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Acetone-soluble cellulose acetates prepared by one-step homogeneous acetylation of cornhusk cellulose in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl)

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Abstract

Cellulose samples extracted from cornhusk have been successfully acetylated in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). Without using any catalyst, cornhusk cellulose acetates (CCAs) with the degree of substitution (DS) in a range from 2.16 to 2.63 were prepared in one-step. Under the homogeneous state, the DS value of CCAs was easily controlled by the acetylation time. The obtained CCAs were characterized by means of FT-IR, ^{13}C NMR, DSC, TGA, and a mechanical test. The NMR results showed that the distribution of the acetyl moiety among the three OH groups of the anhydroglucose unit shows a preference at the C_6 position. The CCAs exhibited good solubility in some organic solvents, such as acetone and DMSO. The cast CCA films from their acetone solutions had good mechanical properties. At the end of each acetylation of cornhusk cellulose, the ionic liquid AmimCl could be effectively recovered. Therefore, this study presents a promising approach and "green process" to make use of crop by-products.

Keywords: Cellulose acetates; Cornhusk; Acetylation; Ionic liquid; AmimCl

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1. Introduction

Cellulose acetate (CA) is one of the most commercially important cellulose derivatives with a wide application in the fields of coating, film, membrane separation, textile, and cigarette industries. The often-used CAs include diacetates having an average degree of substitution (DS) in the range from 2.2 to 2.7 and triacetates having an average DS above 2.8 (Heinze & Liebert, 2001). Because of its limited solubility, cellulose triacetate has not found a great number of commercial applications, while acetone-soluble cellulose diacetates are industrially more important.

Various methods have been developed for producing cellulose acetates, in which acetic anhydride and acetyl chloride are commonly used as acetylating reagents (Heinze & Liebert, 2004). Industrially, cellulose acetates are often produced by reaction of cellulose with an excess of acetic anhydride in the presence of sulfuric acid or perchloric acid as the catalysts (Hummel, 2004). Due to the heterogeneous nature of the reaction, it is impossible to synthesize partially substituted cellulose acetates directly. Therefore, acetone-soluble cellulose diacetates are obtained by hydrolyzing fully substituted cellulose acetate.

Recently, scientists show great interest in a new and promising synthesis path: homogeneous, one-pot derivatization of cellulose, which has several advantages over the heterogeneous path for the followings (Heinze & Liebert, 2001; Heinze, Liebert, Pfeiffer, & Hussain, 2003): (a) the DS of the cellulose derivative can be effectively controlled by adjusting reaction conditions, such as the reaction time, temperature and the molar ratio of derivatizing agent to cellulose; (b) the substituent groups are introduced

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regularly along the cellulose backbone; (c) the physicochemical properties of products thus obtained are much better controlled than those prepared under heterogeneous conditions. For the homogeneous cellulose derivatization reaction, suitable solvent system that can dissolve cellulose and provide a feasible reaction environment is prerequisite. Although, several direct solvents for cellulose have been developed over the past, only a few among them are suitable for chemical functionalization reactions of the cellulose. These solvents include *N*,*N*-dimethylacetamide (DMAc)/LiCl (El Seoud, Marson, Ciacco, & Frollini, 2000; Marson & El Seoud, 1999; Regiani, Frollini, Marson, Arantes, & El Seoud, 1999), dimethyl sulfoxide (DMSO)/tetrabuthlammonium fluoride trihydrate (TBAF) (Heinze et al., 2000; Hussain, Liebert, & Heinze, 2004) and some molten salt hydrate, such as $LiClO_4 * 3H_2O$, and $LiSCN * 2H_2O$ (Fischer, Leipner, Thümmler, Brendler, & Peters, 2003; Fischer, Thümmler, Pfeiffer, Liebert, & Heinze, 2002). However, the drawbacks in the case of above solvent systems are toxicity, high cost, difficulty in solvents recovery, severe side-reaction, and instability during cellulose derivatization.

More recently, room-temperature ionic liquids (ILs), being considered as green solvents, have been successfully used to dissolve and process cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002; Zhang, Wu, Zhang, & He, 2005). As a novel non-derivatizing cellulose solvent, ILs have also been found to be the promising reaction media for cellulose derivatization (Abbott, Bell, Handa, & Stoddart, 2005; Barthel & Heinze, 2006; Heinze, Schwikal, & Barthel, 2005; Wu et al., 2004). The ILs, 1-allyl-3-methylimidazolium chloride (AmimCl) (Wu et al., 2004) and 1-butyl-3-methylimidazolium chloride (BmimCl) (Barthel & Heinze, 2006; Heinze et al., 2005) have been used as reaction media for acetylation of cellulose, and cellulose acetates with various DS ranging from 1 to 3 can be obtained in one step.

On the other hand, up to now, the main source of cellulose for producing cellulose acetates is still cotton and dissolving pulp. This fact makes the raw materials expensive to obtain. In contrast, the low-cost lignocellulosic biomass has become attractive as a renewable resource because it is available in large quantities and routinely cultivated in the world. Among numerous biomass resources, agricultural wastes, woody biomass and related resources form promising feedstock for this purpose because they are underused cellulose resources. During the past several years, many attempts have been made to prepare cellulose materials and cellulose derivatives from the agricultural by-products such as sugarcane bagasse (Liu et al., 2006), wheat straw (Sun, Sun, Su, & Sun, 2004), rice straw (Lim, Son, Lee, Park, & Cho, 2001), and rice hulls (Biswas, Saha, Lawton, Shogren, & Willett, 2006).

Corn is one of the major crops in the world. In 2002, world corn production is about 640 million tons, associated with corn production is a corresponding about 45 million tons annual production of cornhusk which contain 382 g cellulose per kg of dry matter (Hang & Woodams, 2000; Reddy & Yang, 2005). The cornhusk resource constitutes an alternative to wood as a raw material for making pulp because of its high growth rate and adaptability to various soil types. Recently, Reddy and Yang (2005) have developed a fiber extraction method and obtained cellulose fibers from cornhusk with mechanical properties similar to that of the common textile fibers.

In this study, the cornhusk cellulose was used as cellulose resource and acetylated in an IL AmimCl with acetic anhydride as the acetylating reagent. The cornhusk cellulose acetates (CCAs) with the DS ranging from 2.16 to 2.63 were obtained in one-step. The structure and the properties of acetylated cornhusk cellulose, such as solubility, mechanical properties, and the thermal properties were characterized. Finally, the recycling of the ionic liquid, AmimCl was also discussed.

2. Experimental

2.1. Materials

Cornhusk was obtained from AnHui province, China. It was first dried in sunlight and then cut into small pieces (2–3 cm). Commercial cellulose acetate (DS = 2.4, $\eta_0 = 0.3$–0.5 Pa s) was obtained from Cellulose Acetate Factory, Shanghai, China. All other chemical reagents were purchased from commercial resources in China and were used as received.

2.2. Synthesis of AmimCl

The IL AmimCl was synthesized as described in our previous work (Zhang et al., 2005). 1-Methylimidazole (400 mL) and allyl chloride (800 mL) at a molar ratio 1:1.25 were added to a round-bottomed flask fitted with a reflux condenser for 8 h at 55 °C with stirring. The unreacted chemical reagents and other impurities, such as water, were removed by vacuum distillation, and the obtained product, AmimCl, is slightly amber.

2.3. Isolation of cellulose from cornhusk

The isolation of cellulose from cornhusk was carried out according to the method reported in the literature (Kerr, Windham, & Woodward, 1986). The DP of the obtained cornhusk cellulose was measured by Ubbelodhe viscometer applying cuprammonium hydroxide (Cuam) as solvent at 25 °C. The cellulose sample 20 mg (exactly weighted) was dissolved with 5 ml Cuam solution mixed with 5 ml distilled water under magnetic stir for 1 h at room temperature.

2.4. Dissolution of cornhusk cellulose in AmimCl

The obtained cornhusk cellulose sample were cut into small and thin pieces and dried at 70 °C for 3 h in a vacuum oven before use. In a typical dissolution procedure, 0.6 g cornhusk cellulose was dispersed into 14.4 g AmimCl, and the mixture was stirred at 80 °C for 4 h to guarantee the complete dissolution. Finally, a clear cellulose solution with about 4 wt% of polymer concentration was obtained.

2.5. Regeneration of cellulose

The cornhusk cellulose solution was precipitated in a 5-fold amount of distilled water. The resulting mixture was separated by filtration. The solid was washed 3× with distilled water until the IL is free. Finally, the regenerated cornhusk cellulose was dried in the vacuum oven at 60 °C for about 24 h.

2.6. Acetylation of cornhusk cellulose in AmimCl and recycling of the IL

In a typical acetylation procedure, 1.75 ml acetic anhydride (5 mol/mol AGU) was carefully added to a cornhusk cellulose solution (0.6 g cellulose in 14.4 g AmimCl) and the solution was stirred for 2 h at 100 °C. Then the product was precipitated in a 5-fold amount of distilled water and the resulting mixture was separated by filtration. The solid was washed 3× with distilled water until the IL is free, and then collected the solid and drying it in the vacuum oven at 60 °C for about 24 h. At the end of each experiment, the IL AmimCl was recycled by evaporating the filtrate and its purity was determined by ^{1}H NMR spectroscopy.

2.7. FTIR

The cornhusk cellulose and CCAs were ground into powder, and vacuum dried for 24 h. The IR spectra of the samples were recorded with a Fourier transform IR spectrometer (FTIR PE-2000, United States). The test specimens were prepared by the KBr-disk method.

2.8. NMR

The DS of the cellulose acetates was determined by ^{1}H NMR spectroscopy (Bruker AV-400 or DMX-300 spectrometer, at room temperature) after adding a drop of trifluoroacetic acid-d whose function is to shift active hydrogen to low field area, and the DS of the acetate cellulose was calculated according to Goodlertt et al. by equation Goodlett, Dougherty, and Patton (1971):

$$\mathrm{DS} = \frac{7 \times I_{\mathrm{acetyl}}}{3 \times I_{H,\mathrm{AGU}}}$$

Where, I_{acetyl} is the integral of methyl protons of acetyl moieties, I_{AGU} is the integral of all protons of anhydroglucose unit.

The distribution of the acetyl moiety among the three OH groups of the AGU of cellulose acetate was calculated by integrating the spectrum of a solution of cellulose ester in DMSO-d_6 from the ^{13}C NMR spectra (Bruker DMX-300 spectrometer, experiment temperature 100 °C).

2.9. Thermal analysis

The differential scanning calorimetry (DSC) analysis of the cornhusk cellulose, commercial CA and CCAs was recorded on a PE DSC-7. In order to provide the same thermal history, each sample was heated from 50 to 250 °C at 20 °C/min and all the T_g's reported are observed in the second scan. The thermogravimetric analysis (TGA) was performed on a PE TGA-7 from 50 to 600 °C for all the samples, keeping a constant heating rate at 20 °C/min. Both DSC and TGA measurements were carried out under a nitrogen flow.

2.10. Mechanical testing

Each acetylated product including commercial CA was converted into plastic film. The CAs were dissolved in about 30 ml acetone; then the solvent was allowed to evaporate in air at room temperature. The average Young's modulus (E), tensile strength (σ_b) and breaking elongation (ε_b) of the CA films were measured on a universal testing machine (Instron 3365, UK) at a speed of 5 mm min^{-1}. The size of the samples was 70 mm in length and 3–5 mm in width, and 40 mm was the distance between the two clamps. For each plastic, at least five samples were tested and the results for each plastic film are the average of these sample characteristics. All the strength data was collected under the same conditions, such as temperature and air humidity.

3. Results and discussion

3.1. Dissolution of cornhusk cellulose in AmimCl

According to the method reported in the literature (Kerr et al., 1986), the cornhusk cellulose was obtained from corresponding cornhusk by successive removing most of lignin and hemicellulose. The content of α-cellulose is measured by soaking the cellulose in 17.5% NaOH aqueous solution for 45 min at 20 ± 0.1 °C (Liu, 2004). This process can dissolve non-cellulose carbohydrate and leave about 94.1 wt % of α-cellulose. The DP value of the cellulose sample obtained is 530.

In our previous studies, it is shown that the commercially available cellulose samples, such as microcrystalline cellulose, wood pulp, and cotton linters, with the DP in the range from 200 to 1600 can be readily dissolved in the AmimCl. For example, dissolving wood pulp with a DS of 650 could be dissolved in the AmimCl within 30 min at 80 °C without any pretreatment. In the present study, it has been found that the conditions suitable for dissolution of the dissolving pulp or microcrystalline cellulose materials in AmimCl did not yield optically clear solutions for cornhusk cellulose. This might be due to the residual non-cellulose components, such as lignin or ash in the extracted cornhusk cellulose. Both prolongation of the dissolution time and improvement dissolution temperature have been found to be effective for increasing cornhusk cellulose dissolution rate in AmimCl. In a typical procedure of cornhusk cellulose/AmimCl solution, 0.6 g cornhusk cellulose sample was dispersed into 14.4 g AmimCl, and the mixture was stirred at 80 °C for 4 h, a transparent cornhusk cellulose solution with about 4 wt% polymer concentration was obtained. Noteworthy in this regard is the dissolution of cellulose in AmimCl does not need any pretreatment or activation, unlike other cellulose solvent systems such as DMAc/LiCl (McCormick, Callais, & Hutchinson, 1985) and NaOH/H_2O (Isogai, 1998; Zhang, Ruan, & Zhou, 2001), in which the pretreatment or activation for original cellulose is commonly required.

3.2. Effects of reaction time on DS of CCAs

The effect of reaction time on the degree of acetylation was investigated at the reaction temperature of 100 °C and the acetic anhydride/anhydroglucose unit (AGU) mole ratio of 5. The DS values of resultant CCAs were determined by ^{1}H NMR, and the results are shown in Fig. 1. It can be seen that the DS first increased significantly with reaction time, and this increment became slightly after about 3 h. For example, using acetic anhydride as the acetylating reagent, a CCA with a DS of 2.16 (CCA-1) was obtained within only 1 h and after 3 h of reaction time, the DS of CCA could reach to 2.5 (CCA-3), but with further increasing reaction time to 8 h, the DS increased slightly to 2.63 (CCA-8). It should be noticed that, increase of both reaction temperature and molar ratio of acetic anhydride to AGU can result in an increment in DS values of CCAs, which is similar with our previous studies (Wu et al., 2004). These experimental results are not shown here.

3.3. FTIR Spectra

FTIR spectra of the cornhusk cellulose (spectrum a), the regenerated cornhusk cellulose (spectrum b), and the acetylated cornhusk cellulose sample from AmimCl (spectrum c) are shown in Fig. 2. It can be seen that the spectrum a and b are quite similar and no new peaks appear in the regenerated sample, indicating no chemical reaction occurred during the cellulose dissolution and regeneration processes. In other words, AmimCl is a non-derivatizing solvent for cellulose. The spectrum c provides an evidence of acetylation by showing the presence of three important ester bonds at 1752 cm^{-1} (C=O ester), 1375 cm^{-1} (C–H bond in an –O(C=O)–CH_3 group), and 1235 cm^{-1} (–CO-stretching of acetyl group). In addition, decreased peak intensity at 3411 cm^{-1} in spectrum c compared to spectrum a and b, which originates from OH stretching in acetylated cellulose sample, also indicated a partial acetylation.

3.4. NMR spectra

It is well known that the distribution of acetyl moieties among the three OH groups of the AGU has a significant influence on the dissolution behavior of CA. We studied the distribution of acetyl moiety among the three OH groups of the AGU. Fig. 3 shows a ^{13}C NMR spectrum of sample CCA-1 with a DS value of 2.16 in which the signal at 170.5 ppm was attributed to the carbonyl carbon at C_6, 169.6 ppm to that at C_3, and 169.3 ppm to that at C_2. The partial DS value of the acetyl moiety among the three OH groups was calculated from the integration of the ^{13}C NMR spectra, and the results are presented in Fig. 4. It can be seen that, the three hydroxyl groups at C_2, C_3, and C_6 positions exhibit different reaction activities, the order of reactivity is C_6-OH > C_2-OH > C_3-OH for CCA-8, which is similar to that observed in most homogeneous cellulose

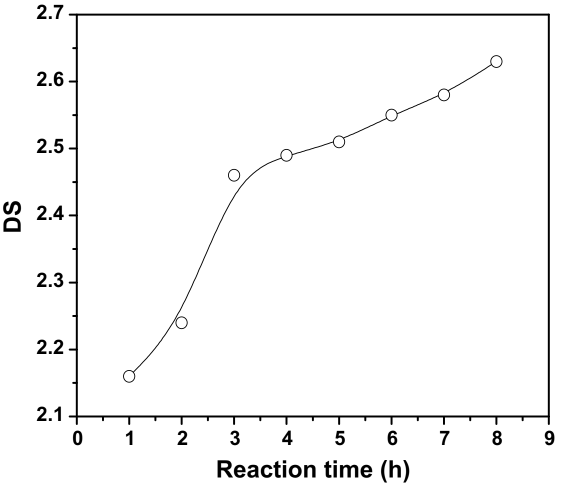

Fig. 1. Reaction time dependence of the DS for CCAs.

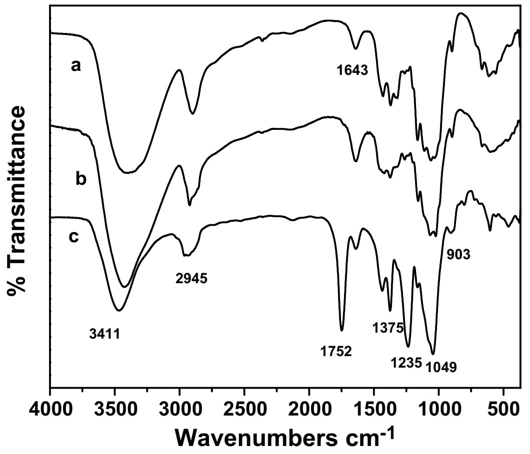

Fig. 2. FTIR spectra of the original cornhusk cellulose (spectrum a), the regenerated cornhusk cellulose (spectrum b), and the CCA-1 with a DS = 2.16 (spectrum c).

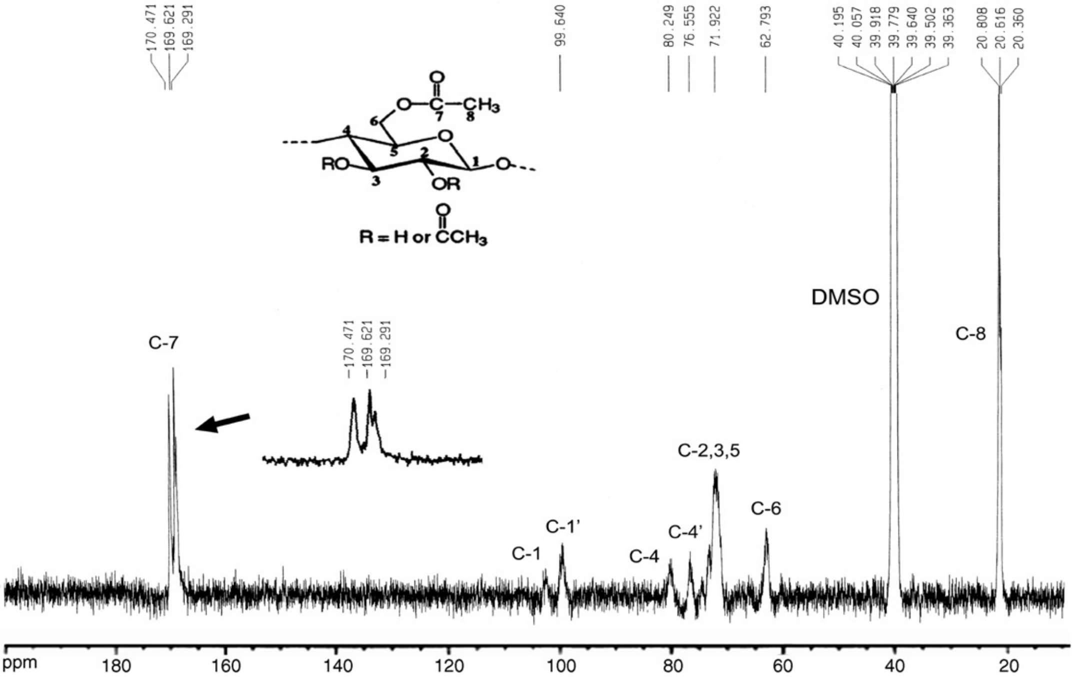

Fig. 3. ^{13}C NMR spectrum of CCA-1 (DS = 2.16).

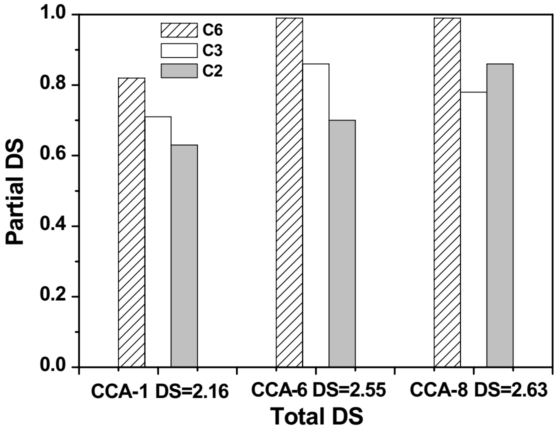

Fig. 4. Distribution of acetyl moiety among the three OH groups of the AGU in CCAs.

acetylation system, such as DMAc/LiCl (Marson & El Seoud, 1999) and 1,3-dimethyl-2-imidazolidinone (DMI)/LiCl (Takaragi, Minoda, Miyamoto, Liu, & Zhang, 1999). While for CCA-1 and CCA-6 the order is C_6-OH > C_3-OH > C_2-OH, which is the same with our previous study (Wu et al., 2004), and this distribution order has also ever been reported in the solvent system DMAc/LiCl (El Seoud et al., 2000; Regiani et al., 1999). However, up to now, no simple explanation can be advanced for the difference in reactivity between C_3-OH and C_2-OH. It is no doubt that, for all the samples, the acetylation of the solvated C_6-OH position is expected to be favored because this hydroxyl group is the least sterically hindered one of the AGU. For example, samples with high DS, such as CCA-6 and CCA-8, whose total DS is 2.55 and 2.63, respectively, their partial DS on C_6-OH position is 0.99 which is considered to be almost completely substituted. It should be noticed that the distribution of acetyl moieties among the three OH groups in the AGU is quite different from CA samples industrially synthesized through heterogeneous acetylation-hydrolysis process, whose partial DS order is C_3-OH > C_2-OH > C_6-OH (Buchanan, Edgar, & Wilson, 1991). The difference in functionalization patterns is considered to be the major reason of the difference in solubility for CA samples synthesized from different paths.

3.5. Solubility

The acetyl groups are more hydrophobic than hydroxyl groups; therefore, replacing some of the hydroxyl groups in cellulose with acetyl groups might significantly alter its solubility properties in organic solvents. In other words, both the DS values and the distribution of acetyl groups of CA have great influence on its solubility. It is well known that the CA samples with the DS > 2.8 (CTA) are only soluble in chloroform, while the CA samples with the DS in the range from 2.2 to 2.7 (CDA) are soluble in acetone. In present work, the solubility of CCAs in chloroform, DMSO, and acetone was investigated and the experimental results are summarized in Table 1. We found that all synthesized CCA samples with DS from 2.16 to 2.63 exhibited good solubility in DMSO and acetone at ambient temperature (25 °C). In the case of chloroform used as the solvent, samples with a DS of 2.49 dissolved slowly. When the DS is above 2.49, the samples readily dissolved in chloroform at ambient temperature.

Table 1
DS and solubility of CCAs homogeneously prepared in AmimCl

Code	DS	Solubility[a]		
		Acetone	$CHCl_3$	DMSO
CCA-1	2.16	+	−	+
CCA-2	2.24	+	−	+
CCA-3	2.46	+	−	+
CCA-4	2.49	+	+	+
CCA-5	2.51	+	+	+
CCA-6	2.55	+	+	+
CCA-7	2.58	+	+	+
CCA-8	2.63	+	+	+

[a] +, stands for soluble and −, stands for insoluble.

Table 2
Mechanical properties of CA films

Code	DS	Tensile strength σ (MPa)	Elongation at break ε (%)	Elastic modulus E (GPa)
CCA-01	2.16	31.1	5	1.69
CCA-03	2.46	38.2	4	1.20
CCA-04	2.49	43.1	9	1.84
CCA-06	2.55	31.9	5	1.77
CCA-08	2.63	44.4	10	1.66
Commercial CA	2.44	50.7	3	2.67

3.6. Mechanical properties

The mechanical properties of CCA films were measured. A commercial available CA with DS 2.44 was also tested for the sake of comparison. The typical stress–strain curves of CA films are shown in Fig. 5, and the average Young's modulus E (GPa), tensile strength σ_f (MPa), and failure strain ε_f (%) of the CA films are summarized in Table 2.

From Fig. 5, it can be seen that no yield point existed in the tensile process for all CA films, indicating the brittle feature of these acetylated cornhusk cellulose. The flexibility of cellulose acetates could be improved by incorporation of some additives, such as plasticizers (Zhang, Ruan, & Gao, 2002).

From Table 2, it can be seen the tensile strength and elastic tensile modulus of the CCA films were in the range from 30 to 45 MPa and from 1 to 2 GPa, respectively. It should be noted that the tensile strength of the CCA films is slightly lower than that of commercial cellulose diacetate films prepared from high grade cellulose resources, such as pulp and cotton. However, it is expected that the cellulose acetate films with better mechanical properties might be obtained under optimized conditions including acetylation and film manufacturing conditions. Even then, the mechanical properties of the present CCA films are slightly higher than those largely used commercial polyolefins, such as polyethylene (PE) and polypropylene (PP), whose tensile strength is usually in a range of 20–40 MPa (Ding, 1995). Therefore, it suggested the potential use of CCA films in some areas, such as packaging and agricultural field (covers), in which currently used is predominately PP and PE. Based on the fact that both PE and PP are non-biodegradable polymers produced from petroleum-based resource, replacement of polyolefin by acetylated cornhusk have a significant benefit to resource conservation, environment, and agriculture.

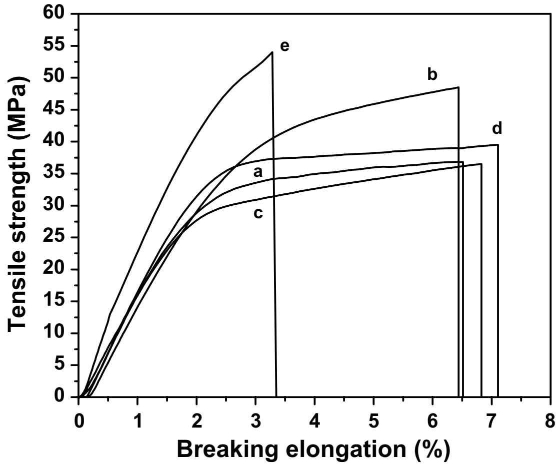

Fig. 5. The stress–strain curves of the CA films for CCA-1 (spectrum a), CCA-4 (spectrum b), CCA-6 (spectrum c), CCA-8 (spectrum d), and commercial CA (spectrum e).

3.7. Thermal analysis

The thermal properties of neat cornhusk cellulose, the commercial CA, and acetylated cornhusk cellulose of samples CCA-3 with a DS of 2.46 and CCA-8 with a DS of 2.63 were characterized by DSC and TGA measurements in an N_2 atmosphere. DSC curves of the neat cornhusk cellulose, commercial CA, and CCAs (CCA-3 and CCA-8) are shown in Fig. 6. In conventional DSC, a reversing event like the glass transition may be hidden by a nonreversing event, such as enthalpic relaxation, so the neat cornhusk cellulose did not show the glass transition temperature (T_g) at standard heating scan (curve a). However, using a more sensitive method, Batzer and Kreibich (1981) reported a T_g of ~230 °C for dry cellulose. From Fig. 6, it can be seen the CCA samples exhibited very clear glass

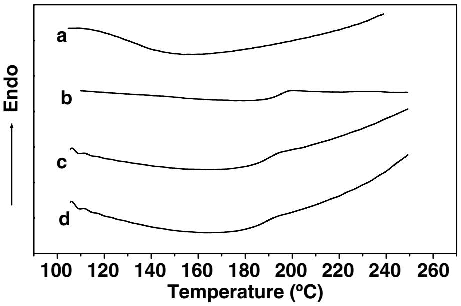

Fig. 6. DSC curves of the neat cornhusk cellulose (curve a), commercial CDA (curve b), CCA-3 (curve c), and CCA-8 (curve d).

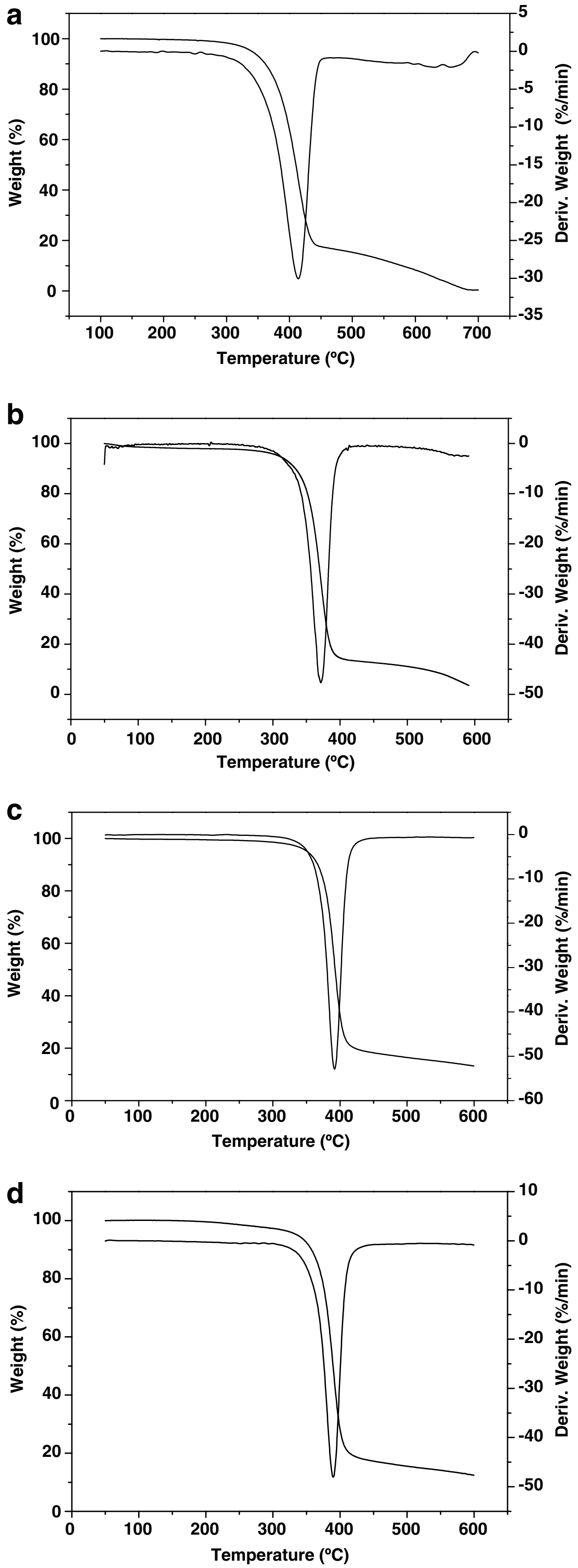

Fig. 7. TG and DTG curves of cornhusk cellulose (spectrum a), commercial available CA (spectrum b), CCA-3 (spectrum c), and CCA-8 (spectrum d) at heating rate 20 °C/min.

transition (196 °C for CCA-3 and 190 °C for CCA-8), which is similar to the commercial CA (198 °C). The T_g of the acetylated cellulose decreased with an increase of DS, which is accordance with the literature (Glasser, Samaranayake, Dumay, & Dave, 1995) and can be explained by the fact that the higher DS leading to less hydrogen bonding and a lower T_g.

Fig. 7 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of neat cornhusk cellulose (Fig. 7(a)), commercial CA (Fig. 7(b)), CCA-3 (Fig. 7(c)), and CCA-8 (Fig. 7(d)) at heating rate 20 °C/min. From these thermograms, it can be seen that the cornhusk cellulose sample starts to decompose at 377.3 °C, the commercial CA starts to decompose at 349.5 °C, whereas the two acetylated cornhusk cellulose samples, CCA-3 and CCA-8, start to decompose at 374.1 and 372.7 °C, respectively. The maximum decomposition temperature of cornhusk cellulose is 413.4 °C, commercial CA is 371.4 °C, and CCA-3 and CCA-8, are 391.7 and 388.6 °C, respectively. This indicates the thermal stability of cornhusk cellulose is slightly decreased due to the acetylation.

3.8. Recycling of the IL AmimCl

From the viewpoint of environmental conservation and economics of the process, after the acetylation of cellulose, effective recycling of the solvent ionic liquids is absolutely required. In our study, at the end of each acetylation of cellulose, the CCA was precipitated with a large excess of water. The polymer was filtered off, and the residual ILs in the filtrate was recovered by a simple evaporation, giving a clean sample of AmimCl. The purity of the recovered AmimCl was above 99%, confirmed by ^{1}H NMR spectroscopy. When the refreshed AmimCl was used as the acetylation media, the CCA with a similar DS was obtained under comparable reaction conditions. However, for the future industrial applications on a large scale, it has been suggested other methods for removal of water may prove to be more practical (Wong, Pink, Ferreira, & Livingston, 2006; Swatloski, Rogers, &Holbrey,Holb). These alternative methods include nanofiltration, reverse osmosis, pervaporation, and salting out of the ionic liquid. Apparently, the advantage of easy recycling of ionic liquids will promote their industrial application in this field.

4. Conclusions

In this work, the cornhusk cellulose was studied as a cellulose resource for homogeneous acetylation in an ionic liquid AmimCl. It has demonstrated that the cornhusk cellulose samples were successfully acetylated with acetic anhydride in the absence of any catalyst. The DS of acetylated products increased with reaction time. The cornhusk cellulose acetates (CCAs) with the DS values in the range from 2.16 to 2.63 can be obtained by controlling the reaction time under a completely homogeneous acetylation. The resultant CCAs were readily dissolved in some organic solvents, such as acetone and DMSO. The CCAs films prepared from their solutions of acetone exhibited good mechanical properties. Based on the fact that the IL AmimCl can be effectively recycled after each acetylation, this study provides a technically feasible and environmentally acceptable method to prepare acetone soluble cellulose diacetates in one step using relatively cheap cornhusk as cellulose resources.

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