

Preparation and Properties of Wheat Straw Fiber-Polypropylene Composites. I. Investigation of Surface Treatments on the Wheat Straw Fiber

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Received 8 September 2008; accepted 21 February 2009

DOI 10.1002/app.30325

Published online 20 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Effects of alkalization, acetylation, and maleic anhydride grafted polypropylene (MAPP) treatments on the thermal and chemical properties of the wheat straw fiber were investigated using thermogravimetric analysis, infrared spectrophotometer, X-ray diffraction, and scanning electric microscopy techniques. It was found that the wheat straw fiber was not prone to weight loss at 170°C and the treated wheat straw fiber exhibited more thermal stability than the untreated wheat straw fiber. Alkalization increased relative cellulose content and exhibited more crystalline due to a rearrangement of the crystalline regions. It also prolonged the degradation of the wheat

straw fiber at higher temperatures due to the increased crystallinity of cellulose. Compared with alkalization, acetylation had more effect on the thermal and chemical stability in the wheat straw fiber contributing to a formation of ester bonding. MAPP improved the thermal stability partly because of a lower grafted ratio of maleic anhydride. Acetylation and MAPP treatment both decreased the crystallinity of the wheat straw fiber. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3049–3056, 2009

Key words: fibers; morphology; poly(propylene); (PP); thermal properties; modification

INTRODUCTION

In recent years, thermoplastic composites reinforced with natural fiber, such as wood, wheat straw, hemp, and flax fiber have enjoyed steady growth due to the superior properties of the resultant products.^{1,2} Compared with inorganic fiber, natural fiber is a renewable and abundant resource. It has less negative impact on the environment because of its ability of recycling and biodegradability. However, natural fiber possesses inherently complex structure, thermal degradation, and adsorption properties. Furthermore, when the natural fiber is processed to the thermoplastic composites, the weak interfacial adhesion between the natural fiber and matrix has negative influence on interfacial bonding and the properties of resultant products. Therefore, extensive studies^{3–7} have examined the pretreatments of the natural fiber and their effects on the interfacial adhesive mechanism of natural fiber and thermoplastic composites.

Alkalization is an attractive method to modify natural fiber surface. This method can eliminate a large amount of hemicellulose and other impurities of the natural fiber and thus produce void on the fiber surface and make a rougher surface. As a result, adhesive characteristics of the fiber surface are enhanced.^{8–10} This treatment leads to fiber fibrillation, i.e., breaking the fiber into smaller ones, and increasing the effective surface area available for the contact with the matrix. Furthermore, it is found that the jute and flax fiber changes in crystallinity during alkali process. The increase in the percentage of crystallinity index of the alkali-treated fiber occurs as a consequence of the removal of the hemicellulose, which leads to a better packing of cellulose chain.^{8,11} It is commented that the concentration of alkalization has a significant influence on the properties of the natural fiber and the resultant composites. However, higher concentration can lead to poorer mechanical properties of the polypropylene (PP) composites filled with wood powder.¹¹

A number of studies^{12–16} have been carried out to modify natural fiber using acetylation method. The principle of acetylation is to react the hydroxyl groups (—OH) of the natural fiber constituents with acetyl groups (CH₃CO—), which known as esterification. It is reported¹⁴ that the weight percent gain of flax fiber was increased at high levels (15–17 wt %) of acetic anhydride. This indicated that esterification

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Contract grant sponsor: Natural Science and Engineering Research Council of Canada (NSERC).

occurred on the fiber surface. Acetylation increases the disperse free energy and the polar interaction ability of flax fiber using inverse gas chromatography technique.

Maleated polyolefins are a more effective method to modify the natural fiber surface and the most commonly used is maleic anhydride grafted polypropylene (MAPP), which functions through esterification between natural fiber hydroxyl groups and anhydride functionality of MAPP through hydrogen bonding. MAPP has a positive effect on tensile strength of the wood fiber-PP composites and a negative effect on the tensile elongation at break in the system. The tensile properties of wood fiber-PP composites showed the best tensile performance with the addition of 5 wt % MAPP.^{17,18} Furthermore, the introduction of natural fiber into a polyolefin melt provides a surface upon which polymer may nucleate. It is observed that MAPP was collected at the edge of the transcrystalline layer; however, FTIR spectroscopy of the interphase did not confirm covalent bonding of the wood with the MAPP because spectra of the MAPP and wood overlapped.^{19,20} Furthermore, it is still unclear whether the improvements in material strength with the addition of MAPP are the result of improved natural fiber-plastic interaction, better dispersion of the natural fiber component, or changes in the thermoplastic morphology.

Although the effects of pretreatments on the properties of natural fiber and the resultant composites have been studied extensively, there is little information available on the effect of pretreatments on the thermal stability of natural fiber. When natural fiber is processed into the thermoplastic composites through extrusion, injection or other processes, natural fiber is exposed to thermal and oxidative degradation at high temperatures corresponding to the melt temperature of polymer. The objectives of this study is to investigate the effect of alkalization, acetylation, and MAPP treatments on the thermal stability and chemical properties of wheat straw fiber using thermogravimetric analysis (TGA), infrared spectrophotometer (IR), scanning electric microscopy (SEM) and wide angle X-ray scattering (WAXS) techniques. In the following study (Part II), the treated wheat straw fiber will be processed to the PP composites and the properties of the wheat straw fiber-PP composites affected by these treatments will be evaluated.

EXPERIMENTAL

Materials

Wheat straw fiber samples were obtained from Fortek MDF refining facility under the following refining conditions: steam pressure of 8 bar and

refining speed of 2500 rpm. The length of refined wheat straw fiber ranges from 0.04 to 6.29 mm with an average length of 0.30 mm, measured with a HiRes fiber quality analyzer (FQA) - LDA02. Acetic anhydride, supplied by Laboratoire MAT and MAPP Polybond[®]3000, supplied from Crompton Company, were used as modifiers. Polybond[®]3000 has 1.22 wt % MA, 0.91 g cm⁻³ density at 23°C, and melt flow index (190°C /2.16 kg) of 400 g/10 min. Another treatment, alkalization, was used with an aqueous solution of sodium anhydride.

Fiber surface modifications

Alkalization

Two grams of wheat straw fibers, with the moisture content of 4.6% were first placed in 40 mL aqueous solution of sodium hydroxide with 2, 4, 6, 8, and 10% concentrations, respectively. The mixture was then placed in a water bath, which was preheated to 20°C and 45°C, respectively, and kept for 1 h. Afterward, the alkalized wheat straw fibers were washed with distilled water for several times, followed by neutralization with 20 mL of 10% acetic acid solution. Wheat straw fibers were then washed with distilled water again and dried at 105°C to a constant weight. The weight percent loss (WPL) as result of the alkalization was calculated according to the eq. (1):

$$\text{WPL}(\%) = 100 \times \frac{m_0 - m_1}{m_0} \quad (1)$$

where m_0 is the initial oven-dried mass of the sample before alkalization, and m_1 is the oven-dried mass of the sample after alkalization.

Acetylation

Acetylation followed the method developed by Rowell.¹² Two grams of wheat straw fibers with the moisture content of 6.4% were placed in a stainless steel mesh container and dipped into a beaker containing acetic anhydride for 1 min; afterward, the wheat straw fibers were drained for 3 min at the room temperature and then placed in a preheated (120°C) oven for 0.5, 1, 1.5, 2, 3, and 4 h, respectively. After that, the wheat straw fibers were placed in a vacuum oven (-30 mmHg) for 2 h at 120°C and dried at 105°C to a constant weight. The weight percent gain (WPG) from the acetylation was calculated according to the eq. (2):

$$\text{WPG}(\%) = 100 \times \frac{m_3 - m_2}{m_2} \quad (2)$$

where m_2 is the initial oven-dried mass of the sample before acetylation and m_3 is the oven-dried mass of the sample after acetylation.

Treatment with MAPP

Two grams of over-dried wheat straw fibers were extracted with alcohol/benzene (1 : 2, v/v) mixture in a Soxhlet extractor for 8 h and dried at 105°C in an oven for 12 h before treated with MAPP. The extracted wheat straw fibers were then placed in hot xylene at 120°C for 3 h, with 4 g of predissolved MAPP. To remove the untreated MAPP, the wheat straw fibers were extracted with xylene at 80°C for 24 h, and then dried at 105°C to a constant weight.

Fiber characterization

ATR spectroscopy

Attenuated total reflection infrared (ATR-IR) spectra of the wheat straw fiber, after the treatments, were obtained using a Specac FTLA 2000. All sample spectra were recorded in the 4000–400 cm^{-1} range, with a resolution of 4 cm^{-1} . Thirty-two scans were carried out for each spectrum. Two replicated measurements were carried out for each sample.

WAXS investigation

The WAXS was performed after the treatments to investigate the ultrastructure of the wheat straw fiber affected by treatments. A small quantity of fiber was mounted on double-sided cello tape and placed in a DX-2000 diffractometer with a Cu anode, operating at 40 kV and 30 mA. The crystallinity index of the untreated and treated wheat straw fiber was calculated according to the eq. (3):

$$\text{CrI} = \frac{I_{(002)} - I_{(\text{am})}}{I_{(002)}} \times 100 \quad (3)$$

where, I_{002} is the counter reading at peak intensity at a 2θ of 22°, and I_{am} is the amorphous counter reading at a 2θ of 18°. ¹⁴

TG measurements

The TG measurements of the wheat straw fibers after the treatment were carried out on a TGA Q500 analyzer (TA Instruments) at a heating rate of 10°C min^{-1} , from 20 to 700°C in a continuous nitrogen and air atmosphere, respectively. The other TG measurements of the wheat straw fiber after the treatments were also conducted isothermal held at 170, 190, 210, and 230°C for 1 h on air atmosphere. Five milligrams of samples were used for a TGA test.

Surface morphology

A JEOL JSM-840A SEM was used to observe the surface morphology of the wheat straw fiber after treatments. All samples were coated with palladium and gold before examination.

RESULTS AND DISCUSSION

Effect of treatments on weight and morphology

Before treatments, fiber roughening can be observed on the surface, and partial breakage of the wheat straw fibers along the longitudinal direction is occurred in the surface of the wheat straw fiber, as illustrated in Figure 1(A). Surface fibrillation phenomenon in the surface of wheat straw fiber is a result of the high shear, twist, and tensile loads during the thermomechanical refining process. For alkalization, with increasing concentration of aqueous solution of sodium hydroxide from 2 to 10 wt % at the temperature of 45°C, the WPL due to alkalization for the wheat straw fiber is increased from 34.6% to 45.0%, indicating that WPL increases gradually with increasing concentration of alkalization. At a lower temperature of 20°C, the WPL is reduced from 34.6% to 26.7%. This means that higher temperature can accelerate the processing of alkalization. SEM micrographs of the wheat straw fibers after alkalization are showed in Figure 1(B). After alkalization, fine voids are produced in the surface of the wheat straw fiber. That results from the fact that alkalization can eliminate hemicellulose and other pectin of the wheat straw fiber, making the wheat straw fiber surface rougher. It is noted that alkalization improves the adhesive characteristics of natural fiber surface^{8–10} by making surface rougher and increasing more contacts.

The WPG due to acetylation for wheat straw fiber increases slightly with increasing reaction time. The maximum WPG is 14.4% after 4 h of reaction time. It has been reported that the WPG of acetylated wood does not exceed 20% with an absence of a catalyst^{12,16} and the results obtained in this study is in agreement with the previous findings. As shown in Figure 1(C), many breakages are obvious after acetylation, and the wheat straw fiber becomes more breakable and fragile. Following the MAPP treatment, it is interesting to note that a layer of polymer appeared in the wheat straw fiber surface, shown in Figure 1(D). This indicates that the MAPP is likely grafted with the wheat straw fiber or covered the wheat straw fiber surface, which helps improve better interface bonding strength between the wheat straw fiber and PP.

Effect of treatments on ultrastructure

Table I shows the effect of treatments on crystallinity indices of the wheat straw fiber. As it can be seen, the controlled wheat straw fiber, from thermomechanically refining processing, has the crystallinity index of 64.9%. Alkali treatment significantly increases the crystallinity index of the wheat straw fiber to 74.7%. This may be due to two reasons. First,

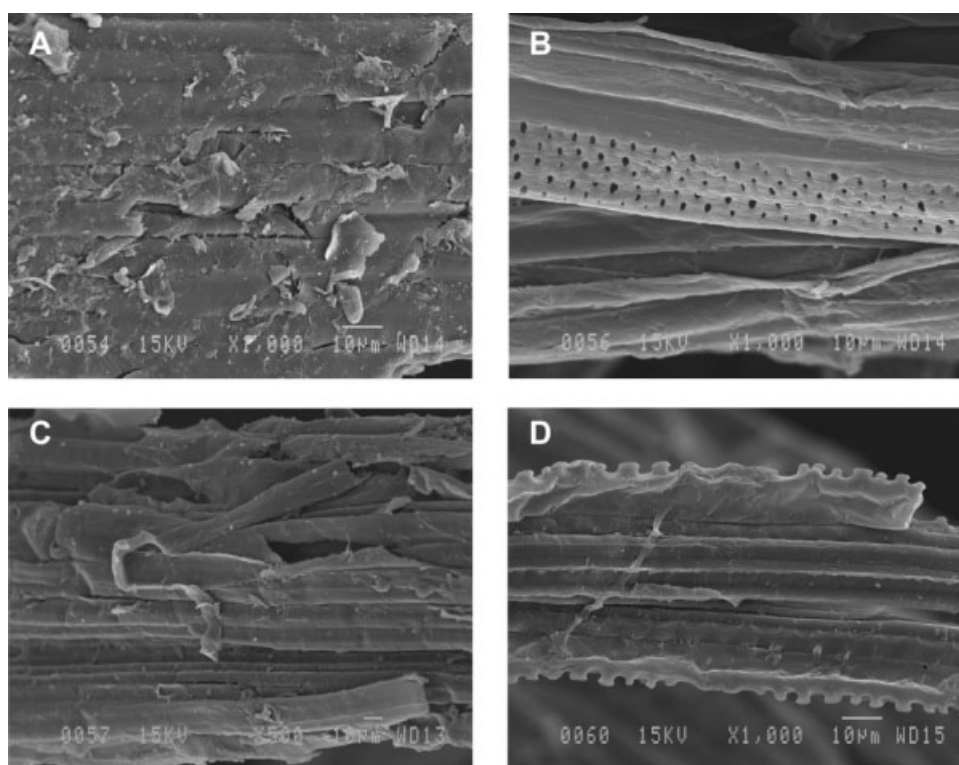


Figure 1 SEM micrographs of samples after treatment (A) control, (B) alkalization, (C) acetylation, and (D) MAPP treatment.

alkalization caused a removal of some of the amorphous constituents of the fiber, hence, increasing the presence of relative crystalline cellulose. Second, there may be a rearrangement of the crystalline regions in such a way that the fiber obtains a more crystalline nature.^{21,22} However, both acetylation and MAPP treatment decreases the crystallinity index of the wheat straw fiber. This is probably due to the steric hindrance introduced by esterification, which does not allow a rearrangement of the crystalline regions. It should be noted that the crystallinity index is useful only on a comparison basis, and it does not provide an accurate determination of the crystallinity content.¹⁴

ATR-IR spectra analysis

ATR-IR spectra of the wheat straw fiber sample after acetylation are shown in Figure 2. The strong absorptions at 3342 cm^{-1} are assigned to hydroxyl

stretching vibrations, and these hydroxyl groups are mainly present in cellulose, hemicellulose, and lignin of the wheat straw fiber. The appearances of peaks at 2890 cm^{-1} are attributed to stretching vibrations of methyl and methylene groups found in cellulose, hemicellulose, lignin, and extractives^{23,24} of the wheat straw fiber. The wheat straw fiber inherently possesses ester linkages in the components of hemicellulose and lignin, which is supported by the presence of a weak absorption peak at 1740 cm^{-1} . After acetylation treatment, the intensity of this peak increases, and another absorption peak appears at 1367 cm^{-1} , a characteristic of CH deformation vibration of methyl. The presence of these sharp and well-defined absorption peaks are due to the esterification between hydroxyl groups of the wheat straw fibers and acetyl groups of acetic anhydride. After the MAPP treatment, the weak absorption peak also appears at 1730 cm^{-1} , as shown in Figure 3. However, it is not clear whether this absorption peak is

TABLE I
Crystallinity Indices of the Untreated and Treated Wheat Straw Fiber

Run	$2\theta_1$	I_{am}	I_{bam}	$2\theta_2$	I_{002}	I_{b002}	I_{002}	I_{am}	CrI (%)
Control	18.922	788	288	22.351	1711	285	1426	500	64.9
Alkalization	18.571	851	332	22.390	2383	332	2051	519	74.7
Acetylation	18.610	856	331	22.117	1619	317	1302	525	59.7
MAPP treatment	19.000	838	282	22.234	1650	273	1377	556	59.6

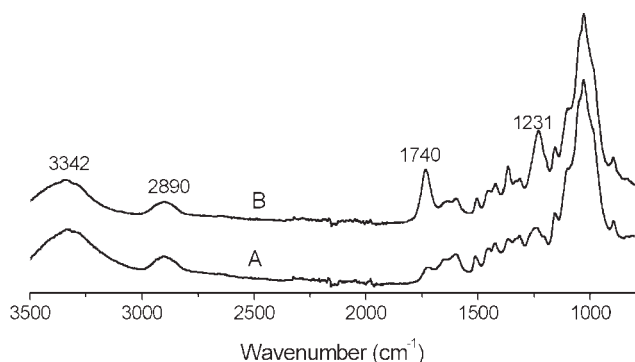


Figure 2 ATR-IR spectra of the wheat straw fiber after acetylation (A) control and (B) acetylation.

due to a formation of ester bonding or the inherent ester bonding in the wheat straw fiber. Assignments of ATR-IR of the wheat straw fiber after the modifications are summarized in Table II.

Thermal properties

Wheat straw fibers possess thermal degradation and combustible properties at high temperatures, which significantly affect the strength and process of the wheat straw fiber-PP composites. Figure 4 shows the TG and its derivatives thermogravimetric (DTG) curves of the wheat straw fibers after the treatments exposed on nitrogen atmosphere. When exposed in a nitrogen atmosphere at 170°C, the weight loss of all samples is less than 5.0% and a significant amount of water is released from the wheat straw fiber. The volatilization of the cellulose, hemicellulose, and lignin is suppressed. At temperatures lower than 170°C, the wheat straw fibers become dehydrated and generate water vapor and other noncombustible gases and liquids, which results in prolonged structural breakdown and discolora-

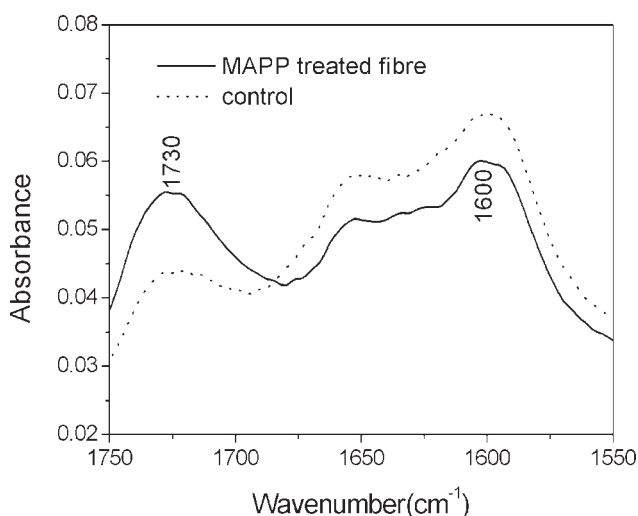


Figure 3 ATR-IR spectra of the wheat straw fiber after MAPP treatment.

TABLE II
ATR-IR Vibrations Peaks and Assignments of Peaks of the Treated Wheat Straw Fiber

Wave number (cm ⁻¹)	Assignments
3342, 3320	OH stretching
2890, 2900	CH stretching of CH ₂ and CH ₃
1730, 1740	C=O stretching
1600	Aromatic or benzene ring stretching
1367	CH deformation of CH ₂ and CH ₃
1031	Si—O—Si vibrations

tion.^{25–27} The DTG curves of the treated wheat straw fiber under nitrogen condition are similar to those of the control, and the peak temperature of the thermal degradation are 368, 361, 361, and 355°C for control, alkalization, acetylation, and MAPP treatment, respectively.

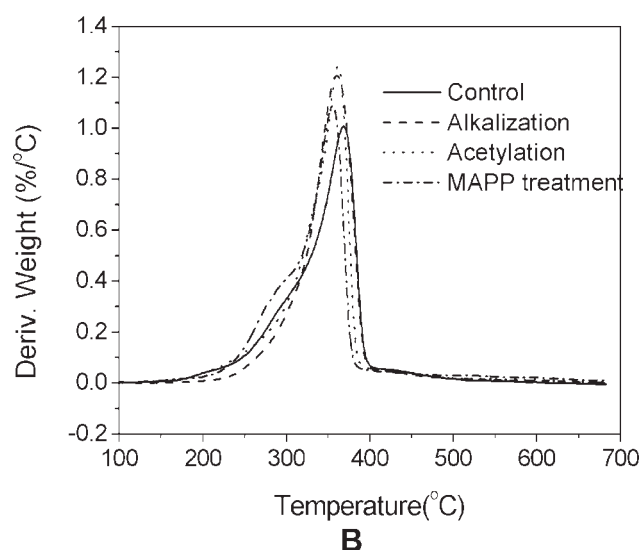
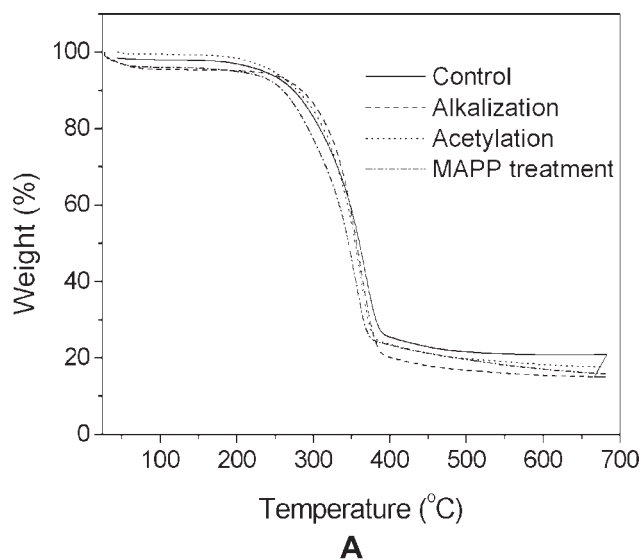


Figure 4 Thermal behavior of the wheat straw fiber after treatment in a nitrogen atmosphere (A) TG and (B) its DTG curve.

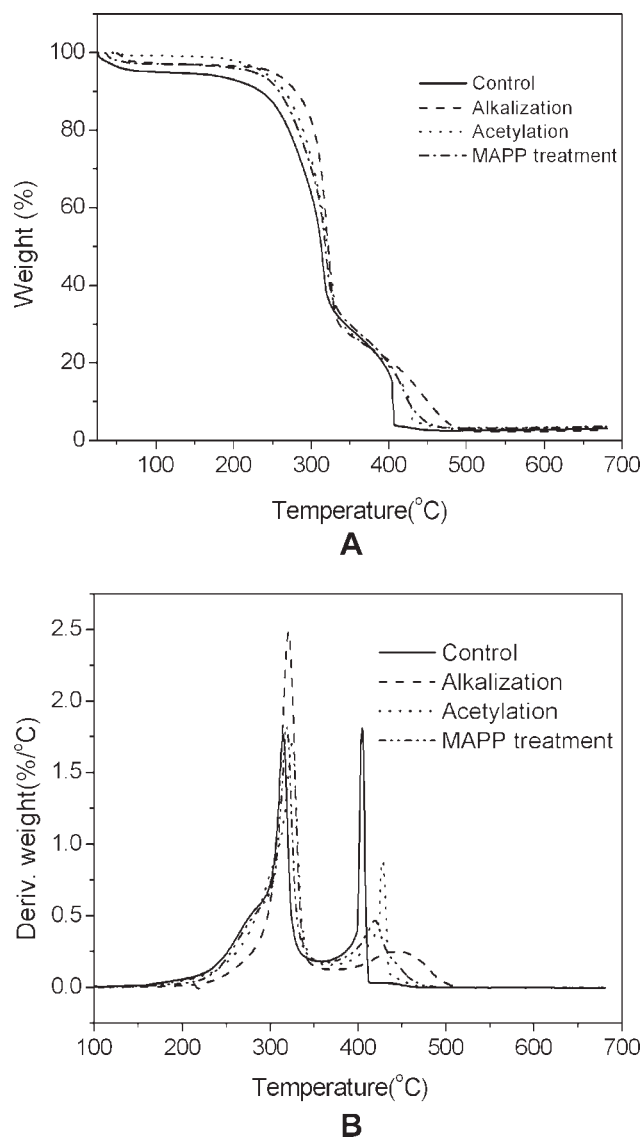


Figure 5 Thermal behavior of the wheat straw fiber after treatment in an air atmosphere (A) TG and (B) its DTG curve.

Figure 5 illustrates TG and DTG curves of the treated wheat straw fiber exposed in an air atmosphere. DTG curves under air condition reveal two

decomposition peaks: one peak at about 320°C is mainly due to the decomposition of the cellulose and the other shoulder, the other peak at around 420°C, can be attributed to the decomposition of the lignin.²⁸ The decomposition peak amplitude of lignin is close to cellulose of the wheat straw fiber; however, it is sharply decreased for the alkali, acetylated, and MAPP-treated wheat straw fiber. At this point, the modification has more effect on lignin than on holocellulose.

When exposed in an air atmosphere at 550°C, the remaining residue of the wheat straw fiber is nearly 2.7%. This indicates that the wheat straw fiber has almost been oxidized, and almost no carbonaceous residue remained. Remaining residue of the wheat straw fiber in air, therefore, reflects the extent of inorganic matter in the wheat straw. The value of 2.7% remaining residue is considered to the silicon content of the wheat straw fiber, which is consistent with the result from burning tests in the previous report.^{25,29} Table III summarizes observations from the TG tests including the onset of degradation, peak temperature for the main degradation, degradation rate, and remaining residues at 550°C.

After exposed at the elevated temperature during the processing of wheat straw fiber-PP composites, the wheat straw fiber is prone to be extremely friable and dark due to hydrolysis, oxygenation during the thermal decomposition. To investigate the effect of exposure temperature and time on chemical structural stability of the wheat straw fiber, the untreated and treated wheat straw fiber was isothermally held for 1 h at 170, 190, 210, and 230°C under an air atmosphere, and the results of weight loss are summarized in Table IV.

From the TGA, the weight loss of the control sample is 6.1, 8.8, 11.6, and 19.7%, respectively, when held for 1 h at 170, 190, 210, and 230°C. Between 170 and 230°C, the wheat straw fiber becomes dehydrated and generates water vapor and other non-combustible gases and liquids including carbon dioxide, formic acid, acetic acid, glyoxal, and water.³⁰ By holding the wheat straw fiber for 1 h at

TABLE III
Degradation Characteristics of the Wheat Straw Fiber After Treatments

Run	Atmosphere	Onset of degradation (°C)	Peak temperature (°C)	Rate of degradation (wt % min ⁻¹)	Residue at 550°C (wt %)
Control	Nitrogen	179	368	3.26	21.13
	Air	213	315,405	4.36	2.71
Alkalization	Nitrogen	237	361	4.63	15.20
	Air	212	321,449	3.08	2.38
Acetylation	Nitrogen	250	361	4.95	19.04
	Air	213	325,429	3.46	3.31
MAPP treatment	Nitrogen	216	355	4.01	18.21
	Air	223	319,419	3.68	3.18

TABLE IV
Weight Loss of the Untreated and Treated Wheat Straw
Fiber Held for 60 min in Air

Time (min)	Run	Weight loss (wt %)			
		170°C	190°C	210°C	230°C
10	Control	4.69	6.66	6.66	7.84
	Alkalization	4.45	4.74	4.68	4.31
	Acetylation	1.66	2.08	2.43	3.40
	MAPP treatment	3.51	4.10	4.62	4.70
20	Control	5.32	7.80	8.60	12.24
	Alkalization	4.63	4.98	5.29	6.19
	Acetylation	2.06	3.17	4.19	7.44
	MAPP treatment	3.84	4.82	6.04	8.64
30	Control	5.64	8.18	9.57	14.77
	Alkalization	4.75	5.17	5.72	7.46
	Acetylation	2.27	3.72	5.21	10.05
	MAPP treatment	4.00	5.19	7.02	11.29
40	Control	5.84	8.42	10.30	16.67
	Alkalization	4.83	5.33	6.07	8.41
	Acetylation	2.40	4.11	6.01	12.11
	MAPP treatment	4.10	5.48	7.84	13.33
50	Control	5.99	8.63	10.96	18.25
	Alkalization	4.91	5.47	6.38	9.18
	Acetylation	2.50	4.43	6.70	13.83
	MAPP treatment	4.21	5.73	8.58	15.04
60	Control	6.11	8.84	11.56	19.65
	Alkalization	4.97	5.59	6.65	9.88
	Acetylation	2.58	4.70	7.32	15.37
	MAPP treatment	4.29	5.96	9.26	16.53

temperatures higher than 170°C, they become slightly charred. With alkalization, the weight loss of the wheat straw fiber is 5.0, 5.6, 6.7, and 9.9%, respectively, when held for 1 h at 170, 190, 210, and 230°C. It is known that alkalization removes almost all hemicellulose, and increases relative cellulose content. Cellulose has better thermal and chemical stability, due to its higher crystallinity.^{31,32} After exposure at 170, 190, 210, and 230°C for 1 h in air, the weight loss of the acetylated wheat straw fiber is 2.6, 4.7, 7.3, and 15.4%, respectively, because of oxygenation and hydrolysis of cellulose, hemicellulose and lignin. The MAPP-treated wheat straw fiber is more stable than the controlled sample but less stable than the acetylated wheat straw fiber due to a lower grafted ratio of maleic anhydride used in this study. Esterification is involved to keep the wheat straw fiber more stable thermally, due to the substitution of hydroxyl groups with acetyl groups.

When all samples were exposed at 170, 190, 210, and 230°C for 10 min in an air atmosphere, it is clear that the degradation rate of the wheat straw fiber, with or without the treatment, exhibits a gradual increase with increasing temperature, especially for the control with 4.7, 6.7, 6.7, and 7.8% of weight loss. After acetylation, the weight loss is 1.7, 2.1, 2.4, and 3.4% at the same testing condition; and that is 3.5, 4.1, 4.6, and 4.7% for the MAPP treatment. Acetylation has a more significant effect on the improve-

ment of the thermal stability of the wheat straw fiber, which can be attributed to esterification between the wheat straw fiber hydroxyl groups (—OH) and acetyl groups (CH₃CO—) of acetic anhydride. Acetylation increases the structural stability, leading to higher thermal stability of the wheat straw fiber. The MAPP treatment does not improve the thermal stability as much as acetylation does because of a lower grafted concentration of maleic anhydride.

CONCLUSIONS

The thermal and chemical properties of the wheat straw fiber after alkalization, acetylation, and MAPP treatments at different temperatures are investigated in this study. In all cases (and when the temperature is lower than 170°C from TGA), chemically pretreated wheat straw fiber exhibits more thermal stability than the control. Alkalization removes almost hemicellulose, thus increases the relative cellulose content and exhibits more crystalline. It also produces more voids in the surface of the wheat straw fiber. Because of the higher crystallinity of cellulose, degradation of the wheat straw fiber is prolonged at higher temperatures. Acetylation has more effect on the thermal and chemical stability, contributing to the ester bonding formation. The wheat straw fiber held for 1 h in air at 170, 190, 210, and 230°C indicates that no obvious thermal decomposition exist in holocellulose and lignin, but the wheat straw fiber is prone to be extremely friable and char. Furthermore, both acetylation and MAPP treatment decreased the crystallinity of wheat straw fiber.

The authors thank Xiangming Wang and Antoine Henry of FPInnovations—Forintek Division for their assistance with the preparation of the wheat straw fibers, and Prof. Mosto Bousmina and his Research Assistant Steve Pouliot of the Department of Chemical Engineering at Laval University for their technical assistance, and Guanxia Yu of Nanjing Forestry University for his assistance with the WAXS experiments.

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