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Acetylation of rice straw for thermoplastic applications

Guangzhi Zhang[a], Kai Huang[a], Xue Jiang[a], Dan Huang[a,*], Yiqi Yang[a,b]

[a] Key Laboratory of Eco-Textile, Jiangnan University, Ministry of Education, Wuxi, China
[b] Department of Textiles, Clothing and Design, University of Nebraska-Lincoln, Lincoln, NE, USA

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ABSTRACT

An inexpensive and biodegradable thermoplastic was developed through acetylation of rice straw (RS) with acetic anhydride. Acetylation conditions were optimized. The structure and properties of acetylated RS were characterized by fourier transform infrared (FTIR), solid-state ^{13}C NMR spectroscopy, X-ray diffractometer (XRD), scanning electron microscope (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results showed that acetylation of RS has successfully taken place, and comparing with raw RS, the degree of crystallinity decreased and the decomposition rate was slow. The acetylated RS has got thermoplasticity when weight ratio of RS and acetic anhydride was 1:3, using sulphuric acid (9% to RS) as catalyst in glacial acetic acid 35 °C for 12 h, and the dosage of solvent was 9 times RS, in which weight percent gain (WPG) of the modified RS powder was 35.5% and its percent acetyl content was 36.1%. The acetylated RS could be formed into transparent thin films with different amount of plasticizer diethyl phthalate (DEP) using tape casting technology.

1. Introduction

Rice straw (RS) is one of the largest agricultural residues in the world. However, rice straw is often considered as solid waste because of its limited industrial application due to its insolubility in common organic solvents and poor thermoplasticity. There is a growing urgency to develop novel bio-based products and other innovative technologies that can unhook widespread dependence on fossil fuel (Esteban & Carrasco, 2011; Mistri, Bandyopadhyay, Ghosh, & Ray, 2010). Now, many countries have imposed new regulations to restrict field burning of agricultural residues in response to restrictions on carbon dioxide emission due to global warming. This also helped stimulating the interests on the utilization of agricultural residues as a renewable natural resource (Liu et al., 2008). Agricultural resources have been utilized as renewable resource of energy and production of a diversity of chemicals, including ethanol production, activated carbon, and ion exchangers (Edgar et al., 2001; Orlando, Baes, Nishijima, & Okada, 2002; Sengupta & Pike, 2012). The interest in rice straw (RS) is growing especially over the last decade due to its abundant availability, low-cost, and good biodegradability.

There is a great amount of agricultural residues in China, in which RS is one of the most abundant (Bi, Gao, Wang, & Li, 2009). According to statistics provided by the Ministry of Agriculture of China, the annual amount of RS produced in China is estimated to be 205×10^6 t in 2009 that accounted for 25% of total amount of straw resources.

RS is formed of a rigid polymer (cellulose) in a thermoplastic matrix (lignin and the hemicelluloses). As is known to all, RS will be decomposed before melting temperature, because there is no sufficient temperature gap between that temperature sufficient to open the intermolecular bond and that temperature at which degradation of the entire material starts (Schroeter & Felix, 2005), which means it is difficult to make RS form sheet or any other shape without using an adhesive like urea resin or isocyanate resin (Rowell, Anand, Caulfield, & Jacobson, 1997). So it is necessary to substitute hydrogen group to endow RS plasticity.

Acetylation is an inexpensive and environmentally friendly approach to make biopolymers thermoplastic and has been widely used in wood modification (Rowell, Tillman, & Simonson, 1986). Acetylation of wood has been already practiced on a commercial basis in Japan and may soon be so in other countries (Rowell, 2006a,b). Acetylation of other biomass also was practiced. Hu et al. reported acetylation of chicken feathers and corn distillers dried grains for thermoplastic applications, respectively (Hu, Reddy, Luo, Yan, & Yang, 2011; Hu, Reddy, Yan, & Yang, 2011).

Acetylation of RS is highly considered in current research of modification of RS in order to get thermoplastic materials. Mohammadi-Rovshandeh reported thermoplasticity and thermal stability of acetylated product of different pretreated rice straw (extracted or prehydrolyzed). Two modifications, acetylation and benzylation, are studied in their work. The result shows that the extracted and prehydrolyzed rice straw can be

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* Corresponding author at: College of Textiles & Clothing, Jiangnan University, Wuxi, China. Tel.: +86 510 85912007; fax: +86 510 85912009.
E-mail addresses: huangdan6@163.com, huangdan@jiangnan.edu.cn (D. Huang).

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benzylated by benzyl chloride and acetylated by a mixture of acetic acid and acetic anhydride, respectively. TGA and TMA are employed to characterize the thermal property of the modified RS (Mohammadi-Rovshandeh & Sereshti, 2005). Based on the research of Mohammadi-Rovshandeh, the mechanism of the variation of the thermoplasticity of the modified RS, such as the crystal structure and the relationship of structure and properties, is highly important and should be taken into account. In this paper, the RS has been acetylated and the effect of acetylation conditions on the weight percent gain (WPG), percent acetyl content (PAC) and thermal properties of the acetylated RS have been investigated in order to mold the entire lignocellulosic resource into films. The acetylated RS with thermoplastic has been prepared and used as the starting material to cast to form the thin films (rice straw fiber film). What's more important, the mechanism of the variation of thermoplasticity of the modified RS is explained based on the characterization of chemical and crystal structure, morphology, thermal properties, and mechanical properties of the prepared modified RS.

2. Experimental

2.1. Materials and reagents

The rice straw was obtained from a local countryside (Wuxi, China). 95% ethanol, benzene, acetic anhydride, glacial acetic acid, 98% sulphuric acid were purchased from Sinopharm Group Inc. All chemicals were used as received without further purification.

2.2. Acetylation of rice straw

RS was pretreated before modification. RS was dried in sunlight and then milled in a crushing machine to 40 mesh, the powdered straw was soaked for 4 h in water, filtered and dried at 80 °C, and then the cleaned powder was dewaxed with toluene–ethanol (2:1, v/v) in a Soxhlet for 6 h, and the dewaxed powder was dried at 60 °C for 24 h in vacuum drying oven. The RS had an approximate composition of 78.5% holocellulose, 48.4% cellulose, 8.5% lignin and 8.0% ash. Holocellulose in the RS was determined according to GB (China national standard) T2677.10-1995. The amount of cellulose in the RS was determined in terms of the acid detergent fiber (ADF) according to Van Soest method. Lignin in the samples was determined as Klason lignin according to GB T2677.8-1994, and ash was determined according to GB T2677.3-1993.

The RS was acetylated using acetic anhydride as the acylation agent, glacial acetic acid as solvent, and sulfuric acid as catalyst. Initially, glacial acetic acid (90 g) was added to the RS (10.0 g), and the mixture was stirred at 40 °C for 3 h to swelling RS. Then the system was cooled to 10 °C and was added pre-cooling mixture of acetic anhydride (30 g) and sulphuric acid (0.90 g) at about 5 °C and allowed to react for 12 h at 35 °C. After the reaction, the mixture was allowed to cool to room temperature, and solid–liquid separated through filtration. The solids obtained were washed with water until the pH became neutral to remove unreacted anhydride, sulphuric acid, acetic acid and by-product. After that, the acetylated rice straw powders were oven dried at 80 °C to constant weight (13.55 g).

2.3. WPG (weight percent gain) and PAC (percent acetyl content)

WPG, which describes the percent increase in the weight of acetylated RS compared to the weight of unmodified RS used for the reaction, was obtained to quantitatively determine the efficiency of acetylating RS. The acetylated RS was thoroughly washed as described earlier to remove chemicals and soluble impurities and later dried in an oven at 50 °C until constant weight was obtained. WPG was calculated according to following equation (1).

$$\mathrm{WPG\%} = \frac{W_{\mathrm{mod}} - W_{\mathrm{unmod}}}{W_{\mathrm{unmod}}} \times 100 \tag{1}$$

where W_{unmod} is the initial oven-dried weight of RS before chemical modification and W_{mod} is the oven-dried weight of the acetylated RS.

PAC is defined as the percentage of acetyl (CH_3CO–) groups. The acetyl content of RS acetates was calculated by the amount of sodium hydroxide which was used to neutralize the acetate acid which was obtained by thoroughly hydrolyzed acetylated rice straw powder (Radiman, 2008). Calculating equation was as follows:

$$\text{Acetyl content} \quad (\%) = [(D - C) + (A - B)]N \times \frac{4.305}{W} \tag{2}$$

where A was volume (mL) of NaOH used for sample titration; B was volume (mL) of NaOH used for blank titration; C was volume (mL) of HCl used for sample titration; D was volume (mL) of HCl used for blank titration; N is 0.5, the molar concentration of NaOH and HCl used for titration; 4.305 is related to the molecular weight of the acetyl group (CH_3CO), the unit conversion from liters to milliliters, and fraction to percentage; W was the sample weight in grams.

2.4. Characterization

2.4.1. Fourier transform infrared (FTIR)

FTIR spectra of the unmodified RS and acetylated RS were collected on an attenuated total reflectance ATR spectrophotometer (Nicolet iS10; Thermo-Fisher Scientific). The samples were placed on a germanium plate, and 16 scans were collected for each sample at a resolution of 4 cm^{-1}.

2.4.2. Solid-state ^{13}C NMR spectroscopy

Solid state ^{13}C NMR analysis of the original RS and acetylated RS (WPG = 35.5%) were performed with a 400 MHz NMR spectrometer (AVANCE III, Bruker company, Switzerland) at a ^{13}C frequency of 101 MHz, using the combined techniques of proton dipolar decoupling (DD), magic angle spinning, and cross polarization (CP/MAS ^{13}C SSNMR). ^{13}C and ^{1}H field strengths of 101 kHz corresponding to 90° pulses of 4 ms were used for the matched spin-lock cross-polarization transfer. The spinning speed was set at 3 kHz. The contact time was 1 ms, and the acquisition time was 10 ms. A typical number of 10,000 scans were acquired for each spectrum. Chemical shifts were referred to tetramethylsilane (TMS) as the internal standard.

2.4.3. Thermal analysis

Thermogravimetric analysis (TGA) was performed on the unmodified and acetylated RS using SDT Q600 (TA instruments) thermogravimetric analyzer. The sample was heated at 10 °C/min in a temperature range of 30–600 °C under nitrogen atmosphere. The DSC thermograms were measured using a TA instruments Q-200(TA Instruments) thermal analyzer. The samples were completely dried at 105 °C for 4 h before DSC determination. The measurement was conducted by heating the samples from 80 °C to 300 °C with a heating rate of 20 °C/min under nitrogen atmosphere.

2.4.4. Wide-angle X-ray diffraction (XRD)

XRD patterns of the unmodified RS and acetylated RS were obtained at room temperature using a D 8 Advance instrument (WAXD, Bruker AXS Company) with a scan speed of 4°/min for 2θ ranging from 3° to 60° at a voltage of 40 kV and current of 40 mA.

2.4.5. *Scanning electron microscope (SEM)*

SEM studies were made using SU-1510 (Hitachi). The samples were coated with a thin layer of gold by sputtering before the SEM imaging. An accelerating voltage of 5 kV with accounting time of 100 s was applied.

2.5. *Preparation and properties of acetylated rice straw film*

2.5.1. *Preparation of RS films*

Films were produced by the method of Hyppola (Hyppola, Husson, & Sundholm, 1996). 10 g acetylated RS powders were dissolved in 200 mL CH_2Cl_2 stirring for 3 h under 25 °C, the solution was subjected to centrifugation at 4000 rpm for 15 min at 15 °C to exclude remaining undissolved part about 20% (ash and a small amount polymer contained in RS). Thereafter, the diethyl phthalate was added, and the mixture was stirred for 30 min. Diethyl phthalate (DEP) (0%, 10 wt%, 20 wt%, 30 wt% and 40 wt% to soluble acetylated rice straw) was used as a plasticizer to improve the thermoplasticity of the acetylated RS. The RS acetate films were prepared by casting the solution onto the glass plate covered with polyethylene film at 25 °C.

2.5.2. *Properties of RS films*

Tensile strength of the films was measured on a universal strength tester (Zwicki-Line Testing Machine, BZ 2.5, Zwick Roll). Samples with a length of 150 mm and a width of 10 mm were cut with a sharp knife trying to avoid jagged edges. The measuring speed used was 50 mm/min and the initial gauge length was 100 mm. At least five samples were tested for each condition, and the average ± one standard deviation is reported.

3. Results and disscussion

3.1. *Determination of the optimum conditions for acetylation*

The acetylation of RS is a typical heterogeneous reaction. It depends on the one hand on the accessibility of the cellulose elements within the starting RS and on the other on the susceptibility of the individual cellulose crystallites toward acetylation. The rate and perfection of acetylation is therefore greatly influenced by the macro and micro morphology of the initial RS. The control of the acetylation time and temperature can be important aspect to the variable degree of acetylation and acetylated RS's physical structure. Hence, acetylation conditions of RS were optimized. Due to the chemical multicomponent and heterogeneity of RS, the degree of substitution for the acetylation process is hard to measure. Instead, the extent of acetylation was evaluated by determining the weight percent gain and the percent acetyl content.

3.1.1. *Effects of catalyst concentration*

Fig. 1 depicts the effect of changing the percent of catalyst (sulphuric acid) on WPG and PAC of RS at 60 °C for 2 h (Sassi & Chanzy, 1995). WPG was increased while catalyst concentration increased from 4% to 9%. But the further increase of catalyst concentration did not help increase the WPG; instead, it decreased the WPG significantly. The WPG decreased substantially to 22.8% when the percent of catalyst to the weight of RS was increased to 10%. The decrease of WPG was mainly due to the degradation of carbohydrates (cellulose and hemicellulose) under strong acid conditions and high temperatures. The degradation products can dissolve in the reaction solution and cannot be collected in the process of solid-liquid separated through filtration, hence the WPG decreased. However, the highest percent acetyl content of 29.8% was obtained at a catalyst concentration of 10%. The modified RS remaining after washing have molecules with higher degrees of acetylation and therefore, there was an increase in the percent acetyl content. The highest WPG obtained was about 34.8% with a catalyst concentration at 9% and could be used for the optimization of other acetylation parameters.

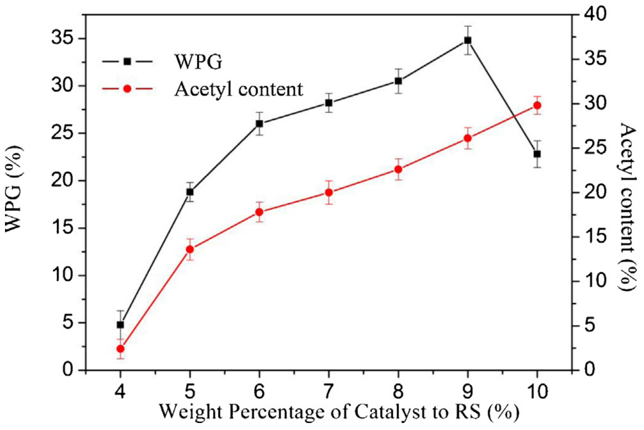

Fig. 1. Effects of catalyst to RS ratio (% w/w) on WPG and PAC. The acetylation was carried out at 60 °C for 2 h with acetic anhydride to RS ratio of 6:1 in glacial acetic acid to RS ratio of 6:1. Data points with same alphabets indicate that they are not statistically different from each other.

3.1.2. *Effects of acetic acid to RS ratio*

Fig. 2 showed that the WPG and PAC all increased significantly with the increase of the weight ratio of glacial acetic acid to RS from 6:1 to 9:1, from 34.5% to 46.2% and from 26.1% to 42.5%. The function of solvent glacial acetic acid is to make RS swelling, that is, to increase the accessibility of the RS hydroxyl groups to the acetylating agents, and dissolves the acetylated product to make the progress of the reaction. Hence, increasing of solvent glacial acetic acid can enhance the extent of RS swelling and increase the effect of the acetylation. At the same time increasing concentration glacial acetic acid can accelerate the degradation of carbohydrates (cellulose and hemicellulose) which resulted in decreasing of the WPG. Optimizing weight ratio of glacial acetic acid to RS is 9:1.

3.1.3. *Effects of acetic anhydride to RS ratio*

Fig. 3 shows the effect of weight ratio of acetic anhydride to RS on the WPG and PAC. The PAC increased significantly from 13.6% to 42.0% when the ratio of acetic anhydride was increased from 1:1 to 3:1, but when the ratio was above 3:1, the increase

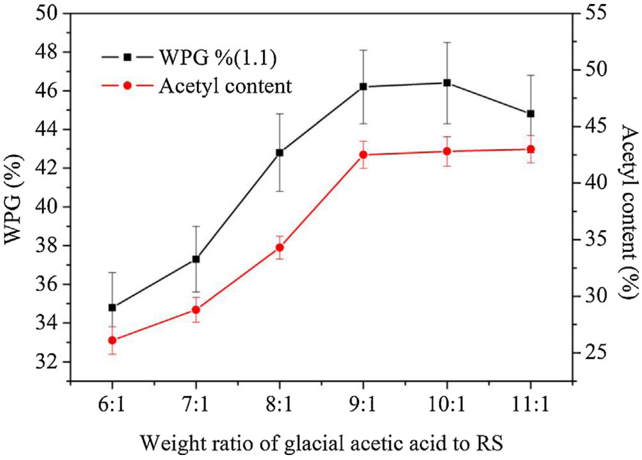

Fig. 2. Effects of weight ratio of glacial acetic acid to RS on WPG and PAC. The acetylation was carried out at 60 °C for 2 h with acetic anhydride to RS ratio of 6:1 and catalyst concentration of 9%. Data points with same alphabets indicate that they are not statistically different from each other.

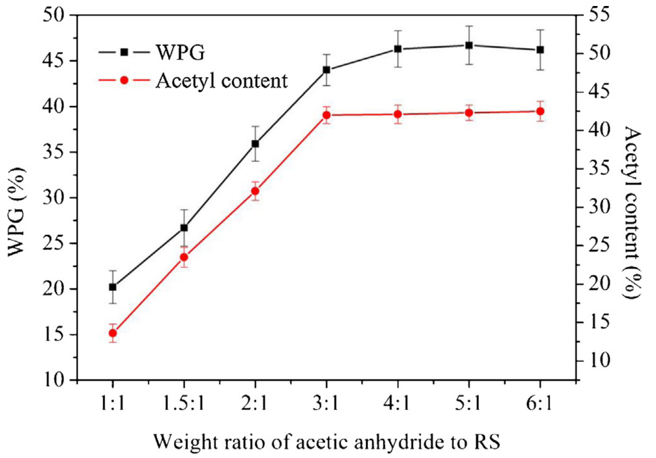

Fig. 3. Effects of weight ratio of acetic anhydride to RS on WPG and PAC. The acetylation was carried out at 60 °C for 2 h with glacial acetic acid to RS ratio of 9:1 and catalyst concentration of 9%. Data points with same alphabets indicate that they are not statistically different from each other.

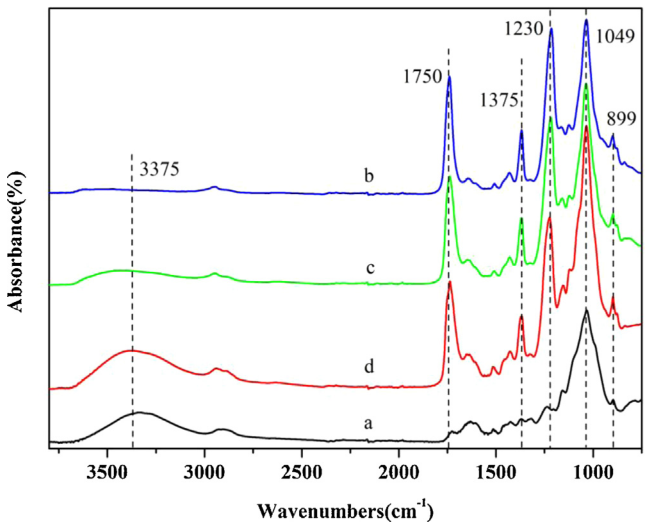

Fig. 4. FT-IR spectra of unmodified RS (a) and acetylated RS of WPG for 44.0% (b), 40.1% (c) and 35.5% (d).

of PAC became extremely small. There is a similar tendency for the effect of weight of acetic anhydride on WPG, the largest rate of increase was 77.7% when weight ratio of acetic anhydride to RS was from 1:1 to 2:1. Increasing the ratio of acetic anhydride to RS above 3:1 marginally increased the WPG to 46.3% and the rate of increase was only 5.2% when weight ratio of acetic anhydride to RS was from 3:1 to 4:1. Further increase of weight ratio of acetic anhydride to RS did not increase the WPG, and the WPG even slightly decreased when the ratio was 6:1. At a low ratio of acetic anhydride to RS, there is insufficient anhydride to react with the hydroxyl in RS, so that the level of acetylation and weight gain is low. The number of accessible hydroxyl groups in RS probably reached equilibrium at an acetic anhydride ratio of 3:1, thus there is no increase in WPG and PAC upon further increase in anhydride ratio higher than 3:1. So, an acetic anhydride ratio of 3:1 was chosen to optimize the other acetylation conditions under comprehensive consideration of the cost of reaction agents, WPG and PAC of acetylated RS. The acetyl content obtained was 42.0%, and the percent weight gain obtained was 44.0% at the condition.

3.1.4. *Effect of reaction time and temperature*

Effect of reaction time and temperature on WPG and PAC was listed in Table 1. When increasing reaction temperature from 35 to 70 °C under the same reaction time, WPG and PAC first increased and then decreased, but the decreasing amplitude of PAC was less. WPG of 44.0% and 43.3% and PAC of 42.0% and 42.5% were obtained when the reaction was carried out at 60 °C for 2 h and 3 h, respectively. Increasing reaction temperature increased the accessibility of RS to chemicals and thus also increased WPG and PAC. However, most of the available hydroxyl groups have been reacted within the amorphous regions of RS, and the reaction reaches equilibrium at 60 °C; therefore any further increase in the WPG was not observed. At high temperatures (>60 °C) and in the presence of acid, some of the carbohydrates in RS were degraded to form the soluble small molecule in water, which led to the decrease of WPG. In addition, the acetylated RS obtained at 60 °C contained some carbonizable substance due to strong oxidation and dehydration property of sulphuric acid resulted in oxidation of the carbohydrates in RS. While the product obtained at 35 °C contained unreacted RS. Therefore a temperature of 50 °C was preferable when reaction time was 2 h. As also seen from Table 1, WPG of 35.5% and PAC of 36.1% were obtained when the reaction was carried out at 35 °C for 12 h, and the quality of the acetylated RS was better than that of the same WPG obtained at high temperature from appearance and uniformity of the samples (also see Sections 3.2.3 and 3.2.4). The result is consistent with acetylation of cellulose, that is, the lower the reaction temperature, the better the quality of the product obtained, but long reaction time is needed (Gettrden, 1967). These can be explained as an erosion mechanism with the acetylation beginning at the exterior of the crystallites and progressing toward their center with prolonging of the reaction time (Glegg, Ingerick, Parmerter, Salzer, & Warburton, 1968; Sisson, 1938).

We can calculate the degree of substitution for the acetylation on the basis of PAC of the acetylated RS and the number of hydroxyl groups per anhydroglucose in cellulose, if the RS was assumed as total cellulose. DS of 42.0%, 39.5% and 36.1% of PAC were 2.8, 2.6 and 2.4 corresponding to 60 °C, 50 °C for 2 h of reaction and 35 °C for 12 h, respectively.

Table 1
Effects of reaction temperature and time on acetylation of RS.[a]

Time (h)	WPG (%) (Acetyl content (%))			
	70 °C	60 °C	50 °C	35 °C
0.5	24.5 ± 2.0 (20.4 ± 1.2)	24.8 ± 1.8 (19.6 ± 1.2)	24.5 ± 1.9 (18.1 ± 1.1)	
1	34.6 ± 1.6 (31.4 ± 1.1)	35.2 ± 1.6 (31.1 ± 1.1)	35.0 ± 1.7 (30.6 ± 1.2)	∼0
2	40.5 ± 1.7 (41.1 ± 1.2)	**44.0 ± 1.7 (42.0 ± 1.2)**	**40.1 ± 1.6 (39.5 ± 1.3)**	7.3 ± 1.8 (5.3 ± 1.1)
3	36.3 ± 1.8 (42.0 ± 1.3)	43.3 ± 1.8 (42.5 ± 1.3)	40.2 ± 1.8 (40.4 ± 1.2)	12.1 ± 1.7 (10.5 ± 1.0)
6			39.8 ± 1.5 (40.9 ± 1.1)	25.4 ± 1.5 (23.9 ± 1.2)
12				**35.5 ± 1.6 (36.1 ± 1.1)**

The bold numbers represent three products of characterization of FTIR, XRD, SEM, TG and DSC.

[a] The acetylation was carried out with an acetic anhydride to RS ratio of 3:1 and a catalyst concentration of 9% in a glacial acetic acid to RS ratio of 9:1.

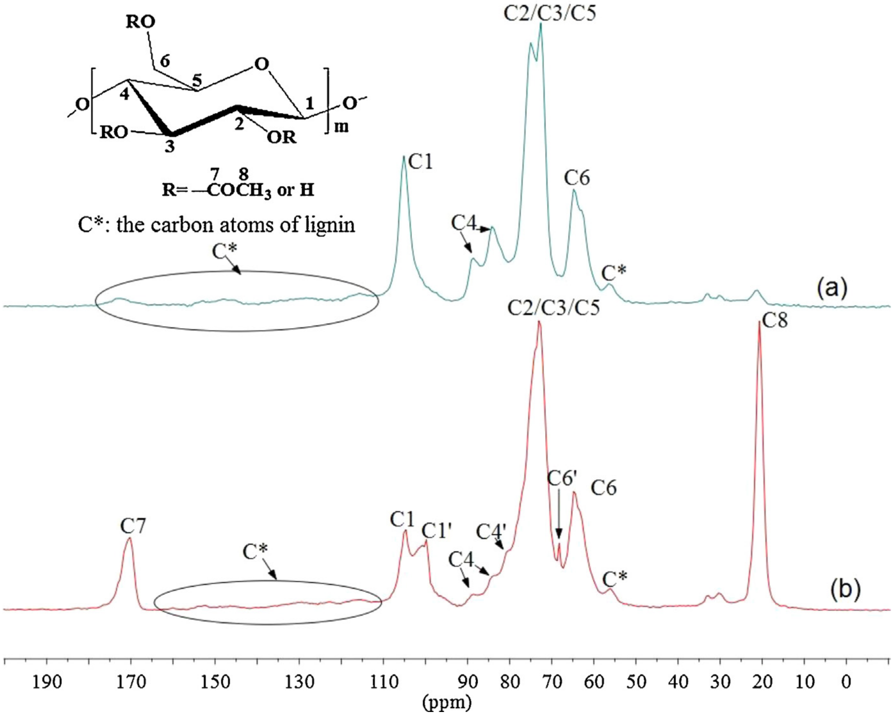

Fig. 5. CP/MAS ^{13}C SSNMR of the original RS (a) and acetylated RS of WPG for 35.5% (b).

3.2. *Characterization of structure and properties of acetylated RS*

3.2.1. *FT-IR spectra*

The FTIR spectra of unmodified RS (a) and acetylated RS of WPG for 44.0% (b), 40.1% (c) and 35.5% (d) are shown in Fig. 4. In comparison, a decrease in the intensity of the O—H absorption band at 3400 cm^{-1} was observed in acetylated RS, indicating that the hydroxyl group contents in RS were reduced after reaction and decreased with increase of WPG. The ester carbonyl absorption peak at 1750 cm^{-1}, carbon–hydrogen peak at 1381 cm^{-1} in acetyl group and 1230 cm^{-1} absorption (C—O) in O—C=O group verified ester bond have been brought in modified RS and their relative intensity is enhanced with increase of the WPG in Fig. 4. The absorption at 2915 cm^{-1} is associated with the symmetric C—H vibration of the CH_3. The presence of above characteristic peaks confirmed acetylation of RS. Using the peak at 1634 cm^{-1} as a reference, the ratio of intensity of the peaks at 1750 and 1634 cm^{-1} was $b > c > d$ (Ohkoshi, 2002). The result was consistent with WPG of RS acetates obtained. The small sharp band at 1634 and 899 cm^{-1} arises from α-glucosidic linkages between the sugar units in hemicelluloses and celluloses (Gupta, Madan, & Bansal, 1987). As expected there were no absorptions in 1840–1760 cm^{-1} and at 1700 cm^{-1}, indicating the absence of free acetic anhydride and the byproduct of acetic acid in the acetylated RS being tested (Hu, Reddy, Luo, et al., 2011).

3.2.2. *Solid-state ^{13}C NMR*

CP/MAS ^{13}C SSNMR of the original RS (a) and the modified RS of WPG for 35.5% (b) was characterized, and the structure with numbered carbons is shown in Fig. 5. Main components of the acetylated RS were lignin and acetylated cellulose. The relative intensities of lignin carbon signals are very low comparing with cellulose in Fig. 5, which is consistent with fact of RS composition. Methoxyl peak of lignin is at 56 ppm, the peaks at 148.30, 147.23, 115.12 and 111.90 ppm can be assigned to the aromatic ring carbons of lignin. Peaks assigned to the carbons in the cellulose backbone at 105.19 (C1), 88.73 and 84.11 (C4), 74.97 and 72.66 (C2, C3, C5) and 64.62, 62.70 (C6), respectively, were evidently detected (Horii, Hirai, & Kitamaru, 1987) in curve a. Among them, the signal of C4 at 88.73 ppm is assigned to crystal interiors, and the signal of C4 at 84.11 ppm to crystal surfaces (Newman & Hemmingson, 1994). The introduction of acetyl groups onto cellulose's molecular chains is confirmed by appearance of the peaks at about 170 and 20.71 ppm in curve b (Witter et al., 2006), which is ascribed to the carbonyl carbons (C7) and methyl (C8) in acetyl. The changes of peaks of C1, C4 and C6 further prove that acetyl has been introduced into RS. The crystalline and disordered components were also detected respectively as upfield and downfield lines for the C4 or C6 carbon (Yamamoto, Horii, & Hirai, 2006).

A peak (99.78 ppm) designated by C1′ is ascribed to C1 carbons adjacent to C2 carbons bearing a substituted hydroxyl group in curve b. As shown in Fig. 5, there are two parts in the peaks of C4 ranging from 84 ppm to 90 ppm (curve a). The signal of C4 at 88.73 ppm is assigned to crystal interiors, the signal of C4 at 84.11 ppm to crystal surfaces (Newman & Hemmingson, 1994). The peaks of C4 were changed in two ways. Firstly, the relative intensities of C4 peaks at 89 and 84 ppm decrease in ^{13}C NMR of modified RS. Secondly, there is a shoulder peak around 80 ppm (designated by C4′) which overlaps with the signals of C2, C3, and C5 carbons. The signal is ascribed to C4 carbons adjacent to C3 carbons bearing a substituted hydroxyl group and can be attributed to the C4 atoms in amorphous regions that are symbolized as N.C. (N.C. means non-crystal) (Newman & Hemmingson, 1994). As can be observed from Fig. 5 (curve b), the intensities of the C6 (64.64 ppm) resonance line decreases, and there is a new peak shifting to downfield (68.22 ppm). Such a downfield shift of C6 carbon signal (designated by C6′) is consistent with the fact that the esterification of hydroxyl groups of cello-oligosaccharides and cellulose causes a strong deshielding; the resonance of the carbon attached to the esterified hydroxyl group is shifted downfield compared to that of the corresponding carbon bearing an unsubstituted hydroxyl group. The modifications and decreasing of the NMR spectra lines, particularly the lines related to C4 and C6, are an indication of chemical modification and changes in crystalline and amorphous

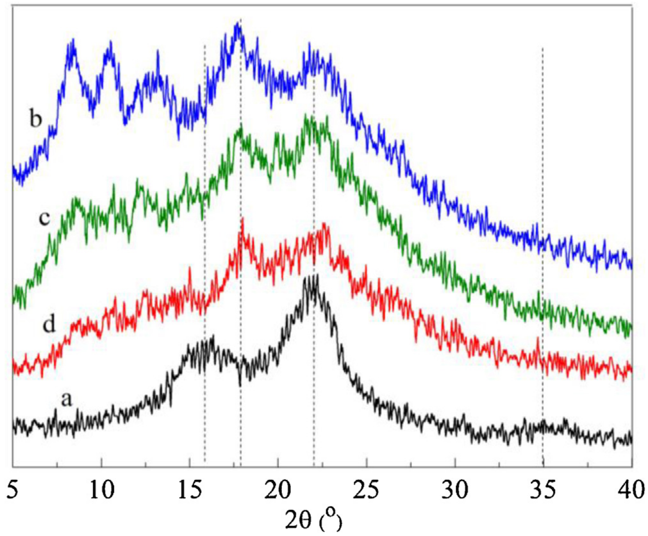

Fig. 6. XRD curves of untreated RS (a) and acetylated RS for WPG 44.0% (b), 40.1% (c) and 35.5% (d).

components in the samples. The chances in these components are observed due to microfibrils modifications reached to an acetylated product less crystalline than unmodified cellulose (Barud et al., 2008).

3.2.3. *X-ray diffraction study*

The morphological changes of polymers can be evaluated via XRD curves. Fig. 6 is the XRD curve of raw RS and acetylated RS. Diffraction peaks localized at 2θ of 14.8–16.4°, 22.1° and 35.6° in the spectrum of raw RS are assigned to crystal planes $(1\,1\,0)$, $(1\,\bar{1}\,0)$, $(2\,0\,0)$ and $(4\,0\,0)$ of cellulose (cellulose I) in raw RS, respectively, and the diffraction peak at 2θ of 18.5° is due to the amorphous regions in cellulose of raw RS (Jiang, Gu, Tian, Li, & Huang, 2012; Wada, Heux, & Sugiyama, 2004). The relative height of the diffraction peak of the amorphous region (18.5°) increases, while the relative height of the diffractions of the four crystal planes obviously decreases, as the WPG of acetylated RS increases from 0% to 44.0%, which is shown in Fig. 6. From Fig. 6, the acetylated RS has a low degree of crystallinity in relation to the original RS, which means the number of hydrogen bonds is decreased due to the substitution of the hydroxyl groups by acetyl groups that have a larger volume and accord with the result of CP/MAS ^{13}C SSNMR. From the XRD curve (b, c and d), the characteristic diffraction peaks of cellulose triacetate located between 5° and 20° are observed and increase with the increase of WPG. On these grounds we speculated that the content of low DS (degree of substitution) cellulose acetate was the largest in acetylated RS of WPG for 35.5% and PAC for 36.1%. This is consistent with the calculating result of the degree of substitution (DS = 2.4) for the acetylation on the basis of PAC of the acetylated RS. Referring to the fact that cellulose diacetate (DS= 2.4–2.5) exhibits the best thermoplasticity, and cellulose triacetate cannot be processed as a thermoplastic because its softening temperature is too close to its decomposition temperature (Vaca-Garcia, Gozzelino, Glasser, & Borredon, 2003), it can be inferred that the acetylated RS obtained at 35 °C for 12 h has best thermoplasticity in three acetylated RS.

3.2.4. *The surface morphology of acetylated RS*

Fig. 7 shows the surface microstructures of modified and raw RS. The photographs reveal that before the acetylation (a), alternate smooth and irregular surfaces can be observed on the epidermis of rice straw. It is suggested that smooth surfaces correspond to small vascular bundles embedded in the subepidermal sclerenchyma. Irregular surfaces had two types of excrescences, and presented trichomes (Pan, Zhou, Zhou, & Lian, 2010). Based on the SEM pictures (b, c and d), it was clear that all cell of surface of RS have been completely destroyed, the fibrillar structures obviously

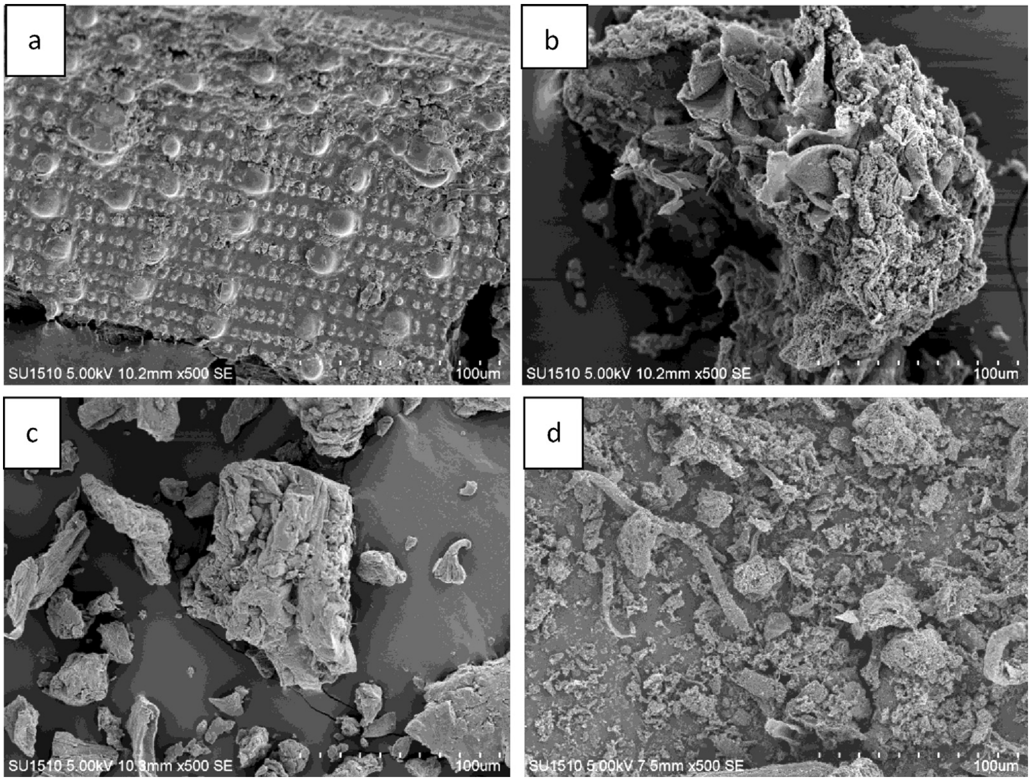

Fig. 7. SEM images of raw RS (a) or acetylated RS for WPG 44.0% (b), 40.1% (c) and 35.5% (d), respectively.

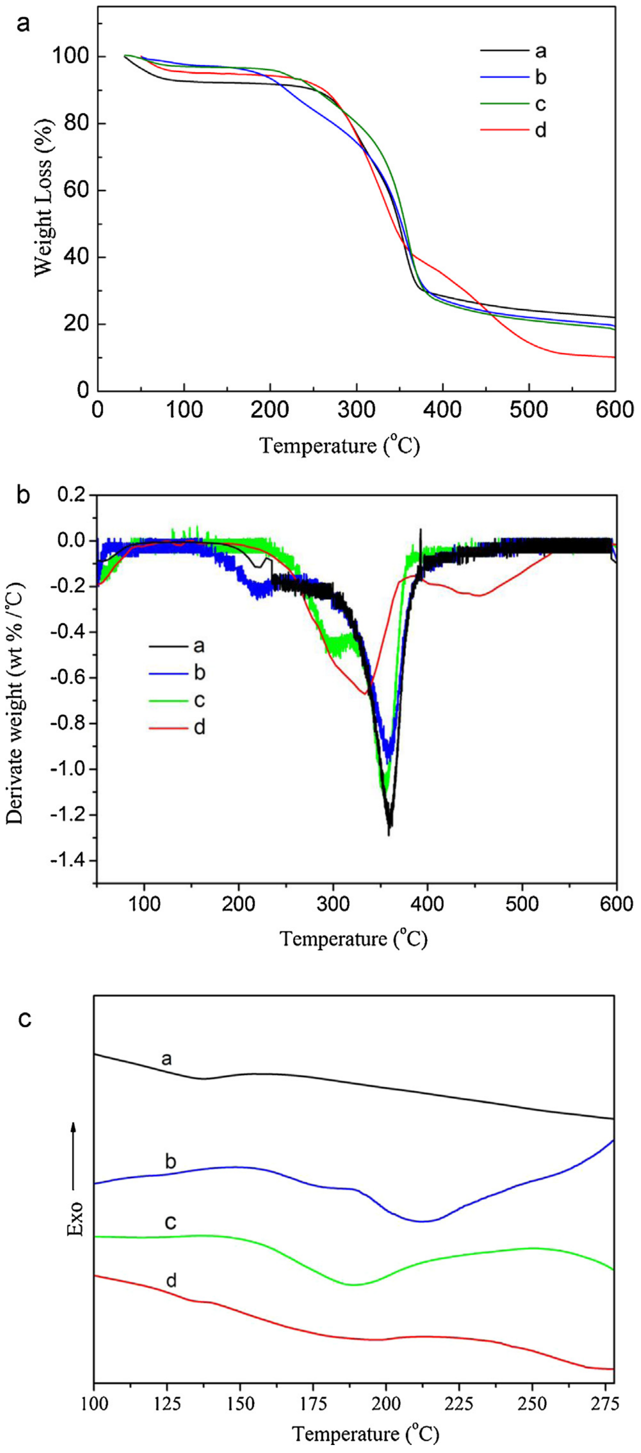

Fig. 8. TGA (A), DTG (B) and DSC (C) plots for raw RS (a) and acetylated RS of WPG 44.0% (b), 40.1% (c) and 35.5% (d).

disappear from the surface of RS. The SEM pictures (b, c and d) also showed that the product obtained under low temperature reaction had best uniformity. This result is consistent with the result of XRD and indicates that acetyl groups have successfully bonded to RS. In comparison, it was clearly observed that uniformity of the acetylated RS decreased with increase of reaction temperature as showed in Fig. 7. The reason may be that some compounds on the surface, which are resulted by the high rate of reaction at the high temperature, inhibit the permeation of the reaction agent into the interior of RS.

Table 2
Tensile properties of acetylated rice straw films.

DEP containing[a] (%)	Tensile strength (MPa)[b]		Breaking elongation (%)[b]	
	RS	Acetylated RS	RS	Acetylated RS
0	0	1.3 ± 0.26	0	0.85 ± 0.02
10	0	1.26 ± 0.20	0	0.98 ± 0.02
20	0	**1.11** ± **0.32**	0	**1.40** ± **0.03**
30	0	0.90 ± 0.35	0	1.81 ± 0.05
40	0	0.78 ± 0.23	0	2.73 ± 0.05

The bold numbers represent higher tensile strength and breaking elongation.

[a] Acetylated RS films with different amount plasticizer DEP (%)(w/w to acetylated RS powder).

[b] The film was cut into strips (150 mm × 10 mm) and stored at 23 ± 2 °C in desiccators (60% relative humidity) for at least 48 h prior to testing. Five samples were tested for each condition and the average with ± one standard deviation was reported.

3.2.5. *Thermal analysis*

Fig. 8 is the TGA (A), DTG (B) and DSC(C) curves of RS and acetylated RS, in nitrogen atmosphere. From this thermo-gram, both of modified and unmodified RS showed a lightly initial decrease of weight below 100 °C due to loss of moisture. But the weight loss of unmodified RS and acetylated RS obtained at low temperature reaction was more obvious due to its high content of hydroxyl group. The phenomenon indicates that the acetylated RS retained un-substituted hydroxyl at low temperature reaction, which coincides with low WPG of product. In Fig. 8(B), it may be observed that for RS there is only one degradation at 360 °C, while for modified RS (WPG: 44.0%, 40.1% and 35.5%) there are two; they are at 219 and 358 °C, 299 and 355 °C, 334 and 453 °C, respectively. This indicated that the acetylated samples were more thermal unstable than the unmodified RS, whereas RS acetates (WPG = 35.5%) formed at low temperature was thermally the most stable polymer among RS acetates and even was more stable than RS because the first decomposing temperature was very close to the unmodified RS and the second decomposing temperature was over unmodified RS. This lower thermal stability of the modified RS was undoubtedly due to the disintegration of intramolecular interactions such as hydrogen bonds, because the strength of the interactions between O-acetyl and OH groups or between OH groups is stronger than that between O-acetyl groups. Besides, at 50% weight loss, the decomposition temperatures (352, 356 and 346 °C) of the three acetylated RS samples were higher than or close to the native RS (349 °C). This indicated that the decomposition rate of acetylated sample was slow comparing with raw RS, probably due to the fact that those easily degradable small molecules have been removed by solution in solvents in the acetylation and aftertreatment process. In addition, for the acetylated RS samples, the residue left at 600 °C (10–19%) was less than that of the unreacted material (22%), which suggested that the acetylated RS was lost with volatile products and did not contribute to char formation.

DSC thermograms of raw RS (a) and the acetylated RS (b, c and d) are shown in Fig. 8 (C). It could be observed that there was no endothermic peak for unmodified RS (a), indicating its poor thermoplasticicty. The acetylated RS exhibited endothermic peaks at 175 and 210 °C for b, 188 °C for c, and 135 and 186 °C for d, respectively, which can be attributed to the melting of crystalline of acetylated RS. The presence of the melting peak demonstrates that the thermoplasticity of the RS was improved due to the acetylating. This shows that melting species have taken place at a WPG of 35.5% and may occur at a lower temperature. The data also show that no lower melting species develops as a result of very high WPGs. The phenomenon is consistent with the result of DS calculating from PAC of acetylated RS.

From the above, the acetylated RS of WPG of 35.5% has better thermoplasticity and can be used to explore its thermoplastic application.

Fig. 9. Digital photo of the acetylated RS (WPG = 35.5%) film (A) and RS (B) with 20% DEP, respectively, and SEM (C) of the acetylated RS (WPG = 35.5%) film with 20% DEP.

3.3. Thermoplastic application of acetylated RS

The acetylated RS (WPG = 35.5%) were cast to form the films under present of DEP (0, 20%, 30%, and 40%) as a plasticizer due to its good compatibility to acetate cellulose. The tensile properties of the films developed from acetylated RS were showed in Table 2. It could be observed that the tensile strength decreased but breaking elongation increased with increasing amount of DEP. This is because that plasticizer can reduce the intermolecular forces, so the film was softened. The film was very brittle without plasticizer, which is the same as cellulose acetate. Acetylated RS film with 20% DEP has relatively higher tensile strength (1.11 MPa) and breaking elongation (1.40%). Fig. 9 shows the digital and SEM image of the acetylated RS film under present of 20% DEP. The acetylated RS formed a transparent film in Fig. 9(A), in which the scales of the ruler under the film can be seen, and the acetylated RS film has a smooth surface as showed in Fig. 9(C). The above results indicate that the acetylated RS has better thermoplasticity, comparing with the raw RS that can not dissolve in any solvent and no film can be made (see Fig. 9(B)). Therefore, the acetylating modification is an effective way to improve the thermoplastivity of raw RS.

4. Conclusions

The thermoplastic acetylated RS was prepared through acetylation of RS with acetic anhydride (weight ratio = 1:3) using 9% sulfuric acid as catalyst in glacial acetic acid at 35 °C. The acetylated RS could be casted to form transparent films under addition or no plasticizer diethyl phthalate (DEP). Acetylation can be a simple procedure to develop inexpensive and biodegradable thermoplastic products from rice straw.

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