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Facile dissolution of wood pulp in aqueous NaOH/urea solution by ball milling pretreatment

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ABSTRACT

The softwood unbleached kraft pulp (UKP) with a lignin content of about 7 wt% was successfully dissolved in NaOH/urea/H_2O solvent by a short time (1 h) ball milling pretreatment. Even though the milling time was only 20 min, the wood pulp fibers (width of around 30 μm and length of higher than 1 mm) of UKP had already become wood meals with a diameter of around 20 μm. After milling 1 h, the wood meals became more uniform and possessed a smaller average diameter of around 5 μm. Meanwhile, the crystallinity indices of the wood pulp decreased remarkably after the ball milling. Especially, the wood pulp became completely amorphous after 1 h ball milling. Furthermore, viscosity-average degree of polymerization (DP_v) of the wood pulp decreased from 1300 to about 330. Moreover, the dissolved proportion of the wood pulp increased from 25.6% to 96.0%. The obtained wood pulp/NaOH/urea/H_2O solution was transparent with yellow color. Moreover, after ball milling 60 min, the delignified thermomechanical pulp with a high lignin content of 13.5 wt% could also be dissolved and used to prepare the lignocellulose hydrogels. It may provide one way to study the structure and properties of the lignin-carbohydrate complex in wood pulp by dissolution of the milled wood pulp in NaOH/urea solvent and also promote the utilization of lignocellulose as novel high-performance materials.

1. Introduction

Wood is widely grown on earth and an important potential source of raw materials for our daily life and the industrial production (Belta et al., 2017). The promotion of the utilization of this abundant wood biomass as materials, together with adequate artificial management of forests and tree plantations, would help to create a sustainable and low-carbon society (Xu et al., 2015; Nechyporchuk et al., 2016; Buzala et al., 2017; Chen et al., 2017; Chen et al., 2018; Yang et al., 2018). It has mainly been used in the fields of housing and furniture timbers, pulp and paper, and wood fuel. In recent years, dissolution of wood pulp to prepare high performance lignocellulose materials has become one promising application of wood (Li et al., 2011; Sun et al., 2011). The main components of wood are cellulose, hemicellulose and lignin, where lignin is present as a network polymer binding with the carbohydrates (cellulose and hemicelluloses) to form a compact structure (Adler, 1977). Development of solvent systems for wood pulp with high lignin content is not only required for examining the nature of the residual lignin and interactions among lignocellulose components but also for utilization of the lignocellulose as a new source of materials (Wang et al., 2009). However, the complicated interactions between lignin and carbohydrates in lignocellulose lead to the difficulty in dissolution of original lignocellulose in the conventional solvents. Moreover, there are several problems when the traditional solvent systems, such as lithium chloride/*N*, *N*-dimethylacetamide (LiCl/DMAc) (Sjöholm et al., 1997), lithium chloride/dimethyl sulfoxide (LiCl/DMSO) (Wang et al., 2009), and ionic liquids (Sun et al., 2011), are applied to dissolve wood pulp, because they are expensive, toxic or require harsh dissolution conditions.

In the recent decade, a serious of harmless, cheap and easy for handing solvents for dissolving cellulose have been developed by Zhang's group, namely alkali/urea solvent at low temperature (Cai and Zhang, 2005; Qi et al., 2008; Yang et al., 2011a,b,c, 2014; Shi et al., 2014a; Wang et al., 2016). Our previous work indicated that the native lignocellulose could not completely dissolve in the NaOH/urea solvent (Shi et al., 2014b). Therefore, pretreatments of lignocellulose are

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necessary for its efficient utilization. Various pretreatment methods (McMillan, 1994; Sun and Cheng, 2002; Mosier et al., 2005; Galbe and Zacchi, 2007; Kumar et al., 2009; Huang et al., 2013) for lignocelluloses have been reported and they can be mainly divided into several categories: physical pretreatment (ball milling, irradiation, sonication, *etc.*), chemical pretreatment (alkali, acid, oxidizing agents, organic solvent treatments, wet oxidation treatments, *etc.*), physicochemical pretreatment (steam explosion, supercritical fluid, *etc.*), biological pretreatment (lignin-degrading micro-organisms, *e.g.* white- and soft-rot fungi), and their combination pretreatments. The previous results indicated that the unbleached kraft pulp with lignin content about 4.2 wt% dissolved in NaOH/urea aqueous solvent after dilute acid treatment due to the reduction of molecular weight of cellulose (Shi et al., 2015). The dilute acid treatment was conducted using 3% H_2SO_4 at 80 °C. Even though the dilute acid treatment condition was not so harsh, the lignin in pulp may be broken at a certain degree in this case. The obtain lignocellulose solution may be sufficient to prepare a series of lignocellulose material, but it is not good to study the property of the native lignin. Ball milling is another important pretreatment method to influence the degree of polymerization and crystallinity of cellulose (Hermans and Weidinger, 1946; Howsmon and Marchessault, 1959; Zhao et al., 2006). It could promote the dissolution of cellulose in NaOH solution (Hermans and Weidinger, 1946; Kamide et al., 1984). Moreover, the milled wood lignin was obtained in a relatively high yield and was less changed than lignin isolated by chemical methods (Björkman, 1956; Chang et al., 1975). In general, the milled wood lignin is regarded as one of the closest lignin to the original lignin in wood. Therefore, ball milling treatment of the lignocellulose may promote its dissolution in the NaOH/urea solvent.

In this work, the wood pulps (unbleached kraft pulp, thermomechanical pulp and delignified thermomechanical pulp) were subjected to the ball milling treatment followed by dissolution in the NaOH/urea solvent. The effects of the ball milling on the morphology, structure, degree of polymerization (DP) and crystallinity index of the wood pulp and the relevant dissolution of the obtained milled wood pulp in NaOH/urea solvent were studied.

2. Materials and methods

2.1. Materials

Softwood unbleached kraft pulp with kappa number about 46 (lignin content of about 7 wt%) and thermomechanical pulp (lignin content of about 28.7 wt%) (Oiji Paper Co., Ltd., Japan) from radiata pine were used as lignocellulose. Epichlorohydrin (ECH) was purchased from Sigma-Aldrich Company; other reagents and solvents were of laboratory grade and used as received from Wako Pure Chemicals, Tokyo, Japan.

2.2. Ball milling of the wood pulp

The softwood unbleached kraft pulp (UKP) was shredded by juice mixer. Then the small pieces of dry pulp with 10 g were milled in a planetary ball mill (Fritsch GmbH, Pulverisette 5) with a 500 ml zirconium dioxide bowl and 80 zirconium dioxide balls (diameter of 1 cm). The milling frequency was 300 rpm. In order to prevent the mill from overheating, the milling was conducted in a 5 °C room and stopped 10 min between every 10 min milling. The milled pulps with different milling degrees were obtained by controlling the total milling time for 0–60 min, and coded as UKP–0 min, UKP–20 min, UKP–40 min, and UKP–60 min, respectively.

2.3. Dissolution of milled pulp in NaOH/urea aqueous solvent systems

The milled pulp was dispersed in the 7 wt% NaOH/12 wt% urea/81 wt% H_2O solvent with milled pulp content of 1 wt% according to the previous reported method (Cai and Zhang, 2005; Shi et al., 2014b, 2015). The pulp dispersion was freezed for 24 h at −20 °C, thawed at room temperature, and then stirred at 1000 rpm. The resulting mixture was centrifuged at 13000 rpm for 15 min at 5 °C. After the removal of the supernatant the corresponding solvent was added to disperse the precipitate and centrifuged. Addition of the solvent and the centrifugation was repeated 4 times to remove the entire soluble fraction. Then the dilute acetic acid with pH 4.5 was added to the precipitate until its pH became 7. After the removal of the supernatant by centrifugation, the precipitate was washed twice by the addition of water followed by centrifugation. Finally the supernatant was removed and the residual precipitate was dried at 105 °C for 2 days and weighed. The dissolved proportion of the milled pulp in the solvent was calculated according to the following equation:

$$\text{Dissolved proportion} = \frac{m_0 - m_1}{m_0} \times 100\% \quad (1)$$

where m_0 was the dry mass of the milled pulp before dissolution, and m_1 was the dry mass of the residual undissolved milled pulp. The dissolved proportion measurements were repeated by more than three times and their average was obtained.

2.4. Preparation of the hydrogel

The thermomechanical pulp (TMP) with weight of 5 g was delignified at 75 °C by the mixture of 1 g $NaClO_2$, 0.3 ml acetic acid and 160 g water for 4 times. It took 40 min for each time. The mixture was occasionally shaken by hand. The delignified TMP was finally obtained after filtration and denoted as BTMP. The lignin content of BTMP was 13.5 wt%. The BTMP pulp was dispersed in the 7 wt% NaOH/12 wt% urea/81 wt% H_2O solvent with pulp content of 4 wt% following the above method to prepare the BTMP solution. The ECH was added to the BTMP solution as cross-linker, stirred at 25 °C for 2 h to obtain a homogeneous solution, and then kept at −20 °C for 24 h to prepare gels. Finally, the gels were washed with water to obtain the BTMP hydrogels.

2.5. Analyses

2.5.1. Lignin determination

The Kappa number method and Klason method were used to determine the lignin content of the samples (Dence, 1992).

2.5.2. Morphology analysis

The dried original pulps and milled pulps were coated with osmium using a Meiwafosis Neo osmium coater at 10 mA for 5 s, and observed with a Hitachi S4800 field emission-type scanning electron microscope (SEM) at 2 kV.

2.5.3. X–ray diffraction (XRD)

The samples were dried in vacuum oven with P_2O_5 at 40 °C for 48 h. Then XRD patterns of the samples were acquired in reflection mode using a RINT 2000 diffractometer (Rigaku, Tokyo, Japan) with monochromator–filtered Cu Kα radiation (λ = 0.15418 nm) at 40 kV and 40 mA. Scans were obtained from 2θ of 4–40° at a speed of 1° per min. Crystallinity index (*C.I.*) was calculated from the height ratio between the intensity of the crystalline region and total region according to the Segal's method (Segal et al., 1959).

2.5.4. Viscosity-average degree of polymerization (DP_v) measurement

The sample (0.04 g) were dissolved in 0.5 M copper ethylenediamine (20 ml) for 30 min. Intrinsic viscosity of the solution was obtained by using a Cannon−Fenske capillary viscometer, and the value was converted to DP_v values by using the Mark−Houwink−Sakurada equation $[\eta] = 0.57 \times DP_v$ (Shinoda et al., 2012).