CELLULOSE CHEMISTRY AND TECHNOLOGY

HOMOGENEOUS SYNTHESIS OF CROSSLINKED CELLULOSE SPHERES FROM HEMP (*CANNABIS SATIVA* L.) STEM AND COTTON

RU YANG, YONG WANG and MIN LI

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology,
Beijing 100029, P.R. China
✉ *Corresponding author: Ru Yang, yangru@bbn.cn*

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Cellulose, extracted from hemp (*Cannabis sativa* L.) stems, was successfully crosslinked with hexamethylene diisocyanate through the homogeneous reaction in the solvent N-methylmorpholine-N-oxide (NMMO). Cotton was also used due to its high cellulose content. The cellulose spheres, about 1 μm in diameter, were obtained through chemical cross-linking reaction. Fourier transform infrared spectroscopy (FTIR) showed that the carbonyl group, NH-group and urethane were introduced. Thermogravimetry (TG) indicated that the crosslinked products had better heat resistance than native cellulose. It was found that the adhesion phenomenon appeared with the increasing amount of cotton cellulose. A possible model of formation of the crosslinked cellulose spheres was also proposed in this paper.

Keywords: cellulose spheres, hexamethylene diisocyanate, crosslinking, NMMO

INTRODUCTION

Cellulose, the most abundant renewable resource in the world, is widely used to prepare cellulose derivatives. Through chemical modification, cellulose materials with new interesting properties can be acquired. However, chemical processing of cellulose is, in general, difficult because this natural polymer is not soluble in common solvents, due to its hydrogen bonds and partially crystalline structure.[1] Therefore, traditional modifications are mostly carried out in the heterogeneous phase. To date, researchers have focused their attention on developing the homogeneous way to obtain more uniform and stable products. Recently, ionic liquid has been used as a medium in cellulose chemistry, and homogeneous chemical modifications of cellulose in ionic liquid have been reported.[2-4] In addition, homogeneous methylation of wood pulp cellulose dissolved in LiOH/urea/H_2O has also been investigated lately.[5,6]

NMMO, as a bulk solvent in industrial fiber-making processes, can regenerate cellulose availably. In NMMO medium, cellulose molecular chains are relatively free and homogeneous chemical reactions may be carried out. However, there are still few reports about the chemical reaction of cellulose in NMMO. Chaudahri *et al.*[7] investigated the carboxymethylation reaction of cellulose in NMMO system in 1987, and Heinze *et al.*[8] published an article to give more experimental details in 1999. Since then, the study on the homogeneous reaction of cellulose in NMMO stagnated. As a basic research, it is necessary to overcome some difficulties to study the reactions in this cellulose solvent system, though NMMO has some defects as chemical reaction medium to some extent. In this paper, hexamethylene diisocyanate (HDI) was chosen to crosslink cellulose molecules in the NMMO system. Isocyanates are a very important industrial raw material to synthesize elastomers, such as polyurethane. HDI, whose isocyanate groups are very sensitive to OH-groups, has been used to modify cellulose in heterogeneous system.[9]

In previous reports, almost all the cellulose spheres or beads were prepared by a suspension

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embedding procedure in the presence of Span 80 or other surfactants.[10-12] Du *et al.*[13] prepared cellulose beads from cellulose solution in ionic liquid by double emulsification formed by Tween 60 and Span 85. The obtained products had a large size, usually greater than 50 μm in diameter. There are hardly any reports on cellulose spheres synthesized by the chemical crosslinking method. The raw materials used are from hemp stems and cotton. Therein, cotton consists almost entirely of cellulose, and hemp (*Cannabis sativa* L.) has been planted agriculturally for centuries to get its bast fiber and hempseed oil. Hemp stems, rich in cellulose, are usually considered as agricultural waste. Undoubtedly, this research is one of the most promising means to convert hemp stems into novel value-added cellulose materials through chemical crosslinking.

EXPERIMENTAL

Materials

Hemp stems from Yunnan province in China were smashed into powders (> 60 meshes) and poached before used. Cotton fibers were obtained from commercial sources without further treatment. NMMO (99.7 wt%), purchased from Huai'an Huatai Chemical Co., Ltd, was dissolved in deionized water to form a 50 wt% solution. Dimethyl sulfoxide (DMSO) was purchased from Beijing Chemical Works. Hexamethylene diisocyanate was acquired from Shanghai Jingchun Reagent Co., Ltd.

Preparation of crosslinked cellulose spheres

Hemp stem powders (0.75 g) were added to 80 mL of 50 wt% NMMO/H_2O solution and soaked with stirring at room temperature for 4 hours. Then, the mixture was heated to 90 °C to remove water through reduced pressure distillation, making the cellulose dissolve out of the hemp stems easily. The temperature was maintained at 90~95 °C for 30 min and a sticky light-yellow translucent solution was obtained. The insoluble substance was filtered with a fine screen, washed, dried and weighed. Subsequently, the filtrate containing 0.15 g cellulose extracted from hemp stem was diluted with 35 mL of DMSO. Then, 2 mL of HDI was added dropwise into the diluted cellulose solution (NMMO/DMSO) under strong agitation for one hour. To separate out the final products, 100 mL of deionized water was added to this cloudy mixture. The light yellow powder was named HC-HDI. If water was directly added without HDI, hemp stem cellulose (HC) could also be acquired.

The preparation process of cotton cellulose (CC) solution was the same as described above. Likewise, 0.15 g and 0.5 g cotton fibers were, respectively, dissolved in NMMO solution without filtering the insoluble substance and 35 mL of DMSO was used to dilute the solution. After that, 2 mL of HDI was added dropwise into both diluted cellulose solutions under strong agitation for one hour. One hundred milliliters of deionized water was added to the cloudy mixture, and the final products were named CC-HDI-0.15 and CC-HDI-0.5, respectively.

The detailed preparation information is provided in Table 1.

Measurement

The morphology was observed by a HITACHI S4700 scanning electron microscope (SEM). Fourier transform infrared spectra (FTIR) were acquired to investigate the chemical structure and groups with a Nicolet 8700 FTIR spectrometer. Thermogravimetric (TG) experiments were carried out under a nitrogen flow with a TG/DTA thermal analyzer from Shanghai Precision & Scientific Instrument Co., Ltd.

Table 1
Detailed preparation information of the three samples

Samples	Cellulose weight (g)	NMMO (mL)	DMSO (mL)	HDI (mL)
HC-HDI	0.15	80	35	2
CC-HDI-0.15	0.15	80	35	2
CC-HDI-0.5	0.50	80	35	2

RESULTS AND DISCUSSION

SEM study of the morphology

Fig. 1 exhibits the SEM images of cellulose raw materials and their corresponding spheres. Fig. 1a shows the cellulose extracted from hemp stems, which appears to be interlaced and ribbon-like. However, the HC-HDI samples synthesized from the crosslinking reaction with HDI are spherical and about 1 μm in diameter (Fig. 1b). These spheres look like clews woven of microfibers in the magnified image (Fig. 1c). Fig. 1d, e and f show the morphology of crude cotton fibers, CC-HDI-0.15 and CC-HDI-0.5, respectively. It can be seen that the cotton cellulose in Fig. 1d is fibriform, of about 10 μm in diameter, while the same clewlike spheres as HC-HDI are also exhibited in Fig. 1e and f. Moreover, with the increasing amount of cotton cellulose, the adhesion phenomenon appeared possibly owing to the excess cellulose in solution.

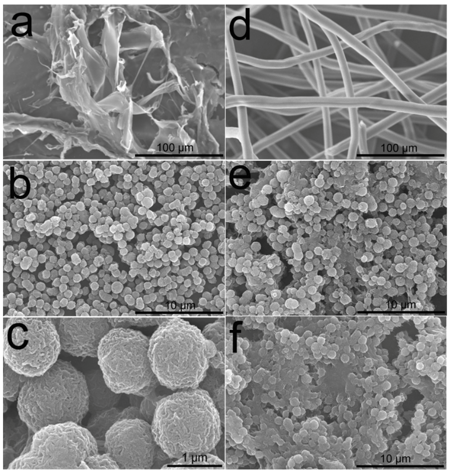

Figure 1: SEM images of (a) cellulose extracted from hemp stems, (b) HC-HDI, (c) magnified HC-HDI, (d) cotton cellulose, (e) CC-HDI-0.15 and (f) CC-HDI-0.5

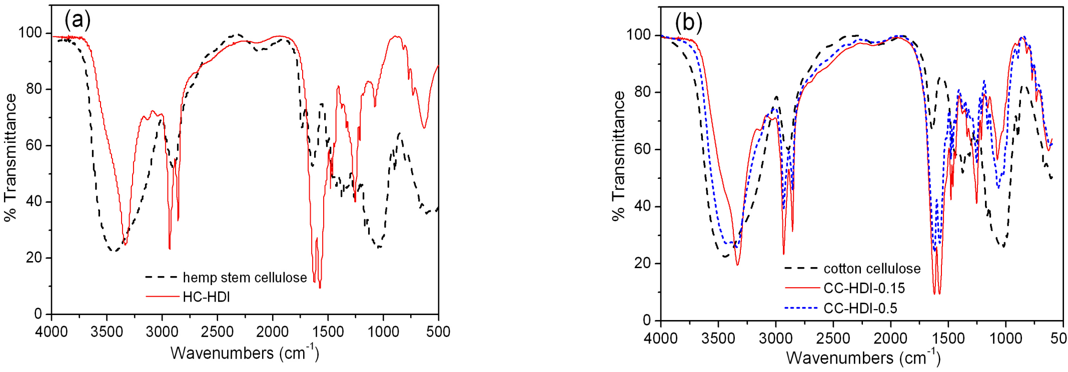

Figure 2: FTIR spectra of hemp stem cellulose and its crosslinked products with HDI (a), and cotton cellulose and its crosslinked products with HDI (b)

Chemical groups characterized by FTIR

Fig. 2 shows the FTIR spectra of pristine cellulose and the reaction products with HDI. Both the regenerated cellulose from hemp stems in Fig. 2a and the cotton cellulose in Fig. 2b exhibit typical absorption peaks of cellulose, which were reported before.[14] After the introduction of HDI, both HC–HDI and CC–HDI show similar FTIR spectra. An intensive band for the –OH (and –NH) groups in the range of 3400 cm^{-1} is also observed. However, this peak became narrower and the relative absorbance decreased with the reduction of cellulose from 0.5 g to 0.15 g (Fig. 2b). That may be attributed to the sufficient reaction of isocyanate groups with hydroxyl groups on the cellulose chains when there was less cellulose.[1] The double peaks at 2933 cm^{-1} and 2857 cm^{-1} show symmetric and asymmetric $-CH_2-$ stretches, which were collectively induced by cellulose and HDI.[15] Further, the peaks at 1622 cm^{-1} and 1574 cm^{-1} can be related to the appearance of carbonyl group (C=O) and the NH-group deformation oscillation, which confirms that cellulose was crosslinked with HDI.[9,15,16] The peak at 1254 cm^{-1} is assigned to the C–O group connecting with Pi bond, which further indicates the presence of urethane introduced by the reaction of –OH with –N=C=O.[15,16]

Possible formation mechanisms of the cellulose spheres

According to the functional group analysis, a crosslinking reaction schematic is proposed in Fig. 3. Cellulose was dissolved in the NMMO system, which was diluted by DMSO. HDI was slowly dropped into the solution under stirring. The HDI droplets were dispersed in this solution just like an emulsion system. The cellulose molecules around droplets reacted with HDI rapidly by following procedures (A) and (B), resulting in the crosslinked clewlike spheres. In procedure (A), a urethane linkage was formed through the reaction between isocyanate and a hydroxyl group. The urethane group continued to react with a new isocyanate molecule to generate an allophanate group in procedure (B).

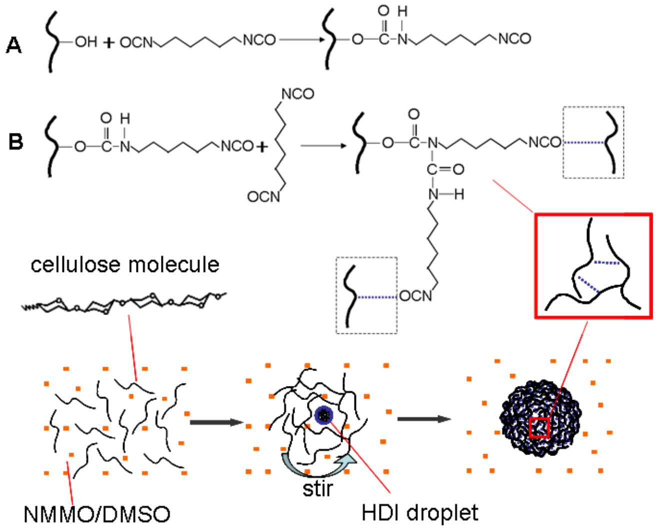

Figure 3: A proposed model for the formation of crosslinked cellulose spheres

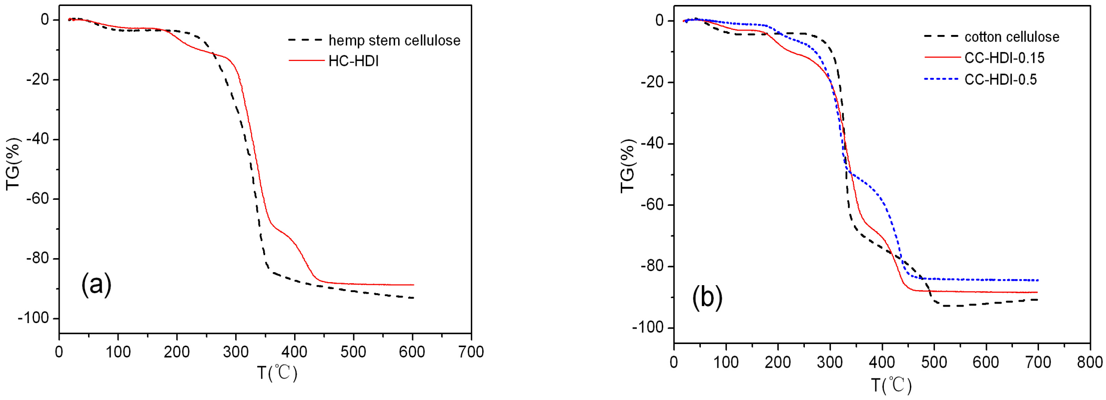

Figure 4: TG curves of hemp stem cellulose and its crosslinked products with HDI (a), and cotton cellulose and its crosslinked products with HDI (b)

Thermostability analysis

Thermogravimetric curves for pristine cellulose and their crosslinked products with HDI are shown in Fig. 4. The curves of both hemp stem cellulose and HC-HDI had an initial loss of moisture and desorption of gases at about 80-110 °C, as shown in Fig. 4a. Next, a major decomposition proceeded from 230 to 370 °C for hemp stem cellulose and its maximum decomposition temperature appeared at 340 °C. However, for HC-HDI, there were two additional weight losses at 180-280 °C and 380-450 °C, which could be attributed to the actual pyrolysis brought by the minor decomposition reaction[1] and the breakage of the crosslinked structure, respectively. The final decomposition temperature of HC-HDI is higher than that of the original cellulose, because the crosslinked structure can improve the thermal stability.[17] In Fig. 4b, the TG curve of cotton cellulose shows one more weight loss at 370-520 °C, compared to the regenerated hemp stem cellulose, which may attributed to the better crystalline region and less amorphous region in the untreated cotton cellulose.[18] Yet, the final thermal stability temperatures of the reaction products are lower than those of the untreated cellulose, possibly because the crosslinked structure of regenerated cotton cellulose from NMMO is still less thermoduric than the perfect natural cotton.

CONCLUSION

Crosslinked cellulose spheres, about 1 μm in diameter, have been prepared by the homogeneous reaction of plant cellulose with HDI in the NMMO system. The characterization results imply that these products have crosslinked structure of urethane and allophanate groups. It was found that the products from hemp stems are more thermoduric than the regenerated cellulose, but the result is opposite for cotton cellulose. Finally, it should be pointed out that NMMO must be handled with caution, as it is oxidizing, labile and even explosive under high temperature, and any incorrect operation may lead to hazards.

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