

Physical Agglomeration Behavior in Preparation of Cellulose-*N*-Methyl Morpholine *N*-oxide Hydrate Solutions by Simple Mixing

Dong Bok Kim,¹ Seong Mu Jo,² Wha Seop Lee,² James Jungho Pak¹

¹School of Electrical Engineering, Korea University, Anam-Dong, Sungbuk-ku, Seoul 136-791, Korea

²Polymer Hybrid Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

Received 27 December 2002; accepted 29 February 2004

DOI 10.1002/app.20607

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The different melting temperatures of *N*-methyl morpholine *N*-oxide (NMMO) hydrates in the cellulose–NMMO hydrate solution may be explained by the rather different crystal structures of NMMO hydrates, which are determined by the amount of the hydrates. The preparative process of cellulose–NMMO hydrate solution may result in cellulose structural change from cellulose I to cellulose II, depending on the amount of the hydrate. Mixtures of cellulose and NMMO hydrate in a blender was changed from the granules to slurry with increasing mixing time at 60–70°C, which is below the melting point of the NMMO hydrate. In the case of 15 wt % cellulose–NMMO hydrate granules, which were made by mixing for 20 min, the melting points of various NMMO hydrates were obtained as 77.8°C ($n = 0.83$), 70.2°C ($n = 0.97$), and 69.7°C ($n = 1.23$), respectively, depending on the hydrate number. However,

the melting points of cellulose–NMMO hydrate slurry and solution were shifted lower than those of cellulose granules, while the mixing time of slurry and solution are 25 and 35 min, respectively. These melting behaviors indicate instantaneous liquefaction of the NMMO hydrate and the diffusion of the NMMO hydrate into cellulose during mixing in a blender. When cellulose was completely dissolved in NMMO hydrate, the crystal structure of cellulose showed only cellulose II structure. In the cellulose–NMMO products of granules or slurry obtained by high-speed mixing, which is a new preparation method, they still retained the original cellulose I structure. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1687–1697, 2004

Key words: cellulose; *N*-methyl morpholine *N*-oxide; agglomeration; solution; lyocell

INTRODUCTION

Viscose processes have been most widely used in manufacturing rayon fibers. The cellulose fibers produced by the viscose process are called “rayon fiber,” which means regenerated cellulose fiber. They are prepared via two chemical steps: blocking, and regeneration of the hydroxyl groups in the cellulose molecule. The viscose processes require the use of toxic chemicals such as carbon disulfide, leading to an environmental problem. Furthermore, they have low productivity and they are intensive energy-consuming processes.

Franks and Varga found that *N*-methyl morpholine *N*-oxide (NMMO) can dissolve cellulose without any chemical treatment.¹ Varga and other researchers also reported that various concentrated cellulose solutions were obtained from an aqueous NMMO solution containing cellulose, depending on effective preparative methods of cellulose solutions.^{2–4} Recently, more production techniques of cellulose fibers were developed

and reported by Courtaulds (Tencel process),⁵ KIST (Cocel process),⁶ TITK-Zimmer (Alceru process),⁷ Lenzing (Lyocel process),⁸ and Akzo-Courtaulds (New-Cell process).⁹ Solvent-spun cellulose fibers obtained by these processes were defined as a generic name, lyocell, in 1992, by the American Federal Trade Commission.¹⁰

Four typical different preparative methods of the cellulose solutions have been reviewed and summarized below. McCorsely et al. reported that the cellulose solution could be prepared by swelling cellulose in 78 wt % NMMO hydrate (degree of hydration, $n = 1.65$), after which excess water was eliminated by evaporation.^{11–14} In 1992, Zikeli et al. reported that cellulose was swollen in 60 wt % aqueous NMMO, and it was passed through a screw extruder with a pan-shaped blade. Here, water in the cellulose solution is evaporated through holes, and the cellulose solution is heated in a thin film evaporator.¹⁵ McCorsely et al. again reported a different preparative method in which a cellulose pulp sheet was used, and it was swollen in 85 wt % NMMO hydrate.¹⁶ They also tried to make cellulose solution by simply mixing cellulose and NMMO hydrate powders, followed by passing them through an extruder at 85–95°C.¹⁷

Correspondence to: J. J. Pak (pak@korea.ac.kr).

Lee et al. made cellulose solution by putting cellulose and NMMO hydrates into a blender at room temperature, then mixing them at 50–60°C, and passing them through a single screw extruder.¹⁸ The premixture of cellulose and NMMO hydrate in a blender showed a round shape, and this premixture was shown to be easily conveyed. It was also shown that this premixture can prevent the degradation of the molecular weight of the cellulose because it can be made within 20 min.¹⁸

Preparative methods of cellulose solution in NMMO solvent can be classified as the evaporation method and direct method. In the evaporation method, cellulose in NMMO hydrate with $n = 1.65$ is swollen, and then it is concentrated to obtain an NMMO hydrate of $n = 1.0$ or $n < 1.0$ by removing water in an evaporator.^{19,20} This method requires a long process time for the elimination of excess water, and tends to degrade the cellulose and NMMO hydrate. In the direct method, which was explained previously,¹⁸ NMMO hydrate with $n = 1$ is used to produce the cellulose solution.

During cellulose dissolving, a small amount of water included in the NMMO swells cellulose fibrils so that NMMO molecules can penetrate them. Cellulose is only swollen in NMMO hydrate when with $n = 1.65$, but cellulose is swollen and then dissolved consecutively when $n < 1.65$.¹ The NMMO hydrate with $n < 1.5$ can completely dissolve cellulose only at temperatures higher than its melting temperature (T_m , 78°C in the case of NMMO monohydrate with $n = 1.0$).²¹ However, it takes a long time to dissolve cellulose because the cellulose solution has a higher viscosity when $n < 1.5$. When the cellulose solution is maintained at a high temperature ($>T_m$) for such a long time, thermal decomposition of cellulose takes place in the absence of an antioxidant such as *n*-Propyl gallate. The cellulose solution is generally very viscous and thermally unstable.²² For example, the degree of polymerization (DP_w) of cellulose in NMMO monohydrate without any antioxidants drops from 600 to 200 in 10 min at 130°C.²³ Also, the cellulose in NMMO hydrate experiences morphological and structural transformations depending on the water content in the NMMO.²⁴

Recently, we reported that the cellulose solution formed pelletized granules without complete dissolving or swelling of the cellulose in which NMMO hydrate penetrated into the cellulose. Solid–solid blending and milling of cellulose and NMMO powders in a blender, while mixing at high speed, yielded an agglomerated cellulose–NMMO. These pelletized granules can be dissolved and solidified rapidly. Generally, solidification of a cellulose solution or swollen cellulose in liquid NMMO is progressed very slowly. Also, the cellulose solution in NMMO hydrates for conventional lyocell fiber spinning is prepared by dis-

solving the swollen cellulose in NMMO hydrate with the removal of excess water, which takes a long time.^{25,26}

This article describes the physical agglomeration behaviors in preparation of cellulose–NMMO hydrate particles by simple mixing, and the structural change of cellulose in a new lyocell fiber processing.

EXPERIMENTAL

Materials

The powder NMMO containing 3 to 22 wt % water was prepared by removing extra water from NMMO/H₂O (50 wt %/50 wt %), which is available from Aldrich Co. (Milwaukee, WI). Aqueous 50 wt % NMMO was condensed in a rotary evaporator at 60–100°C for 3 h at reduced pressure (10^{-3} – 10^{-4} Torr) to various desired water levels. The condensed NMMO was solidified at room temperature, and then it was stored in a dry bottle in nitrogen atmosphere.

The cellulose samples, Rayonex-P and Cellunier-F, were obtained from ITT Rayonier Co. (USA), whose weight-average degree of polymerization was 975 [(IV) = 4.80] and 670 [(IV) = 3.43], respectively. These cellulose samples contained less than 5 wt % water content at room temperature. These cellulose samples were dried in a vacuum oven at 10^{-3} – 10^{-4} Torr, 80°C for 24 h prior to use. The water content of the dried cellulose was below 0.03 wt %.

Measurement of molecular weight of cellulose

To begin with, 1 mol cupriethylene diamine (CUENE) solution was prepared according to ASTM-D 539-51T. The ratio of ethylene diamine to copper ranged from 1.95 to 2.0.

The cellulose solution in NMMO hydrate was immersed in distilled water to eliminate NMMO from the solution. After removing NMMO, the cellulose was dried for 4 h at 10^{-3} – 10^{-4} Torr and 105°C. Cellulose specimens of 100, 200, 300, and 400 ± 0.3 mg were placed in 50 mL of distilled water and then the solution was stirred. Into this bottle, 50 mL of the 1-mol CUENE solution was added and stirred to make a homogeneous solution in nitrogen atmosphere. The solution was filtered through a glass filter in nitrogen atmosphere and the flow time was measured with an Ubbelohde type viscometer (No. 1 C503, No.1 H58; Fischer Co.) at $25 \pm 0.1^\circ\text{C}$ (ASTM-D 1795-62).

Preparation of cellulose–NMMO solution

Powder cellulose–NMMO granules and slurry made with a blender

Cellulose pulp sheets and powder NMMO with specific water content were pulverized and homogenized

TABLE I
Summary of Experimental Conditions of Various Preparative Methods of Cellulose–NMMO Hydrate Samples

Sample code	Experimental conditions			
	Shape type	Temperature (°C)	Time (min)	Equipment type
A	Granules	60	10–20	Blender
B	Slurry	65	20–25	Blender
C	Swollen	70	30	Blender
D	Solution	110	5	Extruder
E	Solution	90	180	Batch reactor

by mixing them in a high-speed blender. The blending was carried out in a blender having knife-edged blades at 1500 rpm.¹⁸ During high-speed blending and milling, the generated heat was removed by circulating cooling water outside of the blender to keep the temperature of the mixture below 70°C. When mixing for 20 min at 60°C in a blender, the cellulose pulp sheets and powder NMMO were converted round granules (sample A). This mixing condition was proven to be sufficient for powder NMMO to diffuse into cellulose and to agglomerate without any swelling or dissolving of cellulose. When the mixing time is 20–25 min at 65°C, cellulose pulp sheets were converted to slurry of cellulose–NMMO hydrate (sample B). When the mixing time is increased to 20–25 min, the formation of the cellulose–NMMO product was changed from granules to sticky slurry with high viscosity. Both cellulose–NMMO granules (A) and slurry (B) exhibited fast solidification behavior. Cellulose–NMMO granules were solidified within a few seconds, while slurry was solidified within a few minutes at room temperature.

Fine cellulose powder was obtained by using a blender with high speed mixing at 1500 rpm. When this fine cellulose powder and liquid NMMO hydrate were mixed at 70°C for 30 min, the liquid NMMO hydrate was impregnated into the cellulose powder, resulting in cellulose–NMMO hydrate slurry with specific water content homogeneously. This cellulose–NMMO hydrate slurry has lower viscosity, and the cellulose in the slurry is in a swollen state. Because of this swollen cellulose in the slurry, this swollen cellulose–NMMO hydrate slurry exhibited slow solidification behavior at room temperature. This swollen slurry required a few hours to be solidified (sample C).

Condensed cellulose–NMMO solutions made by using processing equipments

A homogeneous cellulose solution (sample D) was prepared by dissolving the solidified cellulose–NMMO granules (A) in a single-screw extruder ($L/D = 33$) equipped with degassing units, where L and D are length and diameter of the single-screw extruder, respectively. Temperature of the extruder melting

zone was set to 110°C, and passing time through the extruder was 5 min when the screw was set to 10 rpm. Concentrations of cellulose in the cellulose–NMMO solutions that were made with this extruder were 10 and 15 wt %.

To compare the solution preparation time of the direct method (D) with that of the evaporation method, a cellulose solution was prepared by the evaporation method (sample E). Cellulose was swollen in 78 wt % NMMO hydrate ($n = 1.65$), and excess water was eliminated by evaporation at 10^{-3} – 10^{-4} Torr, at 90°C for more than 3 h. Concentration of cellulose in this solution was 10 wt %. The solution was prepared by using a beaker-type batch reactor with stirring system having four blades.

Table I describes the various preparative methods of cellulose samples A through E.

Measurements of physical properties

The hydrate amount in NMMO was determined using a method suggested by Fischer.²⁷ The measured water content of 3 to 22 wt % in the NMMO hydrates corresponded to the values of n of 0.23 to 1.65.

The thermal properties of NMMO hydrates, cellulose–NMMO granules, cellulose–NMMO slurry, and cellulose–NMMO solution were measured by using the Perkin-Elmer differential scanning calorimeter (DSC) 7 in a nitrogen atmosphere. The DSC was equipped with a stainless steel capsule to withstand high pressure generated by water steam. The temperature scan rate range was set to 2, 5, or 10°C/min. Before the DSC measurements, the instrument was calibrated according to the standard DuPont procedure.

Optical microscopic observation of the samples was performed by using Nikon polarizing microscope (Type 104) equipped with a camera and hot stage (Toledo Co.). Temperature of the samples was measured after placing the sample between parallel slide glasses. The temperature of the hot stage on the optical microscope ranged from room temperature to 120°C.

Wide-angle X-ray diffraction (WAXD) patterns of the samples were obtained by using MX18 X-ray dif-

fractometer (Mac Science Co.) with CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$).

RESULTS AND DISCUSSIONS

Change of molecular weight of cellulose in solution during swelling and dissolving

The NMMO hydrate with $n < 1.5$ can completely dissolve cellulose only at temperatures higher than its melting temperature (T_m , 78°C in the case of NMMO monohydrate with $n = 1.0$).²¹ However, it takes a long time to dissolve cellulose because the cellulose solution has a higher viscosity when $n < 1.5$, and to reduce the water content in the NMMO hydrate. Also, when the cellulose solution is maintained at a high temperature ($>T_m$) for a long time, thermal decomposition of cellulose takes place in the absence of an antioxidant such as *n*-Propyl gallate. This can be explained by a reduction of DPw of cellulose with dissolution time.

Two cellulose specimens were taken from the dissolution system at the desired time and its specific viscosity in CUENE was measured by using a Ubbelohde viscometer at 25°C . Table II shows variation of intrinsic viscosity (IV) in dL/g and DPw of the cellulose specimens at 10 wt % concentration with dissolution time. The molecular weight of cellulose is determined by the following equation,²⁸ which indicates that the intrinsic viscosity is related to the DPw.

$$\text{IV} = 0.98 \times 10^{-2} \text{DPw}^{0.9}$$

When using the evaporation method, a notable reduction of molecular weight of the cellulose is observed. Thus, it can be further determined that a cellulose–NMMO solution made by the direct method with a single-screw extruder is more useful than that made by evaporation method.

TABLE II
Variation of Molecular Weight of Cellulose (Rayonex-P) and Intrinsic Viscosity during Dissolving in NMMO Hydrate with $n = 1.0$ (Cellulose Content: 10 wt %)

	Evaporation method ^a		Direct method ^b	
	DPw	IV(dL/g)	DPw	IV(dL/g)
Cellulose pulp	974.77	4.80	974.77	4.80
Solution	708.08	3.60	851.55	4.25
1 h aging (at 90°C) ^c	673.20	3.44	829.33	4.15

^a Sample E method in Table I—solution preparative time: 180 min.

^b Sample D method in Table I—solution preparative time: 35 min.

^c Sample obtained by heat treatment of 1a and 2b solution samples in oven.

Thermal properties of various NMMO hydrates

The condensed NMMO hydrates of $n = 1.35$ – 0.23 have water content enough to dissolve cellulose completely. NMMO has been known to form anhydrous NMMO or one of two stable crystalline hydrates that are NMMO/ H_2O (monohydrate, $n = 1.0$) and NMMO/ $2.5\text{H}_2\text{O}$ ($n = 2.5$).²⁹ These NMMO and NMMO hydrates have quite different crystal structures. The NMMO hydrates are frequently explained as a series of binary compound consisting of two components and each compound acts as a single substance when reacting with cellulose.

DSC heating thermograms of various NMMO hydrates having specific water content, which were obtained by the removal of excess water from aqueous 50 wt % NMMO ($n = 3.76$), are presented in Figure 1. The NMMO hydrates of 82.05 ($n = 1.35$), 84.97 ($n = 1.13$), 88.03 ($n = 0.9$), 88.96 ($n = 0.83$), 94.02 ($n = 0.45$), and 96.94 wt % ($n = 0.23$) condensed from aqueous 50 wt % NMMO are composed of two homogeneous mixtures of anhydrous NMMO ($n = 0$) and NMMO/ H_2O ($n = 1.0$), or NMMO/ H_2O ($n = 1.0$) and NMMO/ $2.5\text{H}_2\text{O}$ ($n = 2.5$).³⁰ As shown in the DSC heating curves of the condensed NMMO hydrates having less water content than NMMO/ H_2O ($n = 0.9$), solid–solid phase transition point and the depressed melting point of anhydrous NMMO in 94.02 wt % ($n = 0.45$) condensed NMMO hydrate were observed at about 98 and 140°C at heating rate of $5^\circ\text{C}/\text{min}$, respectively. However, those in $n = 0.9$ condensed NMMO hydrate did not exhibit two melting points, but showed a single melting point. The melting points in $n = 0.83$ condensed NMMO hydrate are more prominent with the NMMO hydrate with smaller values of n , verifying the coexistence of various crystal structures.³⁰ In the case of $n = 1.13$ and $n = 1.35$, the endothermic peaks of NMMO hydrates DSC curves were observed at 39°C at heating rate of $2^\circ\text{C}/\text{min}$. The endothermic peaks and the shape of DSC curves are almost identical those reported previously by other researchers.²¹

Figure 1 shows that the melting points of NMMO hydrates increase with decreasing water contents or with increasing heating rate. This may be attributed to different crystal structures because the NMMO hydrates crystal structures are different depending on the amount of water contents. Figure 2 shows an NMMO molecule, crystal structures of NMMO, and two stable NMMO hydrates. Anhydrous NMMO and NMMO hydrates have the crystal structures with the following lattice constants: axis $a = 9.87$, $b = 6.62$, $c = 5.11 \text{ \AA}$, and $\beta = 111.54^\circ$ (anhydrous NMMO, $n = 0$); $a = 25.48$, $b = 6.04$, $c = 9.19 \text{ \AA}$, and $\beta = 99.88^\circ$ (NMMO/ H_2O , $n = 0$); $a = 12.8$, $b = 6.5$, $c = 21.91 \text{ \AA}$, and $\beta = 109.99^\circ$ (NMMO/ $2.5\text{H}_2\text{O}$, $n = 2.5$). All of them are monoclinic lattice unit cells.²⁹

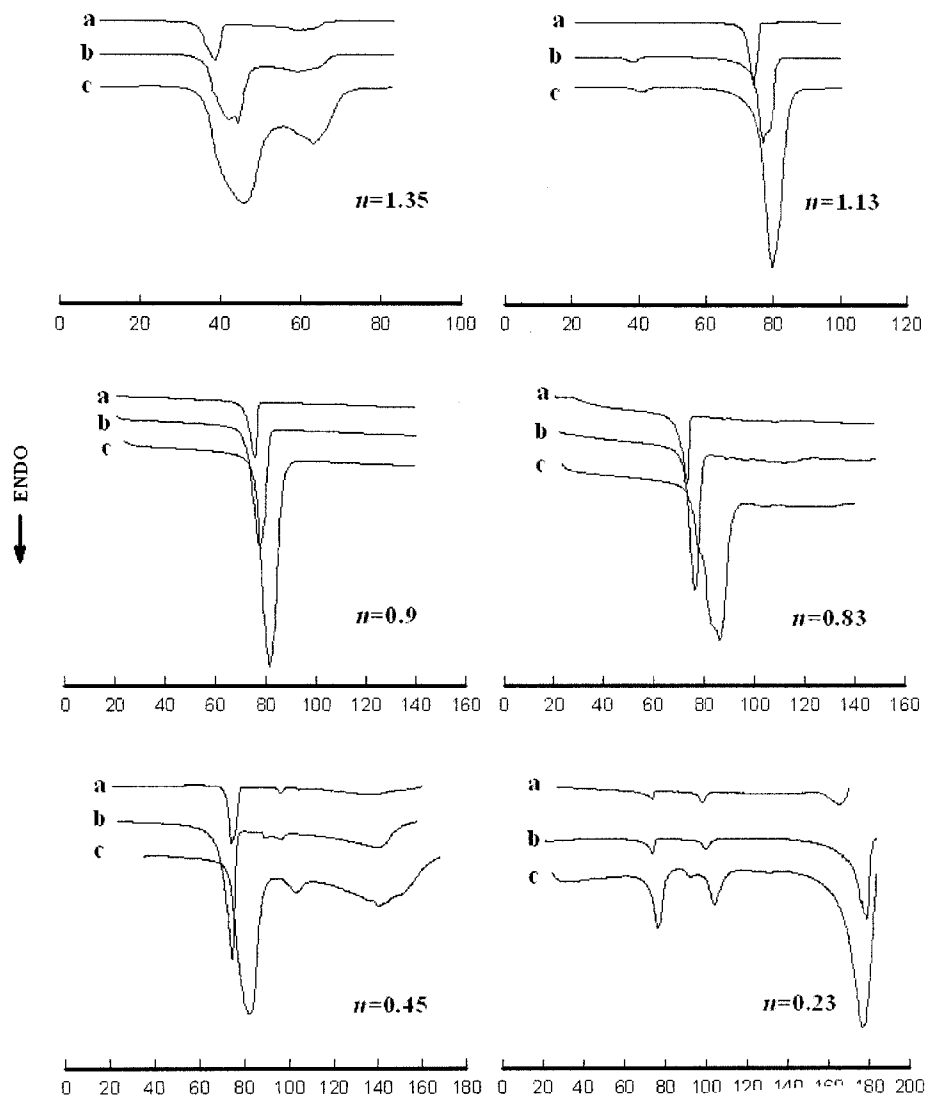


Figure 1 DSC heating thermograms of various condensed NMMO hydrates having specific contents of water [heating scan rate: (a) 2, (b) 5, and (c) 10°C/min].

Thermal properties of cellulose–NMMO hydrate granules and slurry

In general, when making cellulose solution with higher than 5 wt % concentration, specific volume of powder cellulose sample is larger than that of powder NMMO hydrate. Therefore, if the powder cellulose is included in a blender after melting powder NMMO hydrate first, then it is impossible to obtain uniform cellulose–NMMO hydrate solution because the melt NMMO hydrate can dissolve only small portion cellulose having higher volume. Therefore, when powder cellulose and powder NMMO hydrate are simply mixed at a temperature below melting point by high-speed mixing, NMMO hydrates diffuse into cellulose and reduce cellulose volume by pulling the cellulose molecules more closely inside the cellulose. Therefore, the relative volume of NMMO hydrates is larger than

cellulose, and hence, they can be mixed more uniformly. Heating this mixture at a temperature above the melting point of NMMO hydrates can dissolve cellulose homogeneously.

To make a uniform cellulose–NMMO hydrate solution, the mixing temperatures for obtaining agglomerated sample as granules and slurry were set at 60 and 65°C, which are below the melting point (80.9°C) of NMMO hydrate with $n = 0.97$ at heating scan rate of 10°C/min. Powder cellulose–NMMO granules were produced by high-speed mixing in a blender, while keeping the mixture at a temperature high enough for NMMO to diffuse into the cellulose without complete dissolving or swelling of the cellulose.

Figure 3 shows an optical micrograph of a simple homogeneous mixture of powder cellulose and NMMO hydrate without high-speed mixing. Figure 3

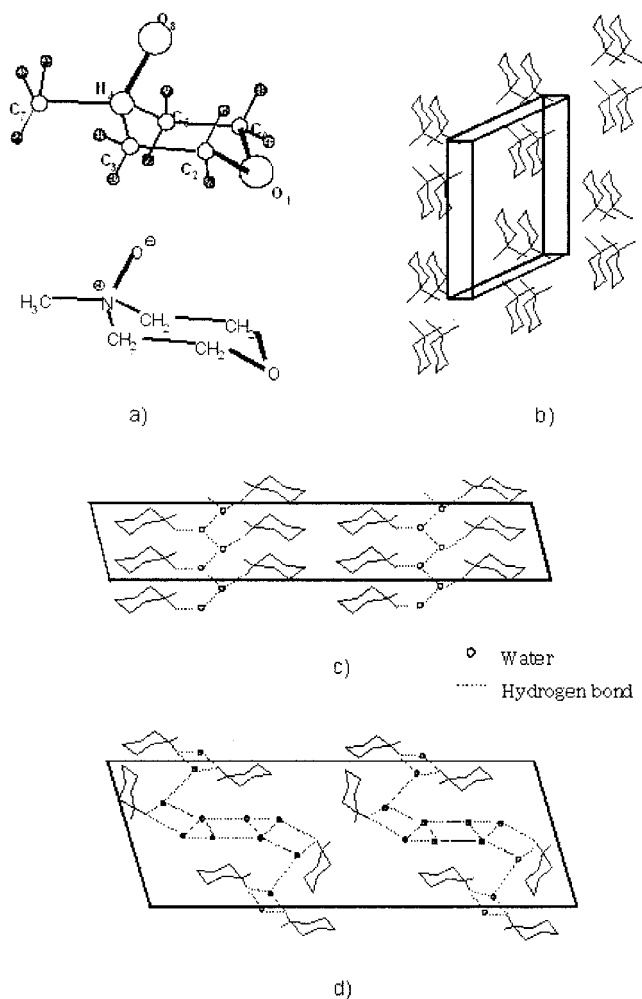


Figure 2 Schematic drawings of (a) NMMO molecule, crystal structures of (b) anhydrous NMMO ($n = 0$), (c) NMMO/ H_2O ($n = 1.0$), and (d) NMMO/ $2.5 \text{ H}_2\text{O}$ ($n = 2.5$).²⁹

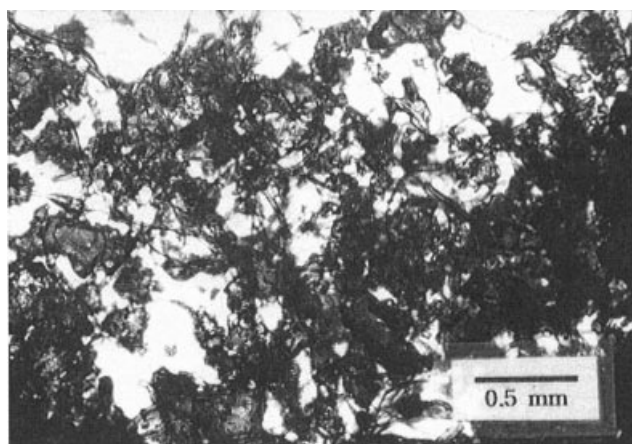
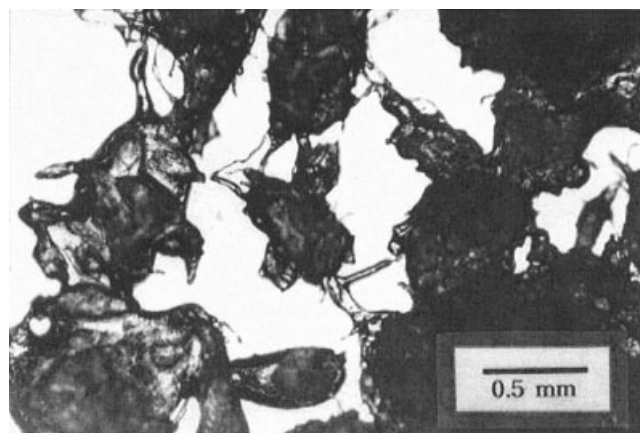
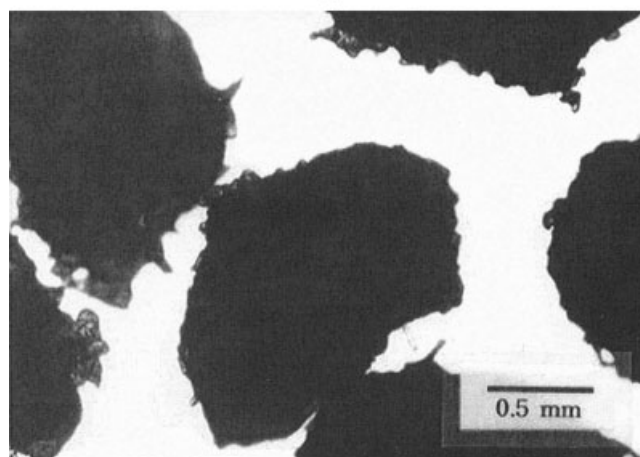


Figure 3 Optical micrograph of a simple homogeneous mixture of powder cellulose and NMMO hydrate having a water content of 12.9 wt % ($n = 0.97$).



(a)



(b)

Figure 4 Optical micrograph of powder cellulose-NMMO hydrate granules formed by high speed mixing at 60°C of powder cellulose and NMMO hydrate having a water content of 12.9 wt % ($n = 0.97$), mixing time: (a) 10 and (b) 20 min.

indicates that this simple mixture of cellulose-NMMO hydrate does not have agglomerated granules at all. When this simple mixture is additionally mixed by high-speed blending, it starts to form granules. Figure 4(a) shows an optical micrograph of powder cellulose-NMMO granules formed by high-speed mixing at 60°C for 10 min. Figure 4(b) shows that the produced granule size increase as the mixing time increase to 20 min from 10 min. When the mixing time was extended 5 min more at 65°C , the granules changed to form sticky slurry completely, as shown in Figure 5. This cellulose-NMMO slurry is very adhesive and viscose that indicates a homogeneous dispersion and penetration of NMMO into the cellulose can be achieved at higher temperature and longer mixing time than the granules preparation conditions.

The DSC heating curves for the cellulose-NMMO granules formed by high-speed mixing are shown in Figure 6. Their melting behaviors are similar to those

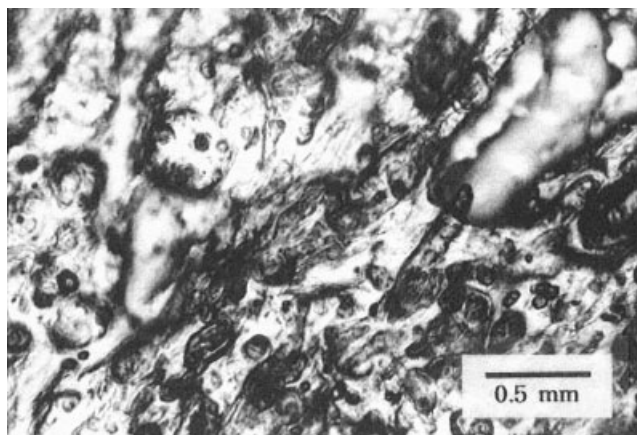


Figure 5 Optical micrograph of viscose cellulose–NMMO hydrate slurry formed by high speed mixing at 65°C of powder cellulose–NMMO hydrate having a water content of 12.9 wt % ($n = 0.97$), mixing time is extended 5 min more than Figure 4(b) at 60°C.

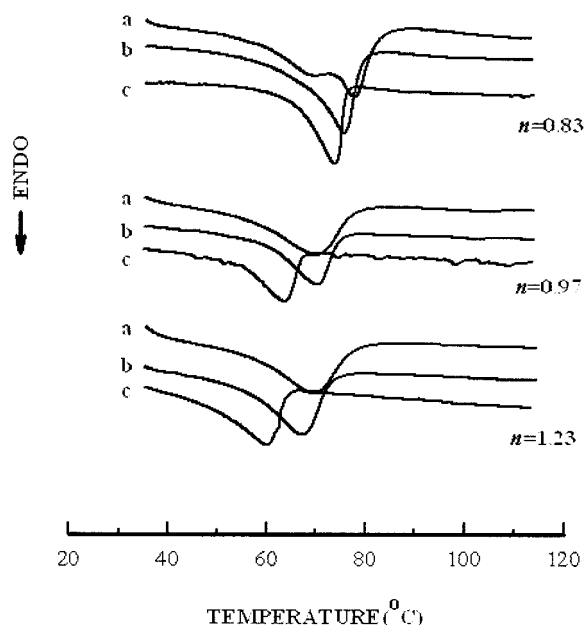


Figure 6 DSC heating curves of powder cellulose–NMMO hydrate granules (A) formed by high speed mixing of cellulose and powder NMMO hydrates [cellulose content: 15 wt %, heating scan rate: (a) 10, (b) 5, and (c) 2°C/min].

of the condensed NMMO hydrates. The melting temperature increased with decreasing water content in the NMMO hydrate or with increasing heating scan rate. All DSC thermograms in this figure show the lower melting peaks than those of the NMMO hydrates of Figure 1, and broader thermograms.

Table III describes the melting point depression of various cellulose–NMMO hydrates samples depending on the cellulose concentration and the water content of NMMO hydrate at heating scan rate of 5 and 10°C/min. When the cellulose concentration is 12 wt % and the water content of NMMO hydrates increases, the melting temperature of NMMO hydrates in cellulose–NMMO samples were shown to decrease (from A to D). The melting point depression depended strongly on the water content of NMMO hydrates rather than the effect of the cellulose concentration in the sample.

Cellulose–NMMO granules were solidified rapidly within a few seconds, while agglomerated slurry was solidified within a few minutes at room temperature. It seemed that the existence of cellulose in the NMMO

hydrate samples may impede the crystallization of NMMO hydrates, as a result of a retarded diffusion of the crystallizing species.³¹ According to the results of Wunderlich³² and Chanzy et al.,²¹ the inclusion of cellulose chains within the solvent crystallites will create defects, which will have an additive effect on the the melting point depression of these crystallites. Therefore, the above melting point depressions in cellulose–NMMO samples indicate the instantaneous melting of powder NMMO hydrate and the diffusion of NMMO hydrate throughout the cellulose during high-speed mixing. In case of 15 wt % cellulose concentration with high-speed mixing, the melting temperatures of NMMO hydrates in cellulose–NMMO hydrate granules and slurry are higher than the melting temperature of cellulose–NMMO hydrate solution as shown in Table III.

TABLE III
Melting Temperature Depression of Various Cellulose–NMMO Hydrate Samples at the Heating Scan Rate of 5 and 10°C/min

Concentration (wt %)	Melting point (°C)							
	12				15			
Heating scan rate (°C/min)	5		5		10		10	
Preparative method	A	B	A	B	A	B	C	D
$n = 0.83/81.3^a$	75.9	75.3	76.3	75.7	77.8	—	—	—
$n = 0.97/80.9^a$	70.5	64.2	73.8	69.7	70.2	69.5	69.2	67.4 (58.6) ^b
$n = 1.23/74.7^a$	65.2	63.2	67.4	65.9	69.7	65.9	64.3 (56.0) ^b	—

^a Melting peaks of NMMO hydrate at heating rate of 10°C/min.

^b Shifted lower melting peaks of cellulose–NMMO hydrate sample.

Thermal properties of cellulose–NMMO hydrate solution

When the cellulose concentration is 15 wt % in a cellulose–NMMO hydrate slurry with $n = 0.83$ as shown in Table III, its melting peak temperature was 75.7°C at a heating scan rate of 5°C/min, which is a slightly lower than the melting peak (76.3°C) of granules. Figure 7 shows the DSC heating curves of cellulose–NMMO hydrate samples made by using various preparative methods. When the hydration number of NMMO hydrate is $n = 0.97$ and the heating scan rate is 10°C/min, the melting peak temperature of cellulose–NMMO hydrate slurry (B) was 69.5°C. This melting peak temperature goes remarkably lower than that of cellulose–NMMO hydrate slurry (B) as the sample preparing time increases (C, D). In case of the cellulose–NMMO hydrate solution (D), the melting peak temperature of NMMO hydrate was 58.6°C.

Figure 8 shows the DSC heating curves of cellulose–NMMO hydrate samples produced by using various preparative methods when $n = 1.23$. These curves B and C have slightly narrower ranges between the start melting temperature and end melting temperature than those of Figure 7. The measured melting peak temperature of the swollen cellulose–NMMO hydrate (C) was lower than that of the slurry (B), and the melting curve shape of (C) was broader than that of (B). The DSC heating curve of the sample C in Figure 8 shows two melting peaks at 56.0 and 64.3°C. It is believed that the lower melting peak at 56.0°C occurs due to the recrystallization of a small position of the

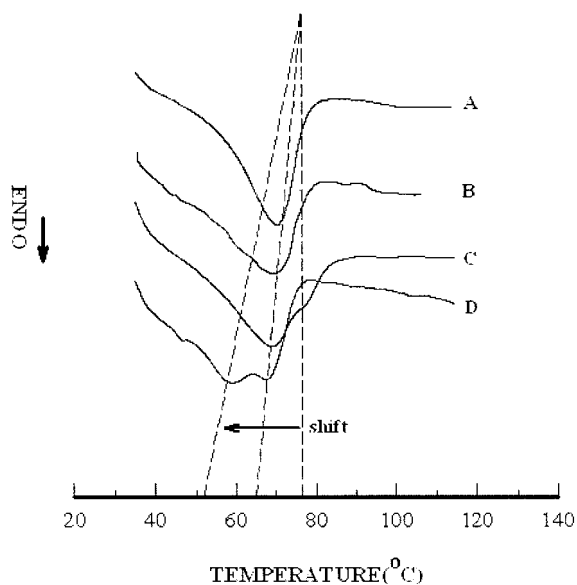


Figure 7 DSC heating curves of powder cellulose–NMMO hydrate granules (A), cellulose–NMMO hydrate slurry (B), swollen cellulose–NMMO hydrate (C), and solidified cellulose–NMMO hydrate solution (D) (cellulose content: 15 wt %, heating scan rate: 10°C/min, $n = 0.97$).

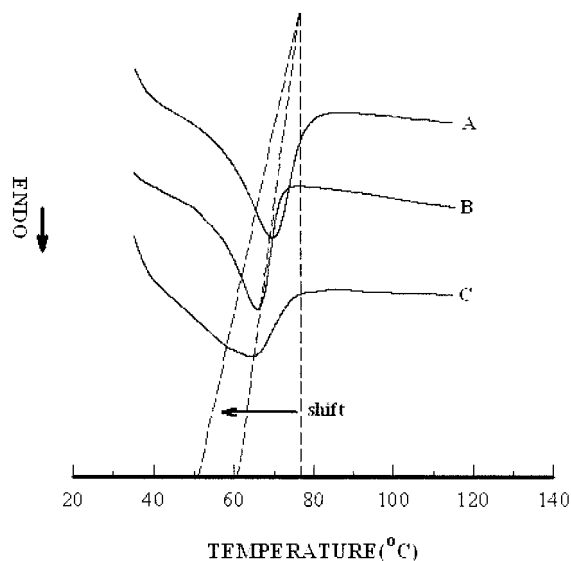


Figure 8 DSC heating curves of powder cellulose–NMMO hydrate granules (A), cellulose–NMMO hydrate slurry (B), and swollen cellulose–NMMO hydrate (C) (cellulose content: 15 wt %, heating scan rate: 10°C/min, $n = 1.23$).

NMMO hydrate molecules, which were not crystallized in the reheating process of the DSC measurement.

All cellulose–NMMO hydrate samples made in a blender were stored at room temperature before use for lyocell processing or DSC measurement. When the solidified cellulose–NMMO hydrate samples were reheated up to its melting point in the DSC, the NMMO hydrate crystals in the swollen cellulose–NMMO hydrate sample were recrystallized into a more organized crystal structure. This recrystallization can be inferred from that the lower melting point of the swollen cellulose–NMMO hydrate sample (C) with $n = 1.23$ appeared at 56.0°C, which is the melting point of the NMMO hydrate. From the DSC heating curves of the swollen cellulose–NMMO hydrates (C), it was observed that the lower melting peak of the NMMO hydrate with $n = 0.97$ (Fig. 7) was not observed, while a very small peak of the lower temperature of the swollen cellulose–NMMO hydrate with $n = 1.23$ (Fig. 8) appeared at 56.0°C. It is believed that this difference results from the solubility difference of the NMMO hydrate, depending on the hydrate number (n) because the hydrate amount bonded to NMMO at $n = 1.23$ is more than that at $n = 0.97$.³³

Change of the crystal structure of cellulose in an NMMO hydrate by simple mixing

We investigated the structural change of cellulose in cellulose–NMMO hydrates during mixing in a blender. Figure 9 shows the X-ray diffractions of simple mixture of cellulose and NMMO hydrate, powder

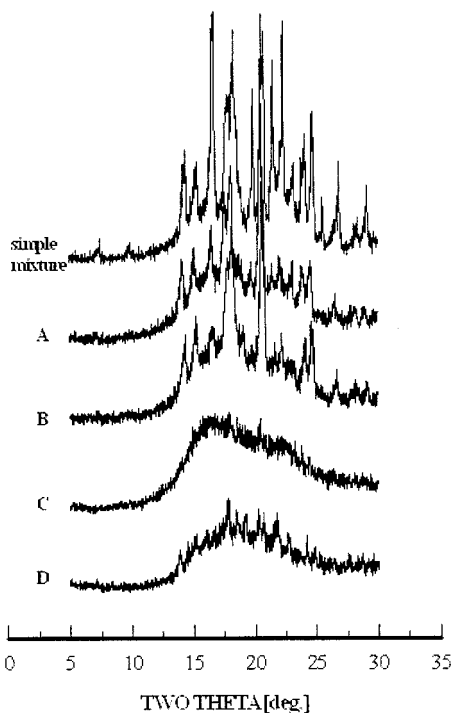


Figure 9 X-ray diffractions of simple mixture of cellulose and NMMO hydrate, powder cellulose–NMMO hydrate granules (A), cellulose–NMMO hydrate slurry (B), swollen cellulose–NMMO hydrate (C), and solidified cellulose–NMMO hydrate solution (D) (cellulose content: 15 wt %, $n = 0.97$).

cellulose–NMMO hydrate granules (A), cellulose–NMMO hydrate slurry (B), swollen cellulose–NMMO hydrate, and solidified cellulose–NMMO hydrate solution (D). In case of (A) and (B) made by high-speed mixing in a blender, the X-ray diffraction peak intensity angles are almost identical to those of the simple mixture of cellulose and NMMO hydrate as shown in Figure 9, and the strong X-ray diffraction intensity peaks in Figure 9 are caused by a NMMO hydrate with $n = 0.97$. However, in the case of the swollen cellulose–NMMO hydrate (C) and the solidified cellulose–NMMO hydrate solution (D), the X-ray diffraction intensity peaks of the NMMO hydrate did not appear. It seems that the NMMO hydrate as a liquid phase penetrates into the cellulose when the mixing time for sample preparation is 25 min or longer at 70°C.

In general, cellulose pulp has cellulose I structure. Only when the cellulose is completely dissolved in NMMO hydrate, this crystal structure of cellulose is converted to the cellulose II structure. Each of the cellulose I and the cellulose II shows three specific X-ray diffraction intensity angles—14.6°(101), 16.4°(101'), 22.6°(002) and 12°(101), 20°(101'), 21.5°(002), respectively. Figure 10 shows six X-ray diffraction curves of dry cellulose samples obtained after removing NMMO hydrate from powder cellulose–NMMO hydrate gran-

ules (A) or cellulose–NMMO hydrate slurry (B), in the case of $n = 0.83, 0.97,$ or 1.23 . Figure 10 shows the X-ray diffraction intensity peaks of the cellulose I and those of the cellulose II as a solid line and a dashed line, respectively. The X-ray diffraction curves indicate that both sample A and B still retain the original cellulose I structure. In the case of cellulose–NMMO hydrate slurry (B) with $n = 0.83$ or 0.97 , two additional X-ray diffraction intensity peaks appeared at 20° and 21.5° (cellulose II), while the intensity peak at 22.6° (cellulose I) decreased. The appearance of two additional intensity peaks indicates that the cellulose crystal structure changes from I to II.

Figure 11 shows the X-ray diffraction curves of three dry cellulose samples obtained after removal of NMMO hydrate from swollen cellulose–NMMO hydrate (C) with $n = 0.97$ or 1.23 , and cellulose–NMMO hydrate solution (D) with $n = 0.97$, respectively. As previously described, the swollen cellulose–NMMO hydrate was made at 70°C, at which the NMMO hydrate diffused into cellulose first and then the cellulose was dissolved in the NMMO hydrate as the mixing time increases. Figure 11 shows that the sample C with $n = 0.97$ or 1.23 was almost converted to cellulose II structure while the sample D with $n = 0.97$ has only cellulose II structure.

Figure 12 shows the X-ray diffraction curves of cellulose pulp, cellulose swollen sample (C) obtained

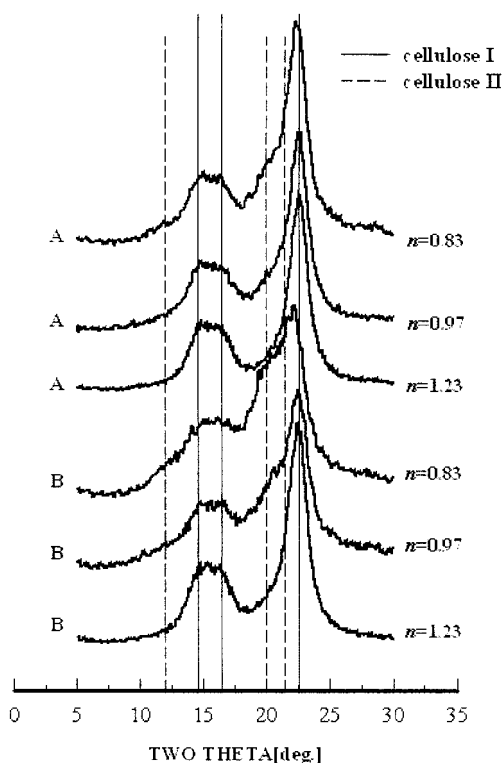


Figure 10 X-ray diffractions of cellulose samples (A: granules and B: slurry) obtained after removal of NMMO hydrate in powder cellulose–NMMO hydrate granules and cellulose–NMMO hydrate slurry.

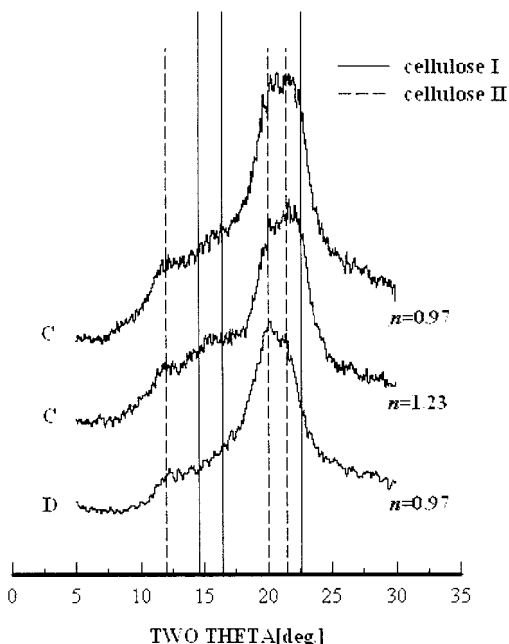


Figure 11 X-ray diffractions of cellulose samples (C: swollen and D: solution) obtained after removal of NMMO hydrate in swollen cellulose–NMMO hydrate and cellulose–NMMO hydrate solution.

from the cellulose–NMMO hydrate with $n = 1.65$ at 70°C , cellulose granules sample (A) obtained from the cellulose–NMMO hydrate with $n = 1.0$ at 70°C , cellulose

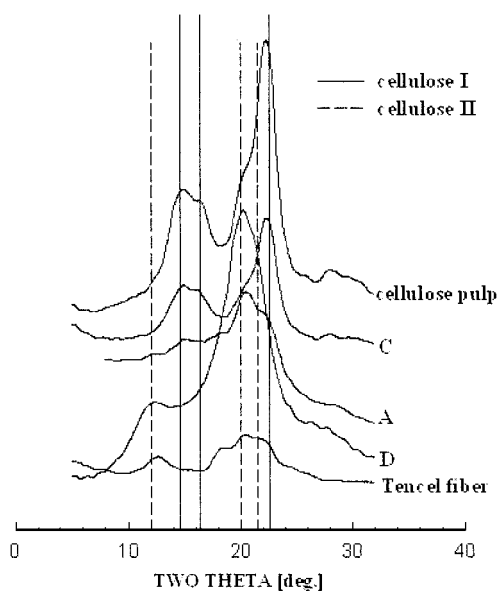


Figure 12 X-ray diffractions of cellulose pulp, cellulose swollen sample (C) obtained from cellulose–NMMO hydrate with $n = 1.65$ at 70°C , cellulose granules sample (A) obtained from cellulose–NMMO hydrate with $n = 1.0$ at 70°C , cellulose solution sample (D) obtained from cellulose–NMMO hydrate with $n = 1.0$ prepared by using extruder at 70°C , and Tencel fiber provided by Courtaulds.

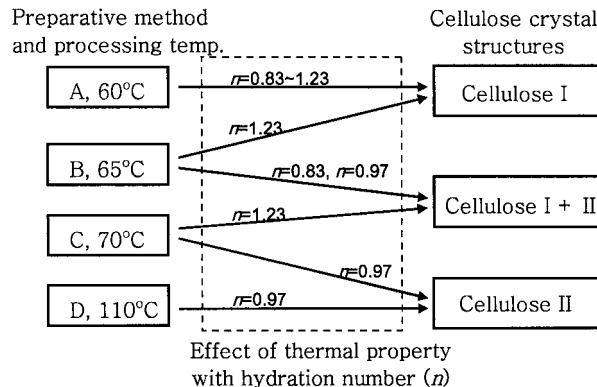


Figure 13 Schematic connection diagram between the preparative method of cellulose–NMMO hydrate samples and cellulose crystal structures.

lose solution sample (D) obtained from cellulose–NMMO hydrate with $n = 1.0$ prepared by using an extruder at 70°C , and Tencel fiber provided by Courtaulds. In the case of both the cellulose pulp and C, the crystal structure of the cellulose still retained the original cellulose I structure. In the case of both the A and D, however, it shows cellulose II structure.

Figure 13 shows the schematic connection diagram between the preparative method of cellulose–NMMO hydrate samples and cellulose crystal structures. Figure 13 also shows a relation between the crystal structures of cellulose samples and thermal property of cellulose–NMMO hydrate samples with various n at various preparative methods. In the case of $n = 1.23$ (A and B), the cellulose crystal structure was retained as cellulose I. In the case of $n = 0.97$ (C and D), however, the cellulose crystal structure was changed from cellulose I to cellulose II.

In particular, it was shown that the NMMO hydrate with $n = 0.97$ (C) dissolved the cellulose completely even at 70°C , which is lower than 110°C (D), and this result implies that the cellulose crystal structure is cellulose II.

CONCLUSIONS

This article described a simple preparative method of cellulose granules or slurry that can be used to make a homogeneous cellulose–NMMO hydrate solution by a direct method in the lyocell process. It was shown that the agglomeration behavior of the mixture of powder cellulose and NMMO hydrate, when being mixed at 1500 rpm in a blender to convert it to granules or slurry, was affected by NMMO hydrate number (n), mixing time, and blender temperature. In the case of the NMMO hydrate with $n = 0.97$, which is very close to $n = 1$ when the cellulose solubility is the best, the melting point of this NMMO hydrate in a solution was 70°C and it decreased as n becomes larger. When the

melting point of the NMMO hydrate in a solution is higher than 70°C, the agglomeration of the mixture of cellulose and NMMO hydrate hardly appears because melting of the NMMO hydrate is accelerated. It was concluded that the proper blender temperature for agglomeration is below 70°C. It is important to set the mixing time of cellulose slurry longer than 25 min and set the blender temperature higher than 65°C to obtain a uniform cellulose solution. The conversion of the cellulose crystal structure from cellulose I (slurry) to cellulose II (solution) was confirmed by using a X-ray diffraction pattern. In conclusion, the cellulose–NMMO hydrate granules or slurry made by using this simple preparative method would result in a small volume because this method is based on agglomeration of the mixture, and hence, it would provide great potential in the lyocell process because this small volume can be easily conveyed into the extruder.

This work was supported by the Brain Korea 21 (BK21) Project in 2003 and was also supported by the Nano Bioelectronics and Systems Research Center (ERC-NBS) of the Korea Science and Engineering Foundation at Seoul National University.

References

1. Franks, N. E.; Varga, J. K. U.S. Pat. 4,145,532 (1979).
2. McCorsley, C. C., III; Varga, J. K. U.S. Pat. 4,211,574. (1980).
3. Henry, C. U.S. Pat. 4,290,815 (1981).
4. Varga, J. K. U.S. Pat. 4,324,593 (1982).
5. Raven, G. *Int Fibers J* 1993, 6, 10.
6. Lee, W. S.; Jo, S. M. *Chem Fibers Int* 1999, 49, 46.
7. Berger, W. *Lenzinger Berichte* 1994, 9, 11.
8. Eichinger, D.; Eibl, M. *Tehtextil* 1997, May, 13.
9. *Japan Textile News Monthly* 1998, May, 43.
10. Federal Trade Commission, FTC File No. P928401 (1992).
11. McCorsley, C. C., III; Varga, J. K. U.S. Pat. 4,142,913 (1979).
12. McCorsley, C. C., III. U.S. Pat. 4,144,080 (1979).
13. Franks, N. E.; Varga, J. K. U.S. Pat. 4,196,282 (1980).
14. McCorsley, C. C., III. U.S. Pat. 4,246,221 (1981).
15. Zikeli, S.; Wolschner, B.; Eichinger, D.; Jurkovic, R.; Firgo, H. U.S. Pat. 5,094,690 (1992).
16. McCorsley, C. C., III; Varga, J. K. U.S. Pat. 4,211,574 (1980).
17. McCorsley, C. C., III. U.S. Pat. 4,416,698 (1983).
18. Lee, W. S.; Jo, S. M.; Kang, H. J.; Kim, D. B.; Park, C. S. U.S. Pat. 5,584,919 (1996).
19. Chanzy, H.; Dube, M.; Marchessault, R. H. *J Polym Sci Polym Lett Ed* 1979, 17, 219.
20. Dube, M.; Deslandes, Y.; Marchessault, R. H. *J Polym Sci Polym Lett Ed* 1984, 22, 163.
21. Chanzy, H.; Nawrot, S.; Peguy, A.; Smith, P. *J Polym Sci Polym Phys Ed* 1982, 20, 1909.
22. Buijtenhuijs, F. A.; Abbas, M.; Witteveen, A. J. *Das Papier* 1986, 40; *Jahrgang. Heft* 1986, 12.
23. Loubinoux, D.; Chaunis, S. *Lenzinger Berichte* 1985, August, Heft 59.
24. Chanzy, H.; Noe, P.; Paillet, M.; Smith, P. *J Appl Polym Sci Appl Polym Symp* 1983, 37, 239.
25. Lenzing, A.-G. EP. 356, 419 (1990).
26. Courtaulds Co., WO 94 06,530 A1 9414 (1994).
27. Fischer, K. *Angew Chem* 1935, 48, 394.
28. Marx, M. *Makromol Chem* 1955, 16, 157.
29. Maia, E.; Peguy, A.; Pérez, S. *Acta Crystallogr* 1981, B37, 1858; Maia, E.; Pérez, S. *Acta Crystallogr* 1982, B38, 849.
30. Kim, D. B.; Lee, W. S.; Jo, S. M.; Lee, Y. M.; Kim, B. C. *Polym J* 2001, 33, 139.
31. Keith, H. D.; Padden, F. J., Jr. *J Appl Phys* 1964, 35, 1206, 1270.
32. Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1976; p 548, vol. 2.
33. Kim, D. B.; Lee, W. S.; Jo, S. M.; Lee, Y. M.; Kim, B. C. *J Appl Polym Sci* 2002, 83, 981.