

論文の内容の要旨

生物材料科学専攻

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氏 名 石 竹 群

指導教員名 松本 雄二

論文題目 Application of aqueous alkali/urea cellulose solvent system to wood pulps
(アルカリ-尿素水系セルロース溶剤の木材パルプへの適用)

Lignocellulose is the most abundant biomass on earth and has potential as a renewable resource for applications in versatile commodity and high-tech materials. Dissolution of lignocellulose is not only important for utilization of the lignocellulose resource but also useful for understanding the interactions among the main components of the plant cell wall (cellulose, hemicelluloses and lignin). The complicated structures and interactions between lignin and carbohydrate in lignocellulose lead to its difficulty in dissolving in conventional solvents in the native state.

In recent years, some cellulose solvents have been used to dissolve lignocellulose. Compared with the other developed cellulose solvents such as lithium chloride/N,N-dimethylacetamide (LiCl/DMAc), N-methylmorpholine-N-oxide (NMMO), and ionic liquids, the alkali/urea (NaOH/urea and LiOH/urea) aqueous system is a simple, low-cost, and environment-friendly route without producing any toxic byproduct. Although pure cellulose could dissolve well in alkali/urea system and the obtained cellulose/alkali/urea solution has been used to produce all kinds of cellulose materials, dissolution of lignocellulose in this system has never been examined in detail until now. If alkali/urea solvent could be successfully applied to lignocellulose, its application will be widely expanded and utilization of lignocellulose as a new source of materials will also be facilitated.

Therefore, the objective of my doctoral research is to do fundamental studies on

dissolution of lignocellulose in aqueous alkali/urea system and analysis of the interactions among the plant cell wall components. The effects of lignin content, hemicellulose content, crystallinity, crystal form, and molecular weight of lignocellulose on its dissolution will be evaluated and different pretreatment methods (dilute acid treatment and ball milling treatment) will also be used to improve the dissolution. It is a new route of an advance environment-friendly technology to prepare lignocellulose solution and materials. The research and application of the new lignocellulose solution will benefit for creating a sustainable society.

Effects of lignin and hemicellulose contents on dissolution

Four species of delignified woodchips with about 1 wt% lignin content (Chlorite–Woodchips) and a series of softwood pulps with different lignin contents were prepared by sodium chlorite delignification. After mechanical defibration, some Chlorite–Woodchips were directly subjected to dissolution treatment in NaOH/urea solvent; the others were first treated with NaOH solution to remove the hemicellulose to obtain NaOH–Chlorite–Woodchips or oxidized with potassium permanganate (OPP) to remove lignin completely to obtain OPP–Chlorite–Woodchips, and then subjected to the dissolution in NaOH/urea solvent. The results showed that the dissolved proportion of the Chlorite–Woodchips ranged from 36% to 46 %, the dissolved proportion of glucan was within 12%, and most of the hemicellulose was dissolved in NaOH/urea solvent. Compared with Chlorite–Woodchips, the dissolved proportion of NaOH–Chlorite–Woodchips was lower, but their dissolved proportion of glucan was higher. After further permanganate delignification, both the dissolved proportion of the OPP–Chlorite–Woodchips and the dissolved proportion of glucan of the OPP–Chlorite–Woodchips were higher than those of the Chlorite–Woodchips. However, the dissolved proportion of glucan was still limited to only 15–30 %. The effect of lignin content of thermo mechanical pulp (TMP) on their dissolution was studied. After delignification, the lignin content of TMP decreased from 28.7 wt% to 11.2 wt%, meanwhile the dissolved proportion increased from 10.5% to 47.8%, which shows a linear relationship with lignin content. However, when the lignin content was not so high, the effect of the lignin content of softwood unbleached kraft pulps on their dissolution is complicated. With the decrease of the lignin content of softwood pulp from 6.9 wt% to 2.8 wt%, the dissolved proportion of the pulp increased from 14% to 26 %. However, further reduction of lignin content from 2.8 wt% to 0.3 wt% led to a

decrease in the dissolved proportion of pulp from 26% to 12%. The dissolved proportion of glucan followed the same tendency. These results indicated that the dissolution of wood cellulose in NaOH/urea solvent is not simply controlled by the hemicellulose and lignin contents, but also by some other factors.

Dissolution of lignocellulose by dilute acid pretreatment

Softwood unbleached (UKP, lignin content 4.2 wt%) and bleached (BKP, lignin content 1.2 wt%) kraft pulp after 3 wt% H₂SO₄ pretreatment were successfully dissolved in aqueous NaOH/urea solution. The lignin and hemicellulose contents of the pulps almost didn't change after the dilute acid treatment; however, crystallinity indices of pulps increased. Moreover, their dissolved proportions increased with the increase in acid hydrolysis time, accompanied by the decrease in their viscosity-average degrees of polymerization (DP_v), as shown in Figure 1.

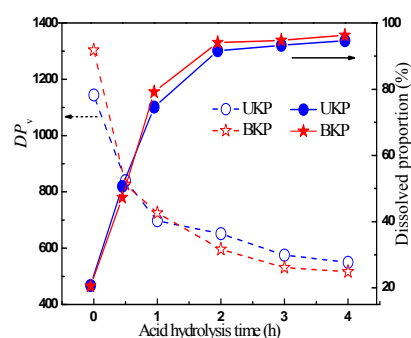


Fig. 1. Effects of acid hydrolysis time on the dissolved proportions and viscosity-average degrees of polymerization (DP_v) of the wood pulps.

After acid hydrolysis 2 h, the wood pulps still possessed a relatively high DP_v of 600; however, they almost completely dissolved in NaOH/urea solution with a dissolved proportion of more than 90%. When the lignin content was not so high (within 4.2 wt%), no significant difference between dissolved proportions of UKP and BKP was found under the same acid treatment condition. Thus, influences of crystallinity indices and lignin contents could be neglected here and the main factor to affect the dissolved proportion of wood pulps should be the DP. However, for the unbleached kraft pulp (UKP') with high Klason lignin content of about 6.1 wt%, after acid hydrolysis 4 h, the dissolved proportion of it increased from 24.7% to 70%. Longer acid hydrolysis time was needed for its complete dissolution. On the other hand, for the delignified thermo mechanical pulp (BTMP), even though the Klason lignin content was as high as 13.5 wt%, after acid hydrolysis 4

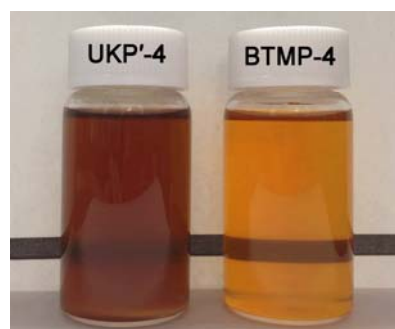


Fig. 2. Photos of UKP'-4/NaOH/urea and BTMP-4/NaOH/urea solutions.

h, it dissolved very well in NaOH/urea aqueous solvent. Although the lignin content of BTMP was higher than that of UKP', after the same acid treatment condition the dissolved proportion of BTMP was higher than UKP', as shown in Figure 2. Maybe it was due to that the different original sources and different pulping making process led to their different lignin structures and lignin carbohydrate complex. This work indicated that even though the lignin content was as high as 13.5 wt%, it could be dissolved in NaOH/urea solvent. Therefore, these lignocelluloses are promising to be used to prepare all kinds of lignocellulose materials by dissolution and regeneration and the applications of lignocelluloses are widely expanded.

Dissolution of lignocellulose by ball milling pretreatment

The unbleached kraft pulp (UKP) with a lignin content about 6.9 wt% was successfully dissolved in NaOH/urea aqueous solvent after ball milling 1 h. The optical transmittances of ball milling treated UKP/NaOH/urea solution prepared by freeze and thaw was much higher than that of ball milling treated UKP/NaOH/urea dispersion prepared at room temperature. Ball milling treatment affected the structures and properties of lignocellulose obviously. Even though ball milling 40 min, the crystallinity indices of lignocellulose decreased remarkably, and it almost became amorphous. After ball milling 1h, DP of cellulose decreased from 1300 to about 330. The dissolubility of cellulose in LiOH/urea aqueous solution is stronger than that of cellulose in NaOH/urea aqueous solution, in terms of dissolution of celluloses with higher molecular weights and preparation of cellulose solutions with higher cellulose concentrations. However, in this work, it was interesting that the dissolved proportions of the unbleached kraft pulps after ball milling in the LiOH/urea solvent were lower than those in the NaOH/urea solvent, even though the difference was not so large (less than 10%).

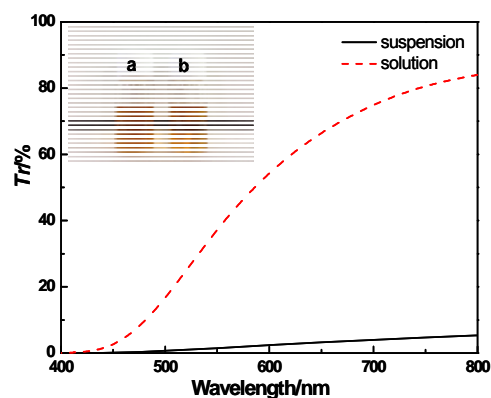


Fig. 3. Optical transmittances (T_r) and photos of the UKP-60min suspension (a, dispersion of UKP-60min in NaOH/urea solvent at room temperature) and solution (b, dispersion of UKP-60min in NaOH/urea solvent at room temperature, followed by freeze and thaw).