.[4,6–9] Thus, as preliminary research to prepare new cost effective regenerated cellulosic fiber, we investigated the fine structure changes, especially the crystal structure and fibrillation, of cellulose films obtained from the cellulose/NMMO/H_2O system with different DP of cellulose, film dope concentration, and coagulation bath condition. The reason we chose film-type samples instead of fiber types in this research was to remove the mechanical effect on the fibrillation during the spinning and drawing processes.

EXPERIMENTAL

Materials

Three different cellulose samples (Buckeye), whose properties are shown in Table I, were used

as powder types after crushing with a mill and vacuum drying. Fifty percent NMMO (BASF) was used after concentrating it to 87% (NMMO/H_2O = 87/13 → expressed with NMMO), in addition to 0.5 wt % n-propylgallate (Aldrich) as an antioxidant to avoid oxidation and degradation during the cellulose dissolving process.

Sample Preparation

Films were prepared by dissolving pulp in NMMO and antioxidant under the process shown in Figure 1. The dissolution of pulp was carried out under nitrogen to avoid moisture regain. Film thickness was controlled with the concentration of the solution. Cast films were immersed in water for 24 h, then washed and dried under a vacuum oven at room temperature. Sample codes and detailed preparation conditions are tabulated in Table II.

Characterization

DP

After the intrinsic viscosity of the pulp or film powder dissolved in 0.5M cupriethylene diamine hydroxide was measured by an Ubbelohde viscometer at 25°C, the weight average DP (DP_w) was calculated with the following equation.

Figure 1   Flow diagram of sample preparation.

Table II Sample Codes and Properties of Cellulose Film Prepared from Various Conditions

Cellulose Pulp	Cellulose Concentration (Cellulose/NMMO: wt %)	Coagulation Condition (H_2O/NMMO: wt %)	Sample Code	DP_w
V60	6	100	V60-1	695 ± 30
		75/25	2	
		50/50	3	
	8	100	4	
		75/25	5	
		50/50	6	
	10	100	7	
		75/25	8	
		50/50	9	
V81	6	100	V81-1	1078 ± 25
		75/25	2	
		50/50	3	
	8	100	4	
		75/25	5	
		50/50	6	
	10	100	7	
		75/25	8	
		50/50	9	
V5	6	100	V5-1	1412 ± 30
		75/25	2	
		50/50	3	
	8	100	4	
		75/25	5	
		50/50	6	
	10	100	7	
		75/25	8	
		50/50	9	

$$DP_w = [\eta] \times 190$$

where $[\eta]$ denotes the intrinsic viscosity.

Thermal Analysis

Cellulose specimens premixed with NMMO were sealed in aluminum pans under dry nitrogen. Thermograms were obtained from 20 to 200°C in a differential scanning calorimeter (Shimadzu DSC-50) at the heating rate of 5°C/min.

X-Ray Diffraction Measurement

Wide angle X-ray scattering (WAXS) measurements were carried out, using Ni-filtered and graphite-monochromated CuKα radiation at room temperature, by a Rigaku D/MAX diffractometer. The diffraction profiles were obtained in para focus mode at 30 kV and 15 mA. All data were counted at intervals of 0.01° and standardized at 0.05° to eliminate air and background scattering. The quantification of crystalline diffraction was obtained by a program made with FORTRAN 77 at our laboratory. This is based on the following assumptions. The cellulose structure has two phases: crystalline and amorphous. All diffracted intensities take the form of a symmetrical Gauss distribution [eq. (1)] centering at its Bragg angle.

Segal et al. reported that in a study on the degree of crystallinity of cellulose the separation of the peak into crystalline and amorphous fractions was carried out at a fixed maximum diffraction angle of $2\theta = 18°$ and 16° related to the amorphous phase.[10]

This separation, however, is in most cases not very well defined and somewhat satisfactory. Kim et al. recently developed peak-fitting techniques for minimizing the effect of the crystal phase by shifting the maximum diffraction angle in the range of $2\theta = 18 \pm 1°$ and $16 \pm 1°$.[11] Particularly

Figure 2 DSC thermogram for powders of cellulose/ NMMO premixed and an NMMO.

in the new regenerated cellulose made from cellulose/NMMO/H_2O systems, there is no approximate diffraction pattern by summation of the resolved major diffraction peak by using the former

Figure 4 X-ray scattering patterns resolved into individual intensities of the corresponding crystal and amorphous planes: (a) V81, (b) V81-1, and (c) fiber.

method. Therefore, the separation of the peak is concurrently accompanied by shifting the maximum diffraction angle of the amorphous phase at intervals of 0.1°. We repeatedly applied a least squares fit [eq. (2)] to obtain the lowest error (ε) from the measured diffraction intensity distribution and deviation (σ_j) between the resolved diffraction intensity distribution of the crystalline and amorphous phases. As a result, we obtained the lowest errors (below 2.5%) at $2\theta = 14.8 \pm 0.2°$.

$$I_j(\phi) = \frac{1}{\sigma_j \sqrt{2\pi}} \exp\left[-\frac{1}{2} \left(\frac{\phi - 2\theta_i}{\sigma_j} \right) \right] \qquad (1)$$

$$\varepsilon = \sum_\phi \left(I(\phi) - \sum_j I_j(\phi) \right)^2, \quad \frac{\partial \varepsilon}{\partial \sigma_j} = 0 \qquad (2)$$

where $I_j(\phi)$ is the intensity of the jth plane at the ϕ angle, ϕ is a measured diffraction angle, and $2\theta_i$ is a maximum diffraction angle of the ith plane.

The DC, apparent crystalline size (t), and Bragg spacing (d) of the reflecting crystal plane of

Figure 3 X-ray scattering patterns resolved into individual intensities of the corresponding crystal and amorphous planes: (a) V60, (b) V60-1, and (c) fiber.

Figure 5   X-ray scattering patterns resolved into individual intensities of the corresponding crystal and amorphous planes: (a) V5, (b) V5-1, and (c) fiber.

new regenerated cellulose film are the results of the following equations.

$$DC = 100 \; \Sigma I_c(\phi)/(\Sigma I_c(\phi) + \Sigma I_a(\phi))$$

where $I_c(\phi)$ and $I_a(\phi)$ denote the integral intensities of the crystal and amorphous planes at angle ϕ, respectively.

$$t = 0.94\lambda/B \cdot \cos \theta,$$

with B as the half-width ($B^2 = B^2_{mea.} - B_{appl}$) and θ as the Bragg angle of the reflecting crystal plane.

$$\lambda = 2 \; d \; \sin \theta,$$

where λ is the X-ray wavelength (1.54 Å).

Density

The density was measured with a density gradient column filled with carbon tetrachloride ($d = 1.59$) and n-heptane ($d = 0.68$) at 23°C.

Surface Morphology

The observations of the film surfaces were made with fractured films. These were coated with gold and examined with a scanning electron microscope (Jeol JSM-6400, Japan) at magnifications of 10,000 and 30,000.

RESULTS AND DISCUSSION

Change of DP

Samples were treated at 110°C for 90 min on the basis of published results on the solubility and degradation of cellulose in NMMO with dissolving time and temperature[4] and our results concerning thermal behavior and remaining cellulose content after dissolution detected by a polarized microscope. The DP_w values of cellulose after dissolution are shown in Table II. Because the DP_w reduction during the dissolving process is caused by oxidative degradation of glucosidic bonds, this

Figure 6   X-ray scattering patterns for (a) V81-1, (b) V81-4, and (c) V81-7, which were prepared with a change of solution concentration of cellulose.

Figure 7 Variation of degree of crystallinity of cellulose films with (a) the degree of polymerization, (b) the cellulose concentration of the solution, and (c) the NMMO concentration in the coagulation bath.

phenomenon will be more serious without adding antioxidant.

Thermal Properties

Figure 2 shows thermal behaviors of several premixed V81 samples with different amounts of NMMO. We believed the structure of the NMMO in premixed samples became monohydrated judging from the endothermic peak for NMMO at 73°C, which is nearly similar to the endothermic peak for monohydrated NMMO (NMMO/H_2O = 87/13) at 78°C. In accordance with the endothermic peak (crystalline melting) for anhydrated NMMO at 180°C confirmed from the study on phase behavior changes of the cellulose/NMMO/H_2O system detected by DSC and an optical microscope by Chanzy et al.,[4] we also found the endothermic peaks at 170 and 180°C, which means anhydrated and monohydrated NMMO both coexist in our concentrated NMMO. Premixed samples showed the maximum endothermic peaks at around 110°C, which we think is the dissolving point of cellulose combined with NMMO, and irregular endothermic behavior at

80–130°C. These various irregular thermal behaviors were caused by the inhomogeneity of hydrated NMMO and cellulose powder with different sizes. The maximum endothermic peak was shifted a little to a higher temperature with cellulose concentration.

Crystal Structure

Resolved diffraction intensity distributions of crystalline and amorphous regions from X-ray diffractograms for various cellulose samples with DP_w are shown in Figures 3–5. From Figure 3, which shows resolved X-ray patterns of powder, film, and fiber of V60 cellulose, the powder had three diffraction peaks at $2\theta = 14.6°$ and 16.4° for (101) and (10$\bar{1}$), respectively, and at $2\theta = 22.6°$ for strong (002), which are characteristic patterns for crystal cellulose I. On the other hand, regenerated cellulose fiber like viscose rayon or mercerized natural cellulose generally show a diffraction pattern for cellulose II at $2\theta = 12°$ for (101), 20° for (10$\bar{1}$), and 21.7° for (002). Significant diffraction peaks for film and fiber appeared at around

Figure 8 Variation of apparent crystalline size of the (002) plane cellulose films with (a) the degree of polymerization, (b) the cellulose concentration of the solution, and (c) the NMMO concentration in the coagulation bath.

Figure 9 Variation of Bragg spacing of the (002) plane of the cellulose films with (a) the degree of polymerization, (b) the cellulose concentration of solution, and (c) the NMMO concentration in the coagulation bath.

$2\theta = 11.8°$ for (101), but peaks at $20–22°$ for $(10\bar{1})$ and (002) were not resolved completely. After separating the unresolved peak, the film showed two nearly superimposed diffraction peaks at $2\theta = 20.7°$. From this result we believe the crystal structure of the film sample is cellulose III, which has a superimposed peak at $2\theta = 20.7°$ for $(10\bar{1})$ and (002). On the other hand, the fiber sample had completely resolved peaks at $2\theta = 20°$ and $21.7°$, which are a typical diffraction pattern for cellulose II. Figures 4 and 5 show trends similar to Figure 3.

Figure 6 shows resolved X-ray diffractograms of V81-1, V81-4, and V81-7. Measured and resolved diffractograms had similar intensities and angles, which strongly supported the result of Figure 4(b). However, judging from the slightly resolved angles of the diffraction peaks of $(10\bar{1})$ and (002) for a higher cellulose concentration, cellulose I and II were coexisting. Therefore, the transformation of cellulose I into cellulose II during regenerated cellulosic fiber production occurred through multistep transformations, depending on processing conditions. This result was

caused by the interaction between cellulose and NMMO, as well as mechanical functioning, such as spinning, drawing, and thermal treatment. We elucidate in detail the shift of the maximum diffraction angle for the amorphous region and the transformation of the crystal structure in the case of the coexistence of cellulose II and III structures.

The changes of the degree of crystallinity and apparent crystalline size with DP_w, cellulose concentration, and NMMO concentration in a coagulation bath were shown (Figs. 7, 8) by calculating the resolved integral intensity of each crystal. Even the degree of crystallinity and apparent crystalline size might be different, depending on the peak separation method; our results were considerably well matched with the known data. The degree of crystallinity was slightly decreased with the DP_w and concentration of cellulose as shown on Figure 7(a,b). Cellulose with semirigid chains can increase its degree of crystallinity just by controlling the spinning condition in the same way that polyethylene with higher molecular weight and flexible chains does. However, we believe the degree of crystallinity of cellulose without applying the spinning and drawing processes

Figure 10 Variation of density of the cellulose films with (a) the degree of polymerization, (b) the cellulose concentration of solution, and (c) the NMMO concentration in the coagulation bath.

V81-1

V81-4

V81-2

V81-7

V81-3

V81-1 (x 30,000)

Figure 11 SEM pictures of cellulose films.

was decreased with the DP_w because of the increase of chain entanglement and consequent interruption of free chain mobility during coagula-

tion. We also believe the increase of cellulose concentration affected the chain entanglement, showing the same trend as above.

As shown on Figure 7(c), the degree of crystallinity was increased with NMMO concentration, because the slower diffusion of NMMO from inside the film to the coagulation bath and the consequent slower coagulation occurred with concentration of NMMO in the coagulation bath. The change of apparent crystalline size based on (002) showed a trend similar to that of the degree of crystallinity (Fig. 8). We believe this result is also closely related to the number of entanglements and the chain mobility.

Figure 9 shows the change of Bragg spacing of (002) with DP_w, cellulose concentration, and NMMO concentration in the coagulation bath. These factors did not affect the Bragg spacing without applying mechanical treatments.

Density Change

For the preparation of fiber and film, polymer concentration and coagulation conditions are very important factors to control their densities,[12] which are closely related to fibril shape and closeness of the inside of the products. Figure 10 shows the changes of film density with cellulose DP_w, cellulose concentration, and NMMO concentration in the coagulation bath. Even though it is generally known that the density is increased with the DP_w of the polymer or dope concentration due to the closeness of the inside of fiber in the wet spinning process,[12] no significant change was detected in our study as shown in Figure 10. This result suggests that density decrease caused by the degree of crystallinity reduction is compensated by the density increase caused by the inside of the fiber being closer. In addition, the density was increased with NMMO concentration. Generally, the microstructures and morphologies of film or fiber samples are generally affected by the relative diffusion rates for the coagulation medium (water) and dope solvent. Moreover, this means increasing density is caused by the homogeneous coagulation to reduce pore size or a defect inside of the film due to the slower diffusion rate of NMMO from inside the film to outside if the concentration of NMMO in the coagulation bath is increased.

Morphology

Figure 11 displays SEM photographs of cross sections of films prepared under different concentrations of NMMO or cellulose. Although the elementary unit structure to form morphologies of natural and regenerated cellulose was known to be slightly different, our cellulose samples sustained microfibril structures judging from the result of Frey–Wyssling, who divided fibril structures of cellulose into three types with the diameter of cross section: 50–60 Å for an elementary fibril, 100–400 Å for a microfibril, and over 1000 Å for a macrofibril.[13] The size of the fibril was decreased with homogeneity and close packing cross section with higher NMMO concentration, but no change was detected with the concentration of the cellulose. This is well matched with the result from the density change experiment. Therefore, we believe the main factor to control fibril formation and close packing is the concentration of NMMO in the coagulation bath, not the cellulose itself.

CONCLUSION

We obtained the following results from the study on the effects of the DP_w and solution concentration (wt %) of cellulose and the concentration (wt %) of NMMO in a coagulation bath on the fine structures of cellulosic fiber, such as crystal structure and fibrillation, in a cellulose/NMMO/H_2O system.

The transformation of a cellulose I structure into a cellulose II structure during regenerated cellulosic fiber production occurred through multistep transformations, depending on the processing conditions.

The degree of crystallinity was slightly decreased with DP_w and the concentration of cellulose, but increased with that of NMMO.

The diameter of the microfibril decreased with the concentration of NMMO, but no change was detected with cellulose concentration. Similar to the morphology observation, no significant density change with DP_w and concentration of cellulose was detected, but the density was increased with the concentration of NMMO in the coagulation bath.

Finally, the main factor to control fibril formation and close packing is believed to be the concentration of NMMO, not of the cellulose itself.

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