COMPARATIVE STUDY OF ACETYLATION OF RICE STRAW FIBER WITH OR WITHOUT CATALYSTS

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ABSTRACT

The reaction of acetic anhydride with rice straw fiber without solvent was investigated, and the extent of acetylation was measured by weight percent gain, which increased with an increment of reaction time or temperature. Meanwhile, the potential of four tertiary amine catalysts (pyridine, 4-dimethylamino pyridine, N-methyl pyrrolidine, and N-methyl pyrrolidinone) for the acetylation at 100°C for 0.5 h was also studied. The hypernucleophile 4-dimethylamino pyridine was found to be the most effective catalyst of those studied. The characterization of acetylated fibers was performed by FT-IR, CP MAS ^{13}C-NMR, and thermal studies. Thermal stability of acetylated rice straw fiber was found to be higher than the unreacted fiber and increased with weight percent gain due to the acetylation.

Keywords: Rice straw fiber, acetylation, catalyst, FT-IR, ^{13}C-NMR, thermal stability.

INTRODUCTION

Chemical modification of wood with organic anhydrides, in particular with acetic anhydride, has been shown to lead to dimensional stabilization and increase biological resistance (Boonstra et al. 1996; Pizzi et al. 1994; Rowell 1982; Rowell et al. 1986). However, the cost of wood fiber is on the rise, and the demand is surpassing supply (Erwin 1997). The possibility of replacing wood fibers with their natural equivalents in the composite materials is currently of interest (Bolton 1995). Application of lignocellulosic materials from renewable resources, such as from agricultural residues, in the reconstituted products (composites) is now competing against reconstituted wood products, e.g. particle- and fiberboards, in markets for floor underlays, furniture, and cabinet construction (Karr and Sun 2000).

Besides seasonality, bulk density, storage, distribution, etc, of using annual plant fibers as composite materials, their main disadvantages are the water sorption and lack of dimensional stability due to the hydrophilic nature of hydroxyl groups in the cell-wall polymers. This leads to undesirable changes in mechanical and dimensional properties as a function of relative humidity, and degradation by decay organisms (Hill et al. 1998a). One strategy to improve the water absorption and dimensional stability of these products is to chemically modify the cell-wall polymers, which will modify the physical and chemical

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properties of the lignocellulosic composites (Karr and Sun 2000). Hydroxyl groups are the most abundant and reactive sites on the cell-wall polymers of a lignocellulosic material (Rowell et al. 1994). Many reagents have been used to modify the cell-wall polymers with varying degrees of success, including anhydrides, acid chlorides, isocyanates, aldehydes, alkyl halides, lactones, nitriles, and epoxide (Rowell 1982). Among these, chemical modification of lignocellulosics using acetic anhydride is perhaps the simplest, safest, and cheapest method for improving the strength, dimensional stability, and rot resistance of biocomposites. Acetyl groups are more hydrophobic than hydroxyl groups; therefore, replacing some of the hydroxyl groups with acetyl groups reduces the hydrophilic property of the cell-wall polymers (Rowell 1992). In addition, such modification causes bulking of the cell wall proportional to the extent of substitution, or weight percent gain (WPG), and renders the material less susceptible to biological decay. Biological protection is afforded by a combination of the lowering of the equilibrium moisture content of the material, and by modifying the chemistry of the cell-wall polymers such that they are no longer recognized by the enzymes associated with the decay organisms (Goldstein 1960; Stamm and Baechler 1960; Tarkow et al. 1950).

Several different methods of acetylation with or without catalysts have been developed, and a number of various catalysts have been examined for accelerating the rate of reaction of acetic anhydride with wood (Rowell 1983). Pyridine-catalyzed acetylation is a standard method for the determination of hydroxyl compounds and other acylable substances (Connors and Albert 1973), since it serves not only to swell the wood structure, thereby permitting effective ingress of reagent, but it also catalyzes the reaction via nucleophilic mediated catalysis (Hill et al. 1998a; Satchell 1963). For many years, 4-dimethylamino pyridine (DMAP) has been used as an acylation catalyst in chemical synthesis. Compared to pyridine, DMAP was found to be approximately 10^4 times more active when used as acylation catalyst (Hofle et al. 1978). Although some studies of the acetylation of lignocellulosic materials, such as jute, cotton, and oil palm trunk fibers (Callow 1951; Hill et al. 1998a; Sen and Ramaswamy 1957), and wheat straw (Bueso et al. 1999), have been reported in the literature, the acetylation of rice straw fiber has not, as far as the authors are aware, been reported. There have also been no reports of using pyridine or DMAP as a catalyst for the acetylation of rice straw fiber using acetic anhydride.

This study is concerned with investigating the acetylation of rice straw fiber by a fast and simplified procedure without or with different catalysts under various conditions. The products were comparatively characterized by their weight percent gain, FT-IR and ^{13}C-NMR CP MAS spectroscopies, and thermal analysis.

MATERIALS AND METHODS

Materials and regents

Rice straw was obtained from the experimental farm of The North-Western Sciences and Technology University of Agriculture and Forestry (Yangling, P. R. China). It was dried in sunlight and then cut into 3–5 cm length small pieces. The cut straw was run through a ring flaker. The resulting fiber was approximately 2 to 5 cm by 0.04 to 0.06 cm. It was further dried in an oven at 60°C for 16 h before use. Acetic anhydride, 4-dimethylamino pyridine (DMAP), pyridine, N-methyl pyrrolidine (MPI), and N-methyl pyrrolidinone (MPO) were purchased from Sigma Company (Xian).

Acetylation of rice straw fiber

In order to determine the relative rates of reaction, the following procedure was adopted. A quantity of the straw fiber (10 g) was placed in a 500-ml flat bottom flask. Then 300 ml acetic anhydride was added. The flask was dipped into an oil bath set at the required temperature (60, 80, 100, 120, and 130°C) fitted with a reflux condenser. After the reaction time (0.5, 1, 2, and 3 h) was completed, the flask was removed from the oil bath and the reagents were filtered off. The fibers were then washed with ethanol and acetone to remove unreacted anhydride and acetic acid by-product as well as the remaining catalysts. The acetylated fiber was oven-dried at 60°C for 16 h. The weight percent gain (WPG) due to acetylation was calculated based on the weight of oven-dried unreacted straw. To reduce errors and confirm the results, each experiment was repeated triplicate under the same conditions, and the WPC represents the average values.

Spectroscopic and thermal characterization

The FT-IR spectra were recorded on a Nicolet-510 FT-IR spectrophotometer, using KBr pellets containing 1% finely ground samples. The solid-state ^{13}C-NMR spectra were obtained using a Bruker MSI-300 spectrometer at 74.5 MHz with magic-angle spinning and cross-polarization (CP-MAS). About 250 mg of sample was packed into zirconia rotors for MAS at approximately 4 kHz. The CP contact time was 5 s, acquisition time 0.1, and total acquisition time 2 h.

Thermal analysis of the unreacted and acetylated straw fibers was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (NETZSCH STA-409). All the measurements were made under nitrogen flow (160 ml/min) keeping a constant heating rate at 10°C/min and using an alumina crucible with a pin hole. Each sample was heated from room temperature to 600°C.

RESULTS AND DISCUSSION

Effects of reaction time, temperature, and catalyst on WPG

In this study, the reaction of acetic anhydride with rice straw fiber was performed using a solvent free system, which increased the reaction rate due to the reducing dilution of modifiers, and avoided a requirement of complicated separation procedures to recover the chemicals after reaction (Rowell et al. 1986). Chemically, the hydroxyl groups can be distinguished as being phenolic, benzylic, or alcoholic in the lignin regions, and alcoholic in the carbohydrate. The alcoholic hydroxyl groups are either primary or secondary, and the phenolic hydroxyl groups are attached to an aromatic ring that has various substituents attached. Thus, each of these groups will exhibit a different reactivity towards acetic anhydride (Hill et al. 1998b; Malm et al. 1953). That is, the rate of reaction is dependent on the relative reactivities of the hydroxyl groups in the substrate, and the rate of diffusion of the reagent into the fiber matrix. On the other hand, based on the modification of wood using acetic anhydride, it has been reported that the wood cell wall polymers react in the order lignin > hemicelluloses > cellulose (Rowell et al. 1994). Similarly, the results, obtained from the chemical modification of coir, oil palm fiber, flax, and jute fibers using acetic anhydride, indicated that the acetylation is proportional to the lignin content of the fibers (Hill et al. 1998a; Rowell 1982; Rowell et al. 1994). In comparison with wood samples, the rice straw fiber used in this study contained much lower amounts of lignin (12.3% dry weight basis) (Sun et al. 2000), which limited its rate of acetylation.

As the data shown in Table 1, a relatively low value of WPG (1.5–15.7%) was obtained for acetylation of rice straw fiber with acetic anhydride under the conditions used. Increase of reaction time from 0.5 to 1, 1.5, 2, and 3.0 h resulted in an increment in the WPG from 9.3 (sample 1) to 10.7 (sample 2), to 11.7 (sample 3), to 12.3 (sample 4), and to 15.7% (sample 5) at 120°C without catalysts, respectively. This enhancement of acetylation by prolonging the duration of reaction was a direct consequence of the favorable effect of time on diffusion and adsorption of the reactants between the acetic anhydride and the straw fiber. The initial step in the mechanism for the reaction of acetic anhydride with an hydroxyl group involves the nucleophilic attack on the acyl carbon center of the anhydride molecule by a lone pair of the alcoholic (or

TABLE 1. *Weight percent gain due to acetylation of rice straw fiber under various conditions.*

Acetylation conditions				Acetylated straw fiber	
Solid to liquid ratio[a] (g/ml)	Temperature (°C)	Reaction time (h)	Catalyst (% dried fibre)	Sample no.	WPG[b] (%)
1: 30	120	0.5	0%	1	9.3
1: 30	120	1.0	0%	2	10.7
1: 30	120	1.5	0%	3	11.7
1: 30	120	2.0	0%	4	12.3
1: 30	120	3.0	0%	5	15.7
1: 30	100	0.5	0%	6	5.3
1: 30	100	0.5	DMAP[c], 3%	7	7.7
1: 30	100	0.5	Pyridine, 3%	8	6.3
1: 30	100	0.5	MPI[d], 3%	9	7.1
1: 30	100	0.5	MPO[e], 3%	10	5.7
1: 30	100	0.5	DMAP, 10	11	10.3
1: 30	100	0.5	Pyridine, 10%	12	6.3
1: 30	100	0.5	MPI, 10%	13	7.2
1: 30	100	0.5	MPO, 10%	14	5.7
1: 30	60	1.0	0%	15	1.5
1: 30	80	1.0	0%	16	3.3
1: 30	100	1.0	0%	17	8.0
1: 30	120	1.0	0%	18	10.7
1: 30	130	1.0	0%	19	11.8

[a] Solid to liquid ratio represents ratio of dried race straw fiber (g)/acetic anhydride (ml).
[b] WPG represents the weight percent gain due to acetylation and was calculated based on the weight of oven-dried unreacted rice straw fiber.
[c] Abbreviation for 4-dimethylamino pyridine.
[d] Abbreviation for N-methyl pyrrolidine.
[e] Abbreviation for N-methyl pyrrolidinone.

phenolic) hydroxyl group, subsequent loss of acetic acid generates the ester. The rate of the reaction, therefore, depends upon the nucleophilicity of the relevant OH group (Hill et al. 1998b).

The effect of different catalysts on the rate of acetylation of rice straw fiber was investigated with catalyst concentrations of 3% and 10% (% dried fiber) at 100°C for 0.5 h, respectively. In comparison with a control sample 6, it is apparent that all the four catalysts accelerated the rate of reaction, with DMAP exhibiting the fastest rate of acetylation. Use of 3% DMAP as a catalyst led to a 2.4% WPG increase over that obtained with neat anhydride, and use of 3% MPO showed a slowest rate of acceleration of the reaction as shown by an increment in 0.4% WPG. Similarly, an increase of DMAP concentration to 10% yielded the product with 10.3% WPG (sample 11), which was approximately two times higher than the WPG obtained at the same condition without catalyst (sample 6). However, no any further increases in WPG of the products were observed when the concentration of the other three catalysts (pyridine, MPI, MPO) increased from 3% to 10%. Such relationships have also been observed during the studies on the potential of several tertiary amine catalysts, such as pyridine, DMAP, MPI, and MPO, for the acetylation of Corsican pine sapwood using acetic anhydride (Hill et al. 2000). The authors stated that at a concentration of only 1% of the catalyst in acetic anhydride, a weight percent gain of 20% was realized, compared with 7% for the uncatalyzed reaction, after 30 min system at 100°C. From computer modeling studies, it has been shown that such increasing rates of the acetylation are a result of reactions where diffusion occurs on a porous interconnected network (the mircovoids located in the cell wall) and where the rates of diffusion and reaction are comparable (Hill and Hillier 1999). In addition, the reaction of acetic anhydride with rice straw fiber generated acetic acid as a single by-product.

Interestingly, it was found that at low concentrations up to *ca.* 10% acetic acid in the anhydride, the reaction was accelerated, but at higher concentrations a retardation occurred (Rowell et al. 1990). Therefore, the acetylation rate with rice straw fiber would be affected by both the rate of reaction of acetic anhydride and the rate of diffusion of acetic acid from the fiber matrix into the surrounding solution.

During the acetylation process, the straw fiber ultrastructure is also another important factor to affect the rate of the reaction, since the anhydride molecules have to diffuse through the fiber matrix to reach the reactive sites. The diffusion is, therefore, a dominant factor to affect the reaction kinetics. The hydroxyl groups of the cell-wall polymers form extensive hydrogen bonding networks within the matrix; and the reaction of the anhydride with hydroxyl group requires the breaking of an hydrogen bond (Hill et al. 1998b; Rowell 1983). Particularly, during the noncatalyzed acetylation process, the fiber swells as the reaction proceeds, requiring disruption of the hydrogen bonding network. In general, increasing temperature favored breaking such hydrogen bonds, swelling the fibers, diffusing the esterifying agent, and moving the reactant molecules, thus enhancing the reaction rate. As shown in Table 1, an increase of reaction temperature from 60, to 80, to 100, to 120, and to 130°C resulted in an increment in the WPG from 1.5% (sample 15), to 3.3% (sample 16), to 8.0% (sample 17), to 10.7% (sample 18), and 11.8% (sample 19), respectively.

From these experiments, it was found that the reaction temperature and time, and the use of catalyst DMAP had significant effects on the WPG of anhydride-treated rice straw fibers. The current results were consistent with the studies of acetylation of Jute using a simplified procedure by Rana et al. (1997). The authors indicated that at higher temperature and longer reaction time, acetic anhydride was able to swell the fiber, making reactive chemical sites more accessible to and therefore enhancing the reaction rate. The highest weight gain (15.7%) was obtained from sample 5, performed at 120°C for 3 h under the uncatalyzed condition used. Meanwhile, the acetylated fibers were found to be lighter in color. This may be attributed to the reaction process that removed some of the extractive components, thus giving light-colored fibers.

FT-IR spectra

In order to determine whether a chemical reaction was taking place between the rice straw fiber and acetic anhydride, the products were subjected to analysis by FT-IR and ^{13}C-NMR CP-MAS. Figure 1 shows the FT-IR spectra of unmodified rice straw fiber (spectrum 1) and acetylated rice straw fiber sample 1 (spectrum 2), prepared at 120°C for 0.5 h without catalyst. The most important features of the spectrum of acetylated rice straw fiber (spectrum 2) are the occurrence of three ester bands at 1752 (C=O ester), 1374 ($-C-CH_3$), and –C–O– stretching band at 1242 cm^{-1} (Saikia et al. 1995). In addition, acetylation of rice straw fiber decreased the peak area at 3436 cm^{-1} due to stretching vibrations of OH, indicating a partial acetylation. An intensive band at 1653 cm^{-1} is assigned to the absorbed water. A small sharp band at 903 cm^{-1} is indicative of β-glucosidic linkages between the sugar units (Gupta et al. 1987). The strong band at 1056 cm^{-1} originated from C–O stretching in C–O–C linkages. The small absorbances at 1520, 1447, and 1334 cm^{-1} relate to the aromatic ring vibrations and ring breathing with C–O stretching in lignins. As to be expected, the absence of absorption region 1840–1760 cm^{-1} in spectrum 2 indicated that the product is free of the unreacted acetic anhydride. The lack of peak at 1700 cm^{-1} for carboxylic group implied that the products are also free of the by-product of acetic acid.

Figure 2 illustrates the FT-IR spectra of acetylated rice straw fiber samples, prepared at 120°C for 1 (spectrum 1, sample 2), 1.5 (spectrum 2, sample 3), and 3 h (spectrum 3, sample 5) without catalyst. Clearly, the bands intensities for ester carbonyl absorbance at 1759 cm^{-1}, a frequency for C–O stretching at

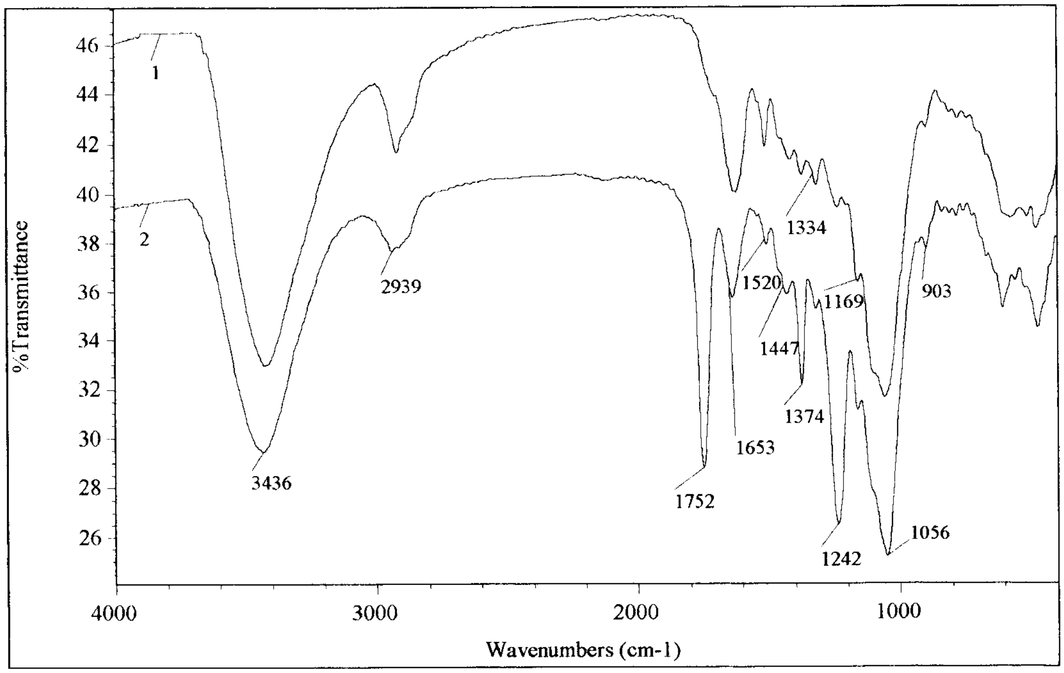

FIG. 1. FT-IR spectra of unmodified rice straw fiber (spectrum 1) and acetylated rice straw fiber sample 1 (spectrum 2), prepared at 120°C for 0.5 h without catalyst.

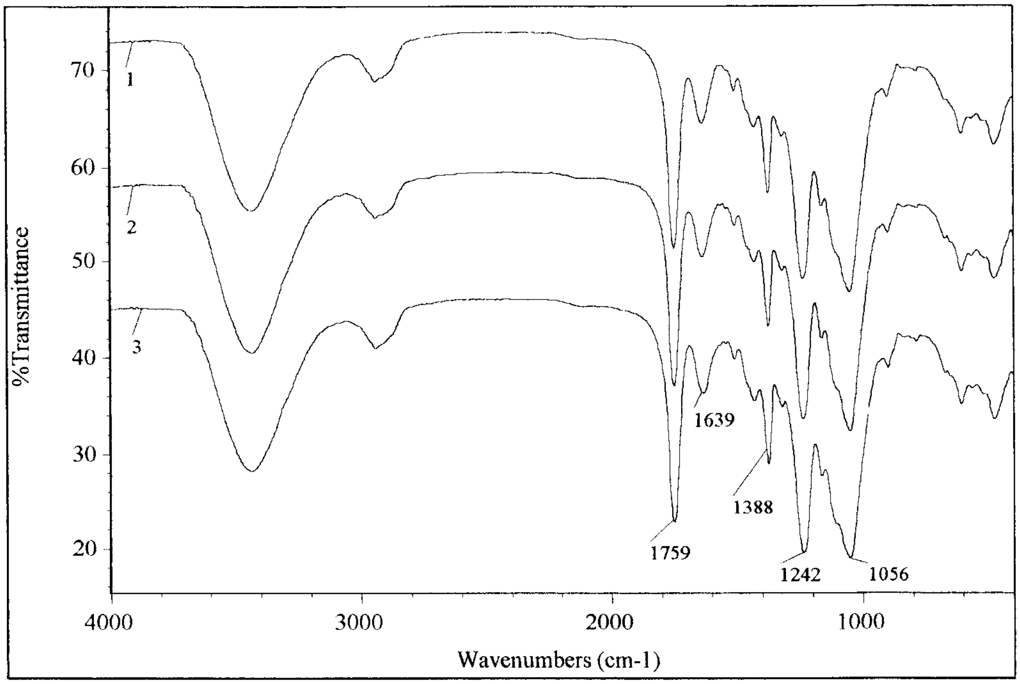

FIG. 2. FT-IR spectra of acetylated rice straw fiber samples, prepared at 120°C for 1 (spectrum 1, sample 2), 1.5 (spectrum 2, sample 3), 3 h (spectrum 3, sample 5) without catalyst.

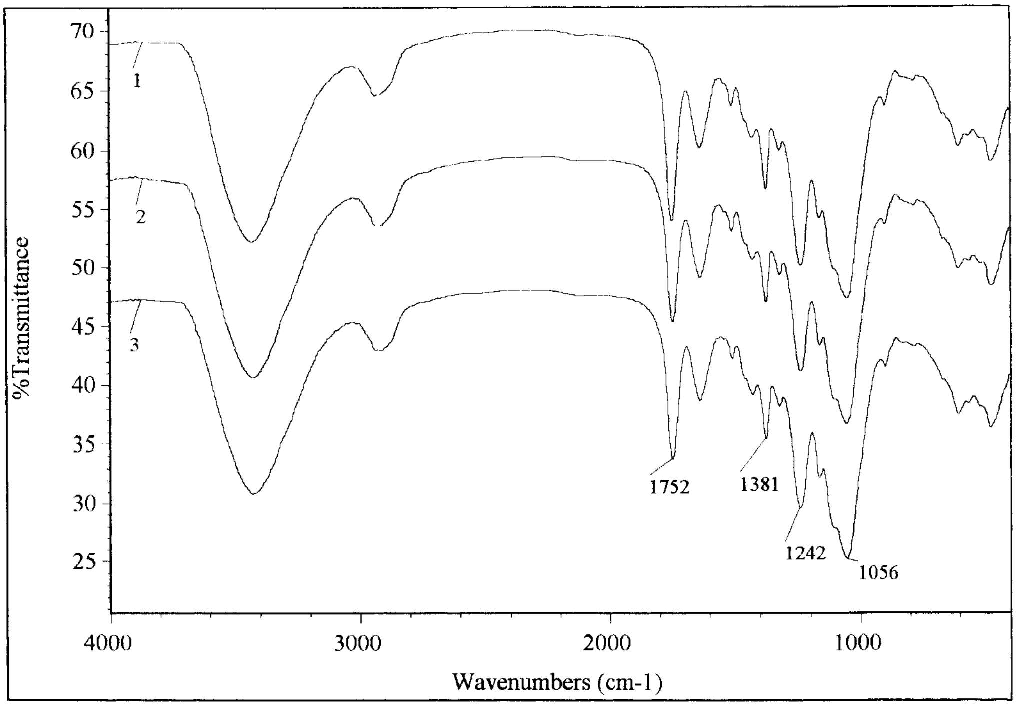

FIG. 3. FT-IR spectra of acetylated rice straw fiber samples, prepared at 100°C for 0.5 h with 3% DMAP (spectrum 1, sample 7), 3% pyridine (spectrum 2, sample 8), and 3% MPI (spectrum 3, sample 9) as catalysts.

1242 cm^{-1}, and a sharp band at 1388 cm^{-1} for C–H bond in $-OOC-CH_3$ group increased with an increase in reaction time from 1 (spectrum 1) to 1.5 (spectrum 2), and to 3 h (spectrum 3), corresponding to an increment of WPG from 10.7, to 11.7, and to 15.7%, respectively. In contrast, the quantitative acetylation is also evident from the decrease of hydroxyl absorption at 3436 cm^{-1} in the spectra, which is proportional to an increase of degree of substitution from spectrum 1 to 2, and to 3.

The effect of different catalysts and reaction temperature on the intensity of the absorption bands of FT-IR spectra was also investigated, and the spectra are illustrated in Figs. 3 and 4, respectively. Obviously, the intensity of ester carbonyl absorbance at 1752 cm^{-1}, a frequency for C–O stretching in acetic groups at 1242 cm^{-1}, and CH_3 bending in acetic groups at 1381 cm^{-1} parallel well the values of WPG in Table 1, indicating again that DMAP is the most powerful catalyst, and an increase of the reaction temperature from 60 to 130°C raises the degree of acetylation significantly.

Solid-state ^{13}C-NMR

The CP MAS ^{13}C-NMR spectra of unmodified rice straw fiber (spectrum a) and acetylated fiber sample 5 (spectrum b), prepared at 120°C for 3 h without catalyst are shown in Fig. 5. Evidently, both of the spectra were dominant and very similar in the carbohydrate region (60–110 ppm), namely C-1 (106.5 ppm), C-4 (90.0 ppm, crystal-interior cellulose, and 84.8 ppm, crystal-surface cellulose), C-2, C-3 and C-5 (75.8 ppm), and C-6 of cellulose and C-5 of xylan (66.0 ppm). This indicated that the carbohydrates were affected to a much smaller extent by acetylation under the condition used. On the other hand, the CPMAS spectrum of acetylated fiber (spectrum b) clearly shows the expected decreases both in the aromatic region between 110 and

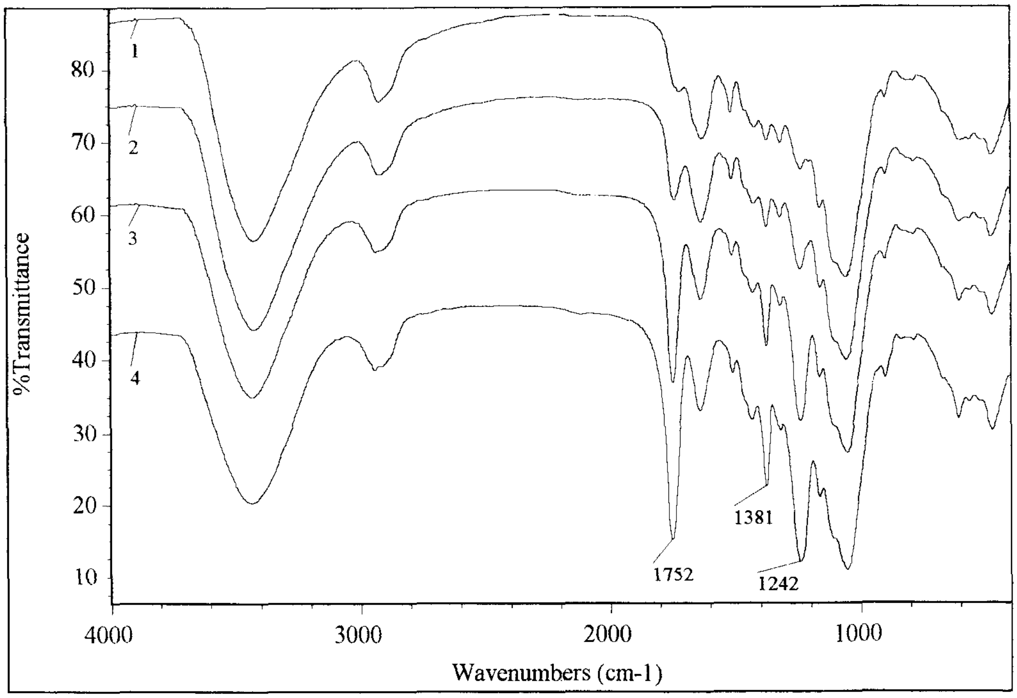

FIG. 4. FT-IR spectra of acetylated rice straw fiber samples, prepared at 60° (spectrum 1, sample 15), 80° (spectrum 2, sample 16), 100° (spectrum 3, sample 17), and 130°C (spectrum 4, sample 19) for 1.0 h without catalyst.

160 ppm and in the aliphatic region for a hydrocarbon CH_2 signal at 35.0 ppm as compared to the spectrum of unmodified rice straw fiber (spectrum a), which is apparent in the aromatic region between 128 and 140 ppm for C-2, C-5, and C-6 of syringyl and guaiacyl units in lignins (Love et al. 1998).This reveals that the acetylation proper is much more extensive on lignins than on carbohydrates. Similar results have been reported by Rowell et al. (1994) in the studies of reactivity of isolated wood cell wall components. They stated that the order of acetylation was lignin > hemicelluloses > holocellulose, and cellulose did not react. For example, the authors showed that at a level of bonded acetyl where all the hydroxyl groups were substituted on the lignin polymer, only about 20% of the total theoretical hydroxyl groups on the holocellulose were substituted. It is therefore clear that, at least in rice straw fiber, the greater proportion of the anhydride has reacted with lignin rather than with the carbohydrates.

In Fig. 5, the spectrum of modified straw fiber (spectrum b) clearly provides the evidence for the occurrence of acetylation as indicated by two strong signals at 171.0 (C=O in esterified acetyl group) and 21.4 ppm (CH_3 in acetyl group). A significant decrease in intensity of the band at 118 ppm (C-5 of guaiacyl and C-3/C-5 of 4-hydroxyphenyl units) confirms again that the new substituents have been introduced in the aromatic ring of lignin. The methoxyl groups in lignin exhibit a small signal at 57.4 ppm. Furthermore, the spectrum of acetylated straw fiber (spectrum b) also clearly shows that acetylation has also occurred on the carbohydrates portion of the fibers. The disappearance of C-6 at 64.8 ppm of the amorphous region in spectrum b reveals that acetylation at C-6 has already occurred (Boonstra et al. 1996), since it appears as a shoulder in spectrum a of the unmodified straw fiber. This is important because it verifies that in the fiber itself reactions of acetic anhydride on straw carbohydrates do occur.

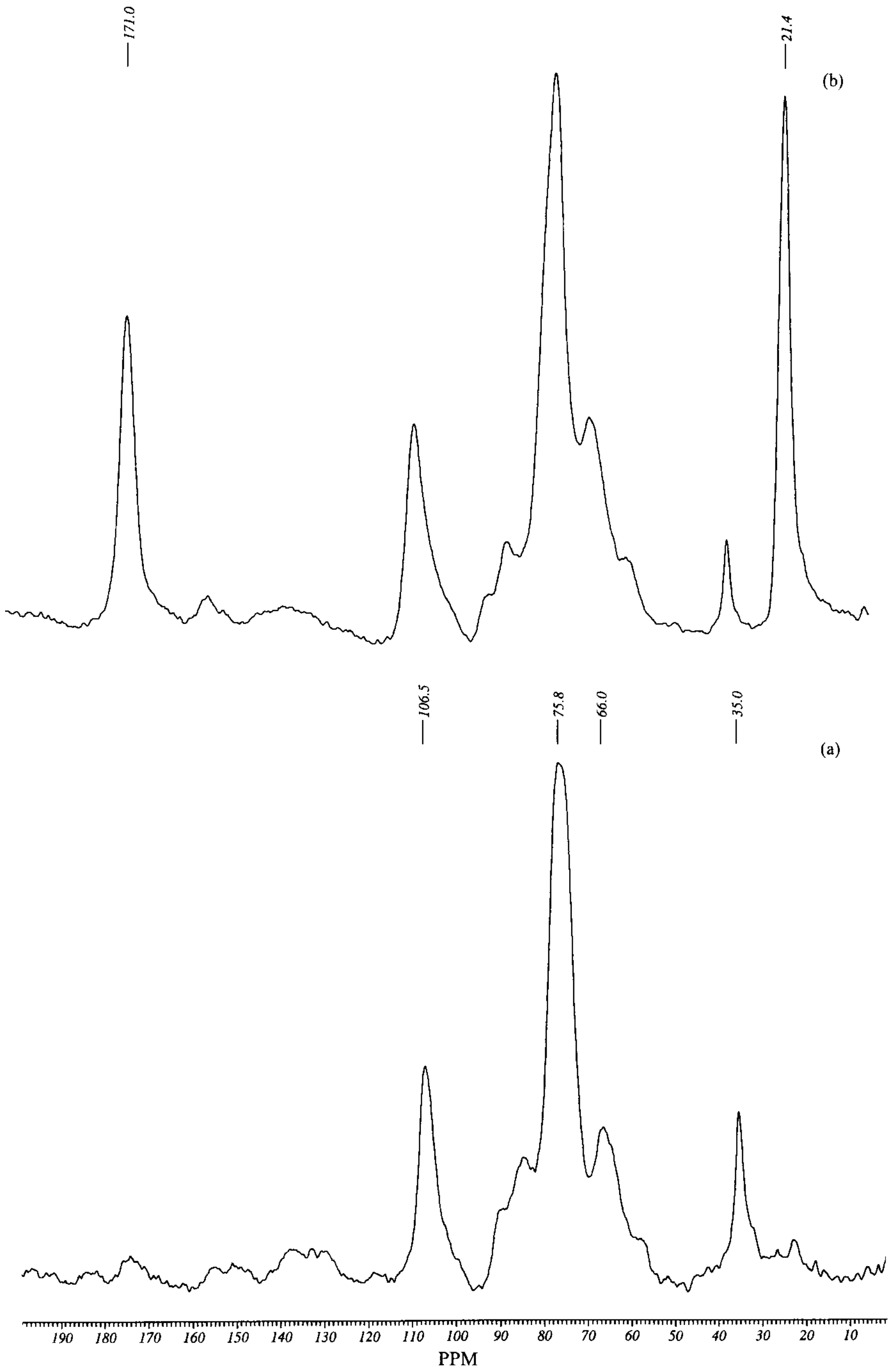

FIG. 5. The CP MAS ^{13}C-NMR spectra of unmodified rice straw fiber (spectrum a) and acetylated straw fiber sample 5 (spectrum b), prepared at 120°C for 3 h without catalyst.

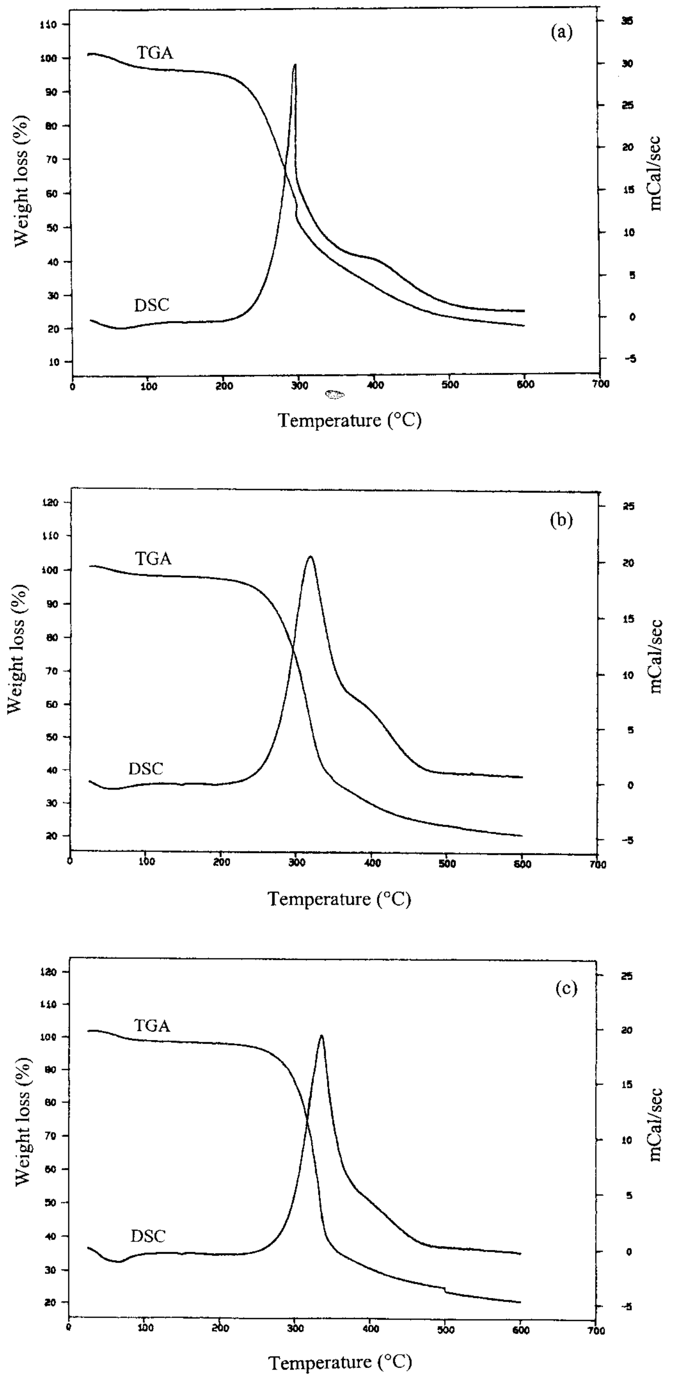

FIG. 6. Thermograms of unreacted rice straw fiber (a) and acetylated straw fiber samples 17 (b), obtained at 100°C for 1 h without catalyst, and 19 (c), prepared at 130°C for 1 h without catalyst.

Thermal analysis

Thermogravimetric analysis (TGA) is one of the techniques used to determine general degradation characteristics and activation energies of materials under pyrolysis and combustion. This analysis includes a precise study of weight loss during programmed exposure to temperature (Beall 1969). Figure 6 gives the thermograms of unmodified rice straw fiber (a) and acetylated straw fiber samples 17 (b) and 19 (c), prepared at 100 and 130°C for 1 h without catalyst, respectively, which gave additional evidence to a higher stability of the acetylated rice straw fiber. As shown in Fig. 6, the native straw fiber started to decompose at 200°C, while the two acetylated fiber samples 17 and 19 started to decompose at 237 and 255°C, respectively. At 50% weight loss, the decomposition temperature was observed at 303°C for native rice straw fiber, 326°C for acetylated straw fiber sample 17, and 338°C for acetylated straw fiber sample 19. This increasing trend indicated that the acetylated rice straw fiber had a higher thermal stability than the unmodified straw fiber, and the thermal stability of the acetylated straw fiber increased with an increment of WPG.

In addition, although the three DSC thermograms of both unreacted rice straw fiber and acetylated straw fiber samples gave only one similar big exothermic peak, the maximum of the peak shifted from 300°C in unmodified rice straw fiber to 331 and 347°C in acetylated straw fiber samples 17 and 19. This confirmed again that the thermal stability of the acetylated rice straw fibers increased with the growth of weight percent gain by the esterification.

CONCLUSIONS

Overall, the acetylation of the free hydroxyl groups in rice straw fiber with acetic anhydride without solvents represents a suitable and effective method for the preparation of rice straw fiber acetates having a more hydrophobic characteristic. The weight percent gain increased with increments of reaction time and temperature. Under an optimum reaction condition (120°C, 3 h), a maximum WPG value of 15.7% was obtained in the absence of catalyst. In addition, DMAP was found to be the most effective catalyst of those studied. At 10% DMAP, a weight percent gain of 10.3% was obtained, compared with 5.3% for the uncatalyzed reaction at 100°C for 0.5 h. Furthermore, the results also showed that a greater proportion of the anhydride reacted with lignin rather than with the carbohydrates in the cell wall of the polymers. Finally, the thermal stability of acetylated rice straw fiber was higher than that of the unmodified straw fiber and increased with an increment of WPG due to the acetylation.

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