SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT WOOD PULP CELLULOSE DERIVATIVE BASED ON SCHIFF BASE REACTION

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The study investigated the effects of different oxidant/cellulose mass ratio on dialdehyde cellulose (DAC) and corresponding cellulose Schiff's base (CSB) with fluorescence. Three DACs were synthesized first from hydrolyzed wood pulp cellulose under 45 °C, and then reacted with 2-methyl-4-nitroaniline (MNA). The morphology, structure, thermal and fluorescence behaviors were characterized by a polarizing microscope, FT-IR, DSC and a fluorescence microscope. The results showed that the oxidant content is the key step to prepare wood pulp CSB. When the mass ratio is 0.5 and 1, the DAC and CSB can retain better rod morphology and thermal stability because the reaction mainly occurs in the amorphous region of the cellulose surface.

Keywords: wood pulp cellulose, Schiff's base, morphology, fluorescence

INTRODUCTION

Cellulose is one of the most abundant biomass materials in the world. According to the different sources in nature, it can be obtained from plant cell walls, algae, tunicates and bacteria. The cellulose macromolecule presents many prominent advantages, such as renewability, biocompatibility, biodegradability, regular structure, and susceptibility to modification by reactive hydroxyl groups.[1] Owing to these features, recently, many research works have been focused on exploring its potential application for more broad fields, as (i) textile material,[2] (ii) composite material,[3] (iii) adsorbent material,[4] (iv) biomedical material,[5,6] (v) membrane separation material,[7] and so on. Many new and specific usages of cellulose are dependent on the chemical modification by changing its bulk or surface properties, which can be realized by homogeneous or heterogeneous synthesis paths. Homogeneous synthesis is usually adopted to change the bulk properties of cellulose to obtain a new polymer easy to dissolve or to transform. On the other hand, since the surface properties of cellulose are crucial in many applications, the heterogeneous reaction is more appropriate to change the surface performance of cellulose.

Up to now, a number of attempts have been made to modify the surface of cellulose, including using some small molecule compounds containing reactive groups,[8,9] oligoether chains,[10] and polymer chains.[11-13] The reported compounds included triazine derivative,[2,3,14] amine compound,[15,16] iron salt,[17] etc. Among them, several amine compounds have been applied to modify cellulose, including aromatic amines,[8] aminosilicones,[18] PEI and EDA,[15] PDM and ASA[16] etc., and their main products are Schiff base.

Schiff base compounds containing an imine group (-RC=N-) are usually formed by the condensation of a primary amine with an active carbonyl. Currently, three paths of cellulose modification with amino derivatives are reported in the literature. That is, the cellulose is directly treated with an amine compound under a certain thermal treatment, indirectly reacted with amino derivatives by an activator N,N'–carbonyldiimidazole, indirectly reacted with an amino compound (PDM, ASA) by dialdehyde carboxymethyl cellulose. Although all modifications proved to form imines from amino and carbonyl groups, which is responsible for the fluorescence, the influencing factors and the mechanism of the modification process have been scarcely reported. In the present work, we modified the wood pulp cellulose with a commercial dye named Spectrolene Red RL (MNA) by the two-step process. The morphology, thermal and fluorescence behaviors of the intermediate and final products are discussed in detail.

EXPERIMENTAL

Wood pulp cellulose board was a commercial bleached eucalyptus pulp from Shanghai Senmao pulp & Paper Co., Ltd. Sulphuric acid, sodium metaperiodate and hydroxylamine hydrochloride were of reagent grade (Nanjing Chemical Reagent No.1 Factory, China). MNA (2-methyl-4-nitroaniline) was a commercial product, also named Spectrolene Red RL (Wujiang Jinsui Chemical Co. Ltd.), which was recrystallized twice from methanol.

The synthesis route of DAC and cellulose Schiff base is shown in Fig. 1, and the specific steps are described below.

Cellulose board was cut into small pieces first, put in a 250 ml beaker, immersed in sodium hydroxide solution (15 wt%) for 0.5 h. Then, hydrochloric acid was added to neutralize the solution up to a neutral pH. After filtering through a sand core funnel and drying, a cleaned and activated sample was obtained.

The sample and sulphuric acid solution (60 wt%) were added into a reaction flask and were hydrolyzed at 45 °C under agitation for 0.5 h. Then, the product was filtered and dried.

A desired amount (1, 2, 4 g) of sodium metaperiodate was dissolved in 100 ml of deionized water and 2 g of hydrolyzed cellulose powder was added to the solution in a flask. The mixture was stirred at 50 °C in the dark for 3 h.[19] After the remaining periodate was decomposed in 10 ml ethylene glycol for 1 h, the product was washed by deionized water, filtered in vacuum and dried.

The amount of the introduced aldehyde was determined by the consumption of alkali in the Cannizzaro reaction.[20,21] The data are presented in Table 1. The DAC samples were converted to nitrogen-containing compounds by Schiff base reaction. MNA (2 ± 0.2 g) was dissolved in 100 ml absolute ethyl alcohol in a 250 ml flask and added to 2 g of DAC. The mixture was stirred at 80 °C for 4 h, filtered and dried. The coarse product was extracted with ethyl alcohol in a Soxhlet extractor at 90 °C for 6 h, and the final cellulose Schiff base was obtained by filtration and dried in vacuum.

A polarizing microscope (MA 1000/MA 2000, Chongqing Optical Instrument Co. Ltd, China) was used to observe the morphology of different wood pulp cellulose and modified samples.

The FTIR spectra of different wood pulp cellulose and modified samples were measured with an ATR (attenuated total reflectance) attachment of VERTEX 70 (Bruker, Germany). The samples were placed on a germanium plate, and 16 scans were collected for each sample at a resolution of 4 cm^{-1}.

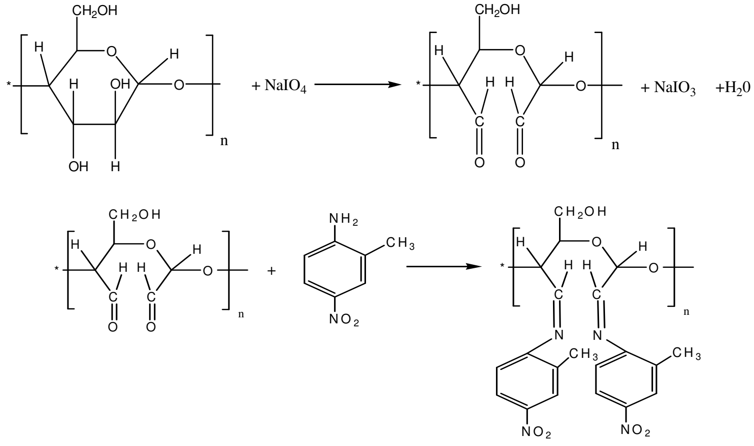


Figure 1: Reaction scheme of the DAC and cellulose Schiff base

Table 1
Reaction conditions and aldehyde contents of DAC

Sample	Hydrolysis temperature (°C)	Oxidation temperature (°C)	pH	$NaIO_4$/cellulose (mass ratio)	Aldehyde content (%)
1.1	45	50	4	0.5	4.29
1.2	45	50	4	1	6.11
1.3	45	50	4	2	12.26

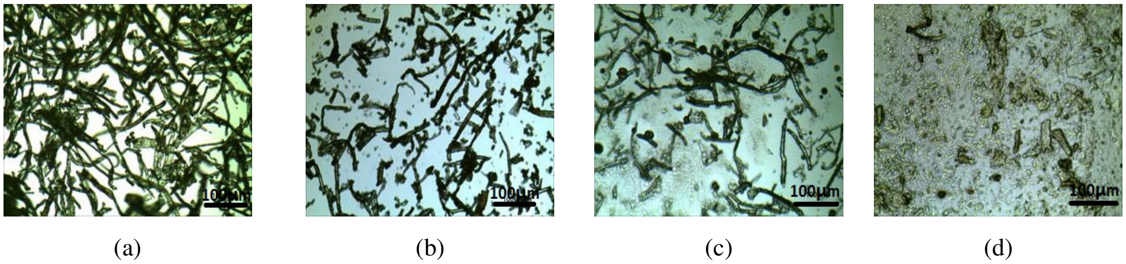
The samples were completely dried at 105 °C for 4 h before DSC determination. The measurement was conducted by heating the samples from room temperature to 400 °C, at a heating rate of 10 °C/min under air atmosphere, using a CDR-4P apparatus (Shanghai Precision Scientific Instrument Co., Ltd., China).

The samples were investigated with a fluorescence microscope IX71 (OLYMPUS, Japan). The fluorescence emission spectra were obtained at excitation wavelengths of 425 and 530 nm.

RESULTS AND DISCUSSION

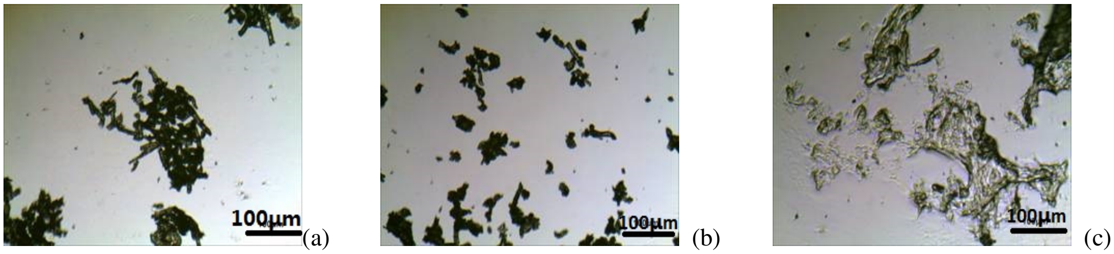
Wood pulp cellulose hydrolyzed at 45 °C and the corresponding dialdehyde cellulose with different oxidant content are shown in Fig. 2. When the m ($NaIO_4$)/m (cellulose) ratio was 0.5, the mean length of DAC shortened obviously compared with the initial cellulose hydrolyzed at 45 °C. With an increasing oxidant content, which is, m ($NaIO_4$)/m (cellulose) changed from 0.5 to 2, the mean length of DAC shortened gradually from about 150, 100 to 30 µm. For the samples containing an m ($NaIO_4$)/m (cellulose) ratio of 0.5 and 1, the DAC retained better rod shape, however, most of the rod shape of DAC disappeared when the ratio was 2.

When the DAC reacted with MNA, and the product was refined in a Soxhlet extractor, the morphology of corresponding cellulose Schiff base was obtained, as shown in Fig. 3. Compared with DAC, the mean length of the cellulose Schiff base shortened after the second reaction. For the DAC where the m ($NaIO_4$)/m (cellulose) ratio was 0.5 and 1, the cellulose Schiff base also retained better rod shape for about 100 to 50 µm, while the rod morphology disappeared completely for the last cellulose Schiff base.



(a) (b) (c) (d)

Figure 2: Wood pulp cellulose hydrolyzed at 45 °C (a) and samples 1.1 (b), 1.2 (c) and 1.3 (d)



(a) (b) (c)

Figure 3: Wood pulp cellulose Schiff base; grafted sample 1.1 (a), grafted sample 1.2 (b), and grafted sample 1.3 (c)

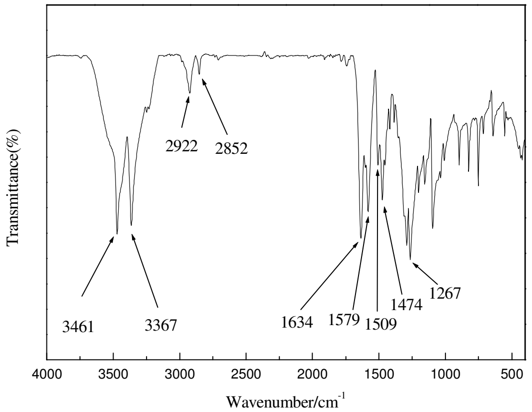


Figure 4: FT-IR of MNA

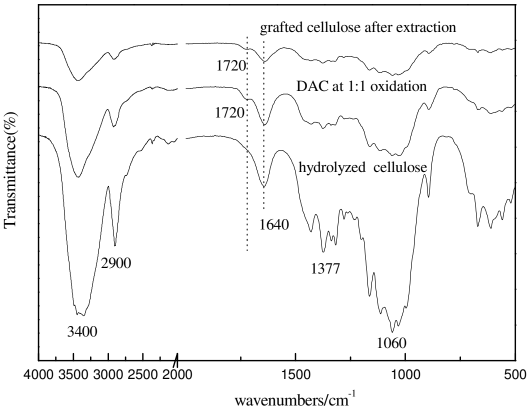


Figure 5: FT-IR of different wood pulp celluloses

The infrared spectra of the amine compound (MNA) are provided in Fig. 4. The peaks at 3461 and 3367 cm^{-1} are assigned to $-NH_2$ stretching vibrations, and that at 1634 cm^{-1} is due to the $-NH_2$ bending vibration. The peak at 2922 cm^{-1} corresponds to C-H asymmetric stretching of $-CH_3$, and that at 2852 cm^{-1} to the C-H symmetric stretching vibration. The bands at 1579, 1509 and 1474 cm^{-1} are associated with benzene skeleton vibration and that at 1267 cm^{-1} is due to the asymmetric stretching of $-NO_2$.

Fig. 5 illustrates the FT-IR spectra of hydrolyzed wood pulp cellulose, DAC, cellulose grafted with MNA after extraction in the Soxhlet apparatus, respectively. The main bands observed in the IR spectra of the original hydrolyzed wood pulp cellulose are as follows: the OH group stretching vibration at 3400 cm^{-1}; the C–H asymmetric stretching vibration at 2900 cm^{-1}; the band at 1640 cm^{-1} can be most likely attributed to the H–O–H bending vibration of water molecules, probably coming from the intermolecular hydrogen bonds between linear polysaccharide chains;[22] the OH bending vibration at 1377 cm^{-1}; the ether bond of C–O–C–O–C is shown as a characteristic peak near 1060 cm^{-1}.

Obviously, DAC shows a characteristic shoulder peak at 1720 cm^{-1}, which must be assigned to the C=O stretching vibration.[23] The IR spectra of the Schiff bases present a strong absorption band between 1631 and 1640 cm^{-1} attributed to the C=N vibrations of imines.[24] However, after further reaction with MNA and extraction in the Soxhlet extractor, there is no obvious characteristic band related to the C=N group, because it may have overlapped the former H–O–H bending vibration at 1640 cm^{-1}. On the other hand, the FTIR cannot detect the C=N vibration probably because the final grafted cellulose product has lower Schiff base content. In spite of this, the FTIR spectra still maintain the former shoulder peak represented by the unreacted acetaldehyde, which appears wider near 1720 cm^{-1}, which probably suggests that the condensation reaction to form the C=N group is incomplete.

Differential scanning calorimetry (DSC) is one of the most important methods for observing the thermal characteristics of materials. After the hydrolyzed wood pulp cellulose was chemically modified with $NaIO_4$ and MNA, the chemical and morphological structures of the modified cellulose changed. The chemical modification had an effect upon the thermal stability of the modified cellulose.

Fig. 6 shows the DSC plots of the hydrolyzed wood pulp cellulose, and cellulose modified with different oxidant contents and MNA, respectively. The data are also listed in Table 2. For the wood pulp cellulose hydrolyzed at 45 °C, the exothermic peak initiated at 232 °C and ended at about 400 °C, as shown in Table 2, accompanied by the decomposition reaction of cellulose in air atmosphere. For the MNA, the characteristic endothermic peak occurred at 120 °C, which is in accordance with its melt process.

When the m ($NaIO_4$)/m (cellulose) ratio was 0.5, the exothermic peak of DAC initiated at 280 °C and ended at 400 °C. The position of the initial exothermic peak was more than 50 °C higher than that of hydrolyzed wood pulp cellulose. The exothermic changes obtained in the DSC plot for DAC are mainly associated with decomposition processes in air, which may occur within the surface area of hydrolyzed wood pulp cellulose during heating, and no apparent change in the crystalline regions of the cellulose is observed. Moreover, for the DAC further modified by MNA, the DSC profile of the obtained cellulose Schiff base resembles that of DAC. This phenomenon shows that the modification processes are possibly due to local surface changes in the non-crystalline regions of the hydrolyzed wood pulp cellulose.

When the m ($NaIO_4$)/m (cellulose) ratio was 1.0, the exothermic peak of DAC initiated at 240 °C, a value that lies between that of the hydrolyzed wood pulp cellulose and that of the sample for m ($NaIO_4$)/m (cellulose) = 0.5. That is, with an increased oxidant content, the surface non-crystalline regions of the hydrolyzed wood pulp cellulose was apparently destroyed, and it would be easy to decompose it and perform the exothermic reaction at an elevated temperature.

Table 2
DSC data of different wood pulp celluloses

Sample*	Initial exothermic peak (°C)	Peak temperature (°C)	Termination of exothermic peak (°C)
45 °C hydrolysis	232	325	400
0.5:1 oxidation	280	324	400
Grafting after 0.5:1 oxidation	280	325	400
1:1 oxidation	240	322	400
Grafting after 1:1 oxidation	241	323	400

*The exothermic peak of DAC disappeared at 2:1 oxidation and grafting

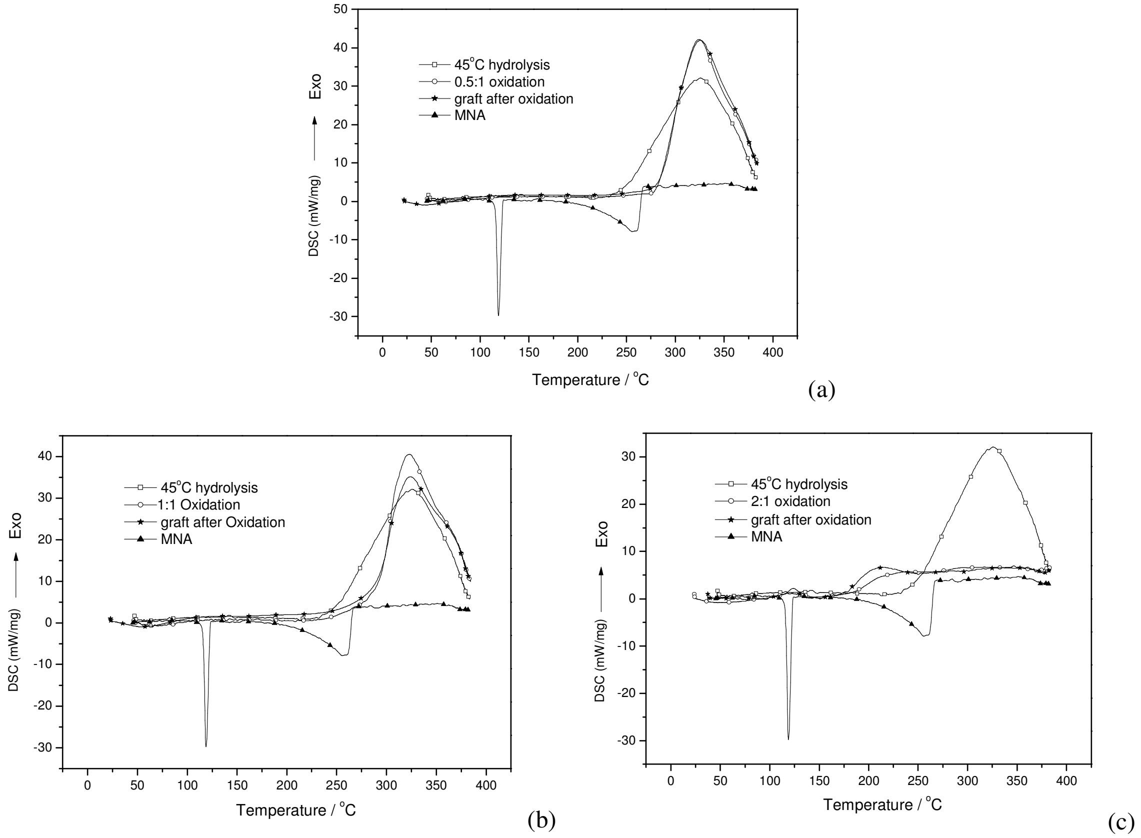


Figure 6: DSC of different wood pulp celluloses

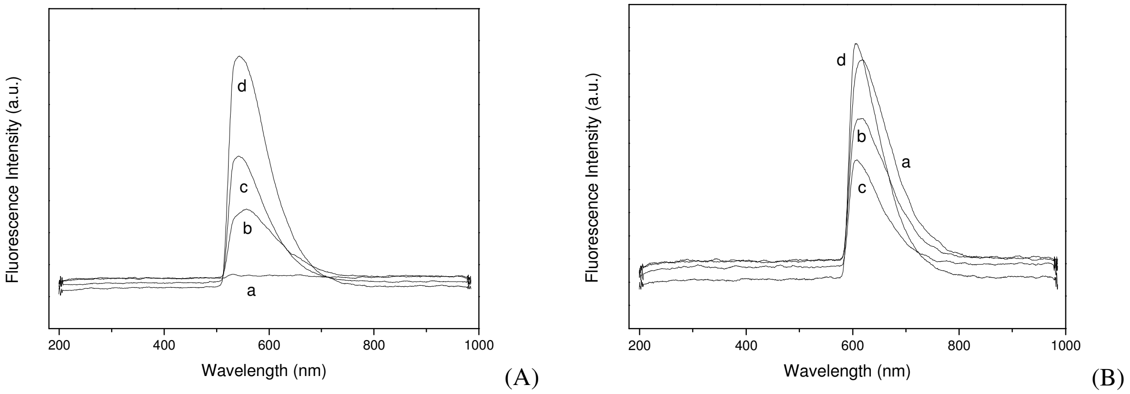


Figure 7: Fluorescence emission spectra at excitation wavelengths of 425 nm (A), 530 nm (B) for MNA (a) and grafted samples 1.1-1.3 (b-d)

However, when the m ($NaIO_4$)/m (cellulose) ratio was 2.0, the characteristic exothermic peak of DAC disappeared, which is explained by the completed breakdown in the crystalline regions of the hydrolyzed wood pulp cellulose at higher oxidation agent content. Moreover, in Fig. 6 (c), an exothermic platform of DAC occurred at about 175 °C, which possibly corresponds to the decomposition of the amorphous DAC.

In addition, comparing the DAC with the product grafted by MNA, it may be noted that their DSC profiles are primarily similar, which suggests that the graft reaction has no obvious effect on the structure and thermal stability of the modified DAC. Therefore, the oxidant content has a key role in preparing wood pulp cellulose Schiff base.

Fig. 7 shows the fluorescence emission spectra corresponding to MNA and cellulose grafted with MNA at excitation wavelengths of 425 nm (1) and 530 nm (2). Apparently, MNA has no fluorescence emission spectra when excited at 425 nm, but an obvious fluorescence emission peak at 617 nm is observed when excited at 530 nm. Moreover, the fluorescence emissions of grafted celluloses excited at 425 nm and 530 are centered at ca. 540 and 610 nm, respectively, and their spectra have a similar profile due to the formation of Schiff bases, although the aldehyde group content is different in the DAC.

The fluorescence of cellulose grafted with MNA may be assigned to imines and reveals the existence of chemical reaction between the acetaldehyde in DAC (or other carbonyl compounds) and MNA. Indeed, it may be explained by the existence of conjugated imines (-CH=N-) with flowable electron bridge, which is responsible for the significant fluorescence and yellow color observed in the samples, produced in condensation processes, as those observed by Bandi *et al.* in the reaction between benzyl amine and acetaldehyde.[25]

CONCLUSION

The morphology analysis showed that the DAC retained better rod shape when the m ($NaIO_4$)/m (cellulose) ratio was 0.5 and 1; and the cellulose Schiff base also retained better rod shape when the m ($NaIO_4$)/m (cellulose) was 0.5 and 1. FTIR showed a characteristic shoulder peak at 1720 cm^{-1} due to the C=O stretching vibrations in DAC, and no obvious characteristic band related to C=N group suggested that the condensation reaction to form C=N group was incomplete. DSC analyses suggested that the graft reaction has no obvious effect on the structure and thermal stability of the modified DAC, while the oxidant content has a key role in preparing wood pulp cellulose Schiff base. The fluorescence spectra at excitation wavelengths of 425 and 530 nm revealed the formation of Schiff bases.

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