

## ACETYLATION OF MICROFIBRILLATED CELLULOSE BY REACTION WITH ACETIC ANHYDRIDE CATALYZED BY N-BROMOSUCCINIMIDE

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### ABSTRACT

Cellulose acetate (DS = 2.3) was prepared by reacting microfibrillated cellulose (MFC) with acetic anhydride using N-bromosuccinimide as a catalyst. The reaction was conducted using dimethyl sulfoxide as the solvent at 60 °C for 120 minutes. Chemical structure of product was determined by IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. The phase structure and the degree of crystallinity of the sample was deduced from the powder X-ray diffraction (PXRD). The thermal stability was investigated by thermal gravimetric analysis (TGA). The results showed that MFC acetate had characteristic of cellulose type I structure with the degree of crystallinity of 50.45 % and the decomposition of the sample took place in the temperature range of 240 – 420 °C.

*Keywords:* microfibrillated cellulose (MFC), microfibrillated cellulose acetate, N-bromosuccinimide (NBS), acetylation.

### 1. INTRODUCTION

Microfibrillated cellulose (MFC) is formed in plant cells during growth and development of plants. It has salient advantages, such as high mechanical strength, low density, natural renewable resources, biodegradability, small size and high specific surface area. Therefore, microfibrillated cellulose has been used to reinforce for polymer nanocomposites, manufacture papers and specific hard covers, make high quality diaphragms for speakers, or thin films in electronics technologies. Besides, MFC has also been used in food, cosmetics and medical products [1 - 2]. However, MFC has polar hydroxyl groups which decrease its solubility in nonpolar solvents and also cause poor compatibility with hydrophobic substrate polymers. Recently, there have been some studies of chemical surface modification of MFC with different agents, such as acetic anhydride, isopropyl dimethylchlorosilane, maleic anhydride, N-octadecyl isocyanate..., in which the hydroxyl groups are replaced by less polarized groups [3 - 9]. In our previous paper [10], we produced MFC from Lung foil wastes (Lung belongs to the bamboo

family, which grows a lot in the western area of Nghe An) and characterized some of their characteristic properties. In this paper, we report the results of the acetylation of MFC including chemical structure, crystallinity and thermal stability of the resulting polymer.

## 2. EXPERIMENTS AND METHODS

### 2.1. Materials

- Lung foil wastes were collected at Duc Phong company located in Nghi Phu, Vinh City Nghe An.

- MFC (the diameter is 4 - 6  $\mu\text{m}$ ) were produced from Lung foil wastes according to the procedure published in [10].

- Acetic anhydride, N-bromosuccinimide (NBS), dimethyl sulfoxide (DMSO) were purchased from Merk company (Germany) and used as received.

### 2.2. Acetylation of microfibrillated cellulose

10 g of the MFC and 1.0 g of N-bromosuccinimide were placed into a 250 ml round bottom flask containing 50 ml acetic anhydride and 100 ml DMSO while stirring. The mixture was heated to 60°C for 120 minutes. After the reaction occurred completely, the MFC acetate was precipitated in saturated NaCl aqueous solution at room temperature, washed to pH = 7 then dried at 80°C in the vacuum oven. The degree of substitution (DS) of the product was determined from the  $^1\text{H-NMR}$  spectrum [9] using the following equation:

$$DS = \frac{\frac{1}{3}(A_{1.87} + A_{1.94} + A_{2.14})}{\frac{1}{6}(A_{3.39} + A_{3.66} + A_{3.82} + A_{4.00} + A_{4.54} + A_{5.06})}$$

where,  $A_{1.87}$ ,  $A_{1.94}$  and  $A_{2.14}$  are areas of proton peaks of three acetyl groups;  $A_{3.39}$ ,  $A_{3.36}$ ,  $A_{3.82}$ ,  $A_{4.00}$ ,  $A_{4.54}$  and  $A_{5.06}$  are areas of the C-H proton peaks of the anhydroglucose unit.

### 2.3. Characterization methods

The chemical structure of the MFC and the MFC acetate was examined by IR spectroscopy using a IMPACT 410 spectrometer at Institute of Chemistry-Vietnam Academy of Science and Technology;  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra in  $\text{D}_6\text{-DMSO}$  were recorded on the NMR spectrometers ADVANCE 125 MHz ADVANCE 500 MHz of Bruker, respectively. The crystallinity of the acetate sample was examined by PXRD method on D8-Advance X-ray diffraction of Bruker company. The degree of crystallinity was calculated based on the empirical method proposed by Segal [11,12] as follows:

$$C = \frac{I_{200} - I_{\text{non-cr}}}{I_{200}} \cdot 100$$

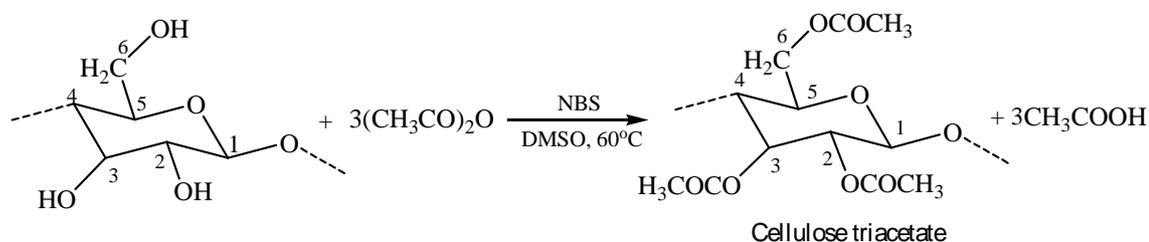
where: C is degree of crystallinity (%);  $I_{200}$ : is intensity of peak maximum with angle  $2\theta$  between 22° and 24°,  $I_{\text{non-cr}}$ : is the peak intensity of the amorphous fraction.

Thermal stability of the polymer was examined by thermogravimetric analysis and was recorded on TGA/DTA Analyzer DTG 60H (Shimadzu, Japan) at Hanoi University of Science-Vietnam National University, at a heating rate of 10 °C/min from room temperature to 800 °C

under nitrogen gas.

### 3. RESULTS AND DISCUSSION

#### 3.1. Chemical structure of the MFC acetate



The IR spectra of MFC and MFC acetate with DS = 2.3 are shown in Fig. 1a and Fig. 1b, respectively. Those bands characteristic of cellulose, as found in the starting MFC, are also found in MFC acetate, such as: C-H bending at 2961  $\text{cm}^{-1}$ , C-H stretch at 1454  $\text{cm}^{-1}$ , C-O-C stretch at 1060  $\text{cm}^{-1}$  and O-H stretch at 3300 - 3500  $\text{cm}^{-1}$ . This indicates that MFC acetate is still having free OH groups. However, the O-H stretch in the latter case is narrower, 3300 - 3500  $\text{cm}^{-1}$ , compared to 3200 - 3600  $\text{cm}^{-1}$  in the MFC, suggesting a partial acetylation of these OH groups. Moreover, there are some other absorption bands supporting the presence of the acetyl group, such as the absorption at 1732  $\text{cm}^{-1}$  and 1257  $\text{cm}^{-1}$  which are characteristic for C=O stretch and C-O stretch of ester group, respectively. And the 1373  $\text{cm}^{-1}$  band could come from the methyl group bending vibration mode. All these data indicate the occurrence of the reaction between MFC and acetic anhydride which partially converts three free OH groups into acetate ester groups.

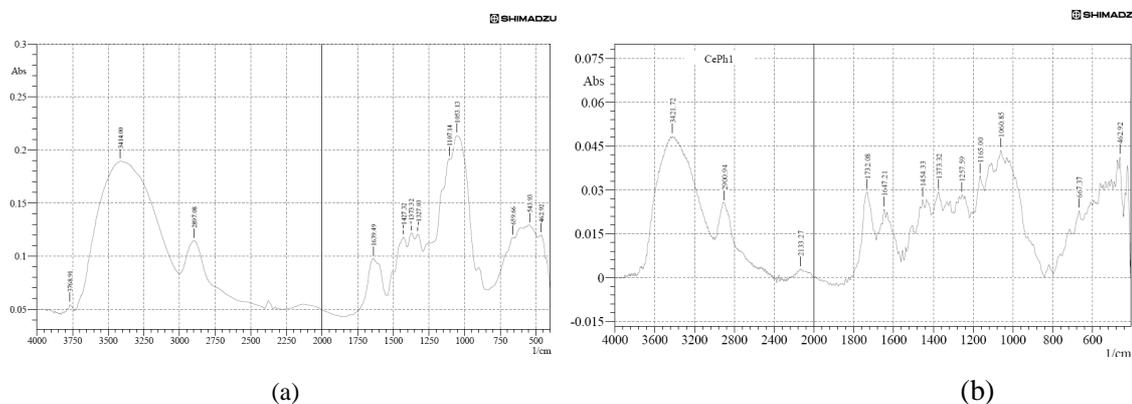


Figure 1. Infrared spectra of MFC (Fig. 3.1a) and MFC acetate (Fig. 3.1b).

Figure 2 shows the  $^1\text{H-NMR}$  spectra of MFC acetate. The proton peaks were assigned based on the ref. [9]: H1 (3.39 ppm), H2 (4.54 ppm), H3 (5.06 ppm), H4 (3.66 ppm), H5 (3.82 ppm) and H6 (4.00 ppm). In addition, new peaks at around 2 ppm indicating the presence of acetyl group, which binds to C2 (1.94 ppm), C3 (1.87 ppm) and C6 (2.14 ppm) through the oxygen atoms.

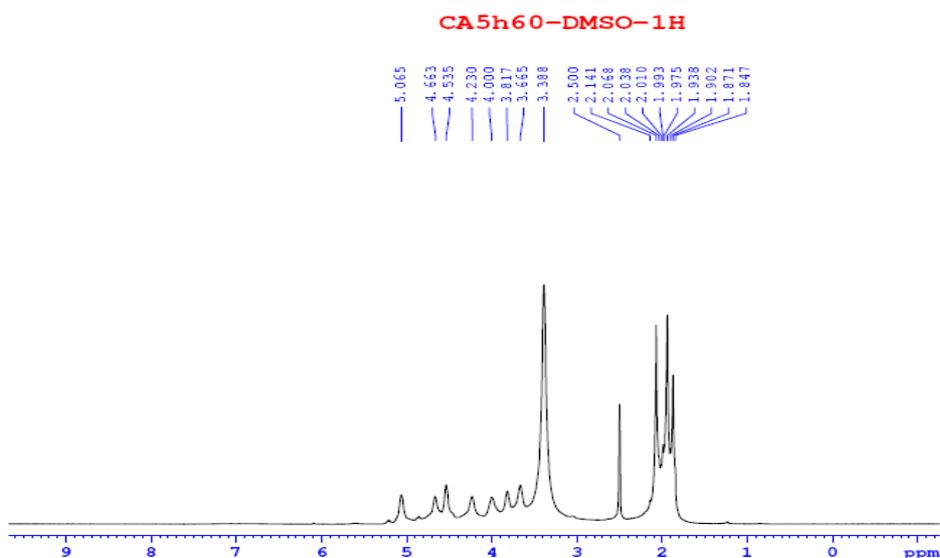


Figure 2.  $^1\text{H}$ -NMR spectroscopy of microfibrillated cellulose acetate (DS=2,3).

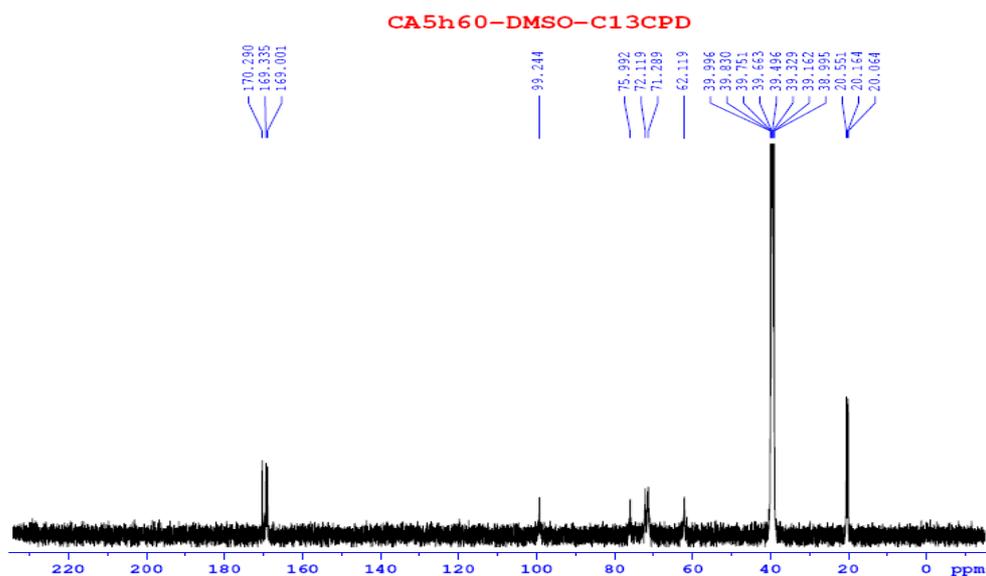


Figure 3.  $^{13}\text{C}$ -NMR spectroscopy of microfibrillated cellulose (DS=2,3).

The  $^{13}\text{C}$ -NMR spectrum is shown in Figure 3 which includes characteristic peaks of 6 carbon atoms on cellulose: C1 (99.2 ppm), C2 (71.3 ppm), C3 (72.1 ppm), C4 (75.9 ppm), C5 (71.3 ppm) và C6 (62.1 ppm). In addition, there are characteristic peaks of carbon atom on acetyl group which replaces H of the OH group binding to C2 atom (169.0 ppm), C3 (169.3 ppm) and C6 (170.2 ppm).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicated that the esterification reaction between the OH groups of MFC and acetic anhydride took place and formed the corresponding MFC acetate.

### 3.2. Thermal stability

The thermal stability of MFC acetate sample is illustrated in Figure 4 which exhibits two weight loss processes corresponding to 5.21 % and 64.24 %. The first process, 5.21 % weight loss, taking place at around 100 °C is believed to be the evaporation of free water in the sample. The second process is more significant, 64.24 % weight loss, and takes place from 240 °C to 420 °C centering around 340 °C, which is believed to be corresponding to a complete decomposition of the sample.

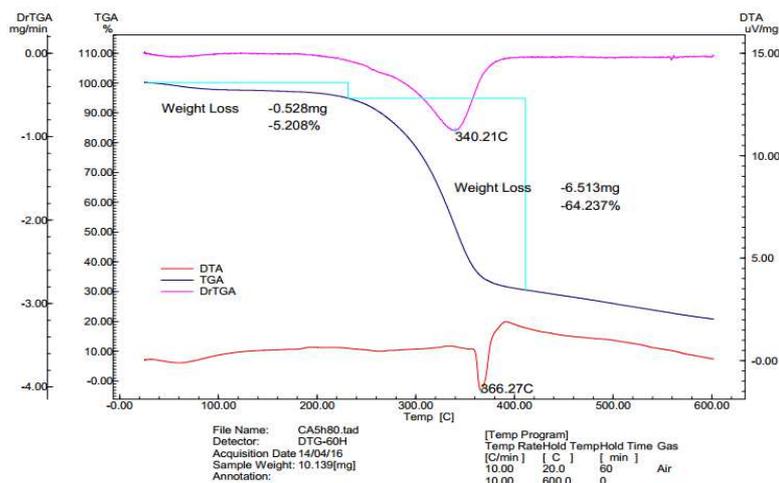


Figure 4. TGA curve of microfibrillated cellulose acetate (DS = 2.3).

### 3.3. Powder X-ray diffraction analysis

The powder X-ray diffraction studies were conducted using a D8-Advance diffractometer at Hanoi University of Science-Vietnam National University, Hanoi. The powder X-ray patterns were taken by using radiation source Cu(K $\alpha$ ) by supplying 40 kV and 40 mA to X-ray generator (Figure 5).

The degree of crystallinity of the MFC acetate sample is 50.45 %, while degree of crystallinity of MFC that reported in [10] was 72.58 %. The acetylation might have decreased the tendency of crystallization of MFC as the results of replacing H bonding source (OH group) by acetyl group. The result of XRD analysis of MFC sample was processed by X'Pert HighScore Plus 3.0 program. The unit cell parameters are  $a = 11.797907 \text{ \AA}$ ,  $b = 2.776298 \text{ \AA}$ ,  $c = 8.008372 \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 107.49^\circ$ . This was asserted that the MFC acetate is still cellulose type I structures as reported in [10].

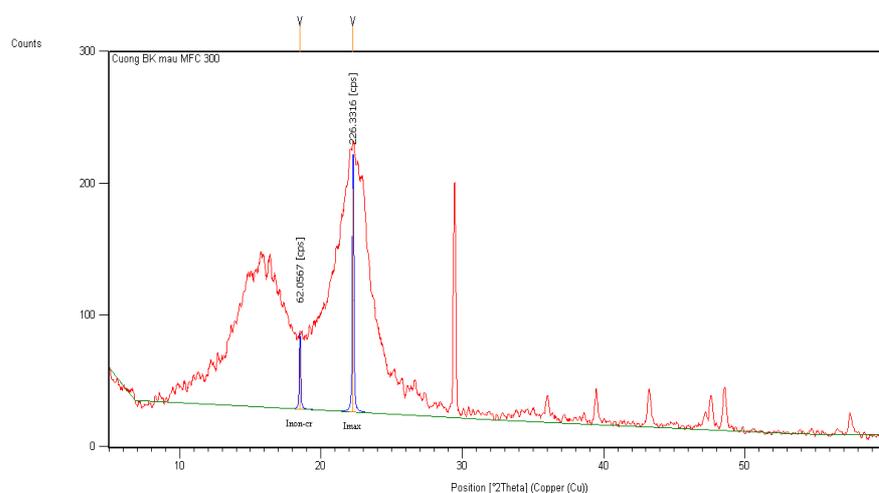


Figure 5. PXRD pattern of MFC acetate (DS=2.3).

#### 4. CONCLUSION

MFC acetate was successfully prepared by the reaction of acetic anhydride with MFC using N-bromosuccinimide as a catalyst at 60 °C. Chemical structure of MFC acetate was examined by infrared and <sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectroscopies. The obtained data confirmed the occurrence of the esterification reaction between hydroxyl groups at carbon atom number 2, 3 and 6 of MFC and acetic anhydride formed MFC acetate.

MFC acetate decomposed strongly from 240 °C to 420 °C. It belongs to cellulose type I structure with the degree of crystallinity calculated from PXRD data was 50.45 %.

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## TÓM TẮT

### AXETYL HÓA VI SỢI XENLULOZƠ BẰNG ANHYDRIT AXETIC VỚI XÚC TÁC N-BROMSUCXINIMIT

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Vi sợi xenlulozơ axetat (DS = 2,3) đã được điều chế bằng phản ứng của vi sợi xenlulozơ từ phôi phế thải của cây Lùng ở Nghệ An với anhydrit axetic. Phản ứng được thực hiện trong dung môi dimetyl sunfoxit (DMSO) với xúc tác N-bromsucinimit (NBS) ở 60 °C trong 120 phút. Cấu trúc hóa học của vi sợi xenlulozơ axetat được xác định bằng phương pháp phổ hồng ngoại và cộng hưởng từ hạt nhân <sup>1</sup>H và <sup>13</sup>C, độ bền nhiệt của polyme được khảo sát bằng phương pháp phân tích nhiệt trọng lượng (TGA) và cấu trúc tinh thể được khảo sát bằng phổ X-ray. Các kết quả nghiên cứu cho thấy rằng vi sợi xenlulozơ axetat có đặc trưng cấu trúc tinh thể xenlulozơ I với độ tinh thể tính được theo phổ nhiễu xạ Ron-ghen dạng bột (PXRD) là 50,45 % và bị phân hủy mạnh trong khoảng nhiệt độ 240 – 420 °C.

*Từ khóa:* vi sợi xenlulozơ, vi sợi xenlulozơ axetat, N-bromsucinimit (NBS), axetyl hóa.