

Unique Structural Characteristics of Nematic Ordered Cellulose—Stability in Water and Its Facile Transformation

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ABSTRACT: Nematic Ordered Cellulose (NOC) film that exhibits a noncrystalline yet highly ordered form was prepared by stretching a water-swollen cellulose gel obtained in a unique manner with coagulation of cellulose molecules dissolved in the N,N-dimethylacetamide/LiCl solvent system. In this article, structural characteristics of this unique film were investigated. Orientation of the molecular chains in the noncrystalline regions across the entire film were stable after immersing in water at room temperature, though conventional amorphous cellulose regions are in any forms believed fairly to be recrystallized under a humid atmosphere. Even 30 days after immersing in water at 50 °C, neither crystallization nor disordering of the chains occurred in the NOC film. On the contrary, the film was capable of being transformed into films composed of cellulose polymorphs domains where the molecular orientation was still maintained as the initial film under various mild conditions that both cotton and cellophane did not show any changes on their structure. These contradictory properties of the NOC film proved to be dependent on its unique supermolecular structure. ©2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 45: 2850–2859, 2007

Keywords: cellulose; crystallization; drawing; nematic ordered cellulose; orientation

INTRODUCTION

Cellulose as a major β -1,4 linked carbohydrate polymer, is assembled mostly to provide both crystalline and noncrystalline regions. Concerning the crystalline regions, the detailed structure including the structure–property relationship have been extensively studied for the last half-century, whereas information on the noncrystalline regions is still much less because of the lack of appropriate specimen and tool to be used. Recently, we proposed the deuteration

monitoring method accompanied with infra-red (IR) spectroscopy and a kinetic interpretation for better understanding of the molecular aggregation in the noncrystalline regions.^{1,2} So far, noncrystalline cellulose domains were prepared principally by three major methods, using mechanical treatments of cellulose, chemical treatments of cellulose derivatives, and coagulation from cellulosic solutions, respectively. These typical methods are (1) grinding cellulose in a ball mill,³ (2) saponification of cellulose diacetate or triacetate in anhydrous alcohol,^{4–6} and (3) regeneration of cellulose solution of SO₂-amine-organic solvent systems, respectively.⁷ However, the preparation of the cellulose substances dominantly occupied by noncrystalline regions requires the considerably

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complicated procedure, which might cause severe degradation or structural modifications.

On the other hand, crystallization of cellulosic materials is categorized into four polymorphs having different unit cells according to the molecular chain packing. The differences of the chain packing in a unit cell, namely, the alignment of the chains, distance between the adjacent chains, direction of the reducing end group of chain, and molecular conformations, should cause polymorph of cellulose. From these, it follows that each polymorph has the respective parameters of the unit cell. Each of the allomorphs depends on the preparation procedure,^{8–10} and is called as cellulose I, II, III, and IV, which can be identified by X-ray diffraction, IR, and CP/MAS ¹³C-NMR spectroscopies.

Native cellulose fibers named as cellulose I, is secreted and assembled by living organisms such as bacteria, algae, plants, and animals, which are distinguished into two crystalline phases, I α and I β . The difference is supposed to be caused by the atmosphere for the crystallization.^{11,12} Cellulose II is prepared by regeneration of cellulose solutions or mercerization of cellulose I in an aqueous alkaline solution (more than ca. 20%). It is also commercially available in the form of fibers and films, as is well known as rayon, lyocell, and cellophane. Cellulose III is, in general, obtained by soaking of native cellulose (cellulose I) or regenerated cellulose (cellulose II) in liquid ammonia at -33 °C. Cellulose IV is usually prepared from cellulose III by heating in glycerol at 260 °C. To elucidate their structure, many attempts have been reported using modern analytical methods.^{13–15} The polymorphs exhibit various chemical and physical properties among them including the elastic modulus and tensile strength. Preparation of each cellulose polymorph, however, is relatively complicated as described above, and in particular the crystalline domains are randomly distributed in the samples. Facile preparations of such fiber and film forms containing oriented crystal domains are required for understanding of the structure–properties relationship, as well as preparation of materials with a high tensile strength.^{16,17}

Recently, we successfully prepared cellulose films having noncrystalline yet highly ordered structure by a facile method.¹⁸ This film was prepared by a slow coagulation of cellulose in N,N-dimethylacetamide (DMAc)/LiCl solution followed by stretching to achieve the molecular

chain orientation. The ordered noncrystalline cellulose also exhibited a quite unique structure attributing to the unique surface properties. The structure of the cellulose film was found to possess nematic ordering molecular chains, which was indicated by X-ray diffraction and the electron microscopic observation.^{19,20} The ordered arrangements of cellulose glucan chains were termed as “nematic ordered cellulose” (NOC). Later, the NOC proved to exhibit the unique surface characteristics derived from the noncrystalline and highly ordered glucan chain associations; for example, it can induce the orientation in deposition of cellulose nanofibers secreted by *Acetobacter xylinum* (*Gluconacetobacter xylinus*), on the surface.²¹

In this work, we will display the other unique properties of the specific noncrystalline regions in NOC films. At first, the structural stability of NOC in water was examined. So far, most conventional noncrystalline cellulose have no orientation in their supermolecular structure, and further it is difficult to avoid the recrystallization in water even at room temperature.^{4–6} Interestingly, the noncrystalline character based on the specific chain orientation of NOC were retained after the treatment in water even at 50 °C for long periods. Moreover, our results have demonstrated that such NOC structure in a film material has provided, under milder treatments, a facile direct transformation into the oriented films having highly aligned domains of cellulose II, III, and IV allomorphs along the initial orientation in the NOC.

EXPERIMENTAL

Preparation of NOC Films

A NOC film was prepared according to the previous reports:^{18,19} cotton cellulose (degree of polymerization; 1300) was dissolved in a 7 wt % LiCl in DMAc. To avoid depolymerization of cellulose molecules, the solvent-exchange technique at room temperature was employed for dissolution. The solution of about 1 wt % concentration of cellulose was coagulated in a glass petri dish under a saturated water vapor atmosphere, which was allowed to stand in a closed box at room temperature for 3 or 4 days until a gel-like film was formed. This precipitated gel-like film was thoroughly washed with water for more than a week to remove the solvent. Finally a

transparent water-swollen cellulose (WSC) film was obtained. After cut into strips, the WSC film was uniaxially stretched with a manual-stretching device under the water-swollen state. The maximum draw ratio was 2.0–2.3. To stabilize the drawn film, it was then air-dried at room temperature with keeping the tension in the stretching device for overnight, followed by vacuum drying at 40 °C for several days. In this manner, we obtained NOC films that had ca. 25 mm in length, 1.5 mm in width, 100 μm in thickness, and 12 mg in weight, respectively.

Stability Test of NOC in Water

Two identical NOC films were prepared by stretching two separated specimens cut from the same WSC sheet simultaneously in the stretching device. One was used for the particular treatment; the other, which was kept in a vacuum oven, was used for the measurement of the density as a control. Morphological changes of NOC were examined after treatments under both wet and dried environments. For examinations in the wetting environment, NOC films were immersed into a large quantity of water in a sealed tube. The two NOC films in water were allowed to stand in water for 30 days, at room temperature and at 50 °C in an oven, respectively. For examinations in the drying treatment, a NOC film was placed in a drying oven at 105 °C for 30 days. Through all the experiments, the specimens were kept in both stressed and relaxed states. The “stressed state” indicates that both ends of NOC films were fixed in the stretching device to maintain the length in the stretching direction all through the treatment, whereas “relaxed state” means no fixation of NOC films. The treated specimens under these conditions were analyzed after vacuum dried as described in the following measurement section.

NOC films, which were allowed to stand for more extended coagulation periods in the petri dishes under the saturated water vapor atmosphere, were also prepared. Namely, the coagulated periods were controlled as 10, 30, and 200 days, respectively. The coagulated cellulose gel-like films were then washed with water and stretched uniaxially to yield the individual NOC films with different coagulation periods.

Preparation of Different Cellulose Allomorphs

The following three treatments were carried out for NOC films earlier prepared to obtain ori-

ented films composed of different cellulose allomorphs. A NOC film was soaked in an aqueous NaOH at room temperature for several hours, followed by washing with water. Secondly, NOC film was immersed into an aqueous solution of ethylenediamine (EDA) at room temperature for overnight, followed by washing with methanol dried over molecular sieve 3A. Thirdly, an NOC film in a stainless steel tube filled with water was heated in an oil bath over 100 °C for 1 h. In fact, the earlier three individual treatments yielded the films of cellulose II, III, and IV, respectively. All through the aforementioned crystallization processes, NOC film was treated in the fixed state mounted on the stretching device. After the treatment, specimens were air-dried with keeping the tensed state, and then vacuum-dried at 40 °C prior to the measurements. The specimens after the earlier crystallization processes were then acid-hydrolyzed with an aqueous hydrochloric acid as well as with sulfuric acid to examine the crystalline transformations. After the hydrolysis, the residue was washed with water and collected by centrifugation, freeze-dried, and then provided for X-ray measurements.

Measurements

Estimation of the Degree of Crystallinity

The density of samples (ρ) was determined pycnometrically using a mixture of *p*-xylene and carbon tetrachloride at 30 °C. The degree of crystallinity based on the density measurement was calculated using the reported density values for crystalline region of cellulose II (1.610 g/cm³) and noncrystalline region of cellulose (1.481 g/cm³). The calculation was performed using the following eq 1:

$$X = (1/\rho_a - 1/\rho)/(1/\rho_a - 1/\rho_c) \quad (1)$$

where ρ_a is the density of the noncrystalline region, ρ_c is the crystalline region, and X is the crystallinity of the sample.

Estimation of the Allomorphs of the Treated Samples and the Orientation of the Crystallites Using Wide-Angle X-Ray Diffraction

Wide-angle X-ray diffraction (WAXD) patterns were measured using nickel-filtered CuK α radiation produced by a Rigaku RINT-2550HF X-ray

generator with a pinhole collimator of 1 mm in diameter at 40 kV and 200 mA. WAXD intensity curves of NOC films were measured by a transmission method using a scintillation counter with a scanning speed $0.5^\circ/\text{min}$. The angular ranges of WAXD curves for the equatorial scan to the drawing direction were $2\theta = 5^\circ\text{--}35^\circ$. The degree of preferred orientation for crystallite,¹⁸ π was estimated by

$$\pi = (360 - (H' + H'')^\circ)/360 \quad (2)$$

where, H' and H'' is the half-width of the azimuthal intensity distribution along the Debye–Scherrer ring at the (004) plane. WAXD patterns were also recorded on an imaging plate (Fuji Film BAS-SR, 127 mm \times 127 mm) at 40 kV and 50 mA for 60 min with a distance of 60 mm, then analyzed using a Rigaku R-AXIS-DS3 system. Most NOC films were measured in an intact film state. On the other hand, the hydrolyzed sample was pressed into a disk with 10 mm in diameter for X-ray measurements, because specimen was broken into small powder-like fragments after the acid treatment.

RESULTS AND DISCUSSION

Structural Stability of Never-Dried Cellulose Gel

The coagulation periods from cellulose/LiCl/DMAc solutions were extended for studying the structural stability of a water swollen cellulose (WSC) gel as the starting material prior to drawing for preparation of NOC. The regenerated and never-dried cellulose gel on the petri dishes were allowed to stand under saturated water vapor atmospheres for 10, 30, and 200 days, respectively. The WAXD profiles of the WSC gels after water washing and drawing into NOC are shown in Figure 1(a–c). The pattern of each intensity curve indicated successful preparation of NOC, when compared with Figure 4(a) and our previous data.^{18,19} The gels remained intact even for 200 days kept under a saturated water vapor condition. Further, there was no influence in the drawability of WSC for NOC. These results indicate that the obtained WSC is stabilized once regeneration of the gels takes place by the coagulation procedure.

The instability of the conventional amorphous celluloses,^{3–6} which attributes to recrystallization by water treatments, is believed to be responsible

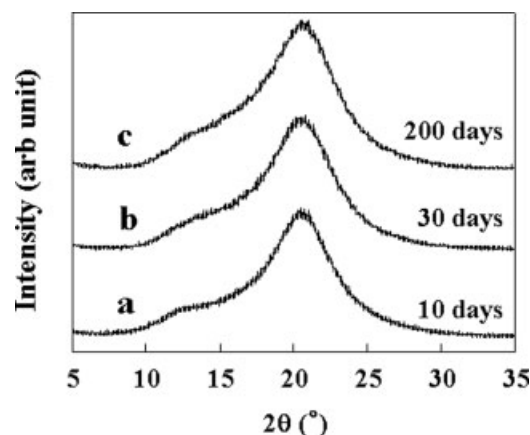


Figure 1. WAXD profiles for NOC of longer coagulation periods; (a) 10 days; (b) 30 days; (c) 200 days.

for their supermolecular structure. As the amorphous celluloses have the mobility of molecular chains and the relatively flexible conformation of a glucose unit, dissociation of the hydrogen bonds and rearrangement of the molecular chains occur easily under such wet conditions.

The superstructure of amorphous celluloses would strongly reflect their preparation process. On the other hand, amorphous cellulose were stable in water when it was prepared by regeneration of cellulose in the SO_2 -diethylamine-dimethylsulfoxide solvent system.⁷ It was reported that in the SO_2 -amine systems, rapid disruption of the cellulose and solvent complex allowed cellulose to have a specific aggregation to keep the amorphous state, but not to form crystallites. In the present DMAc/LiCl system for our NOC preparation, however, the slower coagulation using water vapor yielded the stable noncrystalline cellulose. For both cases, the key to maintain the amorphous or noncrystalline state should be formation of small amounts of the three dimensional cross-linking network. Thus, with such a consideration, certain organic solvent systems for cellulose may provide the stable noncrystalline states.

When the cellulose solution spread on the petri dish was exposed by a saturated water vapor, it turned out to be a gel state with shrinking. The shrinkage is probably due to the interchain hydrogen bonds formed during its coagulation process of cellulose molecules into a sort of network structures. After the solvent was exchanged into water, WSC was composed of ca.93 wt % water and 7 wt % cellulose. During drawing of the WSC, water retained inside of WSC appeared to bleed out from its surface. The exclusion of the

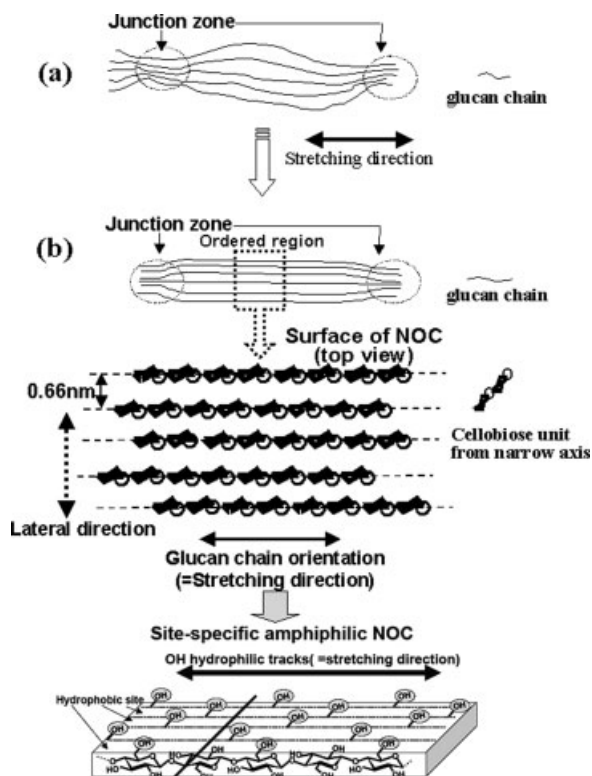


Figure 2. Schematic images of NOC: (a) the initial state before stretching; (b) after stretching; the inserted view is the arrangement of cellulose molecules on the NOC surface.

excess water from the drawn WSC gel may be attributed to adjoining the cellulose chains between the junction zones with accompanying the orientation, as shown in Figure 2(a,b). After drying of the drawn WSC under a stressed state, it showed decrease in thickness more than 80% and shrinking in width over 60%, when compared with the starting sizes of WSC.

Structural Stability of NOC Treated with Water

NOC films exhibited almost perfect transparency as much as the coagulated cellulose solution under water vapor atmosphere. This transparency suggested that the NOC should be consisted of noncrystalline regions. A schematic image of Figure 2 shows how β -glucan chains form the orientation towards NOC, as explained in our previous papers.^{18,19} A junction zone in Figure 2(a) represents the strongly hydrogen-bonded area where even D_2O vapor could not penetrate.¹ The zone probably plays a role as a cross linking point in the water-swollen fixed gel (WSC) of an initial state for NOC. Figure 2(b)

illustrates the state after stretching the gel, namely NOC, and also the inserted figure indicates a schematic zoom up view of the glucan chain arrangement of the NOC. The average distance between two parallel main chains was 0.66 nm as proved by the high-resolution TEM image in a previous article.¹⁹ Most importantly, the TEM image further indicated that the hydroxymethyl groups at the C-6 position that are equatorial-bonded to the anhydroglucose unit of cellulose are vertically stuck up against the surface, which indicates that the neighboring anhydroglucose ring planes are facing with each other, as shown in the bottom image of Figure 2. Simultaneously the stuck up OH groups in the individual molecular chains are also aligned like tracks along the stretching axis (the glucan chain direction). On the contrary, it is noted that the lateral order of the OH groups at the C6 position was at random by indication of the meridional WAXD pattern.^{19,20} It means that the lateral order of the OH groups among the neighboring chains is not well coordinated because of the slipped molecular chain situation with each other. The uniaxial stretching also caused this situation. Therefore, the hydrophilic and polarized OH groups are totally to be oriented as molecular tracks only in the stretching direction across the entire NOC surface. Between the hydrophilic molecular tracks, the hydrophobic phase due to the anhydroglucose plane also appeared, resulting in both hydrophilic and hydrophobic tracks next to each other across the NOC surface.²⁰ These amphiphilic molecular tracks enhance the unique surface properties of NOC. For example, recently we found that the surface induced the oriented deposition of cellulose nanofibers secreted by *Acetobacter xylinum* when the bacteria were incubated on the NOC as a template.^{20,21}

Figure 3 shows the WAXD image for NOC film obtained using the X-ray Imaging plate system. The arcs with the diffused background, which is a unique diffracted pattern for NOC, really indicates that cellulose molecules in NOC are highly oriented, but the coordinate of the glucose ring position is not perfectly fixed. This causes formation of the dominant noncrystalline regions. The typical WAXD intensity profiles of the equatorial scan for NOC film shown in Figure 4(a) also showed the low crystallinity of NOC. There was no significant sharp peak arisen from crystalline regions in the equatorial intensity curve. Only the broad peak maximum

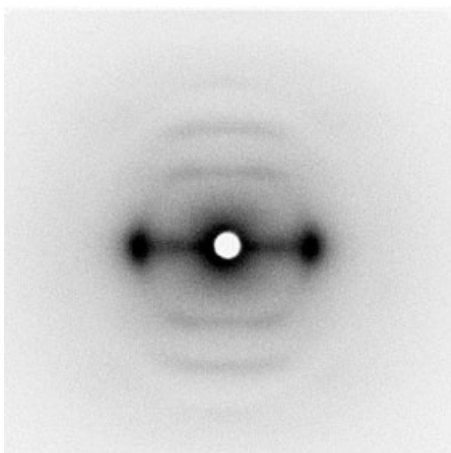


Figure 3. WAXD image for NOC film recorded on an imaging plate.

was observed at $2\theta = 20.5^\circ$. This location was not identical with the corresponding peaks to cellulose crystalline forms of I and II.⁸ The entire information obtained from the diffraction patterns of NOC indicates again the well alignment of the cellulose chains in noncrystalline regions along the drawing direction. The degree of crystallinity based on the density and the orientation parameter of the NOC film was around about 17% and 0.88, respectively, as listed in Tables 1 and 2.

As described in the introduction section, this NOC film exhibited some unique characteristics as templates or scaffolds for several purposes. Thus, it is becoming more important to understand the stability of NOC under various condi-

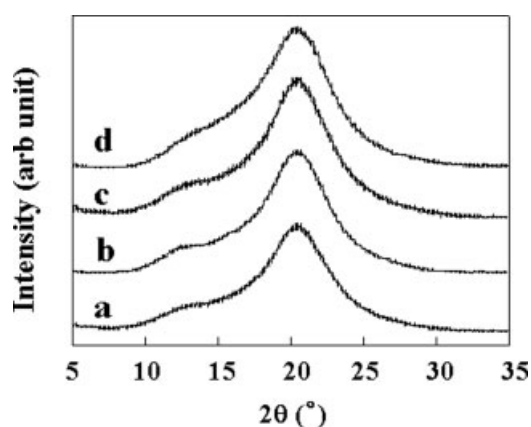


Figure 4. WAXD profiles for NOC films: (a) original; (b) after treatment in water at room temperature for 30 days in a relaxed state; (c) after treatment in water at 50 °C for 30 days in a relaxed state; (d) after treatment in dry heating at 105 °C for 30 days in a relaxed state.

Table 1. Degree of Crystallinity (%) for NOC Films and the Treated NOC Films Estimated from Density

Sample	Before (NOC)	30 Days After Treatments
Wet at room temperature		
Stressed	16.8	18.1
Relaxed	16.7	18.6
Wet at 50 °C		
Stressed	18.4	20.5
Relaxed	17.4	18.6
Dry at 105 °C		
Stressed	17.1	20.5
Relaxed	16.8	18.4

tions. To investigate the influence of water on the structure, NOC films were allowed to immerse into water for 30 days at room temperature and 50 °C, respectively. Both WAXD profiles of the samples after the treatments are shown in Figure 4(b,c). No significant structural change from the initial NOC film was found in the same WAXD curves by the water immersing. Furthermore, the initial NOC film demonstrated no change in the WAXD pattern after immersing in water even at 50 °C for 30 days [Fig. 4(c)]. It was reported that amorphous cellulose prepared by saponification of cellulose triacetate is recrystallized to cellulose II only by the exposure to water vapor at high relative humidity,⁴ and cellulose diacetate was rearranged and crystallized when large amounts of water were supplied.⁵ In general, conventional amorphous celluloses are known to be easily crystallized by water treatments.⁶ At the same time, NOC films were treated with water both under stressed (fixed on

Table 2. Orientation Parameter Estimated from Azimuthal WAXD Profile at the 004 Plane for the NOC Films and the Treated NOC Films

Sample	Before (NOC)	30 Days After Treatment
Wet at room temperature		
Stressed	0.88	0.89
Relaxed	0.88	0.89
Wet at 50 °C		
Stressed	0.89	0.89
Relaxed	0.89	0.89
Dry at 105 °C		
Stressed	0.89	0.89
Relaxed	0.88	0.89

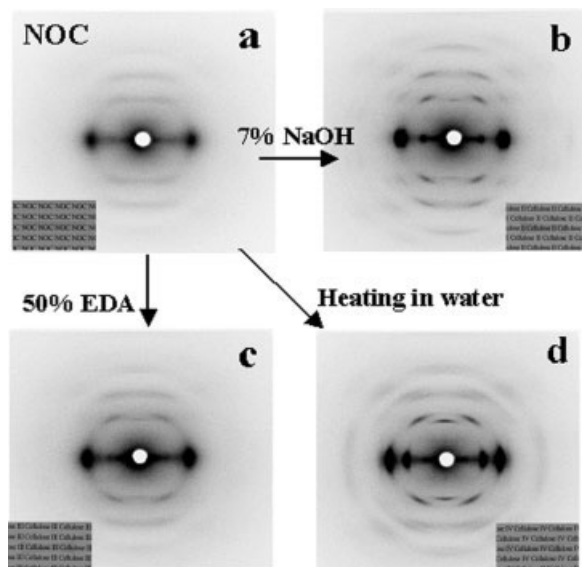


Figure 5. WAXD images recorded on the imaging plate and transparent films (inserted each image) for NOC film and transformed NOC films; (a) NOC, (b) NOC treated with 7% NaOH (c) NOC treated with 50% EDA, (d) NOC heated in water at 180 °C for 3 h.

a drawing device) and relaxed (without fixing on to the device) states. NOC films in the relaxed state would be expected to have a relatively flexible mobility of cellulose chains, which might cause disordering or crystallization. Changes in the degree of crystallinity and the orientation parameters after the water treatments were listed individually in Tables 1 and 2. Both the degree of crystallinity and the orientation parameter did not show significant changes in all conditions. This indicates that NOC were not rearranged and crystallized by water atmospheres, and considerably stabilized under both relaxed and stressed states. Namely, the mobility of cellulose chains and the OH groups in NOC may be restricted appreciably even in the wet conditions. The stability on the structure of NOC under water atmospheres would be dependent on the intermolecular hydrogen bonded domains^{1,2,18–20,22,23} that inhibit as a cross-linking to be loosed or dissociated by water molecules. The domains correspond to the junction zones shown in Figure 2(a,b).

Structural Stability of NOC Under Dry-Thermal Treatments

A WAXD profile of the NOC film treated in the dry state at 105 °C for 30 days in Figure 4(d) was almost the same as that for the initial NOC

film (4a of the same figure), under both the stressed and relaxed states. Instead, the transparent NOC film altered into yellow after the dry-thermal treatment. The coloration may be caused by the disintegration of cellulose, which was depolymerization,²⁴ partial oxidation, or carbonization. However, weight-loss of the samples was negligible after the dry-thermal treatment, and yet the crystallinity index and the orientation factor remained almost the same values. Thus, the structure of NOC proved to be significantly stable in both wet and dry states.

Transformation from NOC into Transparent and Oriented Cellulose Polymorphic Films

NOC exhibited the other unique aspects except the stability against water treatments. Nematic ordered regions as shown in Figure 2(b) of the NOC films facilitate transformation into polymorphs. Figure 5 shows the X-ray fiber diagrams and the photographs (inserted) of cellulose polymorphs prepared from NOC films. Figure 5(a) exhibits the initial NOC structure as the starting material prior to the following crystallization processes. Each crystallized structure transformed from NOC [Fig. 5(b–d)] owned an orientation of crystallites along the molecular orientation axis of NOC. Moreover, the obtained films were all transparent as the inserted photos in Figure 5 indicated. Thus, the orientation of molecular chains and transparency of NOC was maintained thoroughly, even after the crystallization took place.

The equatorial WAXD profiles corresponding to Figure 5(a–d) were shown in Figure 6(a–d),

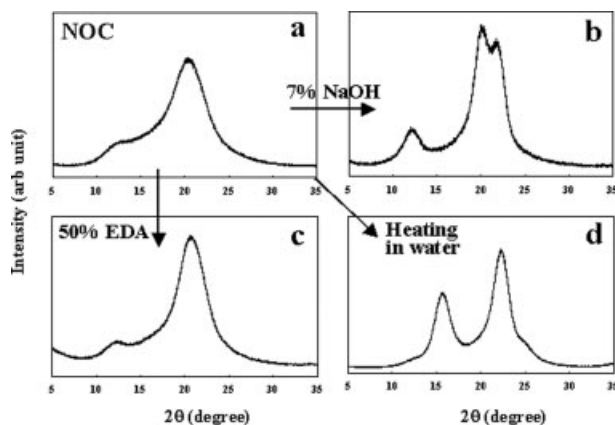


Figure 6. WAXD profiles for NOC and transformed NOC; (a) NOC, (b) NOC treated with 7% NaOH, (c) NOC treated with 50% EDA, (d) NOC heated in water at 180 °C for 3 h.

respectively. The individual patterns of the profiles in Figure 6(b–d) were easily identified as cellulose II, III, and IV, respectively. The results suggest that transformation into each allomorph was completed. It should be noted that all of the transformations were accomplished under milder conditions than the conventional methods reported for the preparation of each allomorphs.^{25,26} For example, 16.5% NaOH aqueous solution has been so far required for transformation from cellulose I into cellulose II, when cotton fibers are used as the starting cellulose.²⁶ Using NOC as a starting cellulose assembled state, 7% NaOH was enough for the transformation. In particular, NOC yielded cellulose IV directly by a hydrothermal treatment by over 100 °C without a pass way of formation of cellulose III as an intermediate. In a similar manner, we employed cotton cellulose and a commercial available cellophane film as a reference of the starting cellulose to transform into polymorphs under the same conditions used for NOC. However, both cotton and cellophane could never be transformed into each allomorph. The facile transformations are attributed only to the supermolecular structure of NOC, which is well ordered, but composed mainly of noncrystalline regions. In fact, the degree of crystallinity of the three crystallized films from NOC were around 45%.

Figure 7 displays the meridian WAXD profiles of each cellulose allomorph converted from NOC. The profiles of Figure 7(a–d) correspond to the intensity profile along the fiber axis of Figure 5(a–d), respectively. The meridional reflections of NOC film appeared obviously as the five planes. The observed half widths of 004 reflections of the polymorphs in Figure 7(b–d) were almost the same value as those among the three samples. Judging from Scherrer's eq 3:

$$t = 0.9\lambda/B\cos\theta \quad (3)$$

where t = size of the crystallite, λ = wave length of X-ray (0.154 nm), B = half width of the peak, and θ = Bragg angle (radian).

It means that the crystalline longitudinal length of all the allomorphs may be in the comparable size. Such similarity of the crystallite size among the different allomorphs transformed from NOC indicates that the junction zones in the initial NOC should hinder growth of the crystallites. In other words, the super-

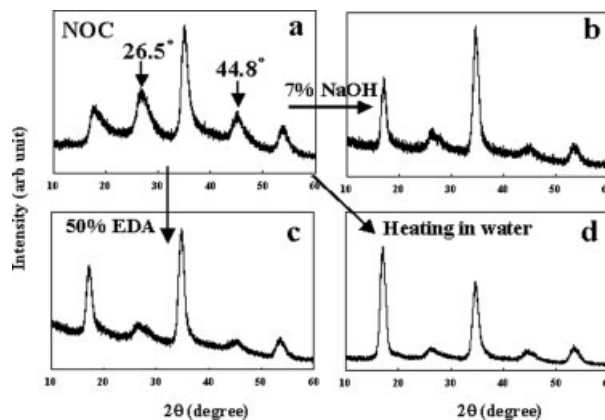


Figure 7. Meridional WAXD profiles for NOC and transformed NOC; (a) NOC, (b) NOC treated with 7% NaOH, (c) NOC treated with 50% EDA, (d) NOC heated in water at 180 °C for 3 h.

structure of the ordered regions between the junctions may only be transformed into the crystallites. In addition, the relative intensity of the reflections at $2\theta = 26.5^\circ$ and 44.8° was decreased after crystallization, but still remained. The reason of the appearing odd-order reflections would be due to coexistence of the different hydroxymethyl group rotations at the O(6)-C(6) position. This may be due to mixture of gauche-gauche and gauche-trans conformation,²⁷ which are largely exist in the initial NOC film.^{19,20} Interestingly, the intensity of 002 in the transformed cellulose IV from NOC exhibited higher than that of 004 as shown in Figure 7(d), differing from other transformation shown in Figure 7(b,c). The relative intensity ratio of 002 to 004 was about 1.4 for cellulose IV in this study, while it was reported about 0.65 for cellulose IV prepared from cellulose III_{II}.²⁸ This disagreement might be dependent on the difference of the molecular arrangement of the starting materials. Alternatively, a heat treatment of the NOC film in water may provide the transformation into another type of cellulose IV allomorph, although it was converted into the oriented cellulose IV easily in a single step because of well-ordered, but noncrystalline characteristics.

As already described earlier, the treated films having a crystallite of each allomorph exhibited transparency. This indicates that the domain sizes of the crystallites were quite small even though they were well oriented along the same molecular orientation direction of the initial NOC film.

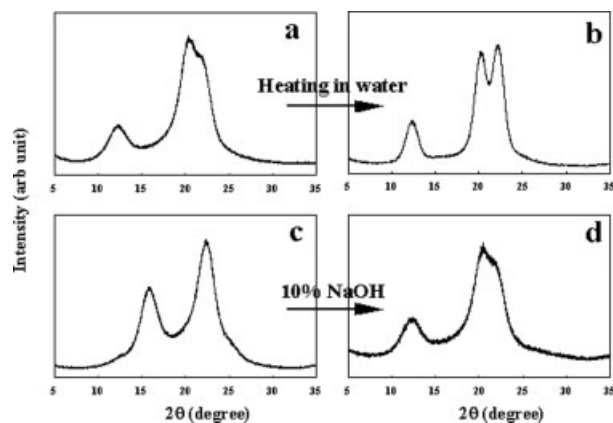


Figure 8. WAXD profiles for transformed NOC; (a) NOC treated with 10% NaOH, (b) after treatment of "a" by heating in water at 180 °C for 3 h, (c) NOC heated in water at 180 °C for 3 h, (d) after treatment of "c" with 10% NaOH.

Structural Stability of Ordered Films Having Polymorphs Prepared from NOC

The stability of crystalline structure was studied using cellulose II and IV obtained from NOC. Cellulose II prepared from NOC by 10% NaOH treatment [Fig. 8(a)] was heated in water at 180 °C for 3 h. This condition is normally sufficient for the initial NOC to be transformed into cellulose IV, as mentioned earlier. However, the cellulose II from NOC was not transformed into cellulose IV. Instead, the heating process of cellulose II in water provided the sharper profile of cellulose II form as shown in Figure 8(b). Two crystalline reflections about at $2\theta = 20^\circ$ and 22° were clearly resolved, and further the profile around 18° indicating noncrystalline region was fairly depressed. This result indicates that the thermodynamic energy of the hydrothermal treatment was not enough for a driving force to transform cellulose II into IV, but enough to decompose noncrystalline regions or transform them into cellulose II. Further study will be needed in terms of kinetics on crystallization under this condition. On the other hand, cellulose IV prepared from NOC by heating in water at 180 °C for 3 h [Fig. 8(c)] was transformed into cellulose II by 10% NaOH treatment completely as illustrated in Figure 8(d). In both experimental conditions, cellulose samples were partly broken or disintegrated into thin fibrils after the treatment. This suggests that the second step of crystal-crystal transformation of cellulose may occur by accompanying with a considerable depolymerization of the molecular chains.

For studying the stability of the crystallites of cellulose IV, acid hydrolyzing treatments of cellulose IV obtained from NOC were performed using aqueous HCl and sulfuric acid under different conditions of concentrations, temperatures, and reaction times. Typical WAXD patterns after the acid hydrolyses are presented in Figure 9(a–d). In comparison of the three profiles of Figure 9(a–d), the acidolyzed residues showed intact cellulose IV except for the sample treated with 66% sulfuric acid for 2 h at room temperature shown in Figure 9(d). An earlier report²⁹ described that cellulose IV_{II} was converted reversibly into cellulose II by an acid hydrolysis using HCl. However, the present results showed no indication of clear transformation from cellulose IV to II. The crystallites of cellulose IV from NOC were appreciably stable against transformation by the acid hydrolyses. It suggests that NOC may be transformed into cellulose IV completely. Moreover, the cellulose IV had no history through cellulose II because of the single step preparation. Thus, the cellulose IV could not be transformed into cellulose II by an acid hydrolysis without such a memory. On the contrary, as shown in Figure 9(d), the cellulose IV after the hydrolysis with 66% sulfuric acid at room temperature for 2 h, was transformed into cellulose II. In this case, it may be explained by that the cellulose II was regenerated with water, following dissolution of cellulose IV into the sulfuric acid. The phenomenon may be similar to the usual recrystallization into cellulose II from cellulose solution.

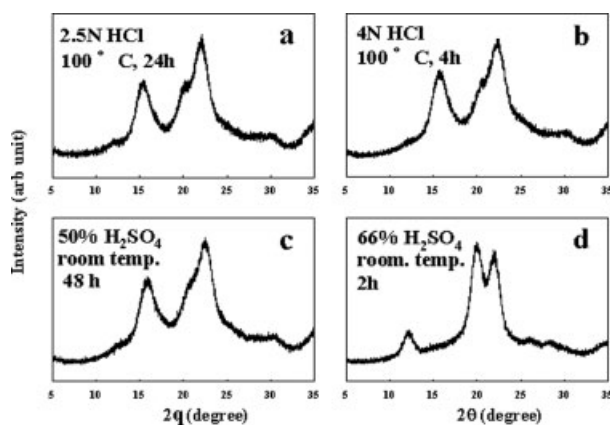


Figure 9. WAXD profiles for acid hydrolyzed cellulose IV prepared from NOC by heating in water at 180 °C for 5 h; (a) 2.5N HCl at 100 °C for 24 h, (b) 4N HCl at 100 °C for 4 h, (c) 50% sulfuric acid at room temperature for 48 h, (d) 66% sulfuric acid at room temperature for 2 h.

CONCLUSIONS

In previous articles, we proposed our concept of glucan chain association for cellulose.^{19,20} A non-crystalline state in the ordered domain should be an intermediate from amorphous to crystalline state. We also showed that oriented crystallization of cellulose did not occur during the drawing process of WSC.¹⁸ This was explained by the consideration of hindrance of the crystallization due to the sturdy three-dimensional hydrogen-bonding network structure of glucan chains in both WSC and NOC. Therefore, in this study, we attempted to elucidate the unique properties of NOC, which is considered as the intermediate between the randomly ordered amorphous phase and crystalline phase. Differing from the conventional amorphous cellulose, the structure of NOC film was stable against the treatment with water. The stability should be also due to the intermolecular hydrogen bonded domains. However, the intermolecular hydrogen bonds in NOC films are probably weak when compared with those in the crystalline phase. This character on NOC enabled a facile crystallization of each allomorph under milder conditions than the conventional crystalline-crystalline transformation. In this sense, NOC should be categorized between the random amorphous state and the crystalline state.

By this understanding, we could also control the supermolecular structure of cellulose; for example, controlling of the orientation parameter, the crystalline form, and the crystallinity index. Next, it will be important to characterize the mechanical properties of the cellulose materials thus prepared and to correlate them with the structure for more advanced commercial utilization. In particular, measuring the mechanical properties of NOC presumably gives fundamental knowledge of ordered noncrystalline cellulose, which leads to a new material from cellulose.²¹

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