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Effects of reaction conditions on the degree of substitution in acetylated nanocellulose

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ABSTRACT

In this study, cellulose nanocrystals (CNC) were chemically extracted from the waste newspapers and acetylated by reacting CNC with acetic anhydride, using sulfuric acid as a catalyst. Response Surface Methodology based on a three-factor factorial design was applied to analyze the interaction effects of reaction temperature, time, and the ratio of nanocellulose and acetic acid (wt/v) on the degree of substitution (DS) which was calculated and compared. Various experimental conditions as reaction temperature (50-70 °C), reaction time (90-150 min), and the ratio of nanocellulose and acetic acid (wt/v) (1:15-1:25) were under investigation. It was found that reaction temperature and its interaction effects have the most significant effects on DS. The acetylated CNC was characterized by FTIR and ^{1}H-NMR spectroscopy. The highest DS (2.997) was obtained in 90 min and the CNC/acetic acid ratio of 1:15 at 70 °C.

Introduction

Wastepaper, a high-yield cellulosic source, has been recently considered for recycling with an increasing rate. One of the most attractive products from cellulose sources is cellulose nanocrystals (CNC) which have unique properties such as low density, biodegradability, high aspect ratio, high strength, and stiffness. However, the application of CNC in the industry has been facing manufacturing challenges due to the limitations in their solubility.

Efforts have been made to overcome the limitation of cellulosic materials by chemical modification such as esterification [1-3], silylation [4,5], etherification [6,7], carbanilation [8], grafting [9], and so on. Among those various preparation methods developed for cellulosic materials, acetylation is one of the common approaches and has been the subject of several scientific studies [10-15]. Acetylated cellulosic materials obtained by converting part of the hydroxyl groups to acetyl groups were reported to have wide applications [16,17]. The degree of substitution (DS) has been the research interest in which several ways to improve DS have been reported [14,18,19].

To the best of our knowledge, Response Surface Methodology (RSM) has not been applied to find the optimal condition for the highest DS by investigating the effects and interactions of at most three factors (i.e., reaction temperature, time, and ratio of nanocellulose and acetic acid). In this study, a factorial design was conducted to understand the effects of these typical reaction parameters and Figureure out

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the condition in which the highest DS could be obtained for the acetylation process in which CNC extracted from waste newspaper reacted with acetic anhydride and using sulfuric acid as a catalyst.

Experimental

Materials

Waste newspapers that contained inks were collected in Can Tho City, Vietnam, and were used for CNC production. All chemicals including sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) were supplied by Merck (Germany). Sodium hypochlorite (NaClO), acetic acid (CH_3COOH) were purchased from Xilong Scientific Co., Ltd. (China). Anhydride acetic $(CH_3CO)_2O$ was provided by Scharlab S.L (Spain). All chemicals were used without any further purification.

Preparation of CNC from waste newspapers

CNC extracted from waste newspapers by means of alkali and bleaching treatments followed by acid hydrolysis as reported in [20] was used in this study for acetylation. First, 5 g of the ground newspaper containing inks were added to 300 mL of 2 wt% of NaOH solution at 100 ℃ in 3 h under continuous stirring, then rinsed with water until pH = 7. After that, 5 g of dried obtained sample was added to 300 mL of 2 wt% of NaClO solution and 5 mL of acetic acid solution at 70 ℃ in 1 h under continuous stirring. Then the sample was rinsed with water until pH = 7 and dried. The obtained cellulose was then treated with 50 mL of 64 wt% H_2SO_4 under continuous stirring and heating at 45 ℃ in 45 min. The reaction was terminated by 1 L of distilled water and rinsed with water.

CNC modification by acetylation

Acetylation experiments were carried out in a 500-mL three-necked flask equipped with an electromagnetic stirrer, a reflux condenser, and a thermometer. The process was similar to the experimental set up in [10]. 2 g CNC was dispersed in an acetic acid solution with 1.6 mL of 98 wt% sulfuric acid as a catalyst.

Table 1: Experimental conditions to be investigated.

Reaction temperature (°C)	Reaction time (min)	CNC/acetic acid (wt/v)
50 - 70	90 - 150	1:15 – 1:25

The solution was kept in various reaction time, acetic anhydride was added and continuously stirred till all samples were well soluted. Table 1 shows the list of all the factors to be investigated and their ranges in this study.

The used volume of acetic acid and acetic anhydride depended on CNC/acetic acid ratio. In particular, 30, 40 and 50 mL of acetic acid and acetic anhydride were respectively utilized in the mixture with CNC/acetic acid ratio of 1:15, 1:20 and 1:25.

Then 40 mL acetic acid 20% was added before the reaction was terminated by cooling. After that, the acetylated CNC was precipitated in hot distilled water and rinsed with water until pH = 7.

Degree of acetylation (DS) determination

DS was calculated using the method reported in [13]. 0.1 g of the dried acetylated CNC was added to 40 mL of 75 % ethanol and 50 mL NaOH 0.05 N in a flask and kept at room temperature in 72 h and heated at 50 °C for 2 h. The excess alkali was titrated with 0.05 N HCl solution with phenolphthalein as an indicator. 1 mL excess HCl 0.05 N was added and kept at room temperature overnight. The excess HCl was titrated with 0.1 N NaOH solution. Acetyl content (%A) was calculated as

$$\%A = [(V_1-V_2) \times N_a + (V_3-V_4) \times N_b] \times (F/W) \quad (1)$$

where V_1, V_2 are volume (mL) of HCl 0.05 N solution used to titrate reference and blank;

V_3, V_4 are volume (mL) of NaOH 0.05 N solution used to titrate reference and blank;

N_a and N_b are the concentrations of the HCl and NaOH solutions, respectively; W is the mass weight of the dried sample;

F = 4.305

The degree of substitution DS was calculated from acetyl content as

$$DS = 162 \times \%A / [4300 - (42 \times \%A)] \quad (2)$$

Moreover, DS of the optimal sample was calculated from ^{1}H NMR spectrum of the optimal acetylated CNC using the equation described in [10] as

$$DS = 3 \times \frac{\text{peak area}_{1.8-2.3\text{ppm}} / 3}{\text{peak area}_{1.8-2.3\text{ppm}} / 3 + \text{peak area}_{7-8.5\text{ppm}} / 5} \quad (3)$$

where $\text{peak area}_{1.8-2.3\text{ppm}}$ and $\text{peak area}_{7-8.5\text{ppm}}$ correspond to the methyl proton of acetyl groups and six protons of aromatic rings, respectively.

Characterization

FTIR (ATR e FTIR 4700, Jasco, Japan) and ^{1}H NMR (300 MHz, in the solvent DMSO, Bruker 300 Ultrashield) were utilized for elementary analysis of the CNC and the acetylated CNC.

Experimental design

The single-factor analysis was initially performed to determine the range of each factor under investigation. Table 2 presents the experimental design matrix and the observed response from 27 experimental runs. From these data, Design-Expert software (Stat-Ease, Inc.) was used to calculate the RSM regression model.

Table 2: Factorial design matrix and DS value

Run	Reaction temperature (ºC)	Reaction time (min)	CNC/acetic acid (wt/v)	DS 1	DS 2	DS 3	Mean value of DS
1	50	90	1:15	2.07	2.11	2.12	2.10
2	50	90	1:20	1.13	1.02	1.15	1.10
3	50	90	1:25	1.64	1.38	1.87	1.63
4	50	120	1:15	1.99	2.12	2.1	2.07
5	50	120	1:20	2.29	2.32	2.26	2.29
6	50	120	1:25	2.16	2.05	2.18	2.13
7	50	150	1:15	1.59	1.48	1.61	1.56
8	50	150	1:20	2.28	2.42	2.56	2.42
9	50	150	1:25	2.2	2.2	2.17	2.19
10	60	90	1:15	1.13	0.96	1.27	1.12
11	60	90	1:20	0.86	1.12	1.05	1.01
12	60	90	1:25	0.71	0.79	0.63	0.71
13	60	120	1:15	1.36	1.27	1.3	1.31
14	60	120	1:20	1.12	1.77	1.4	1.43
15	60	120	1:25	2.23	2.29	2.14	2.22
16	60	150	1:15	1.23	1.35	0.96	1.18
17	60	150	1:20	1.89	2.09	2.2	2.06
18	60	150	1:25	1.97	2.13	2.23	2.11
19	70	90	1:15	2.62	2.67	2.75	2.68
20	70	90	1:20	2.44	2.42	2.37	2.41
21	70	90	1:25	2.67	2.67	2.64	2.66
22	70	120	1:15	2.64	2.65	2.6	2.63
23	70	120	1:20	2.36	2.42	2.57	2.45
24	70	120	1:25	2.02	2.34	2.42	2.26
25	70	150	1:15	1.98	2.11	2.03	2.04
26	70	150	1:20	2.19	2.57	2.68	2.48
27	70	150	1:25	2.58	2.56	2.3	2.48

Results and discussion

Characterization of obtained CNC before modification by acetylation

The obtained CNC was characterized and reported in [20]. In summary, CNC rods with an average diameter of 12.3 ± 2.8nm. In addition, the typical peaks of cellulose crystal structures were detected at 2θ = 14.8°, 22.8° and 34.32°. The high crystallinity index of 80.15% was obtained. Interestingly, the temperature at the maximum weight loss was 300 ℃ with a weight loss of 45.5 wt%.

Interaction effects of reaction temperature and reaction time

The interaction effect of reaction temperature and reaction time is depicted in detail in Figure. 1. It was noted that when reaction time increased, DS increased. This trend was also observed by [10]. Interestingly, the highest DS could be obtained at the highest temperature (70 °C) although DS decreased as reaction temperature increased from 50 to 60 °C. This might result from the reduction of H^+ due to the reaction between CNC and sulfuric acid. At 70 °C,

reaction rate was accelerated resulting in high DS in short reaction time.

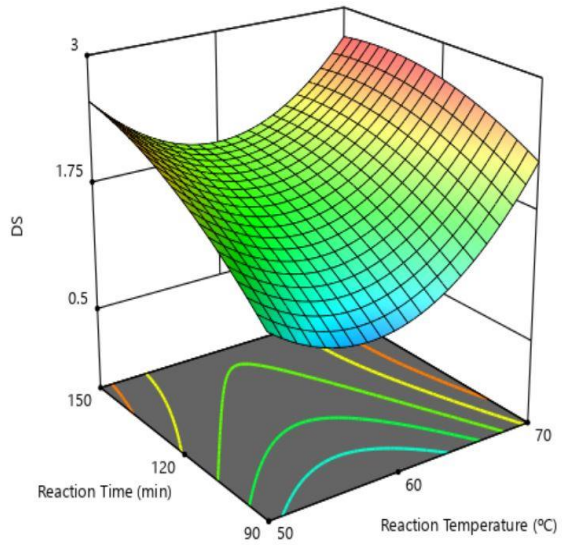

Figure 1: Response surface plot for analysis of the interaction between reaction temperature and reaction time at CNC/acetic acid (wt/v) = 1:25

Interaction effects of reaction time and CNC/acetic acid ratio

The interaction effect of reaction time and CNC/acetic acid ratio was investigated at three different reaction temperatures. The obtained response surface plot obtained at 70 °C is depicted in Figure. 2.

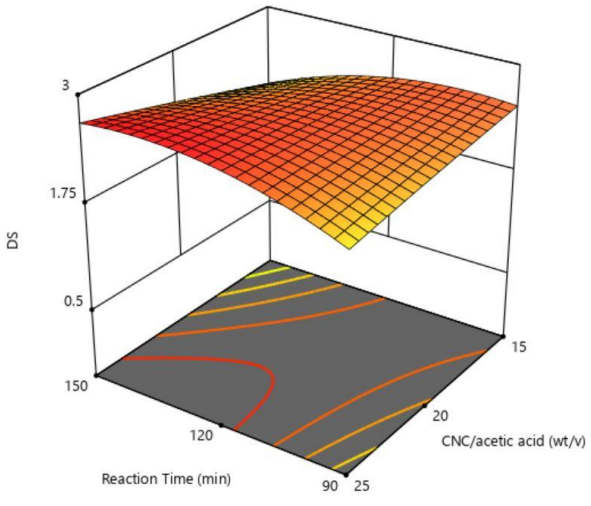

Figure 2: Response surface plot for analysis of the interaction between reaction time and CNC/acetic acid at 70 °C

The change in DS was not significant under the interaction of reaction time and CNC/acetic acid in the investigated range from 50 – 70 °C.

Interaction effects of reaction temperature and CNC/acetic acid

The interaction effects of reaction temperature and CNC/acetic acid ratio is depicted in Figure. 3.

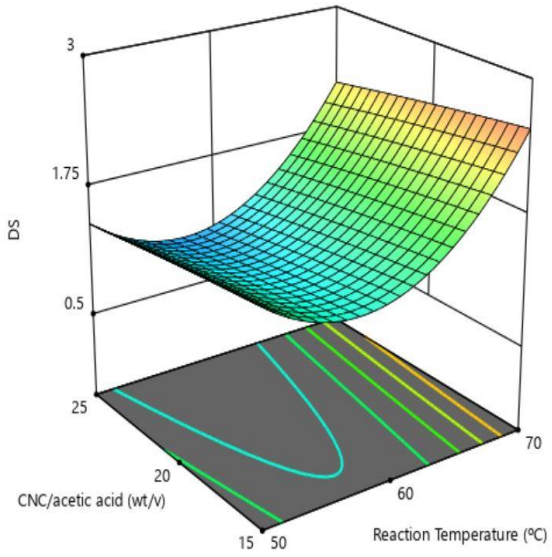

Figure 3: Response surface plot for analysis of the interaction between reaction temperature and CNC/acetic acid in 90 min

At fixed reaction temperature, an increase in the ratio of CNC and acetic acid resulted in DS reduction. In this study, the amount of CNC was fixed as the ratio of CNC and acetic acid was under investigation. Besides, the amount of sulfuric acid was constant. Therefore, the increase in the ratio of CNC and acetic acid demoted the reaction between CNC and hydrogen ion provided by sulfuric acid leading to the reduction of DS. As previously reported [14], the mechanism of nanocellulose acetylation is shown in Figure 4. First, sulfuric acid reacts with nanocellulose resulting in the formation of nanocellulose sulfate. Simultaneously, sulfuric acid reacts with acetic anhydride forming sulfoacetate which then reacts with nanocellulose. Finally, nanocellulose acetate is obtained by the transesterification from nanocellulose sulfate.

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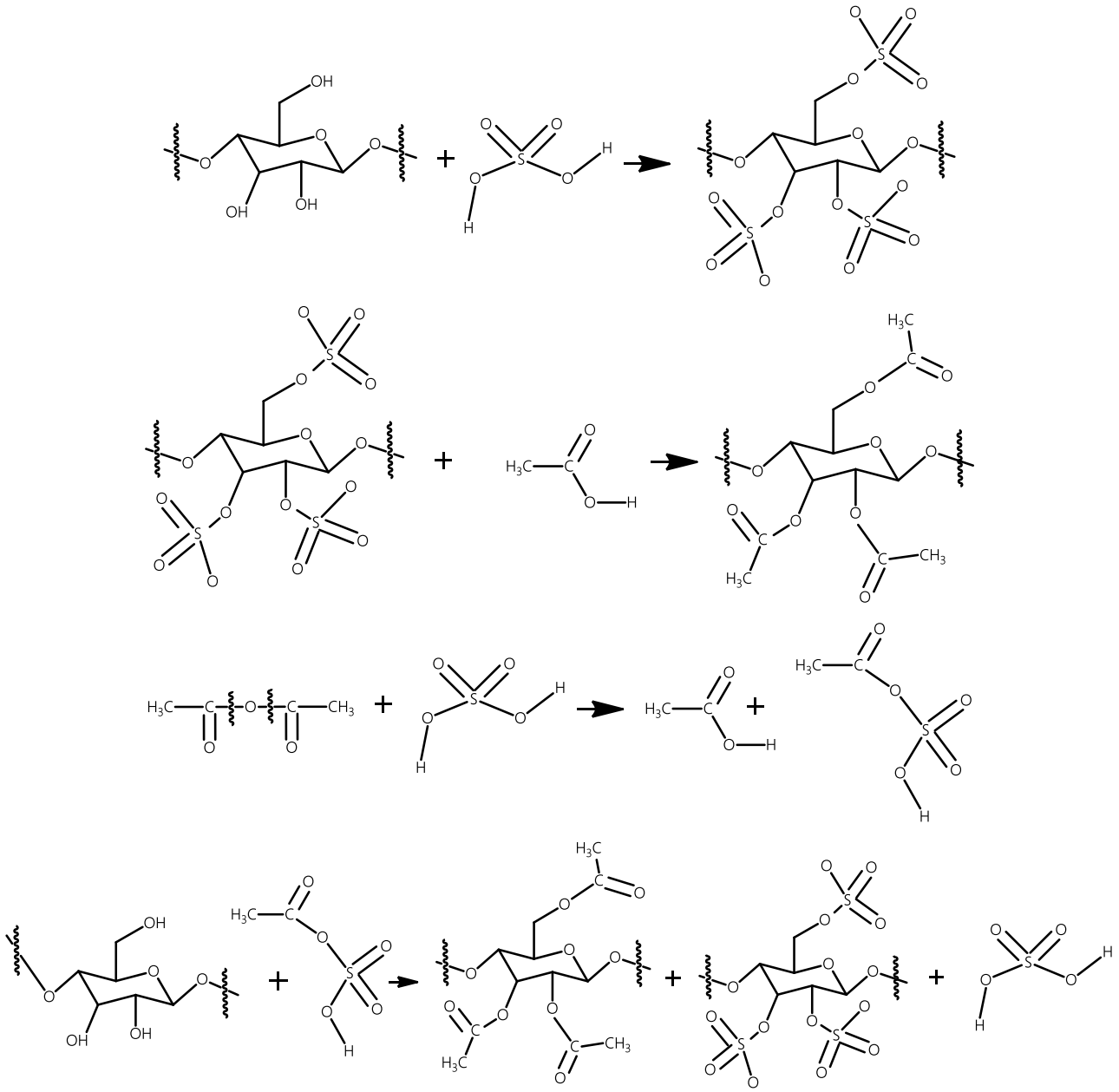

Figure 4: Mechanism of nanocellulose acetylation with acetic anhydride in acetic acid.

Besides, the concentration of sulfuric acid used in the mixture with various ratios of CNC and acetic acid is shown in Table 3.

Table 3: Concentration of sulfuric acid used in the mixture with various ratios of CNC and acetic acid.

CNC/acetic acid	1 : 15	1 : 20	1 : 25
%wt H_2SO_4	8.08	6.28	5.13

As shown in Table 3, the concentration of sulfuric acid reduced with an increased ratio of CNC/acetic acid.

On the other hand, higher DS could be obtained when both reaction temperature and the ratio of CNC/acetic acid increased. The highest DS was obtained in 90 min and the CNC/acetic acid ratio of 1:15 at 70 °C.

FTIR spectroscopy analysis

The FTIR spectra of CNC and optimal acetylated CNC which was obtained in 90 min and the CNC/acetic acid

ratio of 1:15 at 70 °C are presented in Figure. 5 for comparison. The peak at 2908cm^{-1} observed in both samples corresponded to C-H stretching vibration reflecting the general organic content [21]. A small peak in 1610 – 1639 cm^{-1} regions indicated the O–H bending of the absorbed water. As CNC was extracted by conventional acid hydrolysis, the sharp peak at 1040 cm^{-1} signified the presence of S=O stretching.

After acetylation, the peaks in the range of 3300 - 3550 cm^{-1} region corresponding to the O-H stretching vibration had a reduction in intensity after the reaction. The emerged peaks at 1754, 1371, 1234 cm^{-1} associated with C=O stretching vibration of -$COCH_3$, C-H of the acetyl group, and C-O in O-C=O with strong intensity. The results indicated the successful replacement of hydroxyl groups by the acetyl group. The FTIR spectra demonstrated that the acetylation process of CNC extracted from waste newspapers has been successfully carried out.

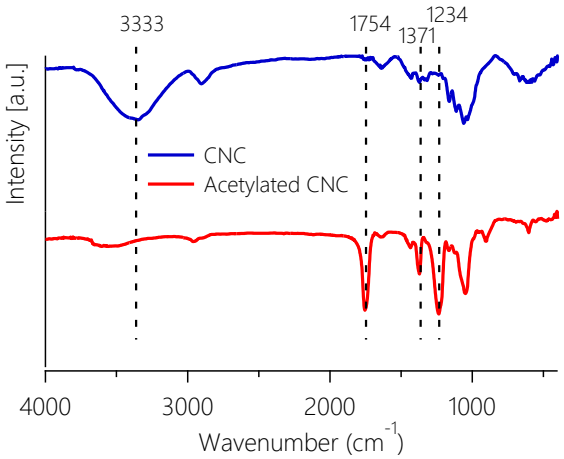

Figure 5: FTIR spectra of the CNC and the optimal acetylated CNC

^{1}H-NMR spectroscopy analysis

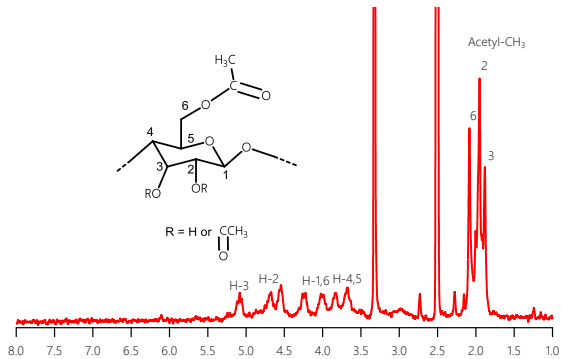

Figure 6: ^{1}H NMR spectrum of the optimal acetylated CNC

The structure of the obtained acetylated CNC was confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (Figure. 6). The signals of a chemical shift in the range of 3.5 – 5.1 ppm represent the peak positions of hydroxyl protons and methylene protons in the glucose anhydride ring. The signals at 1.8 – 2.3 ppm were assigned to the methyl proton of acetyl groups. These FTIR and NMR data are in accordance with those previously reported [14].

Further, DS of the optimal acetylated CNC calculated by Eq (3) was 2.997 which is higher than previously reported as shown in Table 4.

Table 4: Comparison of the obtained DS.

Reference	DS
This study	2.997
Das et al. [11]	2.91
Cao et al. [22]	2.7
Silva et al. [23]	2.7
Luo et al. [15]	2.66
Huang et al. [14]	2.48
Dewi et al. [12]	2.14 – 2.16

Conclusion

In this study, the interaction effects of reaction temperature, time, and the ratio of nanocellulose and acetic acid (wt/v) on the degree of substitution were investigated and analyzed based on RSM with factorial design. The effect of the reaction temperature and its interaction effects were found to have the most significant effects on DS. The highest DS (2.997) was obtained in 90 min and the CNC/acetic acid ratio of 1:15 at 70 °C.

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