ACETYLATION MODIFICATION OF RICE STRAW FIBER AND ITS THERMAL PROPERTIES

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The esterification of rice straw fiber with acetic anhydride, using sulphuric acid as catalyst, under mild conditions in glacial acetic acid, has been investigated. Acetylation conditions, such as dosage of chemicals and catalyst, and time and temperature of acetylation, were optimized. The preferred reaction parameters of acetylation reaction are described as follows: weight ratio of rice straw and acetic anhydride was 1:3, using sulphuric acid as catalyst in glacial acetic acid at 50 °C for 2 h, the dosage of catalyst and solvent was, respectively, 9.0% and 9 times to rice straw powder, in which the acetylation weight percent gain of 40.1% was obtained. The characterization of acetylated rice straw was performed by Fourier transform infrared (FTIR), Nuclear Magnetic Resonance (^{1}H NMR), X-ray diffractometer (XRD), Scanning electron microscope (SEM). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed a slow decomposition rate, compared to raw rice straw, and an endothermic peak at 188 °C. These results demonstrated that the thermal properties of rice straw can be improved by acetylation.

Keywords: acetylation, modification, rice straw, thermal properties

INTRODUCTION

Rice straws (RS) are investable agricultural residues from annual plants and available in large quantities, but have limited industrial applications. Currently, huge amounts of RS are still not used as industrial raw materials on a significant scale, while most of the RS are discarded as waste or burned on the spot. This not only leads to the great loss of a potentially valuable polymer, but also causes environmental anxiety. So, the utilization of agricultural residues as a renewable natural resource becomes a focus of public concern.

Efforts have been made to utilize RS as a renewable resource of energy and production of a diversity of chemicals, including ethanol production, activated carbon, and ion exchangers,[1-4] and as reinforcement for composites.[5,6] Compared with glass fibers or carbon fibers used conventionally, plant fibers have many advantages, like their renewability, environmental friendliness, low cost, light weight and high specific mechanical performance. In addition, through the reaction of their active -OH groups, the chemical modification of natural polymers for thermoplasticization has attracted more and more research interest in the last few decades.[7-9] The benzylation of wood,[10] the acylation of starch and wood,[11-14,15, 16] and the grafting of cellulose[17] or cellulose acetate with aliphatic polyesters[18-24] are typical examples of such modifications. Among all modifications, acetylation is the most common approach to make biopolymers thermoplastic; it is relatively inexpensive and eco-friendly. Cellulose acetates are produced on an industrial scale and used for fibers, films and other applications.[25,26] The esterification of wood makes a totally thermoplastic material. The thermoplasticized woods exhibit good melting properties and are readily moldable into bulk materials or extruded into films and sheets.[11,16,27,28] Acetylation of RS is highly considered in current research of RS modification in order to get

thermoplastic materials. Mohammadi-Rovshandeh reported acetylation of differently pretreated rice straw (extracted or prehydrolyzed). The thermal stability and thermoplasticity of the products was higher than those of rice straw. However, the weight percent gain (WPG) of acetylated RS is smaller, and the factors of influence on acetylation and thermoplastic application have not been discussed.[29-31] The variation of the thermoplasticity of the modified RS, such as WPG and the relationship of reaction conditions and properties, is highly important and should be taken into account.

In view of this, we extensively investigated the acetylation of RS in order to make a thermoplastic material. RS was acetylated using acidic conditions and the effect of acetylation conditions on WPG (weight percent gain) was studied. The structure of the RS acetates obtained was identified. The thermal properties of the RS acetates were also evaluated.

EXPERIMENTAL
Materials
The rice straw was obtained from a local farm (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.

Measurements
FTIR spectra 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}. ^{1}H NMR spectra were recorded using a Varian Mercury 400 MHz spectrometer with CDCl$_3$ as solvent. The polymer decomposition temperatures (Td) were measured using an SDT Q600 (TA Instruments) thermogravimetric analyzer. The sample was heated at 10 °C/min in a temperature range of 30 °C to 600 °C under nitrogen atmosphere. The DSC thermograms were measured using a 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. Wide-angle X-ray diffraction patterns 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. Scanning electron microscope studies were carried out 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.

WPG (weight percent gain)
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 equation (1):

$$WPG\% = ((W_{mod} - W_{unmod}) / W_{unmod}) \times 100 \qquad (1)$$

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.

Pretreatment of rice straw
The RS surface is covered with a cuticle wax silica polymerized layer, which is smooth and flat and functions as a barrier for chemicals.[32] Hence, 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 a vacuum drying oven before usage. The RS had an approximate composition of 78.5% holocellulose, 48.4% cellulose, 8.5% lignin and 8.0% ash.

Acetylation of rice straw
The RS was acetylated using acetic anhydride as acylation agent, glacial acetic acid as solvent, and sulfuric acid as catalyst. Initially, glacial acetic acid (180 g) was added to the RS (20 g), and the mixture was stirred at 40 °C for 3 h until RS swelled. Then the system was cooled to 10 °C and was added a pre-cooling mixture of acetic anhydride (60 g) and sulphuric acid (1.8 g) at about 5 °C and allowed to react for 2 h at 50 °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 distilled water until the pH became neutral to remove the unreacted anhydride, sulphuric acid and acetic acid by-product. After that, the acetylated rice straw powders were oven-dried at 80 °C to constant weight. The WPG was 40.1%.

RESULTS AND DISCUSSION
The chemical modification of RS is represented in the reaction scheme 1, where RS-OH represents the hydroxyl groups present on the polymeric components of RS. Since cellulose constitutes the majority of RS, and lignin contains little hydroxyl,

acetic anhydride has to react mainly with the hydroxyl groups of cellulose. Due to the chemical 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.

The higher the weight gain of acetylated RS, the higher the degree of substitution.

$$Rice\ Straw—OH + (CH_3CO)_2O \xrightarrow{H^+} Rice\ Straw—OOCCH_3 + CH_3COOH$$
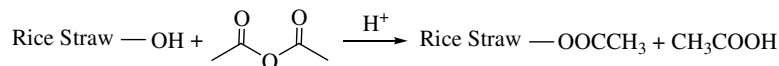
Scheme 1: Acetylation of RS

Optimization of modification conditions
Effects of catalyst concentration on WPG

Fig. 1 depicts the effect of changing the % of catalyst (sulphuric acid) on WPG of RS. WPG was increased, while catalyst concentration increased from 4% to 9%. But further increase of catalyst concentration did not help increase WPG; instead, it decreased WPG significantly. WPG decreased substantially to 22.8%, when the amount of catalyst used was added to 10% of the weight of RS. The decrease in 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 solid-liquid separation processes through filtration, and hence WPG decreased. The highest WPG obtained was about 34.8% with a catalyst concentration of 9% and could be used for the optimization of other acetylation parameters.

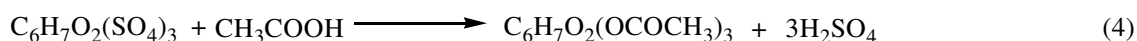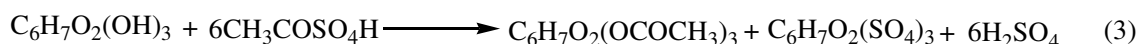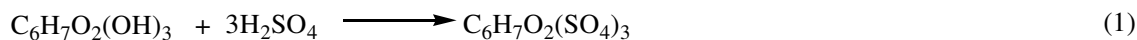### Effects of reaction temperature on WPG

Fig. 2 shows the effects of reaction temperature on WPG of the acetylated RS. When reaction temperature was increased from 35 to 90 °C, WPG increased first and then decreased. The highest WPG of 34.8% was obtained when the reaction was carried out at 60 °C. As also seen from Fig. 2, increasing reaction temperature from 35 to 50 °C increased WPG by 15.1%, and the further increase in reaction temperature from 50 to 60 °C increased WPG by only 4.2%. When reaction temperature got over 60 °C, WPG began to decrease quickly, even negative growth appeared at 90 °C. Growing reaction temperature increased the accessibility of RS fiber to chemicals and also increased WPG. But when temperature was higher than 60 °C and in the presence of acid, some of the carbohydrates in RS were degraded to form soluble small molecules in water and therefore WPG decreased. The acetylated RS obtained at 60 °C contained some carbonizable substance due to the strong oxidation and the dehydration property of sulphuric acid resulted in the oxidation of the carbohydrates in RS. The temperature of 50 °C was the best and was chosen to optimize the other acetylation conditions under comprehensive consideration of the quality and WPG of acetylated RS.

Effects of anhydride and solvent to RS ratio on WPG

The mechanism of cellulose acetylation with acetic anhydride in the acetic acid medium is mainly based on the formation of cellulose sulphate, resulting from the reaction of cellulose with sulphuric acid. The cellulose is transesterifled from sulphate to acetate through a sulphoacetate intermediate stage.[33]

This mechanism of acetylation is presented in the next equations:

$$C_6H_7O_2(OH)_3 + 3H_2SO_4 \longrightarrow C_6H_7O_2(SO_4)_3 \qquad (1)$$

$$(CH_3CO)_2O + H_2SO_4 \rightleftharpoons CH_3COSO_4H + CH_3COOH \qquad (2)$$

$$C_6H_7O_2(OH)_3 + 6CH_3COSO_4H \longrightarrow C_6H_7O_2(OCOCH_3)_3 + C_6H_7O_2(SO_4)_3 + 6H_2SO_4 \qquad (3)$$

$$C_6H_7O_2(SO_4)_3 + CH_3COOH \longrightarrow C_6H_7O_2(OCOCH_3)_3 + 3H_2SO_4 \qquad (4)$$
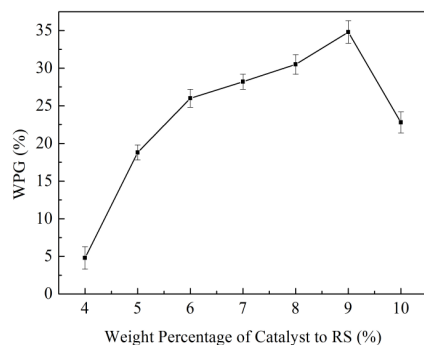
Figure 1: Effect of catalyst to RS ratio (% w/w) on WPG (acetylation conditions: 60 °C, 2 h, acetic anhydride to RS ratio 6:1, glacial acetic acid to RS ratio 6:1
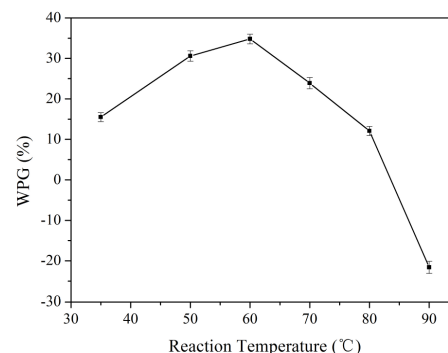

Figure 2: Effect of reaction temperature on WPG (acetylation conditions: 2 h, acetic anhydride to RS ratio 6:1, catalyst concentration 9%, glacial acetic acid to RS ratio 6:1

Glacial acetic acid is not only a medium of the reaction and a solvent that is capable of dissolving the cellulose acetate generated in the reaction, but also is involved in the acetylation of cellulose from the above mechanism. Therefore, the synergistic effect of glacial acetic acid and acetic anhydride on the WPG was discussed. Fig. 3 shows the effect of weight ratio of acetic anhydride and glacial acetic acid to RS on the WPG. Increasing the weight ratio of acetic anhydride to RS from 2:1 to 3:1 increased the WPG significantly. The largest rate of increase was 28.3%, when the weight ratio of glacial acetic acid to RS was 8:1; the lowest rate was 18.8%, when the weight ratio of glacial acetic acid to RS was 6:1. The further increase of the weight ratio of acetic anhydride to RS from 3:1 to 4:1 made the increase in the WPG slow, and when the weight ratio of acetic anhydride was above 3:1, the WPG tended to be constant and was about 30.6%, 34.1%,

37.2%, 42.6% and 42.7% respectively, corresponding to the weight ratio of glacial acetic acid to RS of 6:1, 7:1, 8:1, 9:1 and 10:1. The number of accessible hydroxyl groups probably reached equilibrium at an anhydride ratio of 3:1. Fig. 3 also shows that the WPG increased with increasing the weight ratio of glacial acetic acid to RS and reached the highest by 42.7% at the acetic acid ratio of 10:1, but the WPG remained the same at the glacial acetic acid ratios of 9:1 and 10:1 (42.6% and 42.7%, respectively). The function of solvent glacial acetic acid is to make RS swell, that is to increase the accessibility of the RS hydroxyl groups to the acetylating agents, and to dissolve the acetylated product to allow the progress of the reaction.
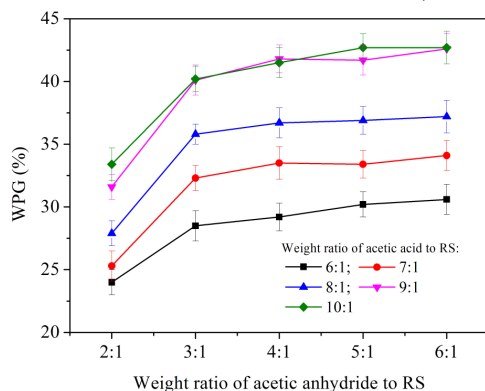

Figure 3: Effect of weight ratio of acetic anhydride and acetic acid to RS on the WPG (acetylation conditions: 2 h, catalyst concentration of 9%, at 50 °C
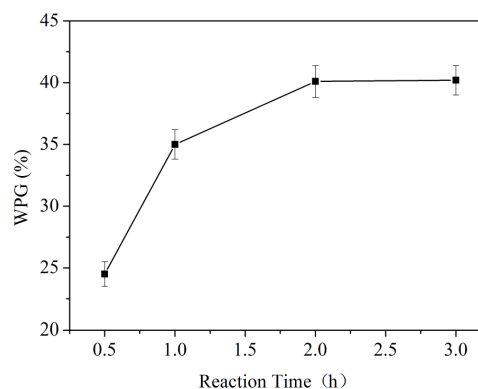

Figure 4: Influence of reaction time on WPG (acetylation conditions: acetic anhydride to RS ratio 6:1, catalyst concentration of 9%, glacial acetic acid to RS ratio 6:1, at 50 °C
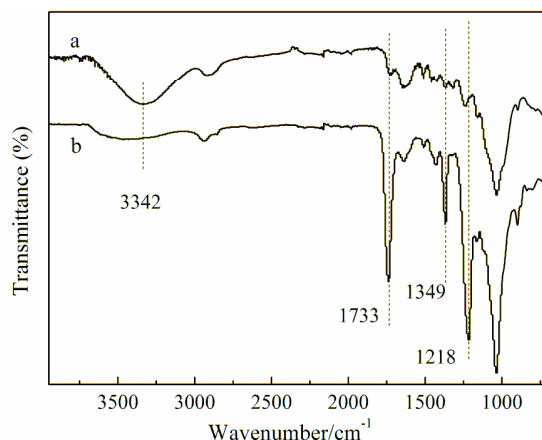
Figure 5: FT-IR spectra of unmodified RS (a) and acetylated RS (b)

Hence, increasing the amount of solvent glacial acetic acid can enhance the extent of RS swelling and increase the effect of the acetylation. It is preferable to use an acetic anhydride ratio of 3:1 and a glacial acetic acid ratio of 9:1, in view of the cost of reaction agents and the effect of acetylation.

Effect of reaction time on WPG

Fig. 4 depicts the changes in WPG of the acetylated RS with increasing reaction time. Increasing reaction time from 0.5 to 1 h and from 1 to 2 h increased the WPG by 10.5% and 5.1%, respectively, as seen from Fig. 4. A further increase in reaction time above 2 h did not change the WPG. The initial rate of acetylation was fast due to the high concentration of reactants. More and more carbohydrates were acetylated with prolonging the reaction time and therefore the WPG increased. Then the reaction rate in the late phase declined because of the decrease in the concentration of reactants. The acetylation reaction reached equilibrium at 2 h and therefore there was no increase in the WPG when the reaction time was more than 2 h under the reaction conditions studied.

Confirming of acetylated RS
FT-IR spectra

The FTIR spectra of unmodified RS (a) and acetylated RS (b) are shown in Fig. 5. In comparison, a decrease in the intensity of the O-H absorption band at 3342 cm^{-1} was observed, indicating that the hydroxyl group contents in RS were reduced after reaction, and the enhanced carbonyl absorption peak at 1733 cm^{-1}, the

carbon–hydrogen peak at 1349 cm^{-1} in acetyl group and absorption peak of C-O at 1218 cm^{-1} in O-C=O group verified that the ester bonds had been obtained in modified RS (Fig. 5b). The presence of a shoulder at 1733 cm^{-1} is due to the carbonyl stretching absorption of ester and carboxyl groups, which are the most abundant in straw hemicelluloses[34] and xylan[35] in spectrum (a). As expected, there was no absorption at 1840-1760 cm^{-1} and 1700 cm^{-1}, which indicated the absence of free acetic anhydride and the by-product of acetic acid in the acetylated RS being tested.[30] The absorption at 2915 cm^{-1} is associated with the symmetric C-H vibration. A sharp and strong band at 1049 cm^{-1} is attributed to C-O stretching in cellulose, hemicelluloses, and lignin or C-O-C, two absorbance peaks at 1510 cm^{-1} and 1454 cm^{-1} correspond to the aromatic skeletal vibrations and ring breathing with C-O. A small sharp band at 900 cm^{-1} arises from α-glucosidic linkages between the sugar units in hemicelluloses and celluloses.[36]

^{1}H NMR spectra of modified rice straw (soluble product)

^{1}H NMR spectroscopy was performed on the soluble products in methylene dichloride obtained after acetylation with CDCl$_3$ as solvent. The ^{1}H NMR spectrum of the soluble product with a WPG of 40.1% is shown in Fig. 6. The weak signals of chemical shift in the range of 6.2-7.5 ppm are due to aromatic protons in lignin. The signals of a chemical shift in the range of 3.5-5.1 ppm represent the peak positions of hydroxyl protons and methylene protons in the glucose anhydride ring, and the methyl protons of acetyl groups display a

resonance signal in the range of 1.8-2.3 ppm. The position of the peaks suggests that the soluble product contains large amounts of carbohydrate esters, indicating successful acetylation, as reported for cellulose acetates and other carbohydrate derivatives. Assuming the acetylated product as acetylated cellulose derivatives, a relative degree of substitution (DS) of hydroxyl groups attached to ring carbon of about 2.68 can be estimated from the ratio of the relative peak intensities between the protons in glucose anhydride ring to the methyl protons of acetyl groups.

X-ray diffraction study

The morphological changes of polymers can be evaluated via XRD curves. Fig 7 represents the XRD curve of raw RS (a) and acetylated RS (b).
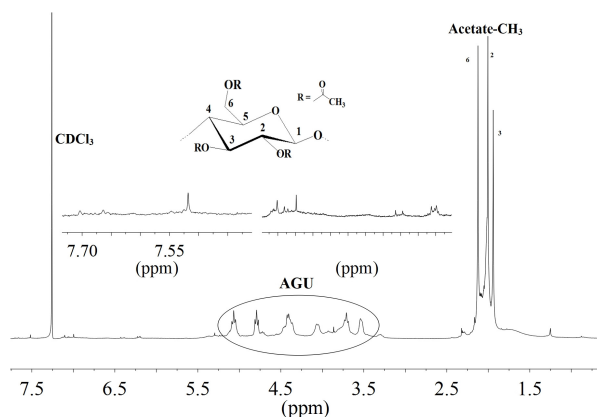
The XRD of the heterogeneous acetylation reaction of cellulose studied by Doyle and Pethrick indicated crystallinity changes during acetylation, when using heterogeneous conditions.[37] The peaks localized at 14.8-16.4^{o}, 22.5^{o} and 35.6^{o} are assigned to reflections of crystalline planes of cellulose (cellulose I) in RS. The peak at 14.8-16.4^{o} has $100_{1\alpha}$, $1\bar{1}0_{1\beta}$, $110_{1\beta}$ and $010_{1\alpha}$; the peak at 22.1^{o} has $110_{1\alpha}$ and $200_{1\beta}$; the peak at 35.6^{o} has 400 in Fig. 7(a).[38] The diffraction peak at 2θ of 18.5^{o} is due to the amorphous regions in the cellulose of raw RS.[39,40] As may be noted from the XRD curve (b), the relative height of the diffraction peak of the amorphous region (18.5^{o}) increases, while the relative height of the diffractions of the four crystal planes obviously decreases and a main broad peak located at around 8° is observed in acetylated RS.

Figure 6: ^{1}H-NMR of acetylated RS corresponding to WPG of 40.1%
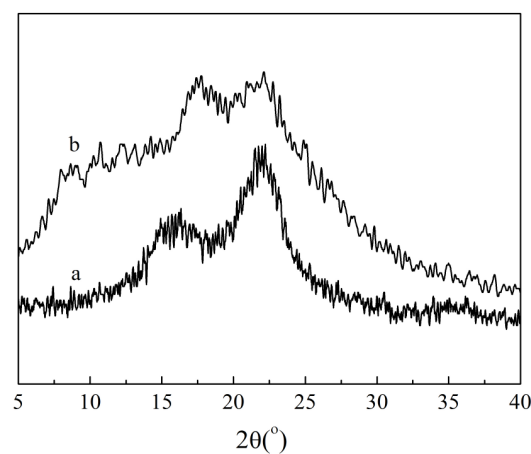

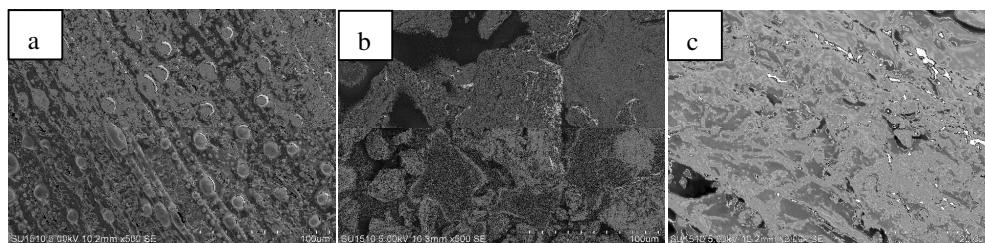Figure 7: XRD curves of untreated RS (a) and acetylated RS for WPG of 40.1% (b)

Figure 8: SEM images of raw RS (a) or acetylated RS for WPG of 40.1% (500 SE (b) and 2000 SE (c))

The peak located at approximately 8° is cited as the principal characteristic of semicrystalline acetylated derivative cellulose.[41] The position of this peak indicates the generation of a disorder when the rice straw is acetylated. The disorder is caused by the projection of the substituting groups (acetyl groups) along the axes and is associated

with an increase in the interfibrillar distance, as well as with the breakdown of microfibrillar structures. The products' degree of crystallinity is much lower than that of original RS, from 38.7% to 29.6%, obtained by the calculation of the integrated intensity of the two types of substance using Crystallinity Calculation Software, which means

the hydrogen bonding was weakened as hydrogen groups were substituted by acetyl groups, which have a larger volume. In addition, some small peaks arisen at 2θ from 10° to 20° show the presence of a small amount of triacetate in the modified product.[42]

Surface microstructures of acetylated RS

The structural variations in the RS are also reflected in their morphologies. Figure 8 shows the SEM micrographs of RS before and after acetylation. The unmodified RS (Fig. 8a) exhibited alternate smooth (small vascular bundles embedded in the subepidermal) and irregular surfaces on the epidermis of rice straw.[43] From the SEM pictures (b and c), it is clear that all the surface cells of RS have been completely destroyed, the fibrillar structures obviously disappear from the surface of RS. This result is consistent with the characteristic result of XRD and indicates that acetyls have successfully bonded to RS.

Thermal analysis
Thermogravimetric analysis

The thermal degradation of cellulose esters is known to take place in various steps, such as removal of water, deacetylation and thermal pyrolysis.[44] Fig. 9 shows the TG and DTG curves of RS. The samples could be differentiated by their characteristic temperature and weight loss. From the thermogram (Fig. 9 I), both modified and unmodified RS showed a slight initial decrease of

weight due to the loss of moisture, but the decrease of unmodified RS was more obvious due to the high hydroxyl group content. After that, the raw RS and acetylated sample started to decompose at 240 °C and 205 °C, respectively. This indicated that the unmodified RS was more stable than the acetylated sample. This lower thermal stability of the modified RS was undoubtedly due to the disintegration of intermolecular interactions, such as hydrogen bonds between polymer molecules. However, by 50.0% weight loss, the decomposition temperatures of the raw RS and the modified sample were recorded at 349 °C and 356 °C, respectively. This indicated that the decomposition rate of the acetylated sample was slow, compared to raw RS, probably due to the increase of the molecular weight of the modified sample. In addition, for the acetylated RS, the residue left at 600 °C (18%) was less than that of the unreacted RS (22%), which suggested that the acetylated RS was lost with volatile products and did not contribute to char formation. From DTG (Fig. 9 II), the temperature of the maximum rate of weight loss for the acetylated RS (362 °C) was higher than that for RS (355 °C). The control specimens showed a shoulder at 298 °C. The low-temperature shoulder in the control is thought to be due to hemicellulose degradation. However, this shoulder was missing in the acetylated RS, which may have two reasons: first, because there was a loss of partial hemicellulose polymers in modification, and second, the stability of acetylated hemicellulose polymers has been increased.
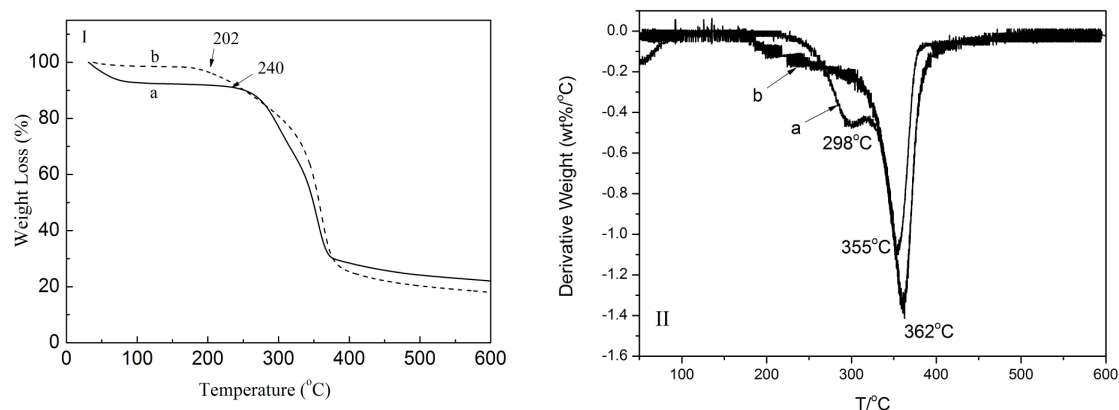

Figure 9: TGA (I) and DTG (II) curves of raw RS (a) and acetylated RS for WPG of 40.1% (b)
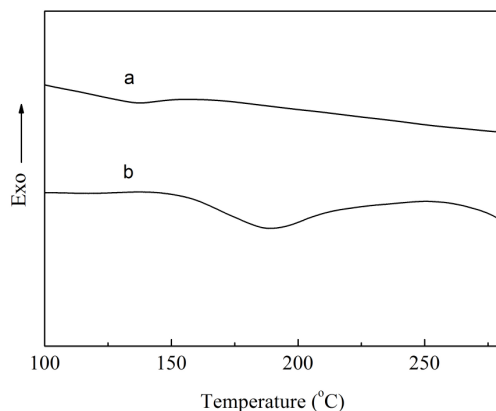
Figure 10: DSC curves of raw RS (a) and acetylated RS for WPG of 40.1% (b)

The results of TG and DTG are different from those of acetylated pine fibers,[14] which may be explained by the difference in the WPG of acetylated products, and the physical and chemical structures, due to different environment and growth cycle.

DSC

DSC thermograms of raw RS (a) and acetylated RS (b) are shown in Fig. 10. It could be observed that there was no endothermic peak for unmodified RS (a), indicating its poor thermoplasticity. Curve (b) exhibited an endothermic peak at 188 °C, 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 acetylating.

CONCLUSION

This research has shown that RS can be made thermoplastic through acetylation, which is a green and relatively inexpensive process. The acetylation was performed in the presence of sulfuric acid, and under optimized conditions (3:1 ratio of acetic anhydride to RS, 9% catalyst, reaction temperature of 50 °C, and reaction time of 2 h), the WPG obtained was 40.1%. Acetylated RS had a melting peak at about 188 °C and a slightly higher overall weight loss after thermal degradation. The lower melting temperature of acetylated RS will provide an opportunity to develop RS thermoplastics, which are inexpensive, biodegradable, and environmentally friendly products.

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