Esterification of Cellulose with Betaine using *p*-Toluenesulfonyl Chloride for the *in-situ* Activation of Betaine

Yu Liu, Fangfang Wang, and Yangyang Sun *

A novel synthesis method was developed for betaine-modified cellulose ester using a mixed N,N-dimethylacetamide/lithium chloride solvent system; *p*-toluenesulfonyl chloride was used for the *in-situ* activation of the betaine. The influence of the reaction temperature and time, as well as the anhydroglucose unit to *p*-toluenesulfonyl chloride to betaine mass ratio on the degree of substitution of the product was evaluated. Increasing the proportion of betaine and *p*-toluenesulfonyl chloride was beneficial to the esterification reaction. The degree of substitution was 1.68 at 90 °C for 32 h with an anhydroglucose unit to *p*-toluenesulfonyl chloride to betaine molar ratio of 1 to 2 to 3. The physicochemical properties of the betaine-modified cellulose were closely related to the degree of substitution. Major changes in the morphologies, crystallinity, thermal properties, porosity, and the average degree of polymerization resulted from the modification. The introduction of betaine made cellulose esters thermally less stable than neat cellulose but more difficult to completely degrade. The crystalline structure of the cellulose esters was destroyed, and the products exhibited a porous nature. Dye sorption studies demonstrated that the betaine-modified cellulose holds the potential of adsorbing anionic substances, which is the premise of its application.

Keywords: Cellulose; Betaine; Esterification; Adsorption

Contact information: State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, Ji'nan, Shandong Province 250353 P. R. China.
** Corresponding author: syyibcas@126.com*

INTRODUCTION

In view of the shortage of fossil-based energy sources and the prevalence of environmental pollution, biobased polymers are of current scientific interest. Cellulose, as one of the most abundant natural polymers in the world, has attracted widespread attention. As a three-dimensional structured polymer, cellulose is composed of an anhydroglucose unit (AGU) linked by β-1,4 glycosidic bonds (Dias *et al*. 2020). Natural cellulose has great properties, *e.g.*, sustainability, biodegradability, biocompatibility, high mechanical strength, and versatile chemical functionality, but it lacks chemical degradation resistance and thermal plasticity (Trache *et al*. 2016; He *et al*. 2021). Cellulose derivatization has been conducted to overcome the drawbacks of cellulose or to give it new capabilities (Eyley and Thielemans 2014). A variety of cellulose materials can be prepared *via* cellulose derivatization, and these products have enabled its application in the pharmaceutical industry, pulp and paper making, food industry construction, and environmental treatment (Lin *et al*. 2016; Almeida *et al*. 2018; Arca *et al*. 2018; Cui *et al*. 2020; He *et al*. 2021).

The physical and chemical properties of cellulose can be modulated by inducing functional groups *via* esterification, etherification, oxidation, and graft copolymerization reactions (Fox *et al*. 2011; Sehaqui *et al*. 2013; Hoeng *et al*. 2015; Fraschini *et al*. 2017; Shojaeiarani *et al*. 2019). Cationic cellulose derivatives have attracted extensive attention, since they are capable of binding electrostatically with anionic substances. This remarkable feature allows cationic cellulose to be used as adsorption material in various fields such as biomedical, pharmaceutical, pulping, wastewater treatment, among many others (Li *et al*. 2015; Gao *et al*. 2016; Aguado *et al*. 2017; Rol *et al*. 2019; Imtiaz *et al*. 2020; Verfaillie *et al*. 2020; Laureano-Anzaldo *et al*. 2021; Liu *et al*. 2021). In general, cationic cellulose can be prepared in several ways, such as direct cationization of cellulose, graft copolymerization of cationic polymers with cellulose, and the introduction of cationic groups into cellulose (Gao *et al*. 2016; Jasmani *et al*. 2016; Li *et al*. 2016; Laureano-Anzaldo *et al*. 2021). Among these methods, the introduction of cationic reagents into cellulose is a feasible technique due to its high efficiency and simplicity (Li *et al*. 2016; Aguado *et al*. 2017; Rol *et al*. 2019).

In this study, an amphoteric ammonium-type alkaloid, *i.e.*, betaine (molecular formula $C_5H_{11}NO_2$), was used to modify cellulose. Betaine, which has been found in a variety of organisms, has a high solubility and is nontoxic to cells even at high concentrations (Craig 2004). In a previous report by Ma *et al*. (2014), betaine-modified cationic cellulose was prepared through the reaction of cellulose with betaine hydrochloride *via* an efficient one-step dry method, and the products exhibited a potential application for reactive dye wastewater treatment. In this work, a new method for synthesizing betaine-modified cellulose esters was developed in which the reaction was performed in a mixed N,N-dimethylacetamide (DMAc)/lithium chloride (LiCl) homogenous solution using *p*-toluenesulfonyl chloride (TsCl) for the *in-situ* activation of betaine. The effects of the reaction conditions, including the reaction temperature and time, as well as the AGU to TsCl to betaine mass ratio, on the product were investigated. The morphological and structural characteristics of the modified cellulose products were characterized to estimate the potential for the application of esters. Overall, this work provided a potential method for preparing cellulose esters.

EXPERIMENTAL

Materials

Cellulose (CAS: 9004-34-6), betaine (trimethylglycine; CAS: 107-43-7), and *p*-toluenesulfonyl chloride (TsCl) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). The particle size of the purchased cellulose is 90 μm. Lithium chloride (LiCl) was purchased from Beijing Solarbio Science & Technology Co., Ltd. (Beijing, China). Ethanol (95%), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), chloroform, and pyridine were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Cupri-ethylene-diamine solution (CAS: 14552-35-3) was purchased from China National Pulp and Paper Research Institute (Beijing, China). The two dyes, acid red 26 (AR 26, CAS: 3761-53-3) and acid black 2 (AB 2, CAS: 8005-03-6), were gifted from the School of Light Industry Science and Engineering, Qilu University of Technology (Jinan, China).

Esterification of Cellulose

Betaine-modified cellulose was synthesized in a cellulose/DMAc/LiCl homogenous solution using TsCl for the *in-situ* activation of betaine. The solvent exchange process was adapted to activate cellulose (McCormick *et al*. 1985; Khaliq and Kim 2016). Then, the activated dry cellulose was dissolved in 50 mL of solvent containing DMAc and LiCl (8 wt.% of DMAc) with magnetic stirring at a temperature of 55 °C for 2 h to prepare a 20 $g \cdot L^{-1}$ solution. The reaction mixtures were prepared by dissolving TsCl and betaine in a cellulose solution, where the molar ratio of AGU to TsCl to betaine were adjusted to 1 to 1 to 1, 1 to 1 to 2, 1 to 2 to 1, 1 to 2 to 2, and 1 to 2 to 3 in order to obtain cellulose esters with different degrees of substitution (DS). It should be noted that betaine was dissolved in water (approximately 0.4 $g \cdot mL^{-1}$) and then added to the reaction system. The reaction mixtures were stirred for 12 h to 32 h at a temperature range of 75 °C to 100 °C and then cooled to room temperature. Then, 200 mL of 95% ethanol was added to the reaction system, and the solid product was collected *via* filtration after full stirring. The washing and filtration operations were repeated three times. The products were freeze-dried and then ground into powder for the following assays.

Determination of the Degrees of Substitution (DS)

The Kjeldahl method was used to determine the nitrogen content of the betaine-modified cellulose, thus calculating the DS according to Eq. 1,

$$DS = 162.15 \times N\% / 14.01 - 136.6 \times N\% \qquad (1)$$

where 162.15 is the molar mass of glucose units in the samples (g/mol), 14.01 is the atomic weight of nitrogen (g/mol), 136.6 is the molar mass of the substituent (g/mol), and N% is the nitrogen content in the sample (Ma *et al*. 2014).

Solubility of Esterified Cellulose

The neat cellulose and betaine-modified product were dispersed in chloroform, pyridine, DMSO, tetrahydrofuran, and DMAc solvents to prepare 10 g/L solutions at room temperature. After ultrasonication at 40 kHz for 30 min, the solutions were centrifuged and then were determined for complete dissolution from a visual inspection.

Characterizations

Fourier transform infrared spectroscopy (FTIR) analysis was conducted to examine the chemical bonds of the samples at a spectral range of 400 to 4000 cm^{-1} (Vertex70, Bruker, Karlsruhe, Germany). X-ray diffraction (XRD) was carried out to measure the crystalline structure of the samples. Specimens were scanned from $2\theta = 5°$ to $2\theta = 60°$ at a scanning rate of 0.3°/s using a diffractometer (Smartlab SE, Rigaku, Osaka, Japan). The Segal peak height method was used to calculate the crystallinity, *i.e.*, the crystallinity index (Segal *et al.* 1959; Wang *et al*. 2018; Liu *et al*. 2021). The sample crystallinity was then calculated according to Eq. 2,

$$C = I_{002} - I_{\text{am}} / I_{002} \times 100\% \qquad (2)$$

where C is the crystallinity index, I_{002} is the maximum intensity of the lattice diffraction at $2\theta \approx 22°$, and I_{am} is the minimum intensity value of the peak at $2\theta \approx 18°$, which accounts for the amorphous part of the samples.

The morphology and microstructure of the cellulose and cellulose esters were observed *via* scanning electron microscopy (SEM). The samples were sprayed with gold and then observed at an accelerating voltage of 5 kV (Regulus 8220, Hitachi, Tokyo, Japan). The thermal stability of the modified cellulose was analyzed *via* thermogravimetric analysis (TGA) using a NETZSCH-STA 449 F5 at a heating rate of 10 °C/min under a nitrogen atmosphere. Nitrogen adsorption porosimetry was used to analyze the Brunauer−Emmett−Teller specific surface areas (S_{BET}) and the pore size distributions (calculated by the density functional theory method) of the samples with a Quantachrome AUTOSORB IQ analyzer (Boynton Beach, USA).

The average degree of polymerization (DP) of the samples was estimated using a viscometer (Viscomat II, BY LAGGE technologies, Sweden). 150 mg of the dried sample was dissolved in 30 mL solution, which consisting of 15 mL cupri-ethylene-diamine and 15 mL deionized water. The reagent was stabilized using red copper sheets. The solution was then immersed in a 25℃ thermostatic water bath for 5 min. The viscosity and the average DP of the samples were determined at 25 ℃.

Adsorption Experiments

The anionic dyes (AR 26 and AB 2) were prepared as simulated dye solutions of different concentrations, and the pH values were adjusted to neutral. A certain amount of betaine-modified cellulose was added to 10 mL of dye solution, and the mixture was stirred at 100 rpm for 60 min at room temperature. The solution was left to settle for 2 h and then centrifuged at 3000 rpm. The supernatant was used to evaluate the adsorption efficiency of the esters by determining the absorbance at the maximum absorption wavelength of the two dyes with the aid of an ultraviolet–visible spectrophotometer (8454, Agilent Technologies, Santa Clara, CA). The dye removal efficiency (E_r) was calculated using Eq. 3,

$$E_r\ (\%) = C_0 - C_e/C_0 \times 100\% \qquad (3)$$

where C_0 and C_e are the concentrations of the dye before and after adsorption (mg·L^{-1}), respectively (Ma *et al*. 2014).

RESULTS AND DISCUSSION

Cellulose Esterification Dependence on the Reaction Conditions

The characteristics of cellulose may be an important factor affecting the efficiency of derivatization. The complex morphology and structure of the crystalline and noncrystalline regions of cellulose as well as the hydrogen bonds generated by the intra- and intermolecular hydroxyl groups make cellulose difficult to dissolve in common solvents, thus limiting the homogeneity of its chemical reactions (McCormick *et al*. 1985; Zhang *et al*. 2014; Ghasemi *et al*. 2017). Therefore, to obtain a better derivatization effect, the swelling or dissolution of cellulose is necessary. To date, alkali, organic solvents, and ionic liquids are commonly used in the pretreatment processing of cellulose to enable its derivatization (Xie and Chai 2016; Ghasemi *et al*. 2017). Here, the DMAc/LiCl solution was employed in synthesis of betaine-modified cellulose esters. Previous studies have found that carbonic acids can be activated by forming mixed TsCl/carbonic acid anhydride, which acts as an intermediate for producing cellulose derivatives *via* nucleophilic substitutions (Sesley *et al*. 2000; Heinze and Liebert 2001). In this work, TsCl was used in the *in-situ* activation of betaine.

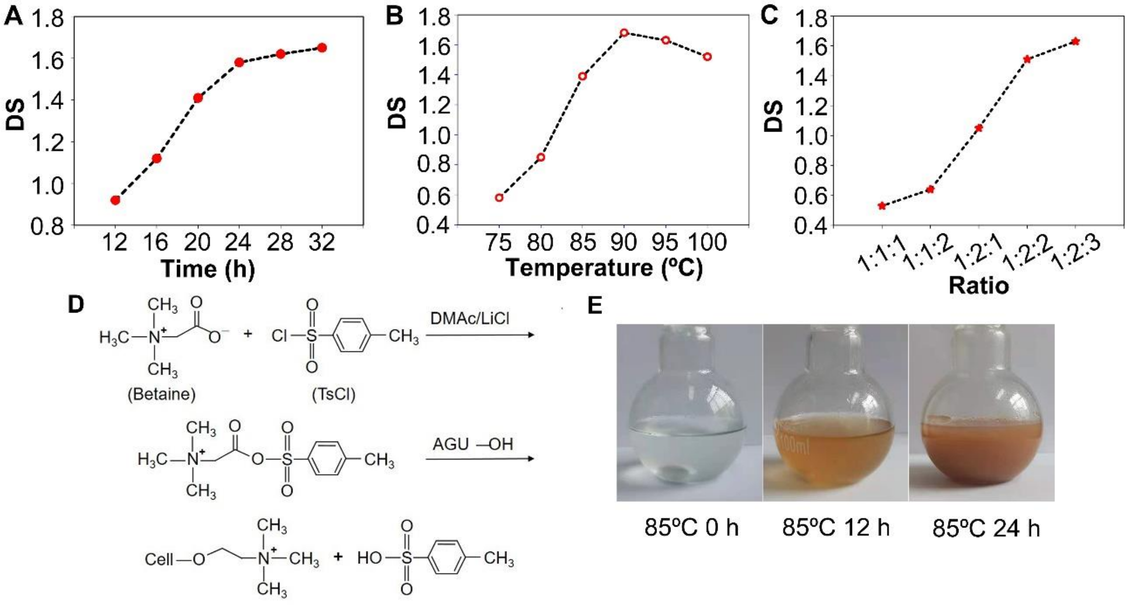

Fig. 1. Effect of the (A) reaction time. (B) temperature. and (C) AGU to betaine to TsCl molar ratio on the DS of betaine-modified cellulose; (D) synthesis of the betaine-modified cellulose (Note: Cell-OH represents cellulose); and (E) the color change of the reaction solution as the reaction time increased

To investigate the effects of the reaction temperature and time, as well as the AGU to TsCl to betaine mass ratio on the DS of betaine-modified cellulose, esterification reactions were carried out under different conditions. The DS of the samples showed an increasing trend, but this trend slowed after 24 h (Fig. 1A). When the molar ratio was 1 to 2 to 2 and the reaction time was 24 h, the DS increased as the reaction temperature increased and reached the maximum value at a temperature of 90 ℃ (Fig. 1B). At a temperature of 85 ℃ after 24 h, the ratio of the reactants had an important effect on the degree of product substitution (Fig. 1C). Increasing the proportion of betaine and TsCl was beneficial to the esterification reaction. This can be explained by the *in-situ* activation mechanism of TsCl on betaine (Sesley *et al*. 2000). In this assay, TsCl and betaine could form mixed anhydrides with higher activity, and these intermediate compounds reacted with the hydroxyl groups on cellulose to form cellulose esters (Fig. 1D). Therefore, the proportionate increase in the amount of betaine and TsCl was conducive to the formation of intermediate products, thus promoting the esterification reaction. As mentioned before, betaine was dissolved in water and then added to the reaction system *via* dropping. The increase in betaine meant additional water in the reaction system, which could affect the fluidity and reaction efficiency of the mixed solution. Given all that, for the purpose of a high DS, the optimum esterification conditions were determined to be a reaction at a temperature of 90 ℃ for 32 h with an AGU to betaine to TsCl molar ratio of 1 to 2 to 3.

It is worth noting that as time increased, the color of the reaction solution deepened, from colorless to brown-yellow (Fig. 1E). This phenomenon was in agreement with a previous study by Shimizu and Hayashi (1988), in which the color of the reaction solution with TsCl changed progressively according to the intensity of the reaction. The reason for the coloring has not been elucidated but is worth pursuing further.

Fourier Transfer Infrared Spectroscopy Analysis of Betaine-modified Cellulose

The spectra of the neat cellulose and modified cellulose are shown in Fig. 2A. In the esterification of cellulose, some hydroxyl groups have been replaced to form ester groups. Therefore, the DS of the betaine-modified cellulose may be related to the peak intensity of cellulose esters. Whenever mentioned in this study, E053, E092, and E152 represent cellulose esters with a DS of 0.53, 0.92, and 1.52, respectively. The characteristic peaks at 3423, 2890, 1643, 1421, and 1062 cm^{-1} in the neat cellulose samples reflected O–H stretching, C–H stretching, C–O–C stretching, CH_2 stretching, and C–O stretching, respectively (Poletto *et al*. 2014; Aalbers *et al*. 2019; Shojaeiarani *et al*. 2019). The infrared spectra of cellulose and regenerated cellulose from the DMAc/LiCl solvent were essentially the same. In the case of the modified cellulose, a new carbonyl stretching vibration at 1745 cm^{-1} (C=O) was identified, suggesting that betaine-cellulose ester linkage was successfully achieved (Ma *et al*. 2014; Her *et al*. 2020). In addition, as the DS increased, the intensity of the peak at 1745 cm^{-1} increased. However, the attenuation of the absorption peak at 1062 cm^{-1} of the modified cellulose indicated that some cellulose may have degraded during the cellulose dissolution and esterification processes.

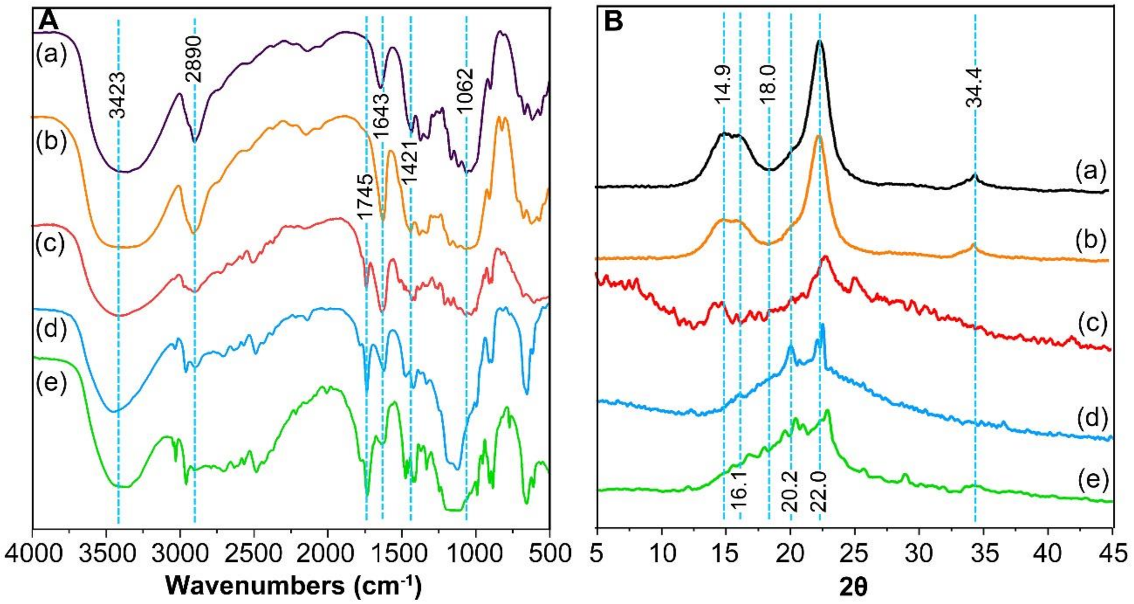

Fig. 2. FTIR spectra (A); and XRD patterns (B) of the neat and betaine-modified cellulose samples (Note: a is cellulose; b is regenerated cellulose form DMAc/LiCl solvent; and c through e are the E053, E092, and E152 betaine-modified celluloses, respectively)

X-ray Diffraction Assay of Betaine-modified Cellulose

Previous studies have shown that the derivatization of cellulose could result in considerable depletion of the intermolecular hydrogen bonding network, especially with a high DS (Eyley and Thielemans 2014; Wang *et al*. 2017). To evaluate the effect of esterification on the physical properties of the samples, two fundamental quantities that describe the structure of cellulose: the crystallinity index (CI) and the average DP, were measured in this study. The crystallinity changes of cellulose after esterification were illustrated by XRD patterns (Fig. 2B). The diffraction profile of neat cellulose exhibited characteristics of cellulose I, with peaks at 2θ angles of 14.9°, 16.1°, and 22.0° (Ju *et al.*

2015; Ahvenainen *et al*. 2016; Dias *et al*. 2020). There was no considerable difference in the diffraction profile between the original and the regenerated cellulose, which indicated that the dissolution and regeneration processes had essentially no effect on the formation of the hydrogen bonds of cellulose molecules. The CI was calculated based on the peak intensity, and the values for the original and regenerated cellulose were 72.9% and 68.8%, respectively. However, the crystalline peaks weakened or disappeared in the modified cellulose, depending on the DS. The XRD patterns of the three modified cellulose samples considerably transformed after treatment, lacking peaks at 2θ angles of 14.9°, 16.1°, and 34.4°, as well as showing a new weak peak at approximately 20.2°. Moreover, the XRD peaks tended to narrow after esterification. The results collected in this assay suggested that the crystallization of cellulose I was destroyed in the modified cellulose.

Average Degree of Polymerization of Betaine-modified Cellulose

According to the XRD patterns of cellulose and the esters, it is reasonable to assume that part of cellulose is degraded during the esterification reaction. Generally, the polymerization degree could be estimated using viscosimetry or size-exclusion chromatography (SEC) (Mattonai *et al*. 2018). After testing the solubility of betaine-modified cellulose with 5 conventional solvents, it was found that none of them could completely dissolve the samples. Thus, the average DP of the samples was estimated by viscometry in this assay. Table 1 shows the viscosity and the average DP of the samples at 25℃ for different DS. The neat cellulose and regenerated cellulose form DMAc/LiCl solvent showed comparable viscosity and DP. For the sample of E053, the average DP was reduced to 78% of the value for neat cellulose. The average DP of E092 and E152 decreased significantly, which were 64% and 58% of the neat cellulose, respectively. It can be seen that the CI and the average DP of cellulose exhibited obvious changes after esterification, which may affect the physical and chemical behaviour of cellulose.

Table 1. Viscosity and Average DP of the Unmodified Cellulose and Betaine-modified Cellulose

Sample	DS	Viscosity (mL/g)	Average DP
Cellulose	−	281	370
Regenerated cellulose	−	275	361
E053	0.53	223	288
E092	0.92	188	237
E152	1.52	173	216

Thermal Stability of Betaine-modified Cellulose

It was speculated that the level of crystallinity and DP may govern the thermal stability (Mukarakate *et al*. 2016; Mattonai *et al*. 2018; Shojaeiarani *et al*. 2019; Leng *et al*. 2020). In view of the results that the crystallinity and the average DP of cellulose esters have been significantly changed compared with neat cellulose in this study, the thermal decomposition of the samples was investigated *via* TGA within a temperature range of 50 to 720 °C under a nitrogen atmosphere (Fig. 3).

By comparing the onset thermal decomposition temperature (T_0) and the degradation trends of the samples, no major difference was observed between the original cellulose and the regenerated cellulose (Fig. 3A). However, the cellulose esters were thermally less stable than neat cellulose, as displayed by the fact that the T_0 values of the esters were shifted toward a lower temperature with a higher DS. As discussed earlier, this was more likely to be attributed to the decrease in crystallinity and the inevasible partial degradation of cellulose during esterification. This result was in consistent with a previous literature, that depolymerization and amorphization of cellulose significantly affected thermal stability (Mattonai *et al*. 2018).

Interestingly, the degradation trend of the betaine-modified cellulose was gentler than the degradation trend of the original cellulose and the regenerated cellulose. This result was also illustrated by the DTG curves. All of the samples showed a single-step degradation process with the primary degradation peak shifting in response to the DS (Fig. 3B). At a temperature of 720 °C, the original cellulose and regenerated cellulose were almost completely degraded, while the ester samples still had at least 20% residue, possibly because the nitrogen compounds were more difficult to degrade than the neat cellulose at that temperature. These results indicated that the introduction of betaine made the modified products thermally less stable but more difficult to completely degrade.

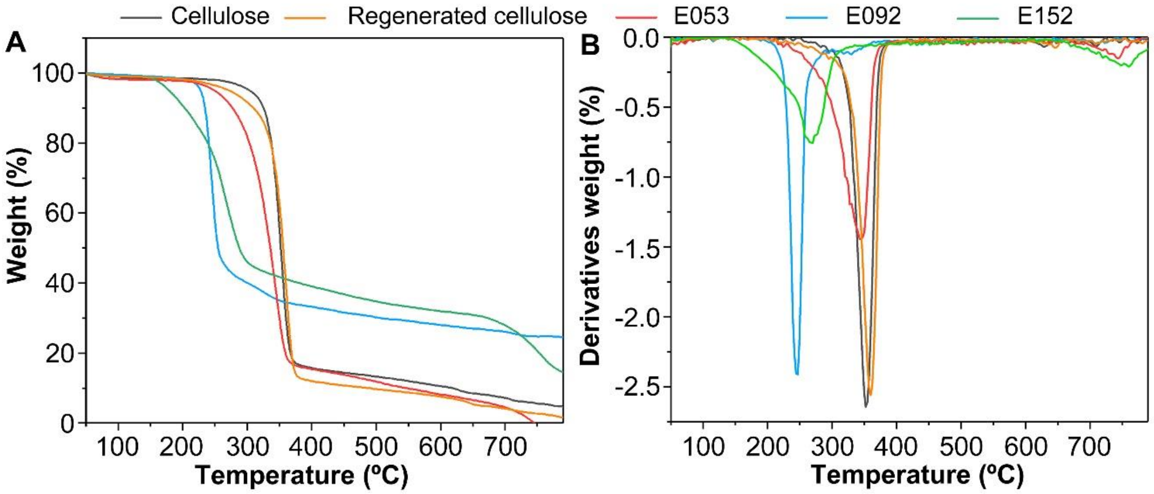

Fig. 3. TGA (A) and DTG (B) curves of the neat and betaine-modified cellulose samples

Morphology of Betaine-modified Cellulose

Subsequently, the morphological change of cellulose *via* esterification was investigated (Fig. 4). It was found that neat cellulose has a compact surface, which is similar to the observations made in previous studies (Salama *et al*. 2015; Wang *et al*. 2017). Compared to neat cellulose, the modified cellulose displayed a porous nature, probably because of the degradation of the sample and the disruption of the hydrogen bonds in the cellulose during esterification, as discussed before. This phenomenon matched the results demonstrating that the crystalline structure of cellulose was destroyed (Fig. 2).

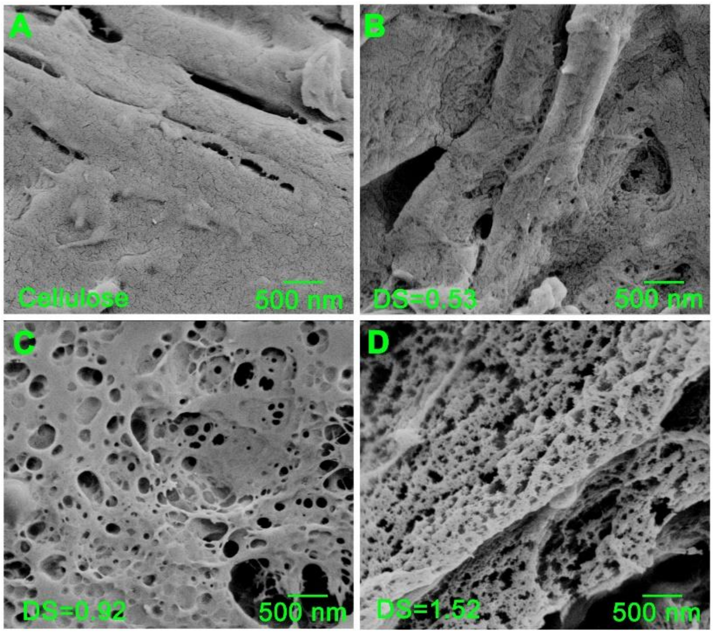

Fig. 4. SEM images of the (A) original cellulose; and (B, C, and D) betaine-modified cellulose with different DS

Porosity of Betaine-modified Cellulose

In the assay for porosity, the absorption-desorption isotherms and pore size distributions of the samples were characterized *via* nitrogen absorption-desorption tests. A summary of the porosity data can be found in Table 2; the higher the DS was, the higher the surface area. As expected, ester sample E152 (DS = 1.52) possessed the highest S_{BET} (45.0 cm·g^{-1}) and total pore volume (V_{total}) (0.89 cm·g^{-1}). The original cellulose showed type I isotherm characteristics, while the three ester samples exhibited type IV isotherm characteristics for mesoporous materials, with a hysteresis loop (as shown in Fig. 5A) (An *et al*. 2017). The steep gas uptake of samples E092 and E152 at high relative pressures was due to the presence of mesopores and macropores (Zubrik *et al*. 2017; Zou *et al*. 2018). Compared with the E092 sample, the E152 sample showed a sharper trend of adsorption behavior at high relative pressures between 0.8 to 1.0, which suggested that the sample consisted of accumulated mesopores.

The pore size distribution of the samples calculated by the density functional theory (DFT) method is shown in Fig. 5B. At a low relative pressure range, the neat cellulose and product E053 exhibited similar pore size distributions of micropores. The negligible adsorption capacity of samples E092 and E152 at a relative pressure range of 0.0 to 0.4 indicated that almost no micropores were detected. Unexpectedly, E152 exhibited a smaller average pore size but a more concentrated distribution when compared to E092. These results agreed with the SEM images showing that E152 has a more evenly distributed porosity. However, it is worth noting that, due to the reduced thermal stability of cellulose esters, the pretreatment temperature was lowered in this assay, which may affect the pore exposure. This may explain why that when compared with cellulose, the morphology of E092 and E152 greatly varied while the increase of the S_{BET} value and pore size was smaller than expected.

Table 2. Values of the S_{BET}, Total Pore Volume (V_{total}), and Average Pore Diameter Calculated (D) from the BET Isotherm and T-Plot Method

Sample	DS	S_{BET} ($m^2 \cdot g^{-1}$)	V_{total} ($cm^3 \cdot g^{-1}$)	D_{ave} ($m^2 \cdot g^{-1}$)
Cellulose	–	2.105	$5.589e^{-03}$	10.618
E053	0.53	3.750	$1.103e^{-02}$	11.766
E092	0.92	4.261	$2.986e^{-02}$	28.032
E152	1.52	44.984	$2.419e^{-01}$	21.066

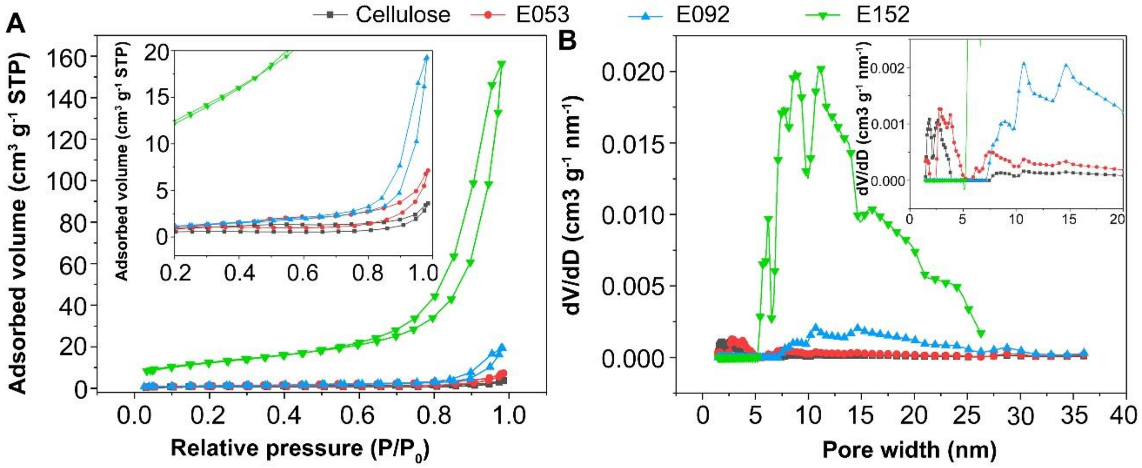

Fig. 5. (A) Nitrogen adsorption–desorption isotherms; and (B) pore size distribution curves of the cellulose and betaine-modified cellulose samples (Note: STP means standard temperature and pressure)

Dye Sorption Studies

The application of cationic cellulose derivatives is worth exploring. Recent studies have shown that cationic cellulose could be widely applied as potential antimicrobial agents, adsorbents, and papermaking additive (Ma *et al*. 2014; Lin *et al*. 2016; Aguado *et al*. 2017; Rol *et al*. 2019; Verfaillie *et al*. 2020). In this paper, the adsorption function of betaine-modified cellulose on anionic substances was investigated by dye adsorption experiment. Two acid dyes (AB 2 and AR 26) were used to estimate the dye-adsorption ability of betaine-modified cellulose (as shown in Figs. 6 and 7). Both dyes are commonly used in textile dyeing, and the wastewater caused by it deserves attention. The schematic illustration for the interaction between the betaine-modified cellulose and the AB 2 and AR 26 anionic dyes is shown in Fig. 6. Considering that both AB 2 and AR 26 dyes contain two sulfonic acid groups, it is speculated that the dyes may be attracted with one or two betaine group when absorbed by cellulose esters. Cellulose esters with different DSs were investigated, and images of the dye solution and adsorbent before and after adsorption were displayed in Fig. 7A. Using the original cellulose as a contrast, it was found that the adsorbent was colored after absorbing the dye, while the color of the solution tended to be lighter. It should be noted that the neat cellulose had almost no adsorption effect on the two dyes, which was demonstrated by determination of absorbance.

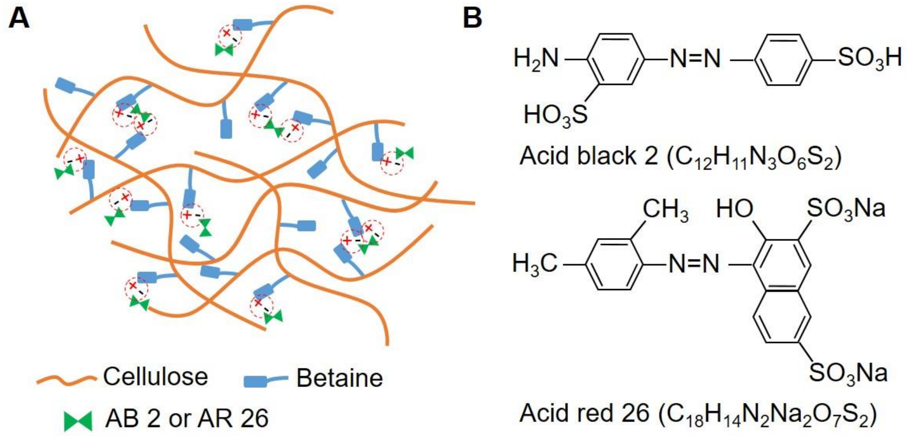

Fig. 6. (A) Schematic illustration for the interaction between the betaine-modified cellulose and the AB 2 and AR 26 anionic dyes; and (B) chemical structures of AB 2 and AR 26.

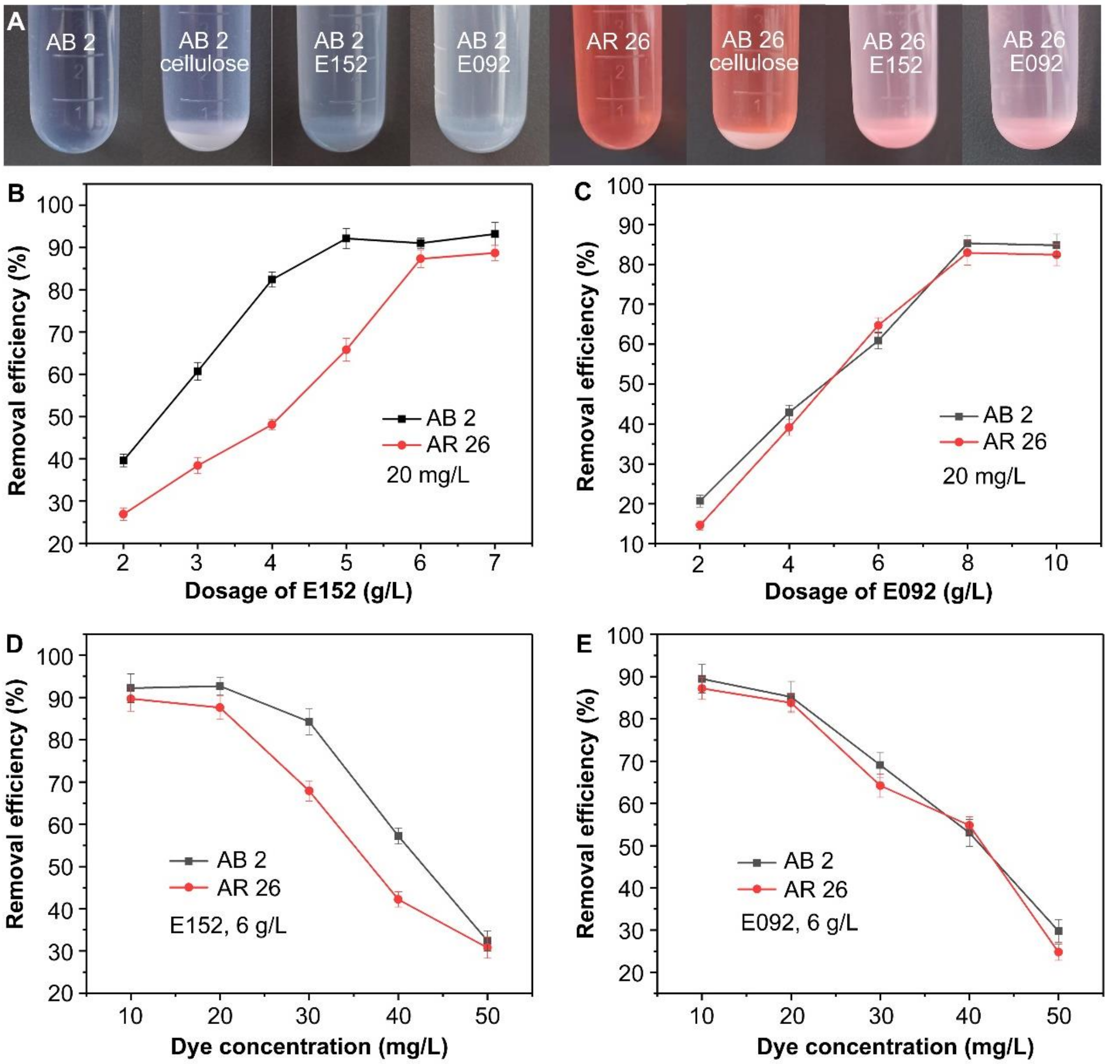

Fig. 7. (A) images of the dye solution and adsorbent before and after adsorption; and (B through E) effects of the adsorbent dosage and dye concentration on adsorption

The effects of the adsorbent dosage and dye concentrations on adsorption were considered. The absorption efficiencies of the two samples showed similar trends (Figs. 7B and 7C). In the case of sample E152, the removal efficiencies of 20 mg/L of AB 2 and AR 26 increased as the adsorbent dosage increased and reached a maximum of 92.1% and 87.3% at adsorbent dosages of 6 g/L and 8 g/L, respectively. For sample E092, it was found that the adsorbent was not as effective as E152, and the removal rate only reached 86% and 82% at an adsorbent dosage of 6 g/L, with respect to AB 2 and AR 26. These results indicated that the higher the DS of the product was, the more conducive it was to the adsorption of dyes. It also suggested that the adsorption effect of the same adsorbent with different dyes is different, so the optimum amount of adsorbent varied. This is probably because the nature of the dye itself has a great influence on the adsorption effect. Both AB 2 and AR 26 have two sulfonic groups, but AB 2 may be less affected by steric hindrance compared to AR 26 and thus tended to be more easily adsorbed by the modified cellulose (Fig. 6B).

The removal tendencies of the two dyes decreased as the dye concentration increased from 10 mg/L to 50 mg/L (Fig. 7D and 7E). When using E152 as an adsorbent, the percent removal of AB 2 gradually decreased from 92.2% to 32.4%, while the removal of AR 26 gradually decreased from 89.7% to 30.8%. In addition, E092 was less effective than E152, as discussed before. These results suggested that the betaine-modified cellulose ester holds the ability to adsorb anions, which provides a theoretical basis for further study of its functions.

CONCLUSIONS

1. A new method for synthesizing betaine-modified cellulose esters in mixed ionic liquid solution, DMAc/LiCl, using TsCl for the *in-situ* activation of betaine was developed.
2. Increasing the proportions of betaine and TsCl is beneficial to the esterification reaction.
3. The physicochemical properties of betaine-modified cellulose are closely related to the degree of substitution (DS). The products exhibited a porous nature and a decrease in crystallinity and the average degree of polymerization. The introduction of betaine made the cellulose esters thermally less stable than neat cellulose but more difficult to completely degrade.
4. Dye sorption studies demonstrated that the betaine-modified cellulose could serves as a promising sorbent for anionic substances, which may lead to a variety of applications.

ACKNOWLEGEMENTS

This research was supported by the National Natural Science Foundation of China (Grant No. 31800219), the National Key Research and Development Program of China (2017YFB0307900), and the Foundation (ZZ20200126 and 2419160205) of State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences.

REFERENCES CITED

Aalbers, G. J. W., Boott, C. E., D'Acierno, F., Lewis, L., Ho, J., Michal, C. A., Hamad, W. Y., and MacLachlan, M. J. (2019). “Post-modification of cellulose nanocrystal aerogels with thiol-ene click chemistry,” *Biomacromolecules* 20(7), 2779-2785. DOI: 10.1021/acs.biomac.9b00533

Aguado, R., Lourenço, A. F., Ferreira, P. J., Moral, A., and Tijero, A. (2017). “Cationic cellulosic derivatives as flocculants in papermaking,” *Cellulose* 24(7), 3015-3027. DOI: 10.1007/s10570-017-1313-y

Ahvenainen, P., Kontro, I., and Svedström, K. (2016). “Comparison of sample crystallinity determination methods by X-ray diffraction for challenging cellulose I materials,” *Cellulose* 23(2), 1073-1086. DOI: 10.1007/s10570-016-0881-6

Almeida, A. P. C., Canejo, J. P., Fernandes, S. N., Echeverria, C., Almeida, P. L., and Godinho, M. H. (2018). “Cellulose-based biomimetics and their applications,” *Advanced Materials* 30(19). DOI: 10.1002/adma.201703655

An, Y., Li, Z., Yang, Y., Guo, B., Zhang, Z., Wu, H., and Hu, Z. (2017). “Synthesis of hierarchically porous nitrogen-doped carbon nanosheets from agaric for high-performance symmetric supercapacitors,” *Advanced Materials Interfaces* 4(12). DOI: 10.1002/admi.201700033

Arca, H. C., Mosquera-Giraldo, L. I., Bi, V., Xu, D., Taylor, L. S., and Edgar, K. J. (2018). “Pharmaceutical applications of cellulose ethers and cellulose ether esters,” *Biomacromolecules* 19(7), 2351-2376. DOI: 10.1021/acs.biomac.8b00517

Craig, S. A. S. (2004). “Betaine in human nutrition,” *American Society for Clinical Nutrition* 80(3), 539-549. DOI: 10.1093/ajcn/80.3.539

Cui, X., Ozaki, A., Asoh, T.-A., and Uyama, H. (2020). “Cellulose modified by citric acid reinforced poly(lactic acid) resin as fillers,” *Polymer Degradation and Stability* 175, pg. DOI: 10.1016/j.polymdegradstab.2020.109118

Dias, Y. J., Kolbasov, A., Sinha-Ray, S., Pourdeyhimi, B., and Yarin, A. L. (2020). “Theoretical and experimental study of dissolution mechanism of cellulose,” *Journal of Molecular Liquids* 312, pg. DOI: 10.1016/j.molliq.2020.113450

Eyley, S., and Thielemans, W. (2014). “Surface modification of cellulose nanocrystals,” *Nanoscale* 6(14), 7764-7779. DOI: 10.1039/c4nr01756k

Fox, S. C., Li, B., Xu, D., and Edgar, K. J. (2011). “Regioselective esterification and etherification of cellulose: A review,” *Biomacromolecules* 12(6), 1956-1972. DOI: 10.1021/bm200260d

Fraschini, C., Chauve, G., and Bouchard, J. (2017). “TEMPO-mediated surface oxidation of cellulose nanocrystals (CNCs),” *Cellulose* 24(7), 2775-2790. DOI: 10.1007/s10570-017-1319-5

Gao, Y., Li, Q., Shi, Y., and Cha, R. (2016). “Preparation and application of cationic modified cellulose fibrils as a papermaking additive,” *International Journal of Polymer Science* 2016, 1-8. DOI: 10.1155/2016/6978434

Ghasemi, M., Tsianou, M., and Alexandridis, P. (2017). “Assessment of solvents for cellulose dissolution,” *Bioresource Technology* 228, 330-338. DOI: 10.1016/j.biortech.2016.12.049

He, X., Lu, W., Sun, C., Khalesi, H., Mata, A., Andaleeb, R., and Fang, Y. (2021). “Cellulose and cellulose derivatives: Different colloidal states and food-related applications,” *Carbohydrate Polymers* 255, 1-13. DOI: 10.1016/j.carbpol.2020.117334

Heinze, T., and Liebert, T. (2001). "Unconventional methods in cellulose functionalization," *Progress in Polymer Science* 26(9), 1689-1762. DOI: 10.1016/s0079-6700(01)00022-3

Her, K., Jeon, S. H., Lee, S., and Shim, B. S. (2020). "Esterification of cellulose nanofibers with valeric acid and hexanoic acid," *Macromolecular Research* 28(12), 1055-1063. DOI: 10.1007/s13233-020-8146-5

Hoeng, F., Denneulin, A., Neuman, C., and Bras, J. (2015). "Charge density modification of carboxylated cellulose nanocrystals for stable silver nanoparticles suspension preparation," *Journal of Nanoparticle Research* 17(6), 1-14. DOI: 10.1007/s11051-015-3044-z

Imtiaz, Y., Tuga, B., Smith, C. W., Rabideau, A., Nguyen, L., Liu, Y., Hrapovic, S., Ckless, K., and Sunasee, R. (2020). "Synthesis and cytotoxicity studies of wood-based cationic cellulose nanocrystals as potential immunomodulators," *Nanomaterials (Basel)* 10(8). DOI: 10.3390/nano10081603

Jasmani, L., Eyley, S., Schütz, C., Van Gorp, H., De Feyter, S., and Thielemans, W. (2016). "One-pot functionalization of cellulose nanocrystals with various cationic groups," *Cellulose* 23(6), 3569-3576. DOI: 10.1007/s10570-016-1052-5

Ju, X., Bowden, M., Brown, E. E., and Zhang, X. (2015). "An improved X-ray diffraction method for cellulose crystallinity measurement," *Carbohydrate Polymers* 123, 476-481. DOI: 10.1016/j.carbpol.2014.12.071

Khaliq, Z., and Kim, B. C. (2016). "Molecular characterization of thermoreversibility and temperature dependent physical properties of cellulose solution in N,N-dimethylacetamide and lithium chloride," *Macromolecular Research* 24(6), 547-555. DOI: 10.1007/s13233-016-4073-x

Laureano-Anzaldo, C. M., Robledo-Ortíz, J. R., and Manríquez-González, R. (2021). "Zwitterionic cellulose as a promising sorbent for anionic and cationic dyes," *Materials Letters* 300, 130236. DOI: 10.1016/j.matlet.2021.130236

Leng, E., Ferreiro, A. I., Liu, T., Gong, X., Costa, M., Li, X., and Xu, M. (2020). "Experimental and kinetic modelling investigation on the effects of crystallinity on cellulose pyrolysis," *Journal of Analytical and Applied Pyrolysis* 152, 1-13. DOI: 10.1016/j.jaap.2020.104863

Li, G., Fu, Y., Shao, Z., Zhang, F., and Qin, M. (2015). "Preparing cationic cellulose derivative in NaOH/urea aqueous solution and its performance as filler modifier," *BioResources* 10(4),7782-7794. DOI: 10.15376/biores.10.4.7782-7794

Li, M. C., Mei, C., Xu, X., Lee, S., and Wu, Q. (2016). "Cationic surface modification of cellulose nanocrystals: Toward tailoring dispersion and interface in carboxymethyl cellulose films," *Polymer* 107, 200-210. DOI: 10.1016/j.polymer.2016.11.022

Lin, Q., Gao, M., Chang, J., and Ma, H. (2016). "Adsorption properties of crosslinking carboxymethyl cellulose grafting dimethyldiallylammonium chloride for cationic and anionic dyes," *Carbohydrate Polymers* 151, 283-294. DOI: 10.1016/j.carbpol.2016.05.064

Liu, Q., Meng, Z., Korpi, A., Kontturi, E., and Kostiainen, M. A. (2021). "Cationic cellulose nanocrystals for fast, efficient and selective heparin recovery," *Chemical Engineering Journal*, 420, 129811. DOI: 10.1016/j.cej.2021.129811

Liu, S., Zhang, Q., Gou, S., Zhang, L., and Wang, Z. (2021). "Esterification of cellulose using carboxylic acid-based deep eutectic solvents to produce high-yield cellulose nanofibers," *Carbohydrate Polymers* 251, 1-10. DOI: 10.1016/j.carbpol.2020.117018

Ma, W., Yan, S., Meng, M., and Zhang, S. (2014). "Preparation of betaine-modified cationic cellulose and its application in the treatment of reactive dye wastewater," *Journal of Applied Polymer Science* 131(15). DOI: 10.1002/APP.40522

Mattonai, M., Pawcenis, D., Del Seppia, S., Lojewska, J., and Ribechini, E. (2018). "Effect of ball-milling on crystallinity index, degree of polymerization and thermal stability of cellulose," *Bioresource Technology*, 270, 270-277. DOI: 10.1016/j.biortech.2018.09.029

McCormick, C. L., Callais, P. A., and Hutchinson Jr., B. H. (1985). "Solution studies of cellulose in lithium chloride and N,N-dimethylacetamide," *Macromolecules* 18(12), 2394-2401. DOI: 10.1021/ma00154a010

Mukarakate, C., Mittal, A., Ciesielski, P. N., Budhi, S., Thompson, L., Iisa, K., Nimlos, M. R., and Donohoe, B. S. (2016). "Influence of crystal allomorph and crystallinity on the products and behavior of cellulose during fast pyrolysis," *ACS Sustainable Chemistry & Engineering* 4(9), 4662-4674. DOI: 10.1021/acssuschemeng.6b00812

Poletto, M., Ornaghi Jr., H. L., and Zattera, A. J. (2014). "Native cellulose: Structure, characterization and thermal properties," *Materials* 7(9), 6105-6119. DOI: 10.3390/ma7096105

Rol, F., Saini, S., Meyer, V., Petit-Conil, M., and Bras, J. (2019). "Production of cationic nanofibrils of cellulose by twin-screw extrusion," *Industrial Crops and Products* 137, 81-88. DOI: 10.1016/j.indcrop.2019.04.031

Salama, A., Shukry, N., and El-Sakhawy, M. (2015). "Carboxymethyl cellulose-*g*-poly(2-(dimethylamino) ethyl methacrylate) hydrogel as adsorbent for dye removal," *International Journal of Biological Macromolecules* 73, 72-75. DOI: 10.1016/j.ijbiomac.2014.11.002

Segal, L., Creely, J. J., Martin Jr., A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Textile Research Journal* 29(10), 786-794. DOI: 10.1177/004051755902901003

Sehaqui, H., Zimmermann, T., and Tingaut, P. (2013). "Hydrophobic cellulose nanopaper through a mild esterification procedure," *Cellulose* 21(1), 367-382. DOI: 10.1007/s10570-013-0110-5

Sesley, J. E., Frazier, C. E., Samaranayake, G., and Glasser, W. G. (2000). "Novel cellulose derivatives. V. Synthesis and thermal properties of esters with trifluoroethoxy acetic acid," *Journal of Polymer Sceience: Part B: Polymer Physics* 38(3), 486-494. DOI: 10.1002/(sici)1099-0488(20000201)38:33.0.co;2-s

Shimizu, Y., and Hayashi, J. (1988). "A new method for cellulose acetylation with acetic acid," *Sen'i Gakkaishi* 44(9), 451-456. DOI: 10.2115/fiber.44.9_451

Shojaeiarani, J., Bajwa, D. S., and Hartman, K. (2019). "Esterified cellulose nanocrystals as reinforcement in poly (lactic acid) nanocomposites," *Cellulose* 26(4), 2349-2362. DOI: 10.1007/s10570-018-02237-4

Trache, D., Hussin, M. H., Hui Chuin, C. T. H., Sabar, S., Fazita, M. R. N., Taiwo, O. F. A., Hassan, T. M., and Haafiz, M. K. M. (2016). "Microcrystalline cellulose: Isolation, characterization and bio-composites application - A review," *International Journal of Biological Macromolecules* 93(Part A), 789-804. DOI: 10.1016/j.ijbiomac.2016.09.056

Verfaillie, A., Blockx, J., Praveenkumar, R., Thielemans, W., and Muylaert, K. (2020). "Harvesting of marine microalgae using cationic cellulose nanocrystals," *Carbohydrate Polymers* 240, 116165. DOI: 10.1016/j.carbpol.2020.116165

Wang, F., Zhao, G., Lang, X., Li, J., and Li, X. (2017). "Lipase-catalyzed synthesis of long-chain cellulose esters using ionic liquid mixtures as reaction media," *Journal of Chemical Technology and Biotechnology* 92(6), 1203-1210. DOI: 10.1002/jctb.5109

Wang, X., Zhang, C., Lin, Q., Cheng, B., Kong, F., Li, H., and Ren, J. (2018). "Solid acid-induced hydrothermal treatment of bagasse for production of furfural and levulinic acid by a two-step process," *Industrial Crops and Products* 123, 118-127. DOI: 10.1016/j.indcrop.2018.06.064

Xie, W. Q., and Chai, X. S. (2016). "A practical method for the determination of degree of substitution in sodium carboxymethyl starch," *Food Analytical Methods* 10(5), 1592-1596. DOI: 10.1007/s12161-016-0731-z

Zhang, C., Liu, R., Xiang, J., Kang, H., Liu, Z., and Huang, Y. (2014). "Dissolution mechanism of cellulose in N,N-dimethylacetamide/lithium chloride: Revisiting through molecular interactions," *The Journal of Physical Chemistry B* 118(31), 9507-9514. DOI: 10.1021/jp506013c

Zou, K., Deng, Y., Chen, J., Qian, Y., Yang, Y., Li, Y., and Chen, G. (2018). "Hierarchically porous nitrogen-doped carbon derived from the activation of agriculture waste by potassium hydroxide and urea for high-performance supercapacitors," *Journal of Power Sources* 378, 579-588. DOI: 10.1016/j.jpowsour.2017.12.081

Zubrik, A., Matik, M., Hredzák, S., Lovás, M., Danková, Z., Kováčová, M., and Briančin, J. (2017). "Preparation of chemically activated carbon from waste biomass by single-stage and two-stage pyrolysis," *Journal of Cleaner Production* 143, 643-653. DOI: 10.1016/j.jclepro.2016.12.061

Article submitted: July 16, 2021; Peer review completed: August 14, 2021; Revised version received and accepted: September 22, 2021; Published: September 28, 2021.
DOI: 10.15376/biores.16.4.7592-7607