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Homogeneous synthesis of cellulose stearates with different degrees of substitution in ionic liquid 1-butyl-3-methylimidazolium chloride

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ABSTRACT

Cellulose stearates with different degrees of substitution (DS) were prepared homogeneously in ionic liquid 1-butyl-3-methylimidazolium chloride ($[C_4mim]^+Cl^-$) solution. Cellulose stearates with DS values of 2.15, 2.19 and 2.57 exhibited good solubility in nonpolar organic solvents. It was indicated by differential scanning calorimetry (DSC) that the melting temperatures of the three cellulose stearates ranged from 38.66 to 56.63 °C. Thermogravimetric (TG) analysis showed that the commencing degradation temperature of the three cellulose stearates were 300 °C, 325 °C and 370 °C, respectively. The cellulose stearate with the DS value of 2.57 has better thermal stability than cellulose.

1. Introduction

Cellulose is the most abundant natural polymer. It is of major commercial and scientific importance with a variety of natural and modified celluloses used industrially. With a view to the changing its solubility and thermoplastic properties, the production of cellulose fatty acid esters is one of the most interesting aspects of its chemical modification.

The chemistry and technology of single and mixed fatty acid esters (acetate, propionate, butyrate, etc.) are well known and have been given much attention in the technical, trade, and patent literature for decades (Heinze & Liebert, 2001). Thermal plastic cellulose long chain fatty acid esters can be dissolved in many organic solvents and identified as potential biodegradable plastics (Wang & Tao, 1995) and nontoxic plasticizer (Coleman & Painter, 1985). When cellulose long chain fatty acid esters are used in polymer composites as a compatibilization agent, not only chemical but also morphological changes, surface energetics, or thermal properties significantly affect their overall behavior in a polymer matrix. Saturated palmic acid ester of cellulose and unsaturated soybean oil fatty acid ester of cellulose have been previously prepared and characterized by heterogeneous reaction (Malm, Mench, Kendall, & Hiatt, 1951; Wang & Tao, 1994). Due to the heterogeneous nature of the reaction, these esters of cellulose have low degree of substitution (DS).

In the previous literatures, solvent systems such as N,N-dimethylacetamide (DMAc) and lithium chloride (LiCl) were reported as cellulose solvents for homogeneous synthesis of cellulose long chain fatty acid esters (Seoud, Marson, Ciacco, & Frollini, 2000). Edgar, Pecorini, and Glasser (1998) described the simple method of reaction of acid chlorides with cellulose in this solvent system, using an acid scavenger such as pyridine. Sealey, Samaranayake, Todd, and Glasser (1996) reported acylation with long chain acids themselves, utilizing in situ conversion to the mixed anhydride with tosyl chloride. Because the derivatization is homogeneous, typically cellulose long chain fatty acid esters of high DS are directly accessible. However, the DMAc/LiCl method is of limited practicality because of the difficulty of recycling the expensive lithium salt. When acid chlorides are used as acylating agents, an acid scavenger must be added to neutralize the hydrogen chloride since the DMAc/LiCl is a neutral system. Very recently, various ionic liquids (IL), so-called green solvents were found to dissolve cellulose as well. Swatloski, Spear, Holbrey, and Rogers (2002) studied various ionic liquids including 1-butyl-3-methylimidazolium chloride ($[C_4mim]^+Cl^-$) with different anions. A conclusion of these studies was that the chloride ion, as a small hydrogen bond acceptor, seemed to be most appropriate for cellulose dissolution. Heinze et al. used $[C_4mim]^+Cl^-$ as reaction medium in the homogeneous preparation of cellulose acetate and high DS (3.0) cellulose acetate was obtained. $[C_4mim]^+Cl^-$ is a ter-

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tiary amine, most of hydrogen chloride formed in the reaction can be neutralized by $[C_4mim]^+Cl^-$, then $[C_4mim]^+Cl^-$ could be washed with water and recycled easily (Heinze, Schwikal, & Barthel, 2005). Based on Swatloski's research, Cao et al. (2007) reported that a series of acetone-soluble cellulose acetates were prepared by one-step homogeneous acetylation of cornhusk cellulose in another novel ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl). But so far no reference about cellulose long chain fatty acid esters prepared in ionic liquids has been reported and lack of the thermal properties of these long chain cellulose esters with different degrees of substitution.

In this work, synthesis and characterization of cellulose stearates with various high DS in the ionic liquid 1-butyl-3-methylimidazolium chloride ($[C_4mim]^+Cl^-$) were reported, and the thermal properties of cellulose stearates with different DS were also carefully studied. Because of the application of cellulose esters in the polyethylene matrix or other polymers in the melt processing usually at a high compounding temperature, it is of utilization and importance to elucidate thermal properties with respect to the different DS.

2. Experimental

2.1. Materials

Microcrystal cellulose (MCC) with a degree of polymerization (DP) of 106 used were purchased from Shanghai Hengxin Chemical Company (China) and dried in vacuum at 80 °C for 12 h. The ionic liquid 1-butyl-3-methylimidazolium chloride ($[C_4mim]^+Cl^-$), melting point: 73 °C (Merck) was used as received. Stearyl chloride was purchased from Aladdin Reagent Company (China) and used as received. Dimethyl sulphoxide, chloroform, toluene, acetone and hexane were all analytical grade reagents purchased from Nanjing Chemical Reagent Company (China).

2.2. Synthesis of cellulose stearate in $[C_4mim]^+Cl^-$

A solution of 1 g (6.17 mmol) MCC in 9 g $[C_4mim]^+Cl^-$ was prepared according to reference Swatloski et al. (2002) and kept at 90 °C. To this solution stearyl chloride 9.055 g (30.85 mmol) was carefully added. The temperature was kept at 90 °C for 1 h. Isolation was carried out by precipitation into 200 ml methanol, washing with methanol in Saxhlet extraction device for 12 h and drying under vacuum at 40 °C for 6 h.

Yield : 5.17 g (80.0%)

DS = 2.57 (determined by means of ^1H NMR spectroscopy). The weight–average molar mass (M_w) of the products were determined by a Waters 1515 gel chromatography (Waters Company). Samples were dissolved and filtrated in tetrahydrofuran which was used as mobile phase. The solubility of the products were tested in the room temperature (25 °C): 1 g product and 20 g solvent was added into a test tube, then an ultrasonic wave equipment (KQ5200B ultrasonic cleanser) was used to assist solubilization.

2.3. NMR

The DS was determined by ^1H NMR spectroscopy (Bruker AV-300 spectrometer) in $CDCl_3$ and was referenced to TMS as an internal standard at 25 °C. The DS of the cellulose stearate was calculated according to equation (Lowman, 1998) as follows:

$$DS = \frac{10 \times I_{CH_3}/3}{I_{AGU} + I_{CH_3}/3}$$

where I_{CH_3} is the integral of methyl protons of the methyl of substituted part and I_{AGU} is the integral of all protons of anhydroglucose unit (AGU).

The specimens of cellulose stearates were analyzed by nuclear magnetic resonance spectroscopy in $CDCl_3$ from the ^{13}C NMR (Bruker AV-300 spectrometer) at 25 °C.

2.4. Thermal analysis

Differential scanning calorimetry (DSC) experiments were run on a Perkin-Elmer Diamond DSC calorimeter to analyze the data. In order to provide the same thermal history, about 6 mg sample was placed in the aluminum pan and then covered by an aluminum lid prior, then heated from −40 to 200 °C at 20 °C/min and fast annealed to −40 °C at 120 °C/min in a nitrogen atmosphere. The DSC data of the first and the second scan were all collected.

Thermogravimetric analysis was conducted using a Netzsch 409PC thermogravimetric analyzer (Netzsch Company). About 10 mg sample was used without predrying. The analysis was carried out in air atmosphere, with a temperature rise rate of 20 °C/min from 60 to 550 °C.

3. Results and discussion

3.1. Synthesis of cellulose stearates

In this acylation reaction, no base as an acid scavenger was added. As the ionic liquid itself was a tertiary amine, the HCl formed in the synthesis of cellulose stearates was fixed by $[C_4mim]^+Cl^-$. In comparison, the insert of $[C_4mim]^+Cl^-$ as reaction media is more efficient than the application of DMAc/LiCl (Heinze et al., 2005). After the cellulose dissolved in ionic liquid $[C_4mim]^+Cl^-$, the solution was very viscous at a low temperature. Since there was no other solvent, we had to rise the reaction temperature so as to lower the viscosity of the solution and facilitate the mix process of the reagents. But after the reaction temperature exceeded 90 °C, the color of the final product became darker. So we set the optimized reaction temperature at 90 °C.

When the reaction time was 1 h and the reaction temperature was 90 °C, to evaluate the effect of the stearyl chloride quantity on DS variation, we studied various stearyl chloride equivalents to per 1 mol AGU. We added to the MCC solution 3–7 mol stearyl chloride per 1 mol AGU. When the reaction time was 1 h and the reaction temperature was 90 °C, it is found that DS rose dramatically from 2.19 to 2.57 when the stearyl chloride varied from 4 to 5 mol. After the stearyl chloride amount rose to 5 mol, The DS was not greatly influenced by stearyl chloride amounts (Fig. 1).

To determine the proper reaction time, 9.055 g (0.03 mol) stearyl chloride was added to 1 g MCC (0.006 mol AGU), different reaction times lead to different yield and DS. When the reaction time was set as 0.5 h, acylation between MCC and stearyl chloride had not accomplished yet. This led to a certain amount of cellulose stearate with low DS which was soluble in methanol and did not lead to solid material, so the yield of the solid cellulose stearate decreased. As the reaction time increased to 1 h, the yield of the cellulose stearate reached the max value 80%. But increasing reaction time did not resulted in an obvious DS increase of the cellulose stearate. When the reaction time increased to 1.5 h, there was no marked change in DS, but there was a little decrease in yield and M_w due to macromolecular degradation of the cellulose in the long time reaction process. After the reaction time reached 2 h, this phenomenon became more remarkable. Actually, this method without any base added to neutralize the HCl produced from the acylation, the degradation of the cellulose is obvious. As the DP of the MCC was 106, the M_w of the product was 31,956 g/mol which is only about 30%

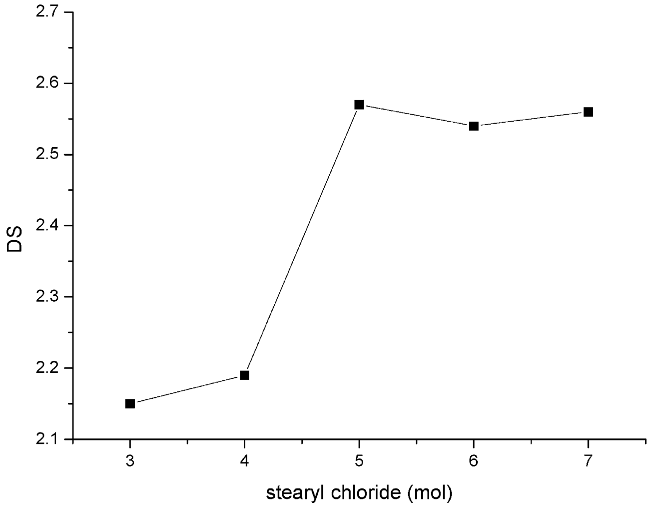

Fig. 1. DS variation in function of stearyl chloride quantity (as mole per 1 mol AGU).

of the theoretical value. However, it will cause trouble for recycle of the ionic liquid to add a base. So, to make the acylation reaction completed, a reaction time of 1 h was appropriate. According to the most appropriate reaction conditions studied above, three kinds of cellulose stearates with different DS were prepared and characterized.

3.2. NMR analysis

The DS of these cellulose stearates were calculated by the integral of the methyl of substituted part and the protons of AGU. The DS values of three cellulose stearates were 2.15, 2.19 and 2.57, respectively.

^{13}C NMR spectra of these cellulose stearates were presented in Fig. 2. The peaks at 14.2 ppm are attributed to C24 of the methyl groups. C8 carbon atoms are indicated by the peaks from 33.5 to 34 ppm. The peaks between 22 ppm and 30 ppm include the signals of C9–23. The detailed ^{13}C NMR of cellulose backbone was displayed in Fig. 3. C1 and C1′ are due to C1 carbon adjacent to C2 carbon bearing unsubstituted and substituted hydroxyl groups, and C4 and C4′ can be affected by C3 carbon in the same manner. C4′ signals are overlied with the signal of $CDCl_3$. The signals of AGU in cellulose stearate at 101.7 (C1), 100.6 (C1′), 76.2 (C4), 77.2 (C4′) 73.1 (C5), 72.1 (C3), 71.5 (C2) and 62.0 ppm (C6) were found. This result is similar to the assignment of cellulose carbon peaks well documented in the literature (Newman, Ha, & Melton, 1994). The resonance of carbonyl groups in cellulose stearate are upfield-shifted by oxygen atom and appears at 171.8–173.2 ppm, suggesting that the esterification reaction took place. Fig. 4 shows the signal at 173.2 ppm was attributed to the carbonyl carbon at C6, 172.4 ppm to that at C3 and 171.8 ppm to that at C2. According to the integration of the carbonyl carbon shown in Fig. 4, we found the order of position reactivity is C6–OH > C3–OH > C2–OH. This result was similar with the previous study (Wu et al., 2004), and this distribution order has also ever been reported in the sol-

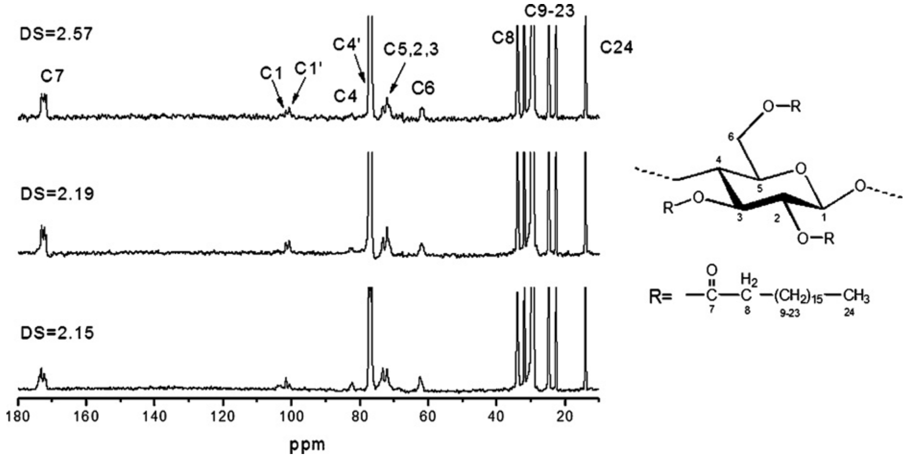

Fig. 2. ^{13}C NMR spectrum of cellulose stearates.

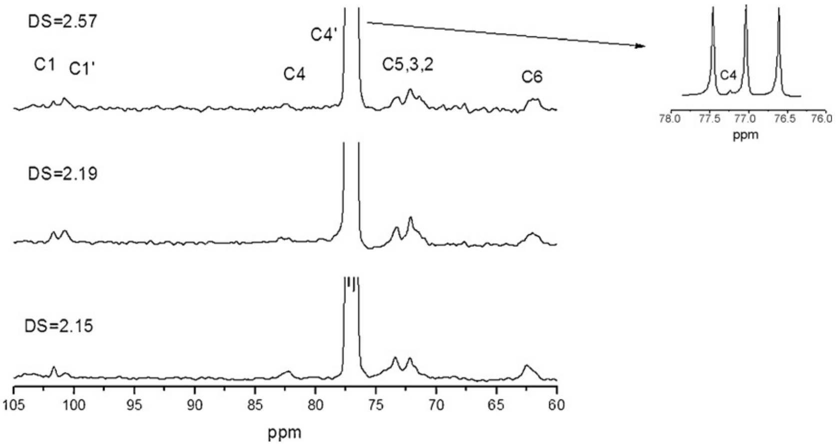

Fig. 3. Detailed ^{13}C NMR spectrum of AGU in cellulose stearates.

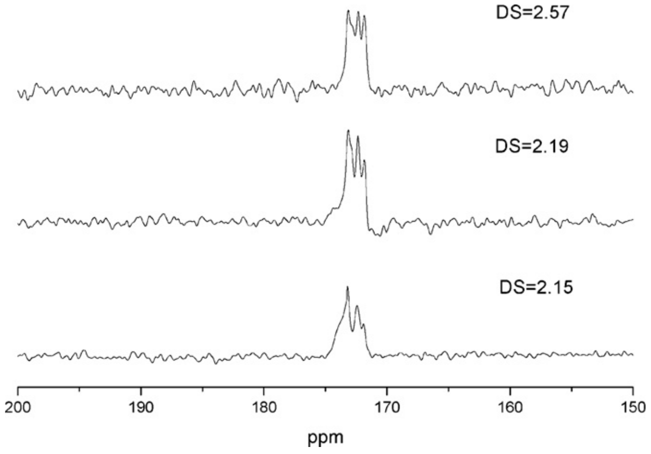

Fig. 4. Detailed ^{13}C NMR spectrum of carbonyl carbons in cellulose stearates.

vent system DMAc/LiCl (Regiani, Frollini, Marson, Arantes, & Seoud, 1999; Seoud et al., 2000). However, up to now, no simple explanation can be advanced for the difference in reactivity between C3–OH and C2–OH. It is no doubt that, for all the samples, the acetylation of the solvated C6–OH position is expected to be favored because this hydroxyl group is the least sterically hindered one of the AGU.

3.3. Solubility

The crystallinity and hydrophilicity of MCC were changed by the stearyl chloride. The stearyl groups are hydrophobic and they can give cellulose good solubility in nonpolar organic solvents. The solubility of cellulose stearates in toluene, chloroform, dimethyl sulphoxide (DMSO), acetone and hexane was investigated. We found that all cellulose stearates with DS values of 2.15, 2.19 and 2.57 exhibited good solubility in toluene, hexane and chloroform at room temperature (25 °C). In term of dimethyl sulphoxide (DMSO) and acetone used as the solvents, all the cellulose stearates were insoluble.

3.4. X-ray diffraction

Diffraction patterns obtained from MCC and cellulose stearates were shown in Fig. 5. As for the cellulose stearates, progressive decrease even vanish of intensities connected with the 1 0 1, $1\,0\,\bar{1}$, 0 0 2 and 0 4 0 planes could be observed with the increasing DS. The intensities of 0 2 1 plane broaden and became blunt. X-ray diffraction spectra of cellulose esters show broader peaks at angles slightly different from those for MCC around 20°. All of these showed that the crystalline of MCC had been destroyed during the acylation and there is an ordered structure in the cellulose stearate, but the crystalline region is anomalous. Until now, there were no studies with X-ray diffraction to determine whether cellulose chains substituted with long-chain organic acids in a homogeneous esterification reaction form an ordered structure. The lack of information about the morphology of such cellulose esters complicates the estimation of the crystallites of cellulose stearates.

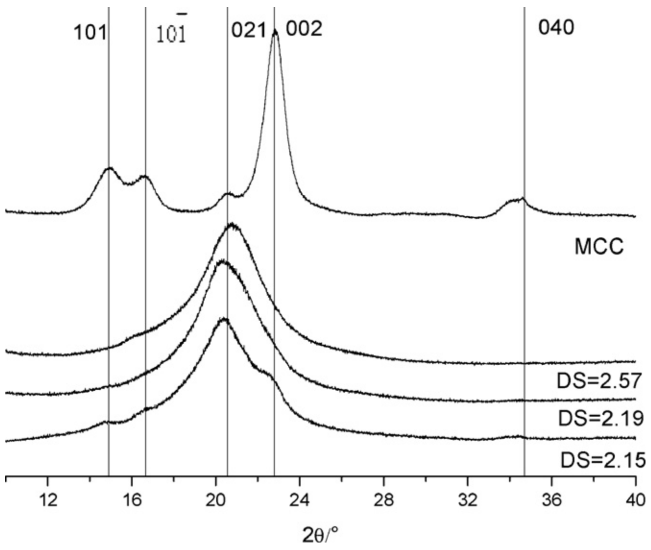

Fig. 5. X-ray diffraction spectrum of MCC and cellulose stearates.

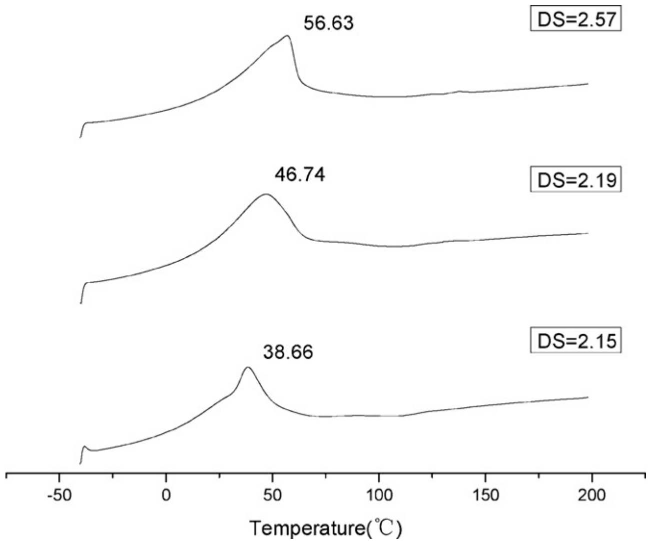

Fig. 6. DSC curves of cellulose stearates in the second scan (after annealing).

3.5. Thermal analysis

The samples with DS of 2.15, 2.19 and 2.57 were analyzed by DSC measurement in a N_2 atmosphere. DSC curves of cellulose stearates were shown in Fig. 6. According to reference (Batzer & Kreibich, 1981), because of massive hydrogen bond association, the glass transition temperature (T_g) of dry cellulose reported was 230 °C, So MCC did not show any glass temperature transition and melting behavior between −40 °C and 200 °C. For all the cellulose stearates were highly substituted by long chain alkyl, most of the hydrogen bond association between the macromolecules dismissed, cellulose stearate samples exhibited low melting peaks (38.66–56.63 °C) couple with glass transitions, the glass transition closed to the disentanglement of the molecular chain, so the separate T_gs could not be observed. Therefore, we can see clearly that the cellulose stearates prepared had been thermoplastic polymers but not polymers like MCC anymore. According to previous literature, Sealey et al. (1996) gave a dimensionally molecular model of a section of a cellulose eicosanoate chain demonstrated the ability of the side chains and the molecule as a whole to adopt a conformation favorable for side-chain crystallization. Similarly, stearyl chloride also gave cellulose stearate long side chains in the cellulose main chain. The increase in melting point was attributed to an increase in side-chain thickness due to the part of the overlapped side chains became larger with increasing DS. To prove this, the first scan of DSC was shown in Fig. 7. There were multiple endotherm peaks in the first scans, but after fast annealing, these peaks did not appear in Fig. 6 anymore. This showed that there were some ordered structures in the cellulose stearates and the result was also confirmed

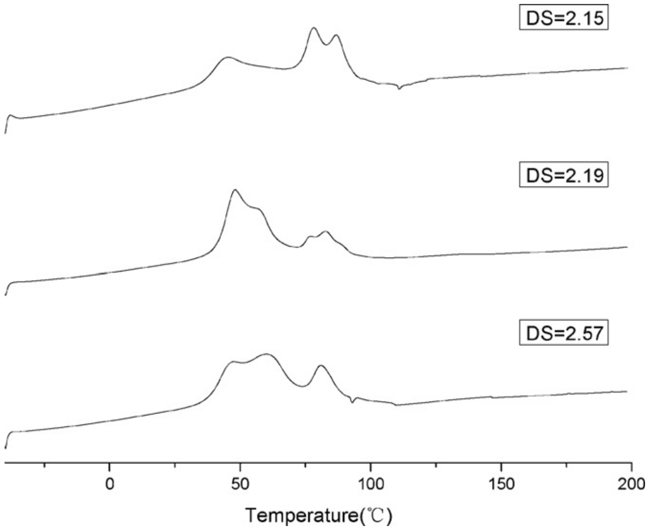

Fig. 7. DSC curves of cellulose stearates in the first scan.

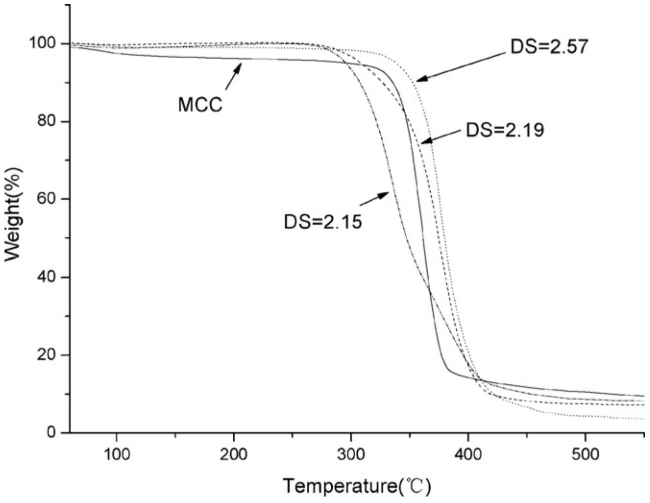

Fig. 8. TG curves of MCC and cellulose stearates.

by the X-ray diffraction analysis. Multiple melting peaks were commonly attributed to different crystal types, recrystallization in the thermal analysis, block copolymers or graft copolymers (Yin & Mo, 2003).

Thermogravimetry (TG) curves of MCC and cellulose stearates in air atmosphere were shown in Fig. 8. A small weight loss around 100 °C can be observed for MCC and the thermal degradation commenced at about 360 °C. This is due to the evaporation of moisture. As the long chain alkyl substituent can decrease moisture sorption of cellulose (Stroeve & Balazs, 1992), the cellulose stearates failed to reveal moisture loss. The first thermal degradation of the cellulose stearate with DS of 2.15 and 2.19 is at 300 °C and 325 °C, respectively, which were lower than that of MCC. This was due to the decrease of molecular weight during the cellulose ester preparation. Even so, the degradation isotherm was shifted to higher temperatures (about 370 °C) for the product with a DS of 2.57, indicating that thermal stability increases with increased stearyl content of the samples. It is worth mentioning that the cellulose stearate with higher DS has better thermal stability than that of MCC in air atmosphere though the M_w of the cellulose stearate was only about 30% of the theoretical value.

4. Conclusions

In this work, cellulose stearates with different DS were successfully prepared from microcrystalline cellulose through homogeneous acylation in $[C_4mim]^+Cl^-$ in the absence of any base but the degradation of cellulose stearates was apparent. The cellulose stearates with various DS values can be obtained by controlling the reaction time and the molar ratio of MCC to stearyl chloride added. The resultant cellulose stearates with the DS values of 2.15, 2.19 and 2.57 were readily dissolved in some nonpolar organic solvents, such as chloroform, hexane and toluene. It was indicated by DSC analysis that the cellulose stearates with low melting range were proved to be thermoplastic polymers. Stearyl moiety could increase the thermal stability of the cellulose in air atmosphere. The cellulose stearate with higher DS showed better thermal stability than MCC.

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