H$_3$PW$_{12}$O$_{40}$·4H$_2$O as an Efficient Catalyst for the Conversion of Cellulose into Partially Substituted Cellulose Acetate

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ABSTRACT: The preparation of partial acetylation of cellulose derived from rice straw was catalyzed by phosphotungstic acid with various numbers of crystal water, and H$_3$PW$_{12}$O$_{40}$·4H$_2$O was found to be as effective catalyst. The yield of the cellulose acetate was significantly enhanced by converting cellulose directly isolated from rice straw into microcrystalline cellulose before acetylation. The optimization of the acetylation was investigated by varying the amount of catalyst and acetic anhydride as well as reaction conditions including reaction time and medium, and a degree of substitution (DS) value of 2.29 and yield of 62.9% were obtained under the optimized conditions. The structure and the formation of the acetylated product were confirmed by Fourier transform infrared spectroscopy (FTIR) and powder X-ray diffraction (XRD) technique, the thermal properties were determined by thermal analysis including thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC), and the morphology was observed by scanning electron microscope (SEM). © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41212.

INTRODUCTION

The need to explore sustainable energy has arisen because of the shortage of resources resulted from the over-exploitation of fossil fuels. Interest in the chemistry of biomass-derived compounds has led to efforts aimed at the use of lignocellulosic materials as alternative sources of chemicals and energy.[1] Cellulose, the major component of plant biomass, is readily available and widely considered a long-term renewable fossil fuel alternative.[2,3] Crop straw, primarily composed of cellulose, hemicellulose and lignin, is a profuse cellulosic by-product from crops production such as wheat, rice, sugarcane, and corn.[4–6] Rice is the largest cereal crop on Earth, accompanying the production of 45% rice straw, which has been used as low-cost feed-stocks for producing value-added products including fuel ethanol,[7] methylcellulose and cellulose acetate after the complete removal of hemicellulose and lignin.[8–11]

Cellulose acetate is one of the most important cellulose derivatives, and is widely applied in the manufacture of fibers, films, paints, plastics, filters, dialyzers, and drugs.[12–16] Generally, wood and cotton are the major resources for the industrial acetylation of cellulose.[17,18] Low-cost lignocellulosic biomass has become an attractive renewable resource because it is available in large quantities and routinely cultivated in the world.[19] The application of cellulose acetate usually depends on its solubility, which typically relates to the degree of substitution (DS) value. Par-

tially substituted cellulose diacetate with DS values ranging from 2.2 to 2.7 is widely used in dialysis membranes, cigar filters and plastics due to its good solubility in acetone.[20] Cellulose diacetate with a desired DS value is generally obtained from the partial hydrolysis of cellulose triacetate produced via the reaction of acetic acid with acetic anhydride in the presence of inorganic strong acids (such as sulfuric acid or perchloric acid).[21] The strong acid–catalyzed processes often result in problems of corrosion and large amounts of generated waste. Therefore, there is a need to develop new catalysts to replace conventional ones for preparing cellulose diacetate.

So far, few studies have been focused on the direct synthesis of cellulose diacetate from cellulose. We have previously reported the acetylation of cellulose catalyzed by H$_3$PW$_{12}$O$_{40}$·6H$_2$O[22] based on its excellent catalytic performance in some reactions,[23,24] so that the influence of the acidity of phosphotungstic acid, which is believed to relate to the number of crystal water, on the catalytic activity wasn't performed. Although partial substituted cellulose acetate with DS values in the range from 1.43 to 2.28 and good solubility in acetone were obtained,[22] the catalyst-to-cellulose molar ratio reached 20%, and a large quantity of catalyst with respect to reagent mass was employed due to the high molecular weight of H$_3$PW$_{12}$O$_{40}$·6H$_2$O. Moreover, poor reactivity of crude cellulose extracted from rice straw led to relatively low yield of the acetylated product. Microcrystalline cellulose presents a novel form of cellulose and exists as fine

crystal powder, offers many advantages such as high reactivity, renewability, and biodegradability.[25]

The aim of this work is to develop a more effective methodology for the direct conversion of cellulose derived from rice straw into partial substituted cellulose acetate. The crude cellulose extracted from rice straw was first converted into microcrystalline cellulose, and the acetylation was then performed using phosphotungstic acid as the catalyst. The catalytic performance of phosphotungstic acid was investigated by varying the number of crystal water contained in it. The acetylation process was further performed with considering the reaction conditions including the amount of catalyst and acetic anhydride, reaction time and medium. The chemical structure, physical properties, and morphology of cellulose diacetate were characterized by using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) technique, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscope (SEM).

EXPERIMENTAL

Materials

Rice straw was obtained from the local farm around Wuhan city (Hubei, China) and the extraction of cellulose from rice straw was reported in our previous work.[22] Phosphotungstic acid was purchased from Aladdin Reagent (Shanghai, China). Dichloromethane (CH_2Cl_2), hydrochloric acid, ethanol, NaOH, acetic acid, acetic anhydride, sodium hydroxide, acetone, chloroform ($CHCl_3$), dimethyl sulfoxide (DMSO) and 1-n-butyl-3-methylimidazolium bromide (BMIMBr) were purchased from Sinopharm Chemical Reagent (Peking, China). They were analytically pure and used without further purification except acetic anhydride was redistilled prior to use.

Preparation of Microcrystalline Cellulose

Microcrystalline cellulose was prepared according to the reported procedures with changes.[26] Generally, 3 g crude cellulose extracted from rice straw and 150 mL 12% hydrochloric acid aqueous solution were added into a 250 mL round-bottom flask, and the mixture was stirred at 70°C for 1 h. The reaction mixture was then cooled to room temperature and diluted by 300 mL distilled water. Powder solid was precipitated after leaving to stand for 24 h, and 100 mL 4% NaOH aqueous solution was added to the solid and continuously stirred at 80°C for 1 h. The mixture was cooled to room temperature again and then washed with distilled water for two to three times before centrifuge. The clear solution in the upper layer was discarded and the solid at the bottom was washed with 95% ethanol solution. The solid was collected by filtration and dried at 80°C to obtain microcrystalline cellulose.

Preparation of Phosphotungstic Acid with Various Numbers of Crystal Water

Phosphotungstic acid with various numbers of crystal water was prepared according to the reported procedures.[27] Typically, 3 g commercial $H_3PW_{12}O_{40} \cdot 21H_2O$ was heated at 9.6 kPa of vacuum degree with different temperature for 1.5 h. Phosphotungstic acid with numbers of crystal water of 14, 10, 6, 4, 2, and 1 was obtained at room temperature, 40, 110, 150, 175, and 220°C, respectively. The pretreated catalyst was then collected and put in a vacuum dryer before use.

Acetylation of Cellulose

In a typical acetylation procedure, 2 g microcrystalline cellulose (ca. 12.3 mmol anhydroglucose unit, AGU), 0.6 g acetic acid, 5 g acetic anhydride, 30 mL CH_2Cl_2 and 0.615 mmol $H_3PW_{12}O_{40} \cdot 4H_2O$ were added into a 100 mL round-bottom flask. The mixture was refluxed for 6 h with vigorous stirring, and the reaction mixture was then cooled to room temperature before centrifugation. The clear solution in the upper layer was transferred into a flask, and the solvent was removed by rotary evaporation, yielding a membrane as crude product. The solid was then collected by filtration after addition of 60 mL deionized water to the membrane, dried overnight at 80°C in a vacuum oven to give the desired product.

Analysis and Calculation

All of the acetylation reactions of cellulose presented in this work were performed in triplicate; both the DS values and yields of acetylated product are the averages of three runs. The DS values of the samples were determined by complete hydrolysis of the samples with sodium hydroxide,[19,28] and the degree of polymerization (DP) values were determined by viscosity measurement of the samples dissolved in copper-ammonium hydroxide solution.[6,29] The yield of cellulose acetate was calculated based on the complete replacement of hydroxyl groups by acetyl groups, and was calculated according to the following equation:

$$\text{Yield}(\%) = \frac{m_p}{\frac{m}{162} \times 288} \times 100\% \tag{1}$$

where m is the mass of cellulose added to the acetylated reaction; m_p is the mass of the acetylated product; 162 and 288 are the molecular weights (in g mol^{-1}) of AGU and cellulose triacetate, respectively.

Measurements

FTIR was carried out on an EQUINOX 55 spectrometer in the range from 4000 to 400 cm^{-1}. The solid samples were grounded with dried KBr powder, and compressed into a disc prior to analysis. XRD measurement was performed on a χ'Pert PRO diffractometer with Cu Kα radiation at 40 kV and 40 mA in the range from 5 to 80°, and the scanning rate is 5° min^{-1}. TGA and DSC were performed using a Perkin-Elemer TG-DSC 7 spectrometer under nitrogen at a heating rate of 10°C min^{-1} in the range from room temperature to 800°C. Approximately 10 mg sample was used in thermal analysis and the gas flow rate was kept at 90 mL min^{-1}. The surface morphologies of rice straw and its derivatives were observed using SEM performed on a Hitachi N-3000 apparatus, and a thin layer of gold is sputtered onto the sample prior to imaging.

RESULTS AND DISCUSSION

Acetylation of Cellulose

Influence of the number of crystal water contained in phosphotungstic acid. The catalytic performance of phosphotungstic acid with various numbers of crystal water was investigated, as shown in Table I. It is believed that the acidity of phosphotungstic acid and catalytic performance are evidently dependent on the number of crystal water contained in it since the acidic strength of phosphotungstic acid, changing in the range from -3.03 to -13.75 (H_o) by varying the number of crystal water from 21 to 1, increases with decreasing the number of crystal

Table I. Acetylation of Cellulose with Various Numbers of Crystal Water

Entry	Number of crystal water	DS	DP	Yield (%)
1	21	1.03	243	8.7
2	14	1.12	257	20.0
3	10	1.43	248	26.7
4	6	1.49	252	36.0
5	4	1.81	245	53.2
6	2	1.87	239	34.7
7	1	1.92	255	27.6
8[a]	4	1.54	254	23.8

[a] Crude cellulose extracted from rice straw was directly employed as raw material for the acetylation.

water.[27] As it can be seen from Table I that DS values were obviously enhanced by decreasing the number of crystal water (Table I, entries 1–5), but were almost kept constant (entries 5–7) when the number of crystal water was reduced to four possibly as a consequence of superacid property of phosphotungstic acid containing 1 to 4 crystal water.[27]

The results in Table I show that the yield of cellulose acetate was also enhanced with decreasing the number of crystal water. A maximum value of 53.2% was achieved in the presence of $H_3PW_{12}O_{40} \cdot 4H_2O$, and a significant drop was then observed with further increase in the acidity. From these results, it is reasonable to speculate that not only the acetylation of cellulose but also the degradation of cellulose acetate is enhanced in the presence of superacid. The decomposition of cellulose acetate possibly occurs by scission of glycosidic linkages followed by pyranose ring rupture and acetic acid evolution resulting from partial deacetylation.[30–32] In addition, the acetylation of cellulose is generally accompanied by the formation of a small quantity of unstable cellulose, leading to the degradation of macromolecular cellulose into smaller molecular glycolipids.[33] The results in Table I show that no obvious differences in DP values, changing in the range from 243 to 257, were observed in the presence of phosphotungstic acid with various numbers of crystal water, further revealing that the degradation of cellulose acetate is mainly due to the deacetylation. As a result, decrease in the yield while almost no change in the DP values was observed.

It also can be seen from Table I that the yield of cellulose acetate was obviously observed to increase using microcrystalline cellulose comparison to that obtained with crude cellulose as raw material for the acetylation process, 53.2% for the former but only 23.8% for the latter was observed (Table I, entries 5, 8), revealing that the acetylation of cellulose was evidently enhanced by converting crude cellulose into microcrystalline cellulose.

Investigation on the Amount of $H_3PW_{12}O_{40} \cdot 4H_2O$. The amount of $H_3PW_{12}O_{40} \cdot 4H_2O$ was further investigated, and the results were listed in Table II. The results in Table II reveal that the DS values, DP values and yields of cellulose ester were evidently dependent on the amount of catalyst. The DS values and the yields increased with an enhancement in the amount of catalyst till the molar ratio of catalyst to AGU elevated up to 5%, a

Table II. Acetylation of Cellulose with Different Amount of $H_3PW_{12}O_{40} \cdot 4H_2O$

Entry	$H_3PW_{12}O_{40} \cdot 4H_2O$/AGU (molar ratio)	DS	DP	Yield (%)
1	0.03	0.37	248	10.7
2	0.04	1.06	252	33.1
3	0.05	1.81	245	53.2
4	0.06	1.54	238	55.1
5	0.08	1.43	224	37.9
6	0.10	1.50	216	25.9

DS value of 1.81 and yield of 53.2% were obtained. The observed drop in the DS values and yields with a further increase in the amount of catalyst is possibly because the addition of excessive catalyst promoted the esterification as well as the degradation of cellulose and cellulose acetate.[34] A DS value of 1.50 and yield of 25.9% were obtained when the amount of catalyst reached 10%. The DP values almost kept constant when the molar ratio of catalyst to AGU below 5%, a slight drop was then observed with further increasing in the amount of catalyst. The amount of water in the reaction system was enhanced with increasing the amount of phosphotungstic acid because hydrated compound $H_3PW_{12}O_{40} \cdot 4H_2O$ was employed as the catalyst. The chain of cellulose acetate is possibly easy to break in the presence of a larger amount of water, thus resulting in a decrease in the DP value.

Influence of Reaction Time. Experiments were conducted by varying reaction time, solvent and the amount of added acetic anhydride to reveal the influence of the reaction variables on the acetylation of cellulose, the results are shown in Table III. The results in Table III indicate that DP values almost kept

Table III. Acetylation of Cellulose Dependent on the Reaction Conditions

Entry	Acetic anhydride/ AGU (molar ratio)	Time (h)	Solvent[a]	DS	DP	Yield (%)
1	4	6	CH_2Cl_2	1.81	245	53.2
2	4	8	CH_2Cl_2	1.93	253	56.8
3	4	10	CH_2Cl_2	2.29	241	62.9
4	4	12	CH_2Cl_2	1.48	238	52.1
5	4	14	CH_2Cl_2	1.25	251	37.5
6	4	16	CH_2Cl_2	1.08	239	33.4
7	2	10	CH_2Cl_2	1.74	250	32.0
8	3	10	CH_2Cl_2	1.91	247	47.8
9	5	10	CH_2Cl_2	2.27	255	45.6
10	6	10	CH_2Cl_2	2.26	260	37.7
11	4	10	Acetone	2.14	246	54.9
12	4	10	$CHCl_3$	0.75	277	21.3
13	4	10	DMSO	0.62	265	5.9
14[b]	4	10	DMSO	0.78	242	18.6
15	4	10	BMIMBr	2.05	258	14.3

[a] The acetylation of cellulose was performed at reflux.
[b] The acetylation of cellulose was performed at 45°C.

constant while the DS values and yields were significantly dependent on the reaction conditions. Both the DS values and yields increased when prolonging reaction time at the initial stage, and the maximum values were obtained for 10 h (Table III, entries 1–3), and a significant drop was then observed with further increasing the reaction time (Table III, entries 4–6). It is believed that cellulose is initially activated by acetic acid in the esterification of acetic anhydride with hydroxyl groups, promoting the accessibility of acetic anhydride to hydroxyl groups contained in cellulose backbone. The ratio of the activated time to the total reaction time was relatively high when the reactions were performed with short time, which correspondingly reduces the esterification time,[35] thus leading to an enhancement in the DS values with increasing the reaction time below 10 h. The observed drop in yield with a further increase in the reaction time beyond 10 h is possibly due to the increased likelihood for the degradation of acetylated product,[3] resulting in part of the product dissolved in water and cannot be collected. No obvious change in DP values was observed, revealing that the degradation of cellulose acetate is mainly due to the removal of acetyl group. This is in accordance with the results in Table I.

Influence of the Amount of Acetic Anhydride. The influence of the amount of acetic anhydride was further examined, as shown in Table III (Table III, entries 3, 7–10). The yield increased monotonously with raising the amount of acetic anhydride till the molar ratio of acetic anhydride to cellulose reached 4 (Table III, entries 3 and 8). The DS values also increased with increasing the amount of acetic anhydride but were almost kept constant when the molar ratio of acetic anhydride to AGU beyond 4. Improvement in the amount of acetic anhydride is helpful to promote the equilibrium shift to the right/product since the acetylation of cellulose is a reversible reaction, thus resulting in an increase in the DS value and yield of acetylation product. Theoretically, the completely acetylated product with a DS value of about 2.8 should be obtained if an excess of acetic anhydride is employed. However, the results in Table III revealed that the observed DS values were much less than the theoretical DS value, even when an excessive amount of acetic anhydride was employed. This result can be ascribed to the loss of acetic anhydride in side reactions as well as the degradation of cellulose. Moreover, the accessibility of acetic anhydride to the hydroxyl groups may be affected by the aggregation among cellulose chains, which arises as a result of intermolecular bonding of cellulose.[12]

Influence of Solvent. Regarding the solvent (Table III, entries 3, 11–15), it was found that both the DS values and yields were maximal using CH_2Cl_2 as the solvent (Table III, entry 3). A slight decrease in the DS value and yield was attained using acetone as the reaction medium (Table III, entry 11), and a lower DS value of 0.75 and yield of 21.3% were observed in $CHCl_3$ (Table III, entry 12). It is well known that the solubility of cellulose acetate is significantly dependent on the substitute degree of hydroxyl group.[6] Solubility tests revealed that the samples with DS values around 2.0 listed in Table III exhibited good solubility in acetone and CH_2Cl_2 but not in $CHCl_3$, which possibly resulted in the differences in the DS values and yields of cellulose acetate. Although partial acetylated product has good solu-

bility in DMSO, both the DS value and yield of cellulose acetate were relatively low (Table III, entries 13 and 14) whether the reaction was performed at 45°C or reflux, further confirming that the temperature is crucial for the acetylation and higher reaction temperature may result in the degradation of cellulose. It has been reported that ionic liquids such as 1-n-butyl-3-methylimidazolium chloride (BMIMCl) and 1-n-butyl-3-methylimidazolium bromide (BMIMBr) are good solvents for cellulose,[6] therefore the reaction performed in BMIMBr was further investigated. However, poor yield of acetylated product was obtained (Table III, entry 15). This is possibly resulted from the high viscosity of ionic liquid, which is not helpful to the reaction.

Characterization

FTIR. The FTIR spectra of crude cellulose extracted from rice straw, microcrystalline cellulose and acetylated cellulose with DS values of 1.50 and 2.29 are shown in Figure 1. The dominant absorption peaks around 3437 and 2926 cm^{-1} are attributed to the stretching vibrations of —OH group and the C—H bond in —CH_2, respectively. Peaks at 897 and 1,165 cm^{-1} are assigned as C—O—C stretching vibrations of the characteristic β-(1–4)-glycosidic bond in glycogen.[36] Although all the characteristic peaks still presented in the spectrum of microcrystalline cellulose in Figure 1(b), a blue shift of the peaks to higher wavenumber values could be observed, confirming the formation of microcrystalline cellulose.[25] New peaks presented around 1758, 1374, and 1234 cm^{-1} in the spectra of acetylated cellulose are related to the stretching vibrations of C=O group, C—H bond in —O(C=O)—CH_3 group and —CO— in acetyl group, respectively,[6] confirming the hydroxyl groups were substituted for acetyl groups during the reaction. Furthermore, the characteristic peaks in Figure 1(d) were obviously stronger than those in the Figure 1(c), indicating the intensity of the characteristics of acetylated products is strengthened with an increase in the DS value.

XRD. The XRD patterns of crude cellulose extracted from rice straw, microcrystalline cellulose, cellulose acetate with DS values
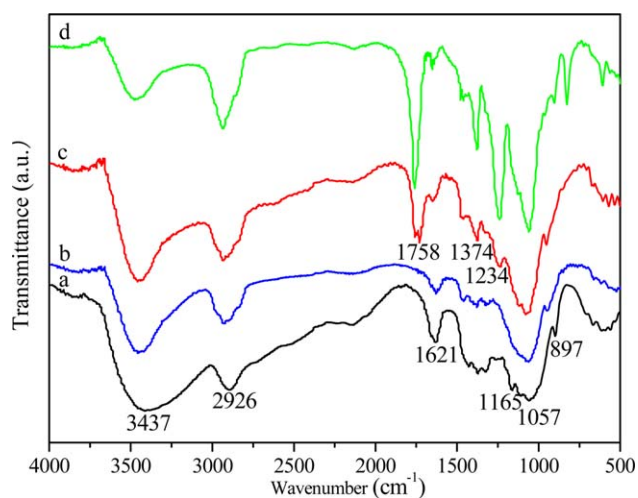

Figure 1. FTIR spectra of (a) crude cellulose extracted from rice straw, (b) microcrystalline cellulose, (c) cellulose acetate with DS value of 1.50 and (d) cellulose acetate with DS value of 2.29. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 1.50 and 2.29 are shown in Figure 2. The peak around 22.4° of (002) reflection in the curves is ascribed to the typical crystal lattice of cellulose I$_\beta$,[8] indicating that all samples exhibit the diffuse characteristic pattern of an amorphous phase. A shoulder peak at 16.1° of (101) reflection and a weak peak at 34.2° of (040) reflection appeared in the spectrum of crude cellulose are assigned to the cellulose phase. The diffraction peak around 22.4° of (002) reflection observed in the plot of microcrystalline cellulose was stronger than that observed in the spectrum of the crude cellulose directly extracted from rice straw, revealing an increase in the degree of crystallinity after the acid pretreatment.[37]

The observation of the diffraction peak around 22° of (002) reflection in the pattern of acetylated cellulose shows that the cellulose acetate still presents the typical crystal lattice of cellulose I$_\beta$.[17] A new weak diffraction peak indexed with the crystalline peaks of CTA II modification[38] appeared around 9.5° but no peak in the range from 15 to 20° ascribed to cellulose triacetate were observed in the diffraction pattern of cellulose acetate, revealing the acetylated cellulose is mainly composed of cellulose diacetate.[39] The peak observed around 22° in the curve of cellulose acetate was wider than that in the XRD pattern of microcrystalline cellulose, indicating a drop in the degree of crystallinity after acetylation.[40] It also can be seen from Figure 2(c,d) that the intensity of the characteristic peaks in the XRD plots of the acetylated product decreased with increasing the degree of acetylation, further indicating the acetylation results in a drop of the degree of crystallinity.[41] This can be ascribed to the replacement of hydroxyl group by acetyl groups, which makes the break of the intramolecularly and intermolecular bonds easier.[42]

Thermal Analysis. The thermal properties of microcrystalline cellulose, cellulose acetate with a DS value of 1.50 and 2.29 were characterized by TGA and DSC measurements in N$_2$ atmosphere, and the results are shown in Figure 3. The mass
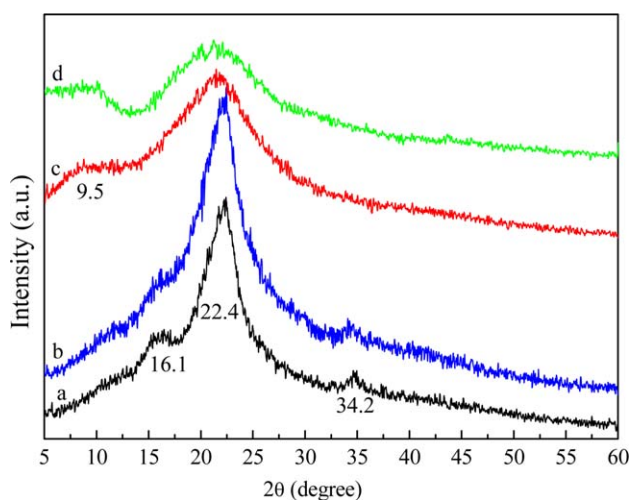

Figure 2. XRD plots of (a) crude cellulose extracted from rice straw, (b) microcrystalline cellulose, (c) cellulose acetate with DS value of 1.50 and (d) cellulose acetate with DS value of 2.29. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
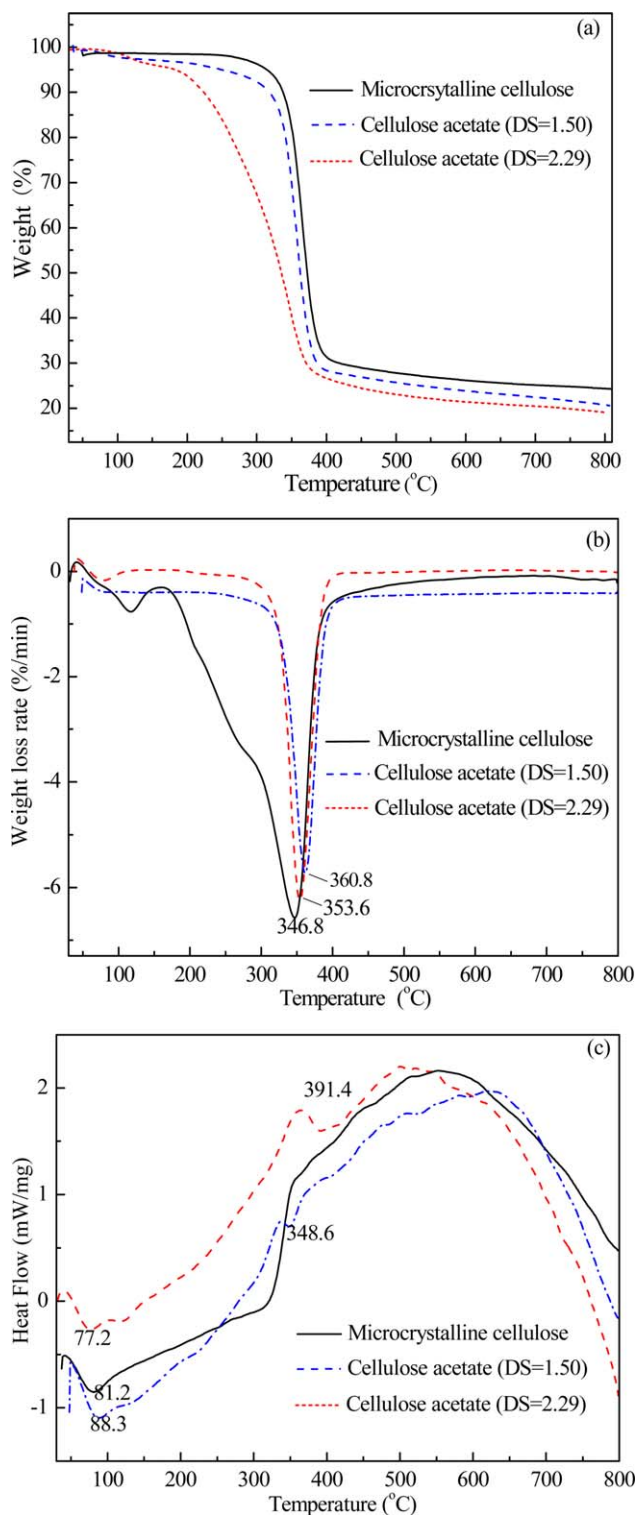

Figure 3. TGA, DTG and DSC curves of microcrystalline cellulose and cellulose acetate (a) TGA, (b) DTG and (c) DSC curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

loss observed within 150°C is associated with the removal of physically adsorbed molecular water.[43,44] It also can be noticed in Figure 3(a) that only one considerable weight loss occurred between 300 and 400°C in TGA curves of all samples.
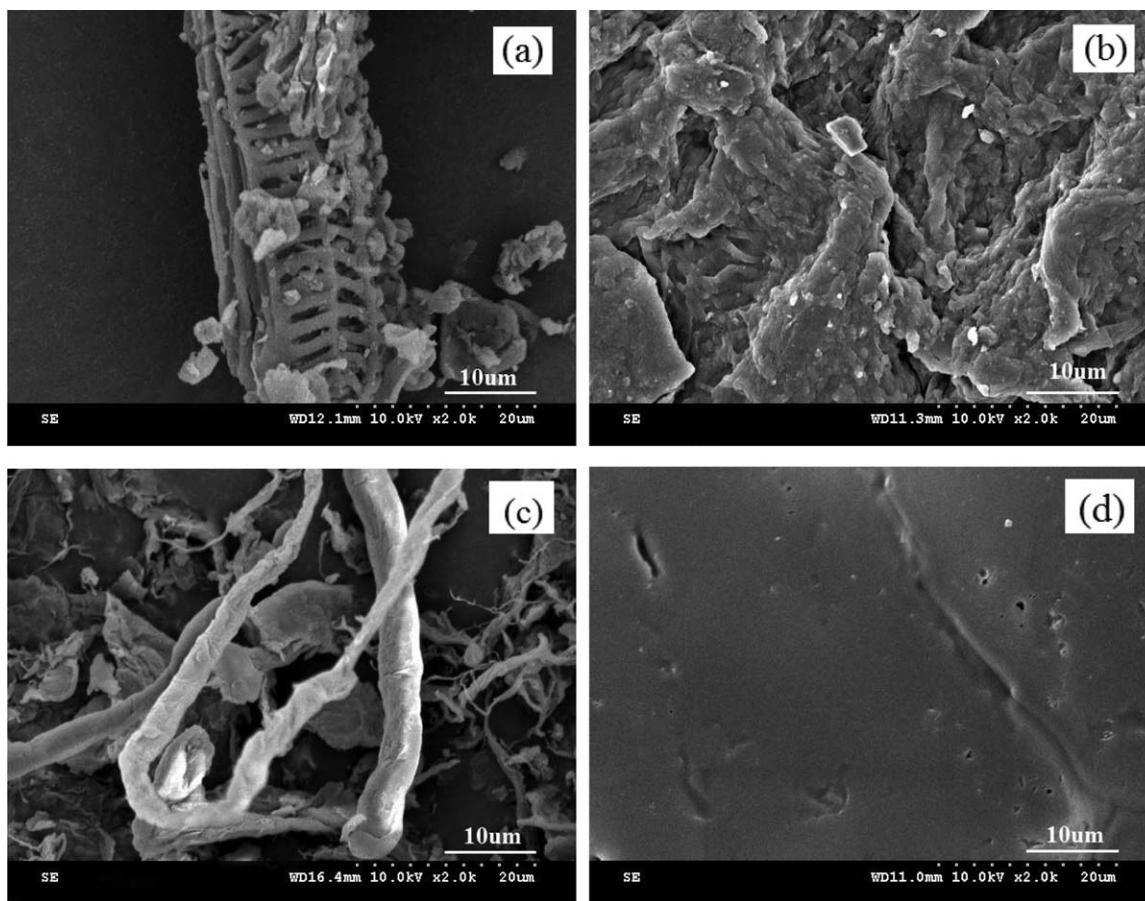
Figure 4. SEM image of (a) rice straw, (b) crude cellulose extracted from rice straw, (c) microcrystalline cellulose and (d) cellulose acetate.

Correspondingly, the maximum decomposition temperature of microcrystalline cellulose and cellulose acetate with a DS value of 1.50 and 2.29 were observed at 346.8, 353.6, and 360.8°C in derivative thermogravimetric (DTG) curves presented in Figure 3(b), respectively. This phenomenon indicates that the thermal stability of cellulose is enhanced after the acetylation and slightly increases with increasing the degree of acetylation. The total mass loss of 80.45, 82.45, and 86.15% for microcrystalline cellulose, cellulose acetate with a DS value of 1.50 and 2.29 were observed in Figure 3(a), respectively. The difference in the mass loss is possibly ascribed to the replacement of hydroxyl groups by acetyl groups.[45]

Endotherms around 80°C in the DSC plots of all samples shown in Figure 3(c) is attributed to the evaporation of the adsorbed water. No other peak was observed in the DSC plot of microcrystalline cellulose likely due to the masking of a reversing event (such as glass transition) by its corresponding non-reversing event (such as enthalpic relaxation). Endothermic peaks located at 348.6 and 391.4°C in the curves of cellulose acetate with DS values of 1.50 and 2.29 were noted, which may be mainly related to the degradation of the acetylated derivatives.[19,46]

SEM. The morphologies of rice straw, crude cellulose derived from rice straw, microcrystalline cellulose and cellulose acetate

with a DS value of 2.29 were observed by SEM; corresponding SEM photographs are presented in Figure 4. It can be seen that the morphology of rice straw without any treatment in Figure 4(a) is hollow but becomes irregular and featureless in the image of crude cellulose in Figure 4(b). Obvious changes are also presented in the images of microcrystalline cellulose and cellulose acetate, stick shape for the former and dense texture for the latter were observed in Figure 4(c,d), respectively. The differences in the morphologies of the samples further support the evidence for the occurrence of chemical processes including the pretreatment of rice straw by alkaline-acid method and the acetylation of cellulose.

CONCLUSIONS

The acetylation of cellulose derived from rice straw catalyzed by phosphotungstic acid with various numbers of crystal water was developed in this work. Both the DS value and yield of partial acetylated cellulose acetate were evidently dependent on the acidic strength and the amount of catalyst as well as reaction conditions including reaction time and reaction medium. $H_3PW_{12}O_{40} \cdot 4H_2O$ was found to be the most effective catalyst among the investigated phosphotungstic acid compounds, and the yield of cellulose acetate was significantly enhanced by converting cellulose into microcrystalline cellulose before

acetylation. Acetone-soluble cellulose acetate with DS value of 2.29 and yield of 62.9% were obtained, respectively, under the optimized conditions.

ACKNOWLEDGMENTS

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