

## Study on the Preparation and Mechanical Properties of Injection-Moulded Wood-Based Plastics

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**ABSTRACT:** The objectives of this study were to prepare injection-moulded wood-based plastics and to characterize their mechanical properties. Injection-moulded wood-based plastics with satisfactory flexural (65.7 MPa) and tensile strengths (30.1 MPa) were successfully obtained through a simple reaction of mulberry branch meal with phthalic anhydride (PA) in 1-methylimidazole under mild condition. The X-ray diffraction results indicated complete disruption of the crystallinity of cellulose because the pattern obtained for esterified fiber was almost a straight line without any peaks. The peaks in the Fourier transform infrared spectroscopy spectra (1738 and 748  $\text{cm}^{-1}$ ) and NMR spectra (173.3 and 133.5 ppm) indicated the attachment of 0-carboxybenzoyl groups onto the wood fibers via ester bonds. The differential scanning calorimetry curves showed that the glass transition temperature decreased with increasing weight percentage gain (WPG). The derivative thermogravimetric analysis curves indicated that esterified wood fiber was less thermally stable than the untreated fiber and that the component tends to be homogeneous with increasing WPG. Scanning electron microscope revealed that the fractured surfaces of most samples were smooth and uniform but that high temperature and less PA dosage could lead to the appearance of holes and cracks. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41376.

**KEYWORDS:** biopolymers and renewable polymers; cellulose and other wood products; mechanical properties; thermoplastics

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### INTRODUCTION

With the increasing depletion of petroleum resources, the search for new eco-friendly materials with excellent performance at an affordable cost as a substitute for petroleum-based plastics has been increasing recently.<sup>1,2</sup> Lignocellulosic biomass, such as agricultural residues and forestry wastes, represents a potential sustainable source of eco-friendly material rather than starch due to its renewability, high yield and low cost.<sup>3</sup> In southern China, substantial number of mulberry branches are discarded after pruning each year. The thermoplasticization of mulberry branches could not only limit the wasting of resources, but also move us one step closer to replacing petroleum-based plastics and wood plastic composites. In addition, in the background of potential food crisis, compared with PLA and other modified starch products, lignocellulose-based plastic is from non-food resources and is more reasonable to be the raw material.

The thermoplasticization of lignocellulosic biomass can be accomplished using several methods, and chemical modification, such as benzylolation,<sup>4</sup> cyanoethylation,<sup>5,6</sup> allylation,<sup>7</sup> etherification, and esterification,<sup>8,9</sup> is one of the most effective methods used for this purpose. Among the various chemical modification methods, benzylolation and esterification were two common methods used to endow wood fiber thermoplasticity. Lu

converted the outer layer of the sisal fiber into a thermoplastic material by benzylolation, while the inner core of the fiber was retained so as to function as a reinforcing element.<sup>10–12</sup> Chen et al. successfully accomplished thermoplasticity of wheat straw though benzylolation in aqueous alkali solution.<sup>13</sup> Unfortunately, benzylolation modification approaches suffers from several drawbacks, such as complex technology, and vigorous reaction conditions. Hassan et al. had made the conversion of bagasse fiber into a thermoformable material using succinic anhydride as the esterifying agent through chemical modification, but the weight percentage gain (WPG) was low and lack of characterization of the mechanical properties of thermoplastic material.<sup>14</sup> Most importantly, the major breakthrough in former works is that lignocellulosic biomass could simply be thermo-moulded by hot pressing.<sup>15</sup> Complete bio-based plastics with sufficient flowability have not yet been successfully developed.<sup>16</sup> Furthermore, among the aforementioned studies, little work has been conducted on thermoplastics of wood-based material; the purpose of most of the previous studies was to enhance properties such as dimensional stability, fungal resistance, photostability, weathering and interfacial compatibility.<sup>17–19</sup> Published studies on the mechanical properties of injection-moulded wood-based plastic obtained through esterification are even more scarce.

**Table I.** WPGs and Mechanical Strengths of Wood Samples After Reacting with PA Under Various Conditions

Samples		Thermoplasticization conditions				Mechanical properties		
No.	Milling time (h)	Reaction temperature (°C)	Reaction time (h)	Reagent dosage		WPG (%)	Flexural strength (MPa)	Tensile strength (MPa)
				BW : PA <sup>a</sup>	NMI (g) <sup>b</sup>			
1	0	15	2	1 : 2	75	48.0		
2	3	15	2	1 : 2	75	104.1	42.5	28.4
3	9	15	2	1 : 2	75	131.3	65.7	30.1
4	15	15	2	1 : 2	75	132.8	56.1	26.4
5	30	15	2	1 : 2	75	132.5	43.5	23.9
6	60	15	2	1 : 2	75	99.7	19.8	8.4
7	15	0	2	1 : 2	75	133.3	64.8	30.6
8	15	5	2	1 : 2	75	129.4	60.9	27.3
9	15	25	2	1 : 2	75	127.9	34.0	15.3
10	15	60	2	1 : 2	75	125.2	24.9	9.4
11	15	15	0.5	1 : 2	75	138.5	52.6	20.1
12	15	15	4	1 : 2	75	129.6	57.5	23.4
13	15	15	8	1 : 2	75	128.2	55.0	18.3
14	15	15	10	1 : 2	75	126.2	53.4	23.7
15	15	15	2	1 : 1	75	52.6	42.1	24.3
16	15	15	2	1 : 3	75	166.2	56.9	27.6
17	15	15	2	1 : 4	75	200.5	65.1	29.8
18	15	15	2	1 : 5	75	211.5	52.5	28.3
19	15	15	2	1 : 2	50	136.6	58.5	28.5
20	15	15	2	1 : 2	100	128.9	59.9	31.9
21	15	15	2	1 : 2	125	116.3	45.2	13.4
22	15	15	2	1 : 2	150	112.5	46.1	19.6

<sup>a</sup>BM : PA represents the mass ratio of dried BM materials to the plasticising reagent PA.

<sup>b</sup>The reagent consumption was calculated when the raw material was 9.0 g.

To overcome these drawbacks, and with the aim of obtaining injection-moulded wood-based plastics with excellent mechanical properties under mild conditions using a simple esterification method, chemical modification of mulberry branch meal with phthalic anhydride (PA) in 1-methylimidazole (NMI) was performed in the present study. The esterification was characterized by WPG calculations, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and <sup>13</sup>C CP-MAS NMR spectroscopy. The thermodynamic stability was characterized by derivative thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC). The mechanical behavior and the fracture surface morphology were also investigated. Mechanisms for the thermoplasticization of wood were briefly elucidated based on the experimental data.

## EXPERIMENTAL

### Materials

After peeling, mulberry branches (Jiangsu, China) were ground in a grinder to pass through a 70 mesh screen. Then, the ground branches were used without any other pretreatments, except ball-milling (BM).

### Chemicals

NMI was purchased from Aladdin Industrial Corporation; acetone, PA, and 4-dimethylaminopyridine (DMAP) were purchased from

Simopharm Chemical Reagent Co. All chemicals were of A.R. grade and were used without further treatment or purification.

### Thermoplasticization

The thermoplasticization of wood was carried out using PA as an acylation reagent, and using NMI as a solvent and catalyst. Wood meal was suspended in a mixture of PA/DMAP/NMI with mechanical stirring. The reaction was performed under the conditions listed in Table I. After thermoplasticization, acetone was slowly poured into the mixture with agitation. The solid was centrifuged and filtered, washed thoroughly with acetone to remove NMI and un-reacted reagents, and dried in an oven. The NMI and acetone were recovered by vacuum distillation.

The WPG was calculated as follows:

$$\text{WPG (\%)} = \frac{M_1 - M_0}{M_0} \times 100\% \quad (1)$$

where  $M_0$  and  $M_1$  are the oven-dried weights of the sample, before and after thermoplasticization, respectively.

### XRD

X-ray measurements were performed on an Ultima IV X-ray diffractometer at 40 KV and 30 mA under the following

conditions: start angle ( $2\theta$ ) =  $5^\circ$ , end angle ( $2\theta$ ) =  $40^\circ$ , and step size ( $2\theta$ ) =  $0.02^\circ$ .

#### FT-IR

Infrared absorption spectra of the native and modified samples derivatives were recorded on an FT-IR spectrophotometer (Nicolet 6700) over the range  $3900\text{--}500\text{ cm}^{-1}$ . Thirty-two scans were recorded for each sample with a resolution of  $2\text{ cm}^{-1}$  in the transmission mode. In each case, dry samples were dispersed in a matrix of KBr and pressed to form pellets.

#### $^{13}\text{C}$ CP-MAS NMR Spectroscopy

Solid-state  $^{13}\text{C}$  CP-MAS NMR spectra of native and modified samples were obtained at room temperature on an AVANCE III 600 MHz NMR spectrometer using MAS rates of 6 kHz at a frequency of 150.90 MHz. Wood meal was packed in MAS zirconia rotors with a diameter of 4 mm. Chemical shifts were relative to glutamate used as an external standard. All the spectra were run collected over 2 h.

#### DTG

The thermal properties of native and modified samples were investigated using thermogravimetric analysis with a NETZSCH TG 209 F1 Iris thermo-gravimetric analyzer. The analyses were conducted at a heating rate of  $10^\circ\text{C min}^{-1}$  under a nitrogen atmosphere.

#### DSC

A Diamond DSC differential scanning calorimeter was used to determine the glass transition temperature of the thermoplasticized wood meal. The heating rate was set at  $20^\circ\text{C min}^{-1}$ , and the measurements were performed under a nitrogen purge.

The samples were held for 1.0 min at  $30.00^\circ\text{C}$ . Then, the samples were heated at  $20.00^\circ\text{C min}^{-1}$  from  $30.00$  to  $200.00^\circ\text{C}$ . After holding for 1.5 min at  $200.00^\circ\text{C}$ , the samples were cooled from  $200.00$  to  $30.00^\circ\text{C}$  at  $20.00^\circ\text{C min}^{-1}$ . A second heating was performed at  $20.00^\circ\text{C min}^{-1}$  from  $30.00$  to  $200.00^\circ\text{C}$ . The DSC thermograms show the second heating process.

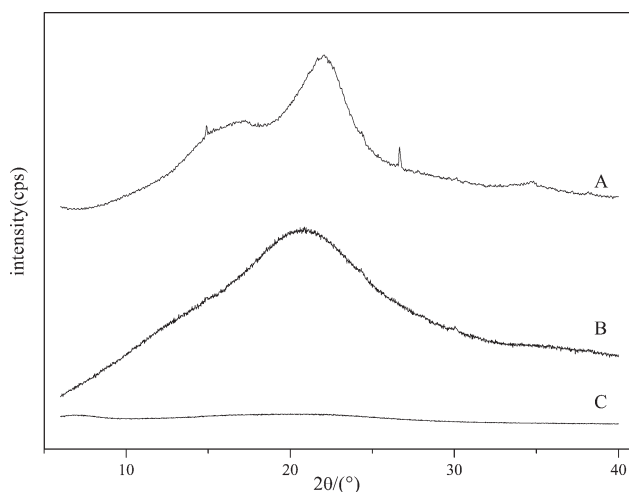
#### Mechanical Behavior

Thermoplasticized products were injection-moulded using a Thermo mini jet under the following conditions: injection temperature of  $175^\circ\text{C}$ , mould temperature of  $80^\circ\text{C}$ , injection pressure of 750 bar, holding pressure of 650 bar, injection time of 30 s, and holding time of 12 s.

The mechanical properties of the injection spline were tested using a UTM4000 computer-controlled electronic universal testing machine. The testing speed for flexural strength was  $5.0\text{ mm min}^{-1}$ , and the testing speed for tensile strength was  $20.0\text{ mm min}^{-1}$ . The dimensions of tensile strength test samples were based on ISO 527-2-A5 and flexural strength test samples were cuboid ( $2 \times 4 \times 10\text{ mm}^3$ ).

#### Scanning Electron Microscope

Samples of the injection spline after mechanical testing were examined with a JSM-7600 FE-SEM. Before performing the scanning electron microscope (SEM) analyses, all of the samples were coated with gold to prevent the accumulation of static charge.



**Figure 1.** XRD patterns of mulberry branch meal without any treatment (a), mulberry branch meal after 15 h of BM (b), and sample 4 (c).

## RESULTS AND DISCUSSION

### Effects of Thermoplasticization Conditions on WPG and Mechanical Properties

Previous investigators have demonstrated that conferring thermoplastic properties to fibers can be achieved through two approaches.<sup>14</sup> One approach was to modify only the thermoplastic matrix of fibers (not meal) and to leave the thermoset component as a reinforcing filler. The other approach focused on rendering the entire fiber structure thermoplastic through chemical modification of fiber meal. Using fiber meal instead of long fibers lost the advantage of utilizing the strength of the fibers. But using fiber meal has the advantage of plasticising more of the chemical components of the fibers, possibly leading to a higher degree of modification, better flowability and improved mechanical properties. Table I presents the WPG and mechanical properties of the esterified fiber as a function of the reaction conditions.

**Effect of BM Time.** Because esterification of the sample without BM (sample 1) occurred, BM was not a necessary treatment for esterifying wood meal with PA in NMI. However, the WPG of the esterified product was as low as 48.0% which indicating the low degree of esterification, and the product was not injection-mouldable which implied the flowability was poor. As shown in the XRD pattern (Figure 1), BM decreased the particle size and the crystallinity of cellulose, increased the specific surface area and the accessibility of reagents and facilitated esterification in the positive direction.<sup>20</sup> Prolonging the milling time from 3 h (sample 2) to 9 h (sample 3) resulted in an increase of the WPG from 104.1 to 131.3% and an increase in flexural strength from 42.5 to 65.7 MPa (Table I). However, when the milling time was increased to 60 h, the WPG of the esterified wood decreased to 99.7% and the flexural strength sharply decreased to 19.8 MPa, possibly because the prolonged intense milling greatly reduced the degree of polymerization of cellulose.

**Effect of Reaction Temperature.** Because high temperatures would impede the exothermic reaction from proceeding in the positive direction and because low temperatures may also block

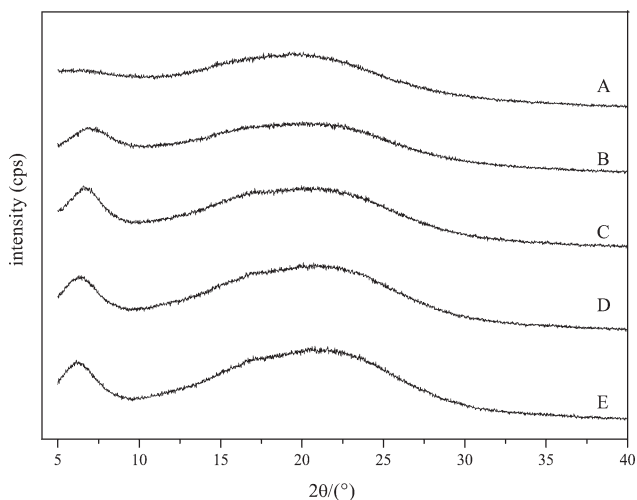
the reaction due to the high viscosity, there was a relationship between temperature and viscosity, resulting in a slight decrease in the WPG from 133.3 to 125.2% as the temperature increased from 0°C (sample 7) to 60°C (sample 10). However, the increase in reaction temperature resulted in a more evident decrease in mechanical strength than in WPG. Clearly, higher temperature impedes the diffusion of heat generated in the reaction, thereby leading to a reaction temperature that is much higher than the ambient temperature, which led to the degradation of the wood meal composition to small molecules. Under the low temperature of 0°C (sample 7), satisfactory flexural and tensile strengths of 64.8 and 30.6 MPa, respectively, were obtained.

**Effect of Reaction Time.** The WPG and mechanical properties were not sensitive to the reaction time. In other words, the reaction of wood meal with PA in NMI was a more rapid reaction (0.5 h) compared with previous studies (8 h).<sup>21</sup> When the reaction time was increased from 0.5 h (sample 11) to 10 h (sample 14), the WPG slightly decreased from 138.5 to 126.2%. Long reaction time will lead to degradation of wood fibers; and, the decrease in WPG was ascribed to such degradation of wood fibers. However, the changes in the mechanical properties were not obvious. It can be concluded from the data that the flexural and tensile strengths fluctuated near 55 and 20 MPa.

**Effect of Reagent Dosage.** Increasing the concentration of reagents caused the reaction to proceed in the positive direction. An increase in the PA dosage had a favorable effect on wood esterification. Increasing the BM : PA dosage from 1 : 1 (sample 15) to 1 : 5 (sample 18), caused the WPG to increase from 52.6 to 211.5%. Unlike the sharp increase in WPG with increasing PA dosage, the flexural strength changed little with increasing dosage. That may be because that changing the dosage of the reagents with other same variables is insufficient to change the mechanical properties of materials.

Increasing the concentration of NMI had an adverse effect on wood esterification. An increase in the concentration of NMI from 50 g (sample 19) to 150 g (sample 22) caused the WPG to decrease from 136.6 to 112.5%. These results appear to be inconsistent with the hypothesis that because the reaction between wood and PA is acid- or base catalyzed, NMI can accelerate the esterification.<sup>22</sup> The difference most likely occurred because NMI is a hydrogen-bond-breaking agent,<sup>23</sup> thus, a large amount of NMI could possibly break the glycosidic bonds in cellulose. The slight decrease in flexural strength from ~60 to 45 MPa with increasing dosage of NMI also confirms that NMI may cause degradation of wood meal.

Note that sample 1 and sample 15 were quite similar but yet different in some respects. The WPGs of sample 1 and sample 15 were 48.0 and 52.6%, respectively, which means that neither reaction was sufficient; however, sample 15 (after BM) was injection-mouldable and possessed good mechanical properties whereas sample 1 (without BM) was not. The reaction conditions in this study were meticulously selected. First, BM was an efficient method for breaking the three-dimensional network structure of lignin and for increasing the accessibility of wood meal,<sup>24</sup> thereby ensuring that agents can penetrate into the



**Figure 2.** Magnified XRD patterns of samples with different WPGs (a: sample 1; b: sample 4; c: sample 16; d: sample 17; e: sample 18).

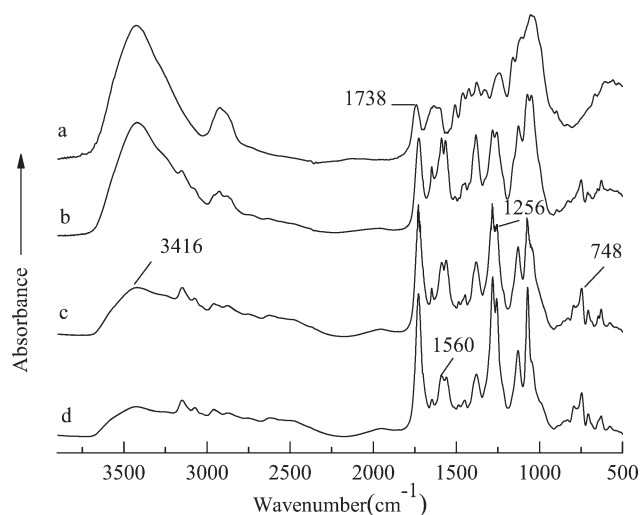
inner space of the wood meal to break the hydrogen bonds to achieve flowability rather than reacting at the fiber surface and, leaving a large number of hydrogen bonds in the cellulose. Second, PA is an excellent esterification reagent with a benzene ring, the presence of which could result in steric-effects that prevent the formation of hydrogen bonds, and virtually no byproducts.<sup>25</sup> Finally, although NMI may cause the degradation of wood meal, it is a perfect solvent, base, and catalyst.<sup>23</sup> Those three factors ensure that an injection-mouldable wood-plastic can be achieved under mild conditions using a simple process, even without a high degree of esterification.

#### Characterization of Injection-Moulded Wood-Based Plastic

**XRD of Injection-Moulded Wood-Based Plastic.** The suprastructures of different samples were investigated using wide-angle XRD. Figure 1 shows the changes that occurred in the X-ray scattering pattern when the raw material was treated by BM and esterification. The original fiber [Figure 1(a)] exhibited the typical cellulose I pattern and eventually transformed after it was BM for 15 h [Figure 1(b)]. The diffraction peak at  $2\theta = 22^\circ$ , which corresponds to the 002 plane of the cellulose I lattice, was observed to shift towards to approximately  $2\theta = 20^\circ$  after BM, and the scattering pattern was lower in intensity and broader in shape. The inner peak at  $2\theta = 15.4^\circ$  was assigned to the 101 and  $10\bar{1}$  lattice planes reflections of cellulose I, and these peaks gradually disappeared after BM. Similar shapes and position changes were reported by Kobayashi et al.,<sup>26</sup> and these changes were suggested to be a result of decrystallization which has a favorable effect on the reaction between wood and reagents.

After esterification, the X-ray scattering pattern of sample 4 was almost a straight line without any peaks (pattern c). This result was considered to be due to the sample being completely amorphous, which is a basic prerequisite for the thermoplasticization of wood meal.

Magnified X-ray scattering patterns of esterified wood with different WPGs are shown in Figure 2. As the weight gain increased

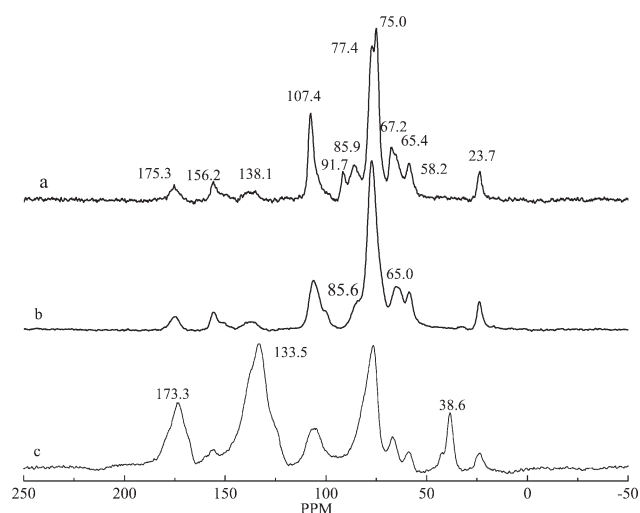


**Figure 3.** FT-IR spectra of unmodified mulberry (a) and samples with different WPG (b: sample 15; c: sample 6; d: sample 16).

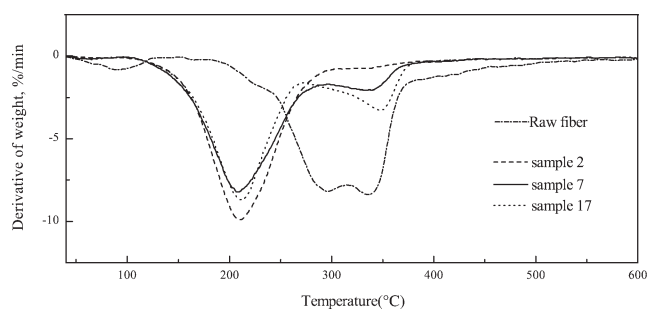
from 48.0% [Figure 2(a)] to 211.5% [Figure 2(e)], a new diffraction peak was formed at approximately  $2\theta = 6.3^\circ$ . With increasing weight gain, the new peaks increased in intensity, became sharper in shape, and moved slightly towards lower diffraction angles. It was clear that the new peak was related to the additional ordering of molecular chains, and the degree of ordering increased as the degree of hydrogen substitution increased, which was a function of the WPG.<sup>27</sup> Because the additional ordering was formed by van der Waals' forces rather than hydrogen bonds, the new crystallization had no adverse effect on flowability.

**FT-IR of Injection-Moulded Wood-Based Plastic.** Figure 3 compares the FT-IR spectra of unmodified mulberry (spectrum a) and samples with different WPGs (spectra b-d) corresponding to samples 15, 6, and 16 in Table I.

Spectrum a exhibits the characteristic signals of lignocellulosics, which include a broad band from the cellulose hydroxyl groups at



**Figure 4.** Solid-state  $^{13}\text{C}$  CP-MAS NMR spectra of raw mulberry branch meal (a), BM mulberry branch meal (b), and esterified mulberry branch meal (c).

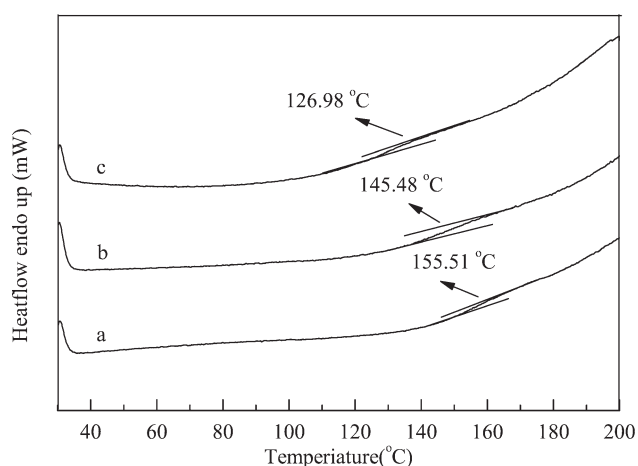


**Figure 5.** DTG thermograms for unmodified fiber (a) and modified fiber with different WPGs.

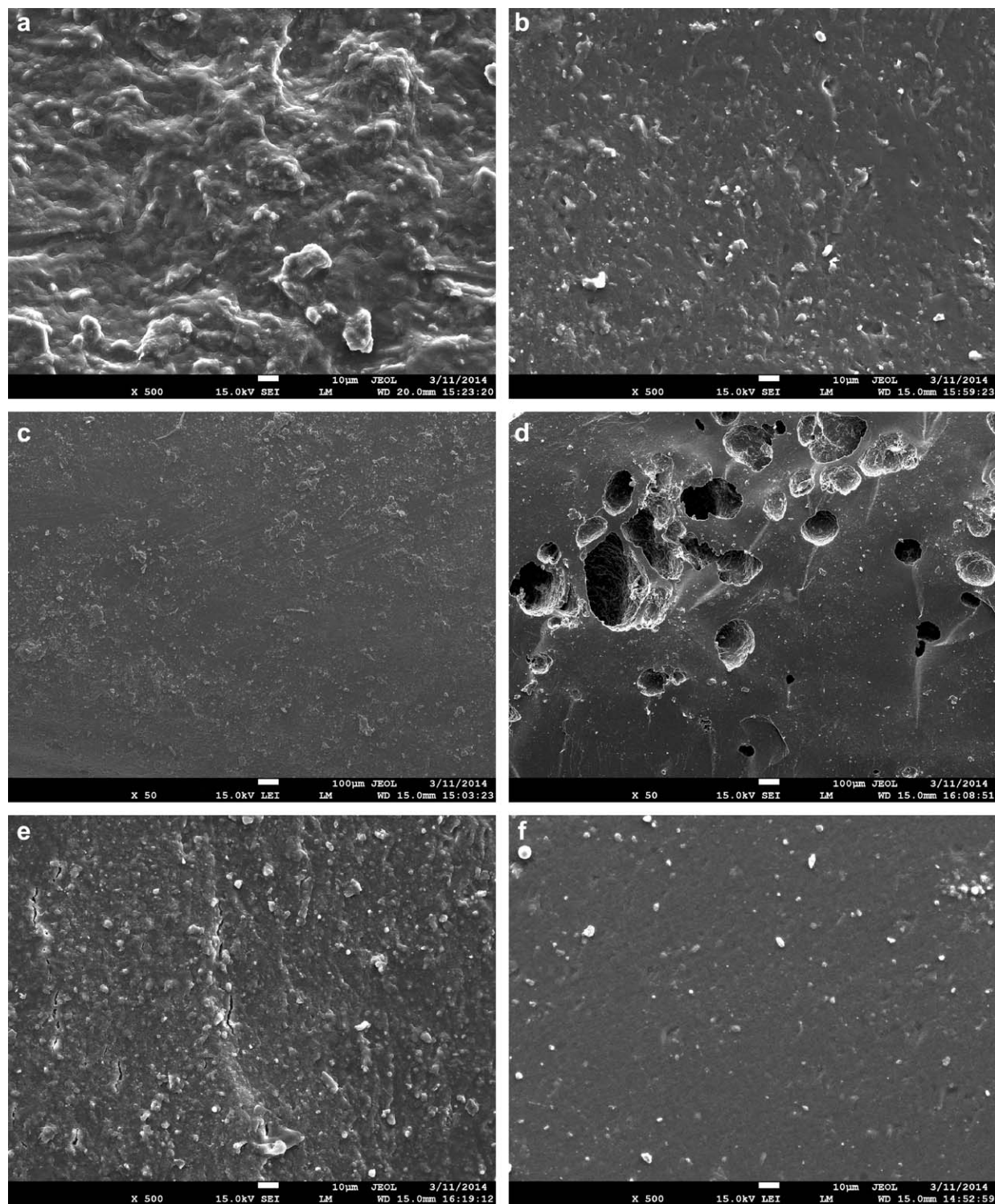
$3416\text{ cm}^{-1}$  and a small band at  $1738\text{ cm}^{-1}$ , corresponding to the carbonyl groups of hemicelluloses and lignin.<sup>28</sup> With increasing WPG (spectra b, c, and d), we can observe a decrease in the band at  $3416\text{ cm}^{-1}$  attributable to the axial deformation of the hydroxyl groups, which were replaced with *O*-carboxybenzoyl groups, in the esterified fibers, as well as an increase in the bands at 1738, 1256, and  $748\text{ cm}^{-1}$  assigned to  $\text{C}=\text{O}$  stretching,  $\text{C}-\text{O}$  antisymmetric stretching, and aromatic  $\text{C}-\text{H}$  angular out-of-plane deformation,<sup>29</sup> respectively, which indicates the formation of ester bonds and the attachment of *O*-formic benzoyl groups onto mulberry. The appearance of a weak peak at  $1560\text{ cm}^{-1}$  characteristic of an imidazole ring indicated the presence of a small amount of NMI.

**$^{13}\text{C}$  CP-MAS NMR of Injection-Moulded Wood-Based Plastic.**  $^{13}\text{C}$  CP-MAS NMR is an appropriate technique for differentiating the signals for crystalline or amorphous carbons in cellulose because of differences in the magnetic environment due to changes in conformation or in packing.<sup>30</sup>  $^{13}\text{C}$  CP-MAS NMR spectra for the raw wood fiber, BM and modified wood fiber are shown in Figure 4.

Figure 4(a) shows the corresponding signals for cellulose, hemicellulose and lignin. The peaks at 107.4 (C1), 91.7 and 85.9 (C4 of crystalline cellulose and amorphous cellulose, respectively), and at 67.2 and 65.4 ppm (C6 of crystalline cellulose and amorphous cellulose, respectively) correspond to cellulose carbons in glucopyranose rings.<sup>31</sup> After BM, the signals at 91.7 ppm and



**Figure 6.** DSC thermograms for modified fibers with different WPGs (a: sample 2; b: sample 7; c: sample 17).



**Figure 7.** SEM micrographs of the fractured surface of injection splines from wood meal esterified under different conditions (a: sample 2; b: sample 3; c: sample 7; d: sample 9; e: sample 15; f: sample 4).

67.2 for crystalline cellulose disappeared in spectrum b, which indicated that the crystalline structure of cellulose was disrupted during BM. A similar phenomenon was observed in the XRD analysis. In addition, the intensity of the overlapping signal at 77.4 and 75.0 ppm attributed to the C2, C3, and C5 of cellulose

and oxylan in hemicellulose completely overlapped after BM, and these signals decreased after esterification. The signals at 65.0 ppm arising from the C6 of cellulose and C5 of xylan also decreased. This result was consistent with the result reported for the esterification of China fir wood by Chang and Chang.<sup>32</sup>

The minor signal at 156.2 ppm is assigned to the C3 and C4 of lignin syringyl and guaiacyl units, and that at 138.1 ppm is assigned to the C1 and substituted C5 of lignin units.<sup>33</sup> Notably, after esterification [Figure 4(c)], the signals at 173.3 ppm for the carboxylic group and at 133.5 ppm for the benzene ring provided evidence for the attachment of the 0-carboxybenzoyl group onto wood fibers via an ester bond, which was consistent with the result observed in the FT-IR spectra. Furthermore, minor signals at 23.7 and 58.2 ppm, belonging to the CH<sub>3</sub> carbon of the acetyl group in hemicelluloses and the methoxy group of aromatic moieties in lignin, respectively, were also observed. The signal at 38.6 ppm is assigned to the carbons belonging to the residual NMI.

#### Thermal Properties of Injection-Moulded Wood-Based Plastic.

The evaluation of thermal stability is of key importance because it is a critical property for thermoplastic bio-material processing.<sup>34</sup> The DTG graphs for the unmodified fiber and for the modified fiber with different WPGs are shown in Figure 5. The results indicate that the esterification of wood meal decreased the hydrophilicity of unmodified fiber, because the water evaporation peak at approximately 100°C disappeared after modification. The disappearance of this peak was most likely due to the esterification, which decreased the number of active hydroxyls in wood fiber that could form strong hydrogen bridges with water.<sup>35</sup> Furthermore, the degradation temperature for esterified fiber starts at 180°C, which is lower than that observed for the unmodified fiber (250°C). A similar decrease in thermal stability had been reported in the literature for the modification of bagasse.<sup>14,36</sup> Un-esterified wood fiber had a significant weight loss temperature of 296.7 and a maximum weight loss temperature of 335.9°C. The former weight loss was most likely due to the pyrolysis of cellulose and hemicellulose, whereas the latter weight loss indicates the pyrolysis of lignin.<sup>37</sup> In comparison, esterified wood fibers had a maximum weight loss at approximately 210°C, which is considered to be pyrolysis of esterified constituent and an unobvious weight loss at approximately 340°C, which gradually disappeared as the ester contents increased and which is considered to be pyrolysis of the unmodified constituent.

The glass transition is the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle state into a molten or rubber-like state (ISO 11357-2). DSC is possible to observe glass transition temperatures. Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. In contrast to previous studies, even though the chemical composition of wood is heterogeneous and complex, as shown in the DSC thermograms for modified fibers with different WPGs (Figure 6), there was a glass transition, such as turning, detected in each curve, and the glass transition temperature decreased as the ester content increased.

**SEM of Injection-Moulded Wood-Based Plastic.** Figure 7 presents the flexural fractured surface under different reaction conditions. The fractured surfaces of most samples were smooth and uniform, implying that the internal molecular structure of

the material is amorphous<sup>38</sup>; the same result was also observed in the XRD analysis. Because BM could successfully reduce the degree of crystallinity, the morphology of the fractured surface for sample 2 [Figure 7(a)] was slightly coarse, whereas that of sample 3 [Figure 7(b)] was quite homogeneous and compact, resulting in a flexural strength that was almost 50% greater than that of sample 2.

Based on the morphologies of the fractured surface of samples with different reaction temperatures, we can clearly conclude that the reduction in flexural strength when the reaction temperature was increased to 25°C [Figure 7(d), sample 9] was mainly attributed to the large amount of holes in the spline. The emergence of holes was most likely due to the carbonization and pyrolysis of small molecules during injection moulding.

Similarly, compared with the homogeneous fractured surface of sample 4 [Figure 7(f)], the morphology for the sample with a smaller PA dosage [Figure 7(e), sample 15] was full of narrow cracks, which resulted in the relatively poor mechanical performance. The cracks could possibly be explained by the weak intermolecular chemical bonding, which was related to the degree of esterification. According to the WPG table and FT-IR spectra, sample 15 was a product with a low degree of esterification.

#### CONCLUSIONS

Injection-mouldable wood-based plastic with satisfactory flexural strength (65.7 MPa) and tensile strength (30.1 MPa) was successfully obtained via reaction with PA and a small amount of DMAP in NMI under mild conditions. Appropriate BM made the material uniform, whereas excess BM greatly reduced the degree of polymerization of cellulose, which had an adverse effect on the mechanical properties. Low temperatures had a favorable effect on the mechanical properties and WPG. The reaction was a rapid process because the influence of reaction time on the WPG and mechanical properties was not significant. The WPG immediately increased when the dosage of PA was increased, but the increase in mechanical properties was slowly. NMI acted not only as a base and catalyst, but also as a degradation agent of esterification.

The XRD, FT-IR, and NMR results indicated the occurrence of esterification and the complete disruption of the crystalline structure of cellulose during esterification. The DSC curves indicated that the glass transition temperature decreased with increasing WPG. The DTG curves showed that esterified wood fibers were less thermally stable than untreated fibers. Although some individual samples exhibit holes and cracks, the fractured surfaces of most samples were smooth and uniform. The utility of the esterified wood as an injection-mouldable plastic is currently under investigation.

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