Modification of cellulose extracted from waste newspaper

C T Mei¹, L Y Jiang¹, M M Jiang¹, X L Zhou² and H Huang¹

¹ School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo 315211, P R China
² School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, P R China
huihuang@nbut.edu.cn

Abstract. The α-cellulose was extracted from waste newspaper, and it was esterified by maleic anhydride. The effect of reaction time, temperature, ratio of maleic anhydride to α-cellulose, dosage of catalyst on the degree of esterification were studied, respectively. The weight percent gain and degree of substitution reached 40.30% and 0.6657, respectively, under the following reaction conditions: reaction time of 2.5 h, reaction temperature of 150°C, ratio of MA to α-cellulose of 1.2 and dosage of catalyst of 10%. The structure and properties of the samples were characterized by FTIR and X-ray diffraction.

1. Introduction
Cellulose is the most abundant organic renewable resource in nature. It is cheap and biodegradable. However, cellulose molecules contain a large number of hydroxyl groups, which are difficult to process because of their poor plasticity. With the aggravation of energy crisis and environmental pollution, the development and utilization of renewable biodegradable polymer materials has attracted worldwide attention. The research and utilization of cellulose has also raised a new level, and the combination of cellulose and plastics is one of the effective ways to realize the value of cellulose. However, the interface compatibility between hydrophilic cellulose and hydrophobic plastics is poor, and the properties of the composites are not good. The modification of cellulose such as esterification, etherification and graft copolymerization is a good way to solve problem. Esterification modification of cellulose by maleic anhydride can endow cellulose with certain hydrophobicity and plasticity, reduce hygroscopicity, and introduce double bonds into the molecule, thus broadening the utilization field of cellulose[1].

Researchers usually esterify cellulose and natural plant fibers by solvent method, which requires a large number of organic solvents[2-4]. The use of organic solvent not only increases the cost of reaction and the difficulty of product post-treatment, but also is not environmentally friendly. In this paper, maleic anhydride was gasified in a reactor, and then esterified into pretreated cellulose. The reaction conditions of maleic anhydride and cellulose were discussed, and the samples were characterized.

2. Experimental
2.1. Materials
Hydrogen peroxide, sodium hydroxide, formic acid, hydrochloric acid, maleic anhydride(MA) and sodium hypophosphite with analytical purity were purchased from Chemical Reagent Co., Ltd. of China Pharmaceutical Group. Waste newspaper was used directly without further treatment.
2.2. Esterification of cellulose

2.2.1. Extraction of α-cellulose. α-cellulose prepared from waste newspaper was got by the following steps: pretreatment of waste newspaper and extraction of α-cellulose. Experimental methods were specified in the reference[5].

2.2.2. Preparation of modified cellulose. 5 g α-cellulose was weighed and mixed evenly with MA and sodium hypophosphite with a certain proportion. It was put into a micro reactor and reacted in an oil bath for a period of time. After the reaction, the micro reactor was cooled to room temperature, and the product was washed to neutral with distilled water and dried to obtain esterified cellulose.

2.2.3. Weight gain rate. The degree of esterification was indirectly expressed by the mass ratio of modified cellulose to α-cellulose. The weight gain rate could be expressed by the following equation:

\[ \text{Weight gain rate} = \frac{(W_1 - W_2)}{W_2} \times 100\% \]

where \( W_1 \) is the weight of α-cellulose in the unit of g, \( W_2 \) is weight of modified cellulose in the unit of g.

2.2.4. Degree of Substitution. The degree of substitution in the esterification was calculated using the following formula:

\[ \text{Degree of substitution} = \frac{(W_1 - W_2)}{W_1} \times \frac{162}{98.06} \]

where \( W_1 \) is the weight of α-cellulose in the unit of g, \( W_2 \) is weight of modified cellulose in the unit of g, 162 and 98.06 are relative molecular mass of a glucose unit in cellulose and maleic anhydride, respectively.

3. Results and Discussion

3.1. Effect of Reaction Time

The effect of reaction time on the esterification degree of α-cellulose is shown in Figure 1 and Figure 2 under the reaction temperature of 150℃, m(MA):m(α-cellulose) of 1.2 and the catalyst dosage of 10wt%.

![Figure 1. Effect of reaction time.](image)

From Figure 1, it can be seen that the weight gain rate of the cellulose increases gradually with time. At the reaction time of 2.5 h, the weight gain rate reached a relatively high level. After that, the increase of weight gain rate was very slow, make it time-consuming and energy-consuming. As shown in Figure 2, samples of modified α-cellulose from left to right was got after the reaction time of 1.0 h,
1.5 h, 2.0 h, 2.5 h and 3.0 h, respectively, the color of the samples became darker or scorch possibly. Reasonable reaction time should be 2.5 h, at which the weight gain rate is 40.30%.

3.2. Effect of Reaction Temperature
The effect of reaction temperature on the esterification degree of α-cellulose is shown in Figure 3 under the reaction time of 2.5 h, m(MA):m(α-cellulose) of 1.2 and the catalyst dosage of 10wt%.

MA was easily sublimated at 130 to 170℃ in this study. With the increase of temperature, the movement rate of MA gas molecule increased, the frequency of collision with hydroxyl groups in α-cellulose increased greatly, and the esterification rate increased. In addition, the esterification reaction is endothermic reaction. Increasing the reaction temperature is conducive to the synthesis of esterified cellulose. 150℃ is the optimum temperature for esterification, because the yield of the sample is relatively high at this temperature, and there is no burning. The yield of the product increased slightly when the reaction temperature was 160 ℃, but the color of the product became darker and some of the products were charred. When the reaction temperature reaches 170 ℃, the product completely turns into coke, which is due to the degradation of α-cellulose at high temperature due to the acidity of MA.

3.3. Effect of ratio of maleic anhydride to α-cellulose
The effect of ratio of maleic anhydride to α-cellulose on the esterification degree of α-cellulose is shown in Figure 4 under the reaction time of 2.5 h, reaction temperature of 150℃ and the catalyst dosage of 10wt%.
Figure 4. Effect of ratio of maleic anhydride to α-cellulose.

As shown in Figure 4, with the increase of the mass ratio of MA to α-cellulose, the weight gain increases gradually, reaching the highest point at the weight gain rate of 40.30%, then decreases slowly. Before the mass ratio of 1.2, the increase of MA can increase the chance of collision with α-cellulose, and further strengthen the positive process of esterification, which leading to the increment of the weight gain rate. However, when the mass ratio exceeds 1.2, the esterification reaction has reached equilibrium. When MA is added to the system, the excess MA has no hydroxyl group to react with it, and side reactions will occur. And too much MA will increase the pressure of the system, which is not conducive to the reversible esterification reaction.

3.4. Effect of Catalyst Dosage

The effect catalyst dosage on the esterification degree of α-cellulose is shown in Figure 5 under the reaction time of 2.5 h, reaction temperature of 150°C and m(MA):m(α-cellulose) of 1.2.

Under the action of sodium hypophosphite, the weight gain rate increased, and the esterification degree of MA with α-cellulose increased significantly. Compared with the two reactions using 10% catalyst and without catalyst, the latter has higher weight gain and better esterification degree. However, when the amount of catalyst reaches 10%, the weight gain increases slowly, and the effect is no longer obvious. Sodium hypophosphite has an obvious catalytic effect on the nucleophilic substitution reaction of MA with cellulose to form esters[6]. Taking the economy and practicability into consideration, the optimum amount of catalyst is 10%.
3.5. *FT-IR and XRD Characterization*

The FT-IR spectra of cellulose samples before and after esterification are shown in Figure 6. Spectra of 3300 cm\(^{-1}\) and 2850 cm\(^{-1}\) showed that the stretching vibration of -OH and -CH\(_2\), respectively. The stretching vibration of esterified cellulose at the peak of 1670 cm\(^{-1}\) was stronger than that of \(\alpha\)-cellulose. The stretching vibration at the peak of 1750 cm\(^{-1}\) was the newly increased peak in esterified cellulose. The stretching vibration of \(\alpha\)-cellulose at this point was C=O, while that of \(\alpha\)-cellulose at the peak of 1150 cm\(^{-1}\) was the stretching vibration of C-O in ester bond. Those confirmed that -OCO-CH=CH-COOH group was successfully introduced into \(\alpha\)-cellulose\(^7\).

![Figure 6. FT-IR spectrum: (a) \(\alpha\)-cellulose; (b) esterified \(\alpha\)-cellulose.](image)

Figure 7 is the XRD spectrum of different cellulose samples. It could be seen that the diffraction peaks of \(\alpha\)-cellulose and esterified \(\alpha\)-cellulose appear near 20 of 14.5°, 23.5°, 35°. The diffraction peak near 20 of 15.5° unitary represents the diffraction intensity of 101 planes, and the diffraction peak near 20 of 35° unitary represents the diffraction intensity of 040 planes. In addition, the diffraction peak near 20 of 23.5° represents the diffraction intensity of 002 plane, which shows the distance between the molecular chains in the crystallization zone of the cellulose. The larger diffraction peak appeared is due to the crystallization zone of the cellulose is highly oriented, the molecular chains are arranged closely and the chain spacing is small. Compared with that of \(\alpha\)-cellulose, the diffraction peak intensity of esterified \(\alpha\)-cellulose decreased, indicating that the crystallinity of \(\alpha\)-cellulose decreased by esterification.
4. Conclusions

α-cellulose was extracted from waste newspaper by using NaOH solution, hydrogen peroxide, formic acid and hydrochloric acid. Modification of α-cellulose was conducted via using MA as esterification reagent and sodium hypophosphite as catalyst. The effect of reaction time, reaction temperature, mass ratio of MA to α-cellulose and catalyst dosage on esterification degree were investigated.

The esterification degree of α-cellulose reached the maximum under the reaction time of 2.5 h, the reaction temperature of 150°C, the mass ratio of MA to α-cellulose of 1.2 and the catalyst dosage of 10wt%. The weight gain rate is 40.30wt%, and the theoretical substitution degree is 0.6657.

Acknowledgments

Authors acknowledge financial support from Zhejiang Xinmiao Plan(2018R428012), Ningbo Natural Science Foundation(2017A610066) and Wang Weiming Foundation of Ningbo University of Technology(2017013).

References

[1] Nenkova S, Dobrilova C, Natov M Vasileva S and Velev P 2006 Polym. Polym. Comp. 14 185
[2] Samir K, Abeer M Mohamed E and Zenat 2008 J. Appl. Polym. Sci. 107 1337
[3] Hadano S, Onimura K, Tsutsumi H, Yamasaki H and Oishi T 2003 J. Appl. Polym. Sci. 90 2059
[4] Rozman H, Musa L and Abubakar A 2005 J. Appl. Polym. Sci. 97 1237
[5] Chen T, Wu N, Huang H, Yang Z, Chen R and Li J 2017 J. Ningbo Univ. Technol. 4 21
[6] Yang C, Wang X and Lu Y 2000 J. Appl. Polym. Sci. 75 327
[7] Liu C, Sun R, Qin M, Zhang A, Ren J, Xu F, Ye J and Wu S 2007 Ind. Crop. Prod. 26 212