

Preparation and characterization of cellulose laurate ester by catalyzed transesterification



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ABSTRACT

The preparation of cellulose laurate was investigated through transesterification in 1-allyl-3-methylimidazolium chloride (AmimCl)/dimethyl sulfoxide (DMSO) cosolvent system by using vinyl laurate as an acylation reagent and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as an effective catalyst. The effects of reaction temperature, reaction time and the molar ratio of vinyl laurate to anhydride glucose unit (AGU) were investigated. The degree of substitution (DS) ranged from 1.47 to 2.74 under the selected conditions and the reaction order of three hydroxyl groups was C-6 > C-3 > C-2. The chemical structure cellulose laurate were explored by Fourier transform infrared (FT-IR) spectroscopy, ¹H-nuclear magnetic resonance (NMR), ¹³C NMR, heteronuclear single quantum correlation (HSQC) and X-ray diffraction (XRD) to confirm the occurrence of transesterification. The improved thermal stability of cellulose laurate was proved by the thermogravimetric analysis (TGA). The tensile analysis and the contact angle measurement confirmed the ductile behavior and the hydrophobicity of the films made from cellulose laurate.

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1. Introduction

With the increase of the environmental awareness, cellulose has been popular in the application of making kinds of materials due to its economic advantages. As the most abundant natural polymer, it has many attractive properties such as renewability, biodegradability and biocompatibility. However, there are some drawbacks because cellulose can not be dissolved in water or common organic solvents due to its strong inter- and intra-hydrogen bonds. The lack of thermal plasticity also makes it hardly to be melted for compression molding. Through chemical modification, the physicochemical properties of cellulose can be significantly changed and more easily applied (Chen, Cho, Kim, Nam, & Lee, 2012).

Cellulose esters are important cellulose derivatives with excellent properties. It has been widely used in many different areas such as filtration, coating, pharmacy, and so on (Edgar et al., 2001). In general, cellulose esters can be obtained by acylation in heterogeneous or homogeneous system, among which the reaction in homogenous solution can get more uniform pattern and control the degree of substitution (DS) (Heinze & Liebert, 2001). For the last few decades, many attempts have been made to develop novel solvent systems to dissolve cellulose, including dimethyl sulfoxide/tetrabutylammonium fluoride (DMSO/TBAF) (Ciacco, Liebert, Frollini, & Heinze, 2003), N,N-dimethylacetamide/lithium chloride (DMAC/LiCl) (Ass, Ciacco, & Frollini, 2006), N-methylmorpholine (NMMO) (Fink, Weigel, Purz, & Ganster, 2011) and NaOH/urea (Cai & Zhang, 2005). However, these solvent systems are either expensive or applied in hard conditions. Extensive use of these solvents would not only do harm to the environment but also violate the economic feasibility.

Ionic liquids (ILs), made up of cations and anions, are promising solvents for dissolving cellulose. ILs have got constant attention since being developed due to their low vapor pressure and recyclability (Liebert, 2009; Wu et al., 2004; Zakrzewska, Bogel-Lukasik, & Bogel-Lukasik, 2010). Moreover, ILs were fine reaction media to produce cellulose derivatives such as carboxylic acid esters, inorganic esters, and so on (Gericke, Liebert, Seoud, & Heinze, 2011). The properties of ILs could be tailored by changing cations and anions, which is also attractive. However, in spite of these fascinating properties, ILs also have some disadvantages: long time to dissolve cellulose and the high viscosity of the solution, which is a hindrance for the following cellulose modification. Lately, IL/dimethyl sulfoxide (DMSO) cosolvent system has been developed to solve these problems and also been applied for broadly dissolving lignocelluloses (Casarano, Pires, & El Seoud, 2014; Chen et al., 2015; Jogunola et al., 2016; Lee et al., 2015; Xu, Zhang, Zhao, & Wang, 2013). It has been found that the cosolvent system are more effective for dissolving cellulose than neat ILs (Rinaldi, 2011). The addition of aprotic

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polar solvents like DMSO could not only reduce the viscosity of the dissolved solution and accelerate the mass transfer rate, but also reduce the steric hindrance (Lee et al., 2015).

Nowadays, most of plastic packing films are usually burned or sent to landfill after use, which causes environmental pollution (Yang, Fukuzumi, Saito, Isogai, & Zhang, 2011). Many green packaging films with biodegradability and proper mechanical properties have been made from natural materials such as starch, chitosan and hemicelluloses (Avella et al., 2005; Chen and Qi et al., 2016). Cellulose laurate, one of long chain cellulose esters, is regarded as biodegradable bioplastic due to the O-glucosidic bond of cellulose and the enzymatically labile ester bond. It can be used to form plastic films without any plasticizer compared to the other biopolymers (Thiebaud, Borredon, Baziard, & Senocq, 1997). According to the previous reports, cellulose laurate is usually produced through esterification by using lauroyl chloride or lauric acid as acylation reagent (Crépy, Chaveriat, Banoub, Martin, & Joly, 2009; Crépy, Miri, Joly, Martin, & Lefebvre, 2011; Huang, Wu, Yu, & Lu, 2015), which could provide acidic environment and always cause the degradation of cellulose. Comparatively, transesterification using related vinyl esters to synthesize cellulose esters is a rather mild and effective reaction (Chen, Xu, Wang, Cao, & Sun, 2016; Schenzel, Hufendiek, Barner-Kowollik, & Meier, 2014). In transesterification, a catalyst is needed to motivate the reaction. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) has been reported as an effective nucleophilic catalyst (Birman, Li, & Han, 2007; Ghosh, 2004; Ji, Qian, & Chen, 2013; Seebach, Thaler, Blaser, & Ko, 1991). In the present study, the preparation of cellulose laurate esters was investigated by transesterification using DBU as catalyst and vinyl laurate as acylation reagent in AmimCl/DMSO cosolvent system. As a harmless acylation reagent, the use of vinyl laurate can significantly reduce the harm to the environment caused by lauroyl chloride and lauric acid. Compared to the catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) used in the transesterification (Schenzel et al., 2014), DBU applied in the protocol are more effective to synthesize long chain cellulose esters with higher DS.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC, DP 280) was purchased from Sinopharm Chemical Reagent Company (Shanghai, China). DMSO and DBU were purchased from Sigma-Aldrich Co. (Guangzhou, China). Vinyl laurate was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). 1-Allyl-3-methylimidazolium chloride (AmimCl) with purity of 99% was supplied by Cheng-Jie Chemical Co., Ltd. (Shanghai, China). Other chemicals were all analytical-grade reagents and used as received without further purification.

2.2. Synthesis of cellulose ester via transesterification

The transesterification reaction was carried out in AmimCl/DMSO. MCC (0.2 g) was suspended in 5 g DMSO (50% wt of AmimCl) in a three-neck flask equipped with a magnetic stirrer. The suspension was agitated until the cellulose was dispersed thoroughly. Then 10 g AmimCl was added to the mixture and heated to a certain temperature (70–120 °C) in an oil bath. After the cellulose was dissolved, different amounts of vinyl laurate and 0.3 mL DBU were introduced into the solution for transesterification with agitation. After the required time, the solution was poured into 500 mL ethanol. The precipitates were centrifuged, washed thoroughly with ethanol and dried in the vacuum oven for 24 h.

2.3. Film preparation

The synthesized cellulose laurate (0.3 g) were dissolved in chloroform (10 mL) at room temperature with magnetic stirring. Then the transparent solution was cast into a polytetrafluoroethylene dish to form wet films. The films were put at ambient temperature for 24 h to evaporate chloroform, then dried in an oven at 50 °C for 5 h in order to further remove chloroform thoroughly, and stored in a plastic bag for characterization.

2.4. Characterization

2.4.1. FT-IR

The FT-IR spectra of MCC and cellulose laurate were recorded on a Bruker spectrophotometer (Bruker, Karlsruhe, Germany) in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. All of the samples and KBr were previously dried at 105 °C in an oven for more than 8 h to remove the moisture. The sample and KBr were mixed together with a ratio of 1:100 (w/w), finely ground and pressed into a disc for the measurement.

2.4.2. XRD

X-ray diffraction of modified samples and raw materials were performed on a D8 Advance instrument (Bruker AXS, Germany) with Nickel-filtered Cu K α radiation (wave length = 0.154 nm) in the diffraction angle 2 θ ranging from 5 to 60°.

2.4.3. TGA/DTG

The thermal stability of the modified samples and raw materials were characterized by using TGA/DTG on a QG500 thermogravimetric analyzer (TA Instruments, New Castle, PA, USA). The device was flushed with nitrogen continually. The samples about 9–10 mg were heated from 30 to 600 °C at a rate of 10 °C/min.

2.4.4. NMR analysis

The ¹H NMR, ¹³C NMR and HSQC spectra of the modified cellulose laurate were recorded from 40 mg samples in 0.5 mL chloroform-d₆ on a Bruker Advance III 600 M (Bruker, Germany) with a 5 mm multinuclear probe according to the reported method (Zhang, Chen, Liu, Zhang, & Sun, 2015).

2.4.5. Determination of DS

The DS of cellulose laurate can be estimated from the ¹H NMR by the calculation with the peak intensity of the corresponding resonances through the following Eq. (1) based on the reported method (Satgé, Granet, Verneuil, Branland, & Krausz, 2004):

$$DS = 10 \times \frac{I_{(CH_3, H)}}{(3 \times I_{(AGU, H)} + I_{(CH_3, H)})} \quad (1)$$

where $I_{(CH_3, H)}$ is the integration of the resonances assigned to methyl protons of methyl group, 10 and 3 are the amounts of protons in the glucose ring and methyl group, respectively, and $I_{(AGU, H)}$ is the integration of the resonances assigned to protons of the glucose ring.

2.4.6. Tensile analysis

The tensile strength of cellulose laurate films was determined at rectangular specimens (30 mm × 10 mm) on a Universal Testing Machine 5565 (Instron, Norwood, MA, USA) fitted with a 100 N load cell at 23 °C with 50% relative humidity (RH).

2.4.7. Contact angle

Contact angles of the film surfaces for water droplets were determined at 23 °C and 50% RH on a contact angle machine (dataphysics,

Table 1

DS and solubility of cellulose laurate prepared by transesterification under different conditions in AmimCl/DMSO cosolvent system.

Entry	T(°C)	Time(h)	AGU:VL ^a	DS	Solubility ^b				
					DMSO	DMF	Acetone	THF	CHCl ₃
1	70	3	1:6	1.47	–	–	–	–	+
2	80	3	1:6	1.60	–	–	–	–	+
3	90	3	1:6	1.62	–	–	–	–	+
4	100	3	1:6	1.72	–	–	–	–	+
5	110	3	1:6	2.32	–	–	–	–	+
6	120	3	1:6	2.41	–	–	–	–	+
7	120	1	1:6	1.97	–	–	–	–	+
8	120	6	1:6	2.74	–	–	–	–	+
9	120	9	1:6	2.55	–	–	–	–	+
10	120	3	1:3	1.80	–	–	–	–	+
11	120	3	1:9	2.62	–	–	–	–	+
12	120	3	1:12	2.63	–	–	–	–	+

^a The molar ratio of AGU to vinyl laurate.^b Insoluble (–) and soluble (+) in different solvents.

OCA40 Micro, Germany). A water droplet of 2 μ L was dropped onto the film and the photos were taken after 10 s.

3. Results and discussion

3.1. Transesterification of MCC

Fig. S1 (Supplementary Materials) shows the transesterification reaction of cellulose and vinyl laurate in the AmimCl/DMSO cosolvent system using DBU as a catalyst. The cellulose laurate esters are synthesized by one step and the byproduct is acetaldehyde, which is volatile and can be removed easily from the reaction system.

As shown in Table 1, DS of the cellulose laurate could be controlled by changing the reaction conditions including reaction temperature, reaction time and the molar ratio of AGU to vinyl laurate. Keeping the molar ratio of AGU to vinyl laurate at 1:6 under 3 h, the DS of cellulose laurate ester increased from 1.47 to 2.41 with the increase of reaction temperature from 70 °C to 120 °C. This increment was probably due to the higher activity of catalyst DBU and the more flexible cellulose chains at higher temperature. Holding the molar ratio of AGU to vinyl laurate at 1:6 and reaction temperature at 120 °C, the improvement of reaction time from 1 to 6 h resulted in an increase in DS from 1.97 to 2.74, while further increase of reaction time from 6 to 9 h led to a slight decrease in DS from 2.74 to 2.55, which was probably due to the degradation of cellulose macromolecules and the hydrolysis of the cellulose laurate ester in AmimCl/DMSO cosolvent system with the increased duration. The DS increased from 1.80 to 2.62 with the increase of the molar ratio of AGU to vinyl laurate from 1:3 to 1:9 and the DS was 2.63 when the molar ratio reached 1:12, which means further increased the molar ratio would not improve the DS value. TBD was reported as an effective catalyst to synthesize cellulose 10-undecenoate through transesterification (Schenzel et al., 2014), and the highest DS value of long chain cellulose esters was 0.4 under 24 h at 115 °C. Comparatively, the transesterification method in the present study was a more effective way to prepare the long chain cellulose ester. From Table S1, the yield of cellulose laurate indicated that the synthesis protocol in the present study was effective and efficient.

The solubility of the synthesized cellulose laurate esters was examined, also as shown in Table 1. Due to the introduction of the long aliphatic side chains onto the cellulose macromolecules, cellulose laurate could not be dissolved in DMSO, N,N-Dimethylformamide (DMF), tetrahydrofuran (THF) and acetone. However, all of the synthesized cellulose laurate could be dissolved in chloroform, providing the possibility to produce films and other composites.

3.2. FT-IR

The FT-IR spectra of unmodified material MCC and modified samples are shown in Fig. S2. Compared to the unmodified MCC, there were several new absorbances in the spectra of the modified samples. The new peaks for asymmetric and symmetric stretching of methylene group appeared at 2924 cm^{-1} and 2850 cm^{-1} , respectively. The band for C=O stretching and that for the scissoring of methylene group exhibited at about 1750 and 1420 cm^{-1} , respectively. The presence of these new peaks indicated that the methylene group and carbonyl moieties were attached onto the cellulose macromolecules, confirming the successful synthesis of cellulose laurate by DBU-catalyzed transesterification in AmimCl/DMSO cosolvent system.

3.3. NMR

The chemical structure of the cellulose laurate was elucidated by ^1H NMR and ^{13}C NMR, as illustrated in Fig. 1. In the ^1H NMR spectrum of the cellulose laurate sample 8, the proton signals from 4.99 to 3.41 ppm are assigned to H-3, H-1, H-2, H-6, H-6', H-5 and H-4 of AGU in cellulose, respectively. The signals at 2.27–2.07, 1.55–1.43, and 1.19 ppm are associated with the methylene protons at H-8, H-9, and H-10–17, respectively. The signals at 0.82–0.80 ppm are attributed to the methyl protons at H-18.

In the ^{13}C NMR spectrum of the cellulose laurate sample 8, the signals at 32.96, 30.91, 23.81, 21.69 and 13.09 ppm are assigned to the carbons of C-8, C-16, C-9, C-17 and C-18, respectively, on the aliphatic side chain. The carbons at C-10–15 positions give the signals at 28.70–28.28 ppm. The carbons at C-1, C-4, C-2, 3, and 5, and C-6 in AGU exhibit the signals at 99.57, 75.82, 72.1–70.46 and 60.99 ppm, respectively. The signals from 171.86 to 170.75 ppm correspond to the carbonyl at C-7, providing the direct evidence of the successful attachment of the aliphatic side chains onto cellulose. Based on the calculation from the integration of carbonyl carbons (C7-O6, C7-O3 and C7-O2) from the ^{13}C NMR in Fig. 1, the partial DS of C-6:C-3:C-2 in the cellulose laurate sample was 1:0.97:0.81, indicating that the reaction order of three hydroxyl groups was C-6 > C-3 > C-2.

To further confirm the assignment of the signals of cellulose laurate, HSQC spectrum was also collected. Fig. 2 shows the cellulose region (A) and aliphatic side chain region (B) of HSQC spectrum of cellulose laurate sample 8. In cellulose region, the strong correlations were well distinguished at $\delta_{\text{H}}/\delta_{\text{C}}$ 5.00/71.04, 4.83/70.29, 4.29/99.56, 4.29/61.03, 3.95/61.03, 3.56/75.28 and 3.42/72.19 ppm for C₃/H₃, C₂/H₂, C₁/H₁, C_{6e}/H_{6e}, C_{6a}/H_{6a}, C₄/H₄ and C₅/H₅, respectively. It should be noted that the proton signal of H₁ was overlapped with that of H₆ from HSQC. In aliphatic

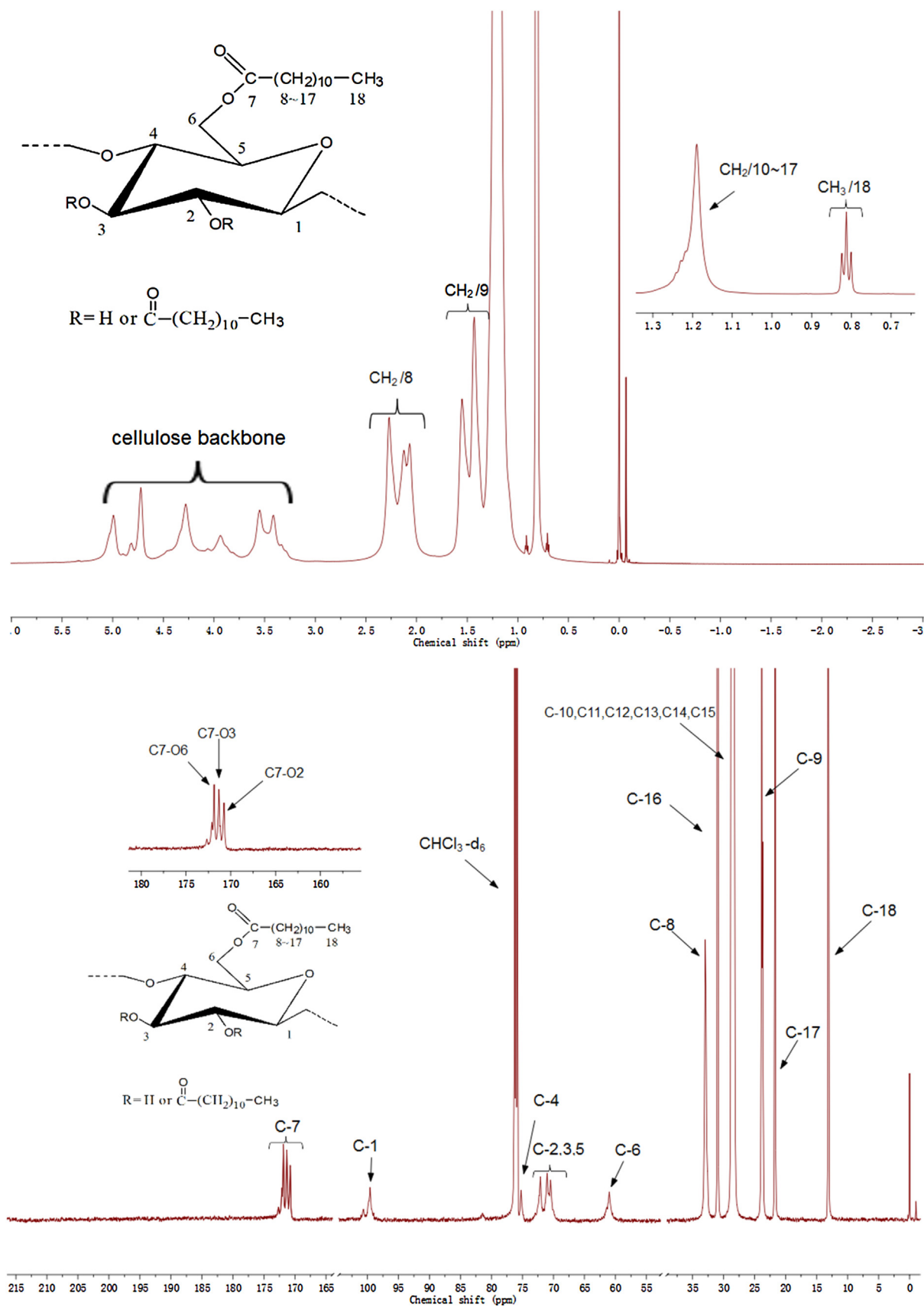


Fig. 1. ^1H - and ^{13}C NMR spectra of cellulose laurate sample 8 (DS = 2.74).

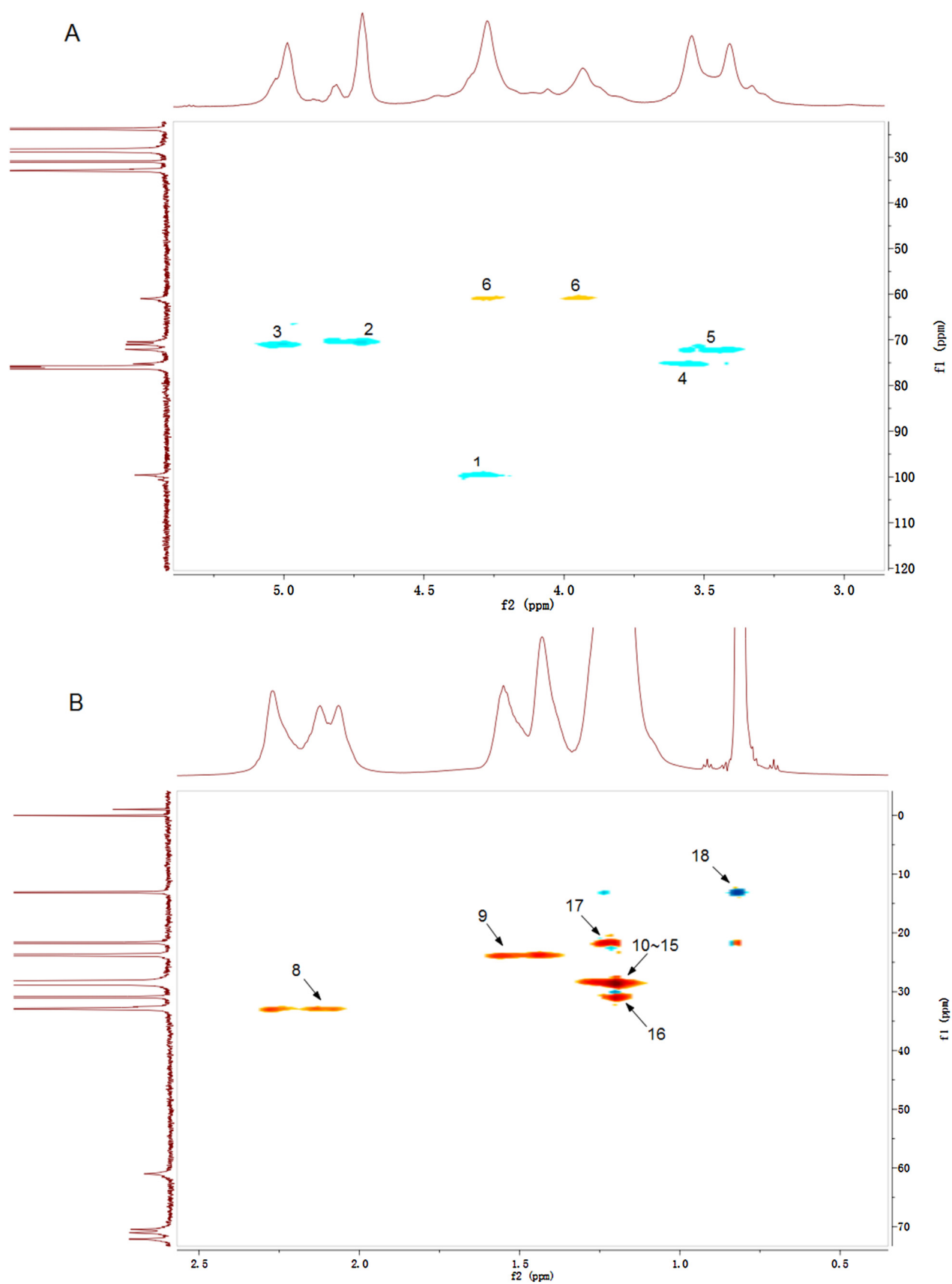


Fig. 2. Cellulose region (A) and aliphatic side chain region (B) of HSQC spectrum of cellulose laurate sample 8.

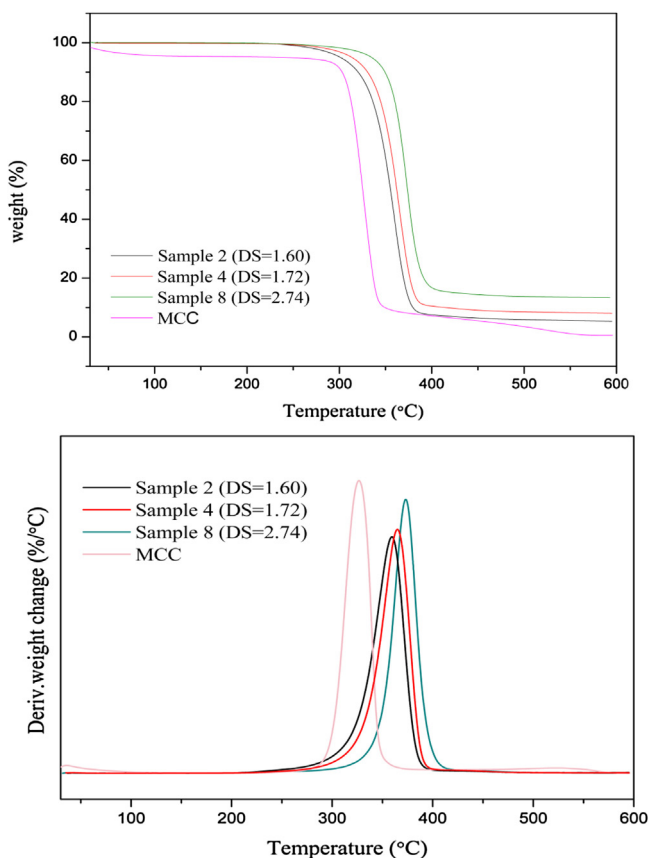


Fig. 3. TGA/DTG curves of unmodified MCC and cellulose laurate esters.

side chain region, the correlations of C_{17}/H_{17} , C_{16}/H_{16} , C_{18}/H_{18} and C_{10-15}/H_{10-15} were located at δ_H/δ_C at 1.21/21.68, 1.20/31.02, 0.82/13.11 and 1.20/28.58 ppm, respectively. The two decentralized signals at δ_H/δ_C from 2.28/33.02 to 2.13/32.91 and 1.56/23.89 to 1.44/23.75 ppm related to C_8/H_8 and C_9/H_9 , respectively.

3.4. Thermal analysis

The thermal stability of unmodified MCC and cellulose laurate samples 2 (DS=1.60), 4 (DS=1.72) and 8 (DS=2.74) was investigated by using TGA/DTG in the range of 30°C to 600°C under nitrogen atmosphere. The corresponding TGA/DTG curves are shown in Fig. 3. As can be seen from TGA curves, the weight loss was divided into three stages. The first stage with minor weight loss below 150°C of MCC was the loss of moisture in the samples. Due to the hydrophobic nature of the attached laurate group, the modified samples almost had no weight loss in this stage. The following substantial weight loss stage was due to the primary decomposition of the samples. MCC began to decompose at about 295°C, while the modified samples 2, 4 and 8 exhibited relatively high thermal stability and started to decompose at about 314°C, 322°C and 340°C, respectively. At 50% weight loss, the decomposition temperature appeared at about 325°C, 355°C, 361°C and 373°C for MCC and modified samples 2, 4 and 8, respectively, implying the increased thermal stability after transesterification. Although the major crystal structure of MCC is destroyed upon chemical modification, the introduced long-chain fatty groups on the cellulose skeleton can be in a regular arrangement and form a new ordered structure, which may be responsible for the improved thermal stability (Huang, 2012). These results were similar to the previous report (Cao et al., 2013). At the last stage, the pyrolysis residues at 600°C were 5%, 8% and 13% for samples 2, 4 and 8, respectively, while it was 0.7%

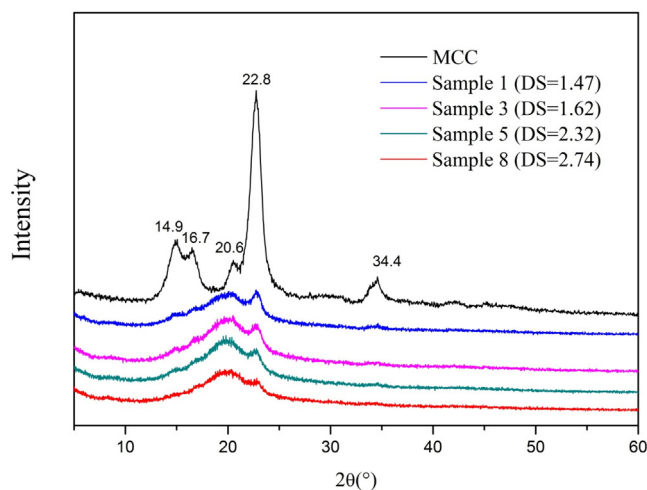


Fig. 4. XRD patterns of MCC and cellulose laurate esters.

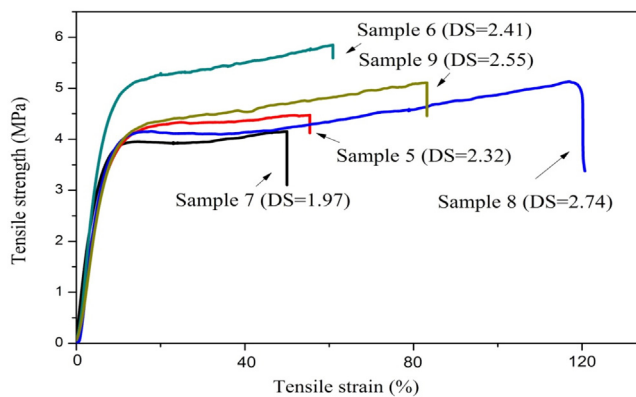


Fig. 5. Tensile strain curves of cellulose laurate ester films.

for MCC. These differences were probably due to the resistant by-product of decomposition (Fundador, Enomoto-Rogers, Takemura, & Iwata, 2012).

DTG curves could reveal the detailed decomposition rate of the samples. As can be seen from DTG curves, the primary peak for the maximum degradation rate appeared at 326°C for unmodified MCC, while it was 359°C for sample 2, 365°C for sample 4 and 373°C for sample 8, implying the increased thermal stability upon the transesterification reaction.

3.5. XRD

In order to investigate the transformation of the cellulose crystalline structure, the XRD patterns are shown in Fig. 4. As can be seen from the curves, MCC exhibits the typical cellulose I crystalline structure with the characteristic peaks at $2\theta = 14.9^\circ$, 16.7° , 20.6° , 22.8° and 34.4° for 101, $10\bar{1}$, 021, 002 and 004 diffraction planes, respectively. However, three diffraction planes including 101, $10\bar{1}$, and 004 almost disappeared in the XRD patterns of the modified samples, and the intensity of the peaks at $2\theta = 20.6^\circ$ and 22.8° became weak with the increased DS. These changes indicated that the crystalline structure of cellulose was greatly destroyed upon transesterification in AmimCl/DMSO cosolvent system. The attachment of long aliphatic side chains was also helpful to avoid the recrystallization of cellulose during regeneration.

Table 2
Mechanical properties of the films produced from cellulose laurate esters.

sample	DS	Tensile strength (Mpa)	Tensile strain at Break (%)	Young's Modulus (Mpa)
7	1.97	4.15 ± 1.01	49.99 ± 5.85	73.28 ± 12.75
5	2.32	4.47 ± 1.03	55.42 ± 3.54	59.86 ± 6.13
6	2.41	5.85 ± 0.85	60.89 ± 6.42	49.88 ± 11.70
9	2.55	5.20 ± 1.02	83.00 ± 10.44	52.14 ± 14.64
8	2.74	5.13 ± 0.56	116.00 ± 27.59	33.65 ± 9.58

3.6. Mechanical properties

It is well known that unmodified cellulose is hard to form films, while cellulose laurate with relatively high DS can easily form films by the casting/evaporation technique after being dissolved in chloroform. Tensile strength, tensile strain at break and Young's modulus are the important parameters of mechanical properties of cellulose laurate film. The tensile strain curves of the cellulose laurate films are presented in Fig. 5, and the relationship of these

parameters versus DS values is shown in Table 2. The Young's modulus decreased from 73.28 MPa to 33.65 MPa with the increased DS from 1.97 to 2.74, suggesting that the cellulose films became more ductile after the introduction of more aliphatic chains onto cellulose. The tensile strain at break increased from 49.99% to 116.00% with the increment of DS from 1.97 to 2.74. The achievement of the largest tensile strain at break 116.00% implied that the cellulose laurate films were deformable. The increase of DS from 1.97 to 2.41 resulted in an improvement of tensile strength of the films

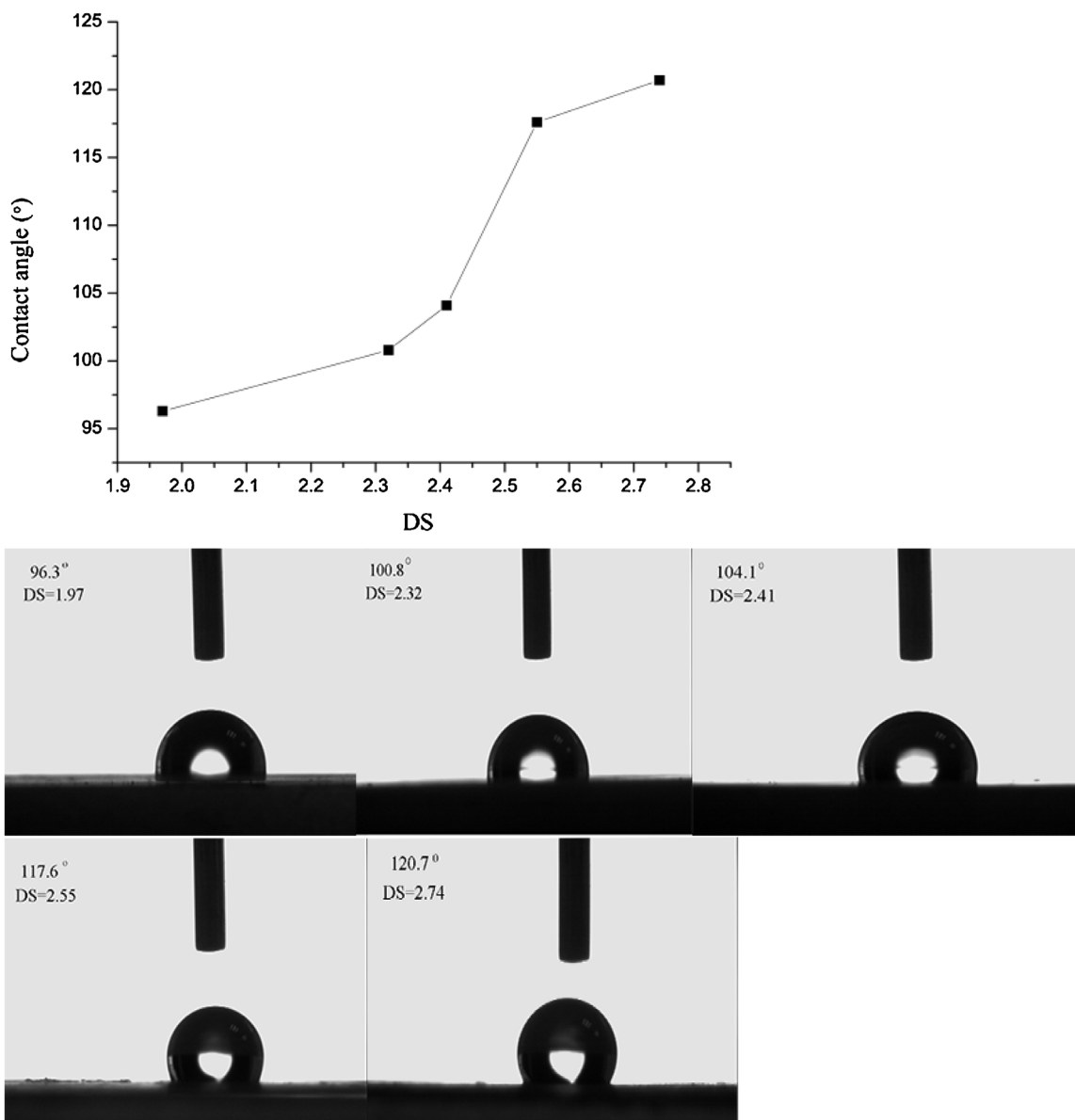


Fig. 6. The curve of water contact angle and optical image of the contact angle.

from 4.15 to 5.85 MPa, while further increase of DS to 2.74 led to a decrease in tensile strength to 5.13 MPa, indicating that tensile strength could be improved by improving DS to some extent. These results were similar with the previous report (Crépy et al., 2009).

3.7. Contact angles of cellulose laurate films

The surface polarity of the cellulose laurate films was evaluated by water contact angle measurements. As shown in Fig. 6, the cellulose laurate films showed high contact angles with water. With the increase of DS from 1.97 to 2.74, the water contact angle increased from 96.3° to 120.7°. To the best of our knowledge, the substrate can be defined as hydrophobic when the contact angle with water is higher than 90° (Crépy et al., 2009). Obviously, the films prepared from the synthesized cellulose laurate were hydrophobic. It is well known that the long aliphatic chains are hydrophobic and cellulose are hydrophilic. Therefore, the more aliphatic side chains were attached onto cellulose, the more hydrophobic the films were. In addition, the decreased content of the hydrophilic hydroxyl groups of cellulose also led to the hydrophobicity of the films.

4. Conclusion

In the present study, cellulose laurate was successfully synthesized by transesterification with vinyl laurate as acylation reagent and DBU as an effective catalyst in the AmimCl/DMSO system. The DS ranged from 1.47 to 2.74 by changing reaction time, temperature and the molar ratio of AGU to vinyl laurate. The chemical structure of the prepared cellulose laurate was investigated to confirm the occurrence of transesterification by FT-IR, ¹H NMR, ¹³C NMR, HSQC and XRD. The thermal stability of cellulose were improved after the attachment of long aliphatic side chains. The mechanical properties of the films showed the ductile behavior, and the contact angle measurements confirmed the hydrophobic characteristic of the films. Considering the ductile behavior and hydrophobicity of the cellulose laurate films, the application of these cellulose esters has great potential in green packaging.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbpol.2017.03.074>.

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