Milling in Seconds Accelerates Acetylation of Cellulose in Hours

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ABSTRACT: A new sustainable synthetic method for cellulose acetate was developed by a combination of I2-catalyzed solid–liquid acetylation of cellulose and a milling process reducing the crystallinity of cellulose within a few seconds. Milled low-crystalline cellulose was acetylated faster than the original cellulose with higher crystallinity. The plausible factors of acceleration were the conversion of the hydroxy group in hydrogen bonds into reactive ones and the efficient formation of the catalytic species. The high conversion was assisted by the amorphous domain of the milled cellulose, while the morphological and structural changes were ignorable.

1. INTRODUCTION

Cellulose is the most abundant polymer in nature, and we use cellulose in a wide range of applications in our daily life as fibers and sheets like papers. Cellulose may also be transformed into various materials by chemical modifications.1−3 Cellulose acetate is a green polymer fabricable only from naturally occurring abundant resources, and its excellent mechanical properties allow wide applications in filters, fibers, plastics, and so on.4

However, typical esterification of cellulose requires long reaction time, harsh conditions, or dissolution requiring specific solvents such as ionic liquids, due to the low reactivity of cellulose originating from the crystalline nature of cellulose and interchain packing by the hydrogen bonding. Exploration of methods enhancing the reactivity of cellulose is a crucial subject. A typical approach is homogeneous reactions dissolving cellulose in solvents. Ionic liquids5−10 including CO2 switchable systems10 and organic solvents with additives11−13 were employed to dissolve cellulose by reducing its crystallinity. However, these methods are accompanied by side reactions, degradation of the cellulose skeleton possibly lowering the performance of the resulting products, high energy, or toxic solvents. These disadvantages give negative impacts on the sustainability of cellulose acetate.14

We reached for an idea for a new sustainable route for cellulose acetate combining the solid–liquid reaction of cellulose in acetic anhydride catalyzed by I2 developed by Biswas et al.15,16 (Scheme 1) and novel rapid decrystallization of cellulose by dry milling with rotational mortars developed by Nishioka et al. in a few seconds.17,18 A unique feature of this I2-catalyzed esterification is the high conversion despite the heterogeneous reaction under mild conditions. In heterogeneous solid–liquid reactions, the state of the solid affects the reaction behavior, and hence, we decreased the crystallinity of cellulose to increase the reactivity by milling. The advantageous feature of this milling is the fast and facile process without requiring additional reagents.18 Other procedures for decrystallization require longer time, energy-consuming ball-milling for mechanical treatments19−24 or chemical modifications or dissolution before regeneration.25−28

Treated cellulose with lower crystallinity has higher activity in hydrolytic degradation.23,24 Mechanochemically assisted esterification of lignocellulose was also reported to improve the efficiency of the heterogeneous esterification, probably due to the decrease in the crystallinity and the promoted penetration of anhydrides.29 This work opened the possibility of the acceleration of esterification of cellulose, while the highest efficiency stayed below 35%. For the practical application of the reduction of crystallinity to esterification, further advances are necessary.

In this work, we investigated the cooperation of heterogeneous acetylation and dry milling for the modification of cellulose. We found that the milling reducing the crystallinity of cellulose accelerates the heterogeneous acetylation of cellulose, leading to quantitative conversion, thanks to both the release of the hydrogen bonds and the sufficient formation of the catalytic species.
2. RESULTS AND DISCUSSION

Acetylation was carried out by a heterogeneous reaction of solid cellulose and acetic anhydride catalyzed by I₂ (0.9 mol % to OH) at 40 °C. The degrees of crystallization of low-crystalline cellulose (LC) obtained by milling and the original crystalline cellulose (CC) were 22 and 62%, respectively. Solids, partially insoluble in dimethyl sulfoxide (DMSO), were obtained by the reactions of LC and CC for 6 h in 83 and 81% yields, respectively. The other parts were oligomers soluble in the resulting liquid consisting of acetic anhydride and acetic acid. The DMSO-soluble part was analyzed by 1H NMR spectroscopy (see the Supporting Information). The products with lower degrees of substitution (DS) were partially insoluble in DMSO-d₆ and this 1H NMR analysis provides quantitative information on the soluble fractions. The degrees of substitution (DSNMR) were 96 and 59% for the products obtained from LC and CC, respectively. Accordingly, the acetylation behavior was monitored by 1H NMR and IR spectroscopies (Figure 1). The DSNMR of the product from LC was higher than the DSNMR of the product from CC, until the quantitative acetylation of LC was attained at 6 h. The acetylation of CC was completed in 8–10 h. This analysis indicates that the formation of soluble cellulose acetate is faster in the acetylation of LC. The IR spectroscopic analysis was carried out by comparing the wavenumber of the stretching vibrational absorption of C==O in the whole solid, which shifts to a lower wavenumber by the hydrogen bonds by the residual hydroxy moieties. This IR spectroscopic analysis evaluates the total environment of the carbonyl groups regardless of the solubility. The wavenumber of the C==O absorption for the product from LC saturated faster than that for the product from CC, and the trend of the shift was identical to that observed in the NMR spectroscopic analysis. This analysis clearly indicates that the hydroxy group in LC was consumed faster than that in CC. Both of the analyses indicate that the reaction of LC proceeded faster than that of the original CC. This investigation revealed that the milling in seconds shortened the reaction time in hours.

We investigated the factors for this acceleration. The possible factors of the acceleration we examined were the release of the hydrogen bond of the hydroxy groups, fragmentation of the cellulose chain by milling, morphological changes, improved affinity of LC toward acetic anhydride, and the change in the activation behavior of acetic anhydride with I₂.

First, we found a difference in the hydrogen bond of cellulose as expected. Figure 2 illustrates the Fourier transform infrared (FTIR) spectra of LC and CC measured by the KBr method using carefully dried KBr. The absorption of the...
stretching vibration of O–H bonds ($\nu_{\text{OH}}$) for LC and CC had peak tops at 3409 and 3391 cm$^{-1}$, respectively, and the peak for CC is broader by the shoulder at a lower wavenumber region. The $\nu_{\text{OH}}$ absorption of the free hydroxy group is reported to be observed at 3580 cm$^{-1}$, and absorption bands observed below 3400 cm$^{-1}$ were assigned to $\nu_{\text{OH}}$ of hydroxy groups with the inter- and intramolecular hydrogen bonds, which were revealed by precedent detailed works on the FTIR spectroscopic analysis of chemically regenerated or modified cellulose. This difference clearly indicates the release of hydroxy groups from hydrogen bonds by the dry milling process.

In addition, the relative intensity ratios of the peaks at 1430 cm$^{-1}$ toward 897 cm$^{-1}$ support the decrease in the crystallinity of LC (Figure 2c). The spectra normalized by the intensity of the peaks at 897 cm$^{-1}$ show that the absorption at 1430 cm$^{-1}$ in the spectrum of LC is significantly weaker than that in the spectrum of CC in a similar manner with ball-milled cellulose.

Second, we also found another difference in the behavior of the activation of acetic anhydride with I$_2$. The cellulose sources were immersed in a solution of I$_2$ in ethyl acetate at 40 °C for 1 h. Then, we measured the UV–vis spectra of the supernatants after filtration (Figure 3). The spectrum of the supernatant originating from LC shows an absorption peak at 300 and 360 nm indicating the formation of I$_3$$. As known, cellulose is not positive to the iodine–starch reaction as can be confirmed again from the spectrum of the supernatant originating from the original CC, while starch is positive by capturing I$_3$ in the helical secondary structure of starch. The weak but positive iodine–LC reaction in a similar manner with the iodine–starch reaction implies accidental formation of starch-like cavity by the randomization of the well-defined cellulose fibril by the milling. The active species of this acetylation is I$^+$ serving as a Lewis acid activating the carbonyl group of acetic anhydride, and the formation of I$_3$$ led to enhanced formation of I$^+$ accelerating the acetylation.

The effects of the following factors were found ignorable. We could confirm that the fragmentation of cellulose and the change in the affinity with acetic anhydride did not take place. The molecular weights and the thermal behaviors of fully acetylated cellulose were almost identical (Supporting Information), indicating that mechanical fragmentation did not take place during the milling. The absorbencies of acetic anhydride in LC and CC were identical 63 and 68 wt %, respectively.

The effect of the morphological change was also ignorable. The milling changed the fibril morphology of cellulose into the plate-like morphology by compression, as observed in the scanning electron microscopy images (Figure 4). We recrystal-
possible negative effect is the reduction of the surface area by compression during milling.

For these experiments, we found that the randomized alignment of cellulose assisting the formation of active I+ and the weakened hydrogen bonding are the important factors for this acceleration of acetylation of cellulose.

3. CONCLUSIONS

We found the significant acceleration of heterogeneous acetylation of cellulose by simple milling of cellulose in seconds. Two plausible factors for this acceleration are the release of the hydrogen bond and the enhanced formation of catalytic I+ species. The enhanced reactivity originating from the amorphous nature will also have positive impacts on other functionalizations, and further studies are ongoing.

4. EXPERIMENTAL SECTION

4.1. Materials. Cellulose (ARBOCEL 600) was obtained from J. Rettenmaier & Söhne GMBH + Co. KG (Rosenberg, Germany). LC was prepared by milling at 10 °C with a rotation speed of 180 rpm with a shear and cooling milling machine based on KGW-G015 (West Co., Ltd., Japan), modified by Nishioka et al.15 The radius of the mortars was 45 mm. The clearance between upper and lower mortars was 10 μm. The upper mortar was fixed and the lower mortar rotated around the center. Samples were injected through a slot located on the upper mortar. The distance between the slot and the center was 20 mm. The samples were grinded in a region of mortars in the radial distance between 20 and 45 mm. The injected samples were discharged out typically in two to five rotations of the lower mortar after injection. Therefore, the estimated processing time in the mill machine calculated from the size of the mortar and the rotation speed is 1 or 2 s. Acetic anhydride was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). I2, acetic anhydride, Na2S2O3, ethanol, and ethyl acetate were purchased from Kanto Chemical (Tokyo, Japan). Acetic anhydride, Na2S2O3, ethanol, and ethyl acetate were purchased from Kanto Chemical (Tokyo, Japan). All of the reagents were used as received.

4.2. Measurements. 1H NMR spectra were recorded on a JEOL (Tokyo, Japan) ECX-400 (400 MHz) and ECX-500 (500 MHz) spectrometer. FTIR spectra were recorded on a Rigaku (Tokyo, Japan) RINT RAPID diffractometer with Cu Kα irradiation. The degree of crystallization was calculated from the intensities of the diffraction of the 200 lattice at 2θ = 22.6° and the diffraction at 2θ = 18.5°.31 Thermogravimetric analysis was conducted using Seiko Instruments (Chiba, Japan) EXSTAR 6000 TG/DTA 6200 instrument under a nitrogen atmosphere. Scanning electron microscopy measurements were conducted on a Hitachi (Tokyo, Japan) SU8000 microscope at an accelerating voltage of 30 kV.

4.3. Acetylation of Cellulose. Cellulose (284 mg, 1.75 mmol-unit), acetic anhydride (1.90 g, 18.6 mmol), and iodine (40 mg, 315 μmol) were added in a glass test tube. The mixture was magnetically stirred at 40 °C. Then, saturated aqueous solution of Na2S2O3 (4 mL) and ethanol (25 mL) were added, and the resulting mixture was stirred for 30 min to wash the solid. The solid was collected by vacuum filtration and washed with hot water (ca. 85 °C) and ethanol. Acetylated cellulose was isolated by overnight drying at 60 °C under reduced pressure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02422.

1H NMR spectra of products, photo images of the reaction, and properties of fully acetylated products (PDF)

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Notes
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