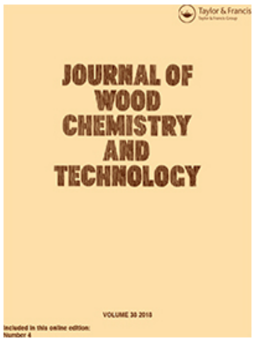
Journal of Wood Chemistry and Technology

ISSN: 0277-3813 (Print) 1532-2319 (Online) Journal homepage: http://www.tandfonline.com/loi/lwct20



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To cite this article: Ying Guo, Jian-Qiang Chen, Meng Su & Jian-Guo Hong (2018) Bio-based Plastics with Highly Efficient Esterification of Lignocellulosic Biomass in 1-methylimidazole under Mild Conditions, Journal of Wood Chemistry and Technology, 38:4, 338-349, DOI: 10.1080/02773813.2018.1488876

To link to this article: https://doi.org/10.1080/02773813.2018.1488876

Journal of Wood Chemistry and Technology, 38: 338–349, 2018
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ISSN: 0277-3813 print/1532-2319 online
DOI: 10.1080/02773813.2018.1488876

BIO-BASED PLASTICS WITH HIGHLY EFFICIENT ESTERIFICATION OF LIGNOCELLULOSIC BIOMASS IN 1-METHYLIMIDAZOLE UNDER MILD CONDITIONS

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Lignocellulosic biomass is regarded as one of the most abundant and sustainable resources for the development of bio-based plastics. The esterification of wood with phthalic anhydride (PA) yields low content due to lack of an efficient modification medium. In the present study, 1-methylimidazole was used as a catalytic medium for the highly efficient esterification of waste lignocellulosic biomass (poplar wood, mulberry wood, and wheat straw) with PA. After modification, the wood particles were plasticized and molded via injection molding. Analyses of the weight percent gain showed that under the same conditions, poplar wood, which has a soft and loose structure, presented the highest extent of esterification, whereas mulberry wood, which has a tight texture, had the lowest extent of esterification. Mulberry wood-based plastics exhibited the best performance in terms of flexural and tensile strength. Notably, short reaction time was favorable to produce bio-based plastics that were light in color. FT-IR spectroscopy and solid-state ^{13}C NMR spectroscopy confirmed the chemical structures of the esterified products. Dynamic mechanical analysis was used to identify the storage modulus and the damping factor of the esterified products. Analyses of the morphologies of the materials demonstrated different composite structures for the bio-based plastics, which played an important role in their mechanical performance.

KEYWORDS. Bio-based plastics, lignocellulosic biomass, heterogeneous esterification, phthalic anhydride, 1-methylimidazole

INTRODUCTION

In past decades, bio-based plastics have shown great potential as substitutes for petroleum-derived plastics and have been developed from various biomass sources.[1–3] For example, as a typical degradable polymer, poly(lactic acid) (PLA) has been widely used in packaging, automobile, tissue engineering, and pharmaceutical industries.[4] The monomer of PLA, lactic acid, is usually derived from food resources in the presence of microorganisms. In addition, natural polymers extracted from plant biomass, such as starch,[5,6] proteins,[7] and plant oils,[8] have been used as raw materials to develop bio-based plastics. Notably, lignocellulosic biomass, including woody plants and cereal crops, is regarded as one of the most abundant and sustainable resources for biofuels, chemicals, and new materials.[9,10] Lignocellulosic biomass has not yet been fully utilized for practical proposes. In particular, every year, hundreds of millions of tons of wheat straw are burnt after the harvest in China, leading to severe pollution in the environment. Therefore, the conversion of waste lignocellulosic biomass into bio-based

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plastics is of great importance to reduce the cost of bio-based plastics.

Lignocellulosic fibers have a reinforced composite structure, wherein cellulose fibrils act as a stiff reinforcement and hemicelluloses and lignin components act as a soft matrix. Lignocellulosic fibers lack a high degree of plasticity, mainly because of strong inter- and intra-chain hydrogen bonds in the crystalline regions of cellulose.[11,12] A large number of hydroxyl groups in cellulose can be substituted chemically by non-polar groups to disrupt hydrogen bonds; thus, lignocellulosic fibers can achieve plasticity.[13] Generally, there are two approaches to the chemical modification of lignocellulosic fibers to obtain plasticity: etherification[14–16] and esterification.[17–19] In our previous studies, mulberry wood and wheat straw have been successfully plasticized by benzylation in an aqueous alkali solution.[20] By comparison, etherification reactions typically require high temperatures and harmful chemicals, e.g., alkali conditions and benzyl chloride, which inevitably pose threats to both researchers and the environment.

Phthalic anhydride (PA), which is similar to benzyl chloride, has a large and flat molecular structure. By performing an esterification of the lignocellulosic fibers with PA, many benzoyl groups can be introduced into the cellulose chains. Accordingly, the robust lignocellulosic structure can be separated due to the reduced intermolecular forces among the cellulose chains. Theoretically, the flowability of the lignocellulosic components can be achieved by increasing their temperature above the melting temperature.[21] Researchers have attempted to modify wood with PA; however, the esterified products, which showed slightly improved plasticity, can only be processed by hot pressing due to the low content of esterification.[22] 1-methylimidazole (NMI) acts as a hydrogen-bond-breaking agent when dispersed into lignocellulosic fibers, and NMI also acts as a catalyst for esterification, assuming that the reaction between the lignocellulosic fibers and PA is acid- or base-catalyzed.[23,24] Therefore, the esterification of the lignocellulosic fibers can be effectively improved under mild conditions in NMI. The use of NMI for the plasticization of different lignocellulosic fibers through efficient esterification has not yet been reported.

In this study, bio-based plastics of different injection levels derived from three kinds of waste lignocellulosic biomass, including poplar-wood chips, mulberry branches, and wheat straw, were successfully prepared by highly efficient esterification in NMI under mild conditions. The esterified products were characterized by weight percent gain (WPG), FT-IR spectroscopy, and solid state ^{13}C NMR spectroscopy. Moreover, the mechanical performances, viscoelastic behaviors, and surface morphologies of the injection-molded plastic specimens were systemically studied.

MATERIALS AND METHODS

Materials

Mulberry wood, poplar wood, and wheat straw were obtained in the Jiangsu province, China. All the raw materials were pulverized to an 80 mesh size and were then ball-milled for 4 h with a planetary ball mill (QM-3SP2, Nanjing University affiliated Instrument Factory, Nanjing). Four 500 mL zirconia milling cylinders and 70 zirconia balls with three diameters (large = 10 mm, medium = 7 mm, and small = 5 mm) were used. The number ratio of large: medium: small of the milling balls was 1:2:4, and the optimal ball milling time was 4 h to achieve minimal sizes of the lignocellulosic fibers without severe degradation. Wheat straw was dispersed in an aqueous NaOH solution (5 wt%) while stirring for 24 h to remove the wax layer, followed by washing with distilled water to reach a neutral pH. NMI was purchased from the Aladdin Industrial Corporation, China, and acetone and PA were purchased from Simopharm Chemical Reagent Co, China. All the chemicals were of A.R. grade and were used without further treatment or purification.

Chemical Composition Analysis

The components of the wheat straw, poplar wood, and mulberry wood were characterized. The cellulose content was determined by the nitric acid-ethanol method. The hemicellulose content was calculated by subtracting the cellulose content from the holocellulose content, which was determined according to Chinese national standard (GB/T2677.10-1995): Fibrous raw material – Determination of holocellulose. The lignin content was calculated by adding the acid-insoluble lignin content (Chinese national standard (GB/T747-2003): Pulps – Determination of acid-insoluble lignin) with the acid-soluble lignin content (Chinese national standard (GB/T10337-2008): Raw material and pulp – Determination of acid-soluble lignin). The extracted content underwent a hot water treatment. The ash content was determined according to Chinese national standard (GB/T 6438-2007): Animal feeding stuffs – Determination of crude ash.

Esterification of Lignocellulosic Biomass

Heterogeneous esterification of three lignocellulosic biomass materials was carried out at room temperature using PA as an acylation reagent and NMI as the dispersion medium and catalyst. After a ball-milling treatment, the lignocellulosic biomass was suspended in a mixture of PA/DMAP/NMI with mechanical stirring. The chemical dosages and reaction times are listed in Table 2. The esterified products were precipitated by pouring the reaction mixture slowly into 400 mL of acetone with agitation. The resultant precipitates were centrifuged, filtered, and washed with ethanol twice to remove NMI and the unreacted PA. Then, the esterified products were weighed to determine WPG, which was calculated using the following equation:

$$\mathrm{WPG}\ (\%) = \frac{M_1 - M_0}{M_0} * 100\%,$$

where M_0 is the initial oven-dried weight of the lignocellulosic biomass and M_1 is the weight of the oven-dried esterified products. Each experiment was performed in triplicate under the same conditions, and each WPG listed in Table 2 represents an average value.

Injection Molding

Dumbbell-shaped specimens based on the ISO 527-2-A5 standard and cuboid specimens ($2 \times 4 \times 10$ mm) were prepared through an injection molding process and were used for tensile and flexural tests, respectively. Before the injection molding process, the esterified products were homogenized with a twin screw extruder (minilab, Thermo) at 155 °C and were extruded under a screw, with a speed of 50 rpm. The extrudate was granulated using a mill (A11, IKA) and then oven-dried at 80 °C for 24 h. The injection molding at 170 °C and under 550 bar was performed using an injection molding machine (Mini-jet, Thermo).

Characterization

FT-IR

Three kinds of lignocellulosic biomass materials and their esterified samples were characterized by FT-IR spectroscopy (Nicolet 6700, USA) with finely ground samples (1%) in KBr pellets. A total of 16 scans were collected for each sample and were recorded in the range of 4000–500 cm^{-1} at a resolution of 4 cm^{-1}.

Solid-state ^{13}C NMR

Solid-state ^{13}C NMR spectra of the lignocellulosic biomass, ball-milled samples, and the esterified products were characterized on an AVANCE III 600 MHz NMR spectrometer using MAS rates of 6 kHz at a frequency of 150.90 MHz. The spin rate of the 4-mm rotor was 8 kHz for the CP/MAS experiments. The acquisition time was 0.0127 s. The delay time was 2 s.

Dynamic Mechanic Analysis

A dynamic mechanical analyzer (Q800, TA Instruments, USA) was used to analyze the storage modulus and the damping factor (tanδ) at a heating rate of 3 °C/min from −50 °C to 100 °C under a multi-frequency-strain module. A dual cantilever system was used to hold the specimens.

Mechanical Testing

The mechanical tests of the injection-molded specimens were conducted using a universal tester (UTM13344 MTS, USA). The crosshead speeds were set at 5.0 mm/min and 20.0 mm/min for flexural strength and tensile strength, respectively.

Scanning Electron Microscope (SEM)

The morphologies of cross-sections of the specimens were observed on a field emission scanning electron microscope JSM-7600F (JEOL, Japan). All the samples were coated with a thin layer of gold by sputtering before the SEM imaging. An accelerating voltage of 10 kV was applied.

RESULTS AND DISCUSSION

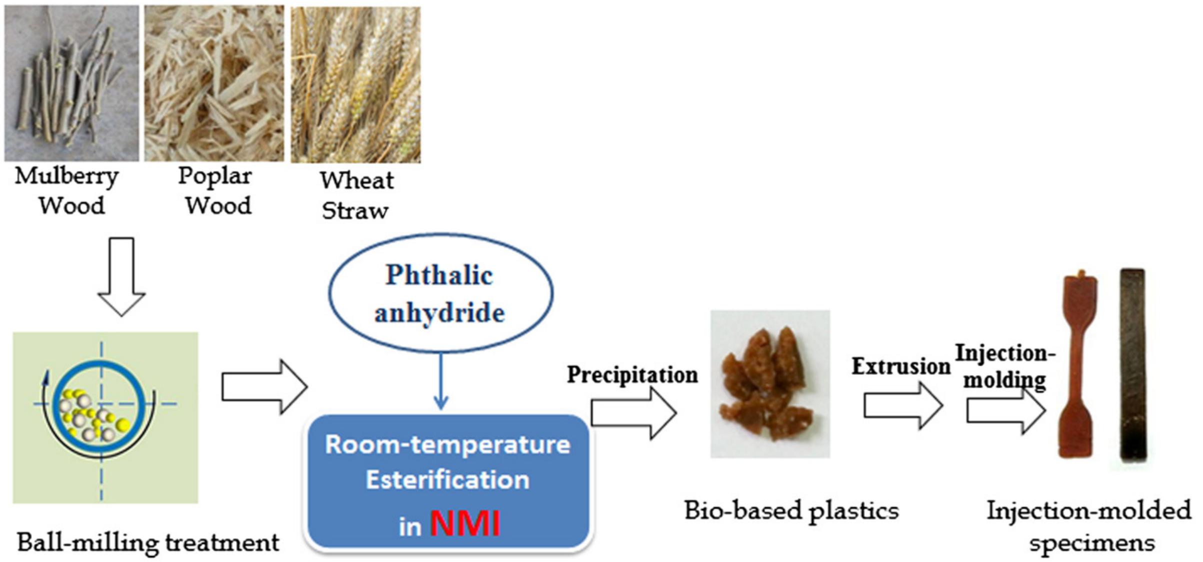
Esterification of Lignocellulosic Biomass

Before esterification, the chemical composition of each lignocellulosic biomass was characterized, and the results are listed in Table 1. Cellulose, hemicellulose, and lignin accounted for more than 85% of the chemical composition in the three lignocellulosic biomass materials. Specifically, the cellulose content in poplar wood (45.3 wt%) and mulberry wood (49.5 wt%) was considerably higher than that of the wheat straw (35.4 wt%), whereas wheat straw contained the highest amount of hemicellulose. The lignin content in each of these lignocellulosic biomass materials was similar. The extracts obtained after the hot water treatment were mainly sugar, tannin, and water-soluble inorganic salts. The high ash content in wheat straw (9.6 wt%) was mainly composed of silicate salts, calcium salts, and potassium compounds.

TABLE 1. Chemical composition of three lignocellulosic biomass materials.

	Content/%		
Components	Wheat straw	Poplar wood	Mulberry wood
Cellulose	35.4 ± 2.1	45.3 ± 1.2	49.5 ± 1.7
Hemicellulose	34.7 ± 1.2	28.5 ± 1.5	25.4 ± 1.1
Lignin	16.5 ± 1.0	17.1 ± 0.8	16.6 ± 0.8
Extracts	2.3 ± 0.5	4.2 ± 0.7	4.6 ± 0.5
Ash	9.6 ± 0.6	2.9 ± 0.2	2.1 ± 0.2

The process used for preparing the bio-based plastics is illustrated in Scheme 1. Prior to esterification, the lignocellulosic fibers were subjected to a ball-milling treatment that reduced the size of the ball-milled particles to 20 µm. At room temperature, homogeneous acylation of eucalyptus wood can occur in NMI.[23] In our study, esterification of the lignocellulosic fibers was achieved in NMI without any additional catalyst. The reaction was heterogeneous because NMI cannot completely dissolve all the woody particles. Table 2 shows the WPG of the materials collected after the chemical dosages were added for the given reaction times. Based on Table 2, the WPG of all the samples is more than 100%, indicating that the reaction was highly efficient under mild conditions. Moreover, in terms of reaction time, the esterification of each lignocellulosic biomass for 0.5 h produced bio-based plastics with comparable WPG values to those reacted for 1.0 h (samples #2 and #4, #6 and #8, #10 and 12), which reflects the high efficiency of the esterification reaction in NMI. The efficiency of the esterification was attributed to the NMI, which acts as an efficient catalyst in the reaction.[23,24] An increase in the NMI dosage from 50 to 75 g had an obviously favorable effect on the WPG for all three types of lignocellulosic biomass materials. However, increasing the added amount of NMI from 75 to 100 g did not result in any obvious increase in the WPG. For the poplar wood and wheat straw, continuous addition of NMI led to a decrease in the WPG. Like ionic liquids, NMI is a hydrogen-bond-breaking reagent for lignocellulosic fibers. Consequently, excessive addition of NMI leads to the breakage of glycosidic bonds in



SCHEME 1. Flow diagram of the preparation process for bio-based plastics derived from lignocellulosic biomass materials.

TABLE 2. Different esterification conditions and corresponding weight percent gains.

		Chemical dosages				
Lignocellulosic biomass (L.B.)	No.	L.B./g	P.A./g	NMI/g	Reaction time/h	WPG/%
Mulberry wood	1#	9	18	50	1.0	113.4
	2#	9	18	75	1.0	129.4
	3#	9	18	100	1.0	130.3
	4#	9	18	75	0.5	126.6
Poplar wood	5#	9	18	50	1.0	126.7
	6#	9	18	75	1.0	157.1
	7#	9	18	100	1.0	148.3
	8#	9	18	75	0.5	141.3
Wheat straw	9#	9	18	50	1.0	129.4
	10#	9	18	75	1.0	138.3
	11#	9	18	100	1.0	121.3
	12#	9	18	75	0.5	133.3

the cellulose and therefore affected the WPG.

By comparing the WPG values of the three materials after reactions under the same conditions, the extents of esterification of the three kinds of lignocellulosic biomass materials were poplar wood > wheat straw > mulberry wood. These results possibly arose from the kinetic diffusion of the reactive reagents throughout the cell walls of the lignocellulosic biomass.[25] Poplar wood is relatively lightweight and soft and has large early wood pores in the texture, which is beneficial for the diffusion of PA to the hydroxyl groups in the poplar wood. In contrast, mulberry wood has a tight texture, which likely led to relatively low accessibility of the hydroxyl groups to the reagents.

Appearance and Mechanical Performance

Notably, the reaction time had an obvious effect on the appearance of the esterified products, as shown in Figure 1. Dumbbell-like specimens prepared from samples #4, #8, and #12 were much lighter in color than those prepared from samples #2, #6, and #10. In ionic liquids/dimethyl sulfoxide, the heterogeneous esterification of mulberry

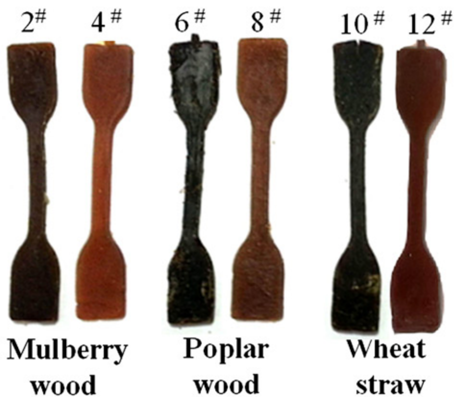


FIGURE 1. Image of dumbbell-like injection-molded specimens.

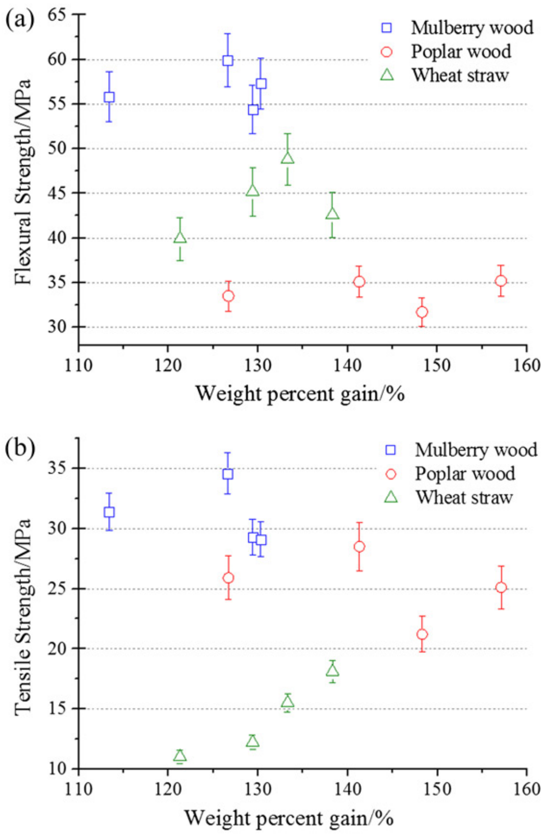


FIGURE 2. Mechanical properties after weight percent gain.

wood over a short time (2 h) can produce all-wood-plastics that are highly translucent in appearance and thus have desirable light-permeability.[26] The heavy coloring of the samples possibly arose from the oxidation of the phenolic lignin into benzoquinones over long esterification reaction times. However, esterification for 0.5 h was favorable for a better mechanical performance, possibly due to the lower extent of modification on the cellulosic components, which acted as reinforcements in the specimens.

The flexural and tensile strengths of all the specimens based on the WPG of the corresponding esterified products are illustrated in Figure 2. Mulberry wood-based plastics demonstrated the best performances in both the flexural and tensile strength tests among the three lignocellulosic biomass materials. Related to the relatively low WPG of the mulberry wood-based plastics, the superior mechanical properties are likely attributed to the fact that, after esterification, the mulberry wood contained a relatively high content of unmodified cellulosic components, which acted as reinforcements in the specimens. The SEM results discussed in a later section revealed this clearly reinforced structure in the mulberry wood-based plastics. Poplar wood-based plastics with high WPG exhibited the lowest flexural strengths, possibly because the modification of the lignocellulosic components in the poplar wood resulted in the collapse of its robust structure. Wheat straw-based plastics exhibited the lowest tensile-strength performances. The cavities in the inner layers of wheat straw-based plastics, as shown in the SEM results, accounted for the relatively low strength. It is worth noting that the consistent synthesis of materials with a certain WPG in their esterified products corresponded to the optimal mechanical performances of the specimens for each lignocellulosic biomass. Occasionally, relatively high WPGs led to inferior mechanical performances.

FT-IR Spectra

Figure 3 shows the FT-IR spectra of the raw lignocellulosic biomass and the esterified products (samples #2, #6, and #10). By comparing the results before and after esterification, the broad peaks at 3430 cm^{-1} corresponding to active hydroxyl groups in the lignocellulosic biomass had noticeably reduced intensities, which indicated that a considerable amount of hydroxyl groups were

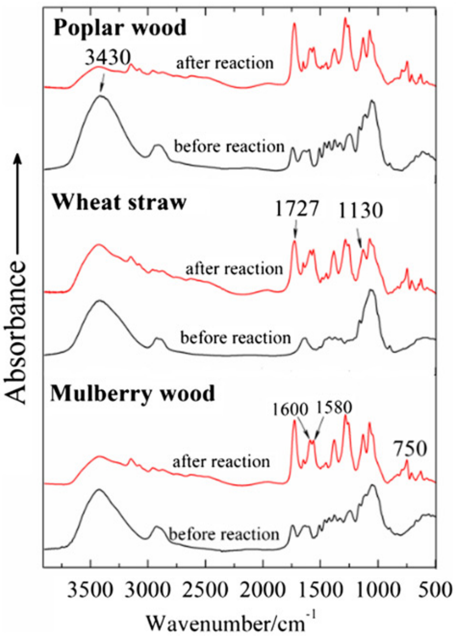


FIGURE 3. FT-IR spectra of lignocellulosic biomass before and after esterification.

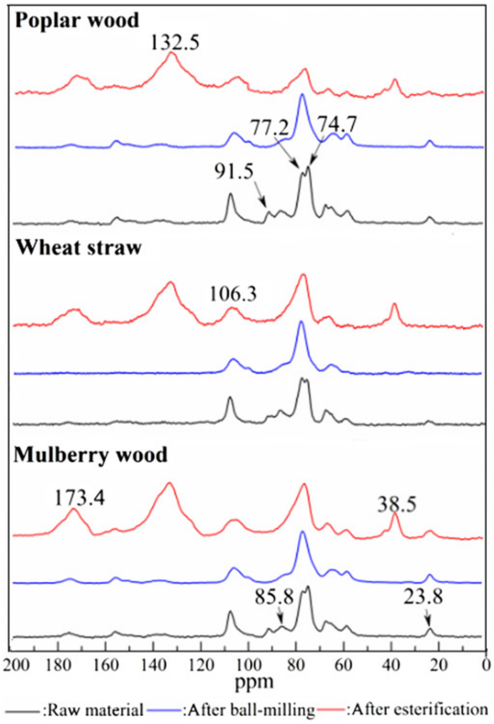


FIGURE 4. Solid-state 13C NMR spectra of lignocellulosic biomass after ball-milling and esterification.

substituted by PA. The peaks at 1727 and 1130 cm^{-1}, corresponding to the C=O stretching and the C−O anti-symmetric stretching, respectively, increased after the esterification, which provided direct evidence of successful esterification. In addition, the peak at 750 cm^{-1}, which is assigned to the aromatic C−H angular out-of-plane deformation, clearly increased after the reaction, which confirmed the successful introduction of carboxybenzoyl groups into the lignocellulosic fibers.[27]

The decreased intensity of the peak at 3430 cm^{-1} after esterification of mulberry wood was more apparent than that of wheat straw, indicating the lower extent of esterification in wheat straw. This result was inconsistent with the results from the WPG analysis. This difference is possibly attributed to the loss of components such as hemicellulose and lignin when the ball-milled wheat straw was subjected to the alkali pretreatment, whereas almost all the hemicellulose and lignin of mulberry wood was retained before esterification. As a result, mulberry wood exhibited intensive esterification by FT-IR but showed a relatively low WPG.

It is worth noting that, in Figure 3, the peaks at 1600 and 1580 cm^{-1} appeared to be split, which was not observed in the unmodified materials. This result indicated strong conjugation of the C=O groups in the ortho and para-positions of benzoquinone moieties in the esterified products, which can explain the heavy coloring in samples #2, #6, and #10.[28]

Solid-state ^{13}C NMR Spectra

Solid-state ^{13}C NMR spectra are shown in Figure 4. After the ball-milling treatment, the raw materials were also characterized to analyze any changes caused by ball-milling. In the spectra of the raw lignocellulosic biomass, the main components of cellulose, hemicellulose, and lignin have specific signals, as previously described.[29] The spectra of poplar wood and mulberry wood were very similar. In contrast, the removal of a portion of hemicellulose and lignin from the wheat straw during the alkali pretreatment caused peaks in the range of 130–180 ppm (corresponding to lignin components), and the peak at 23.8 ppm (corresponding to the $-CH_3$ carbon of the acetyl group in hemicellulose) disappeared in the unmodified wheat straw.

After the ball-milling treatment, obvious changes were observed in the three kinds of raw materials. The peak at 106.3 ppm belonging to the crystalline cellulose became blunt, and the original doublets at 74.7 and 77.2 ppm corresponding to the C2, C3, and C5 of cellulose and oxylan in hemicellulose merged into a sharp peak, which was attributed to the decrystallization of the cellulose by ball-milling. In the spectra of the esterified products, the peak at 173.4 ppm, which was assigned to the carbonyl group, indicated that esterification occurred at the C6 position, which was inconsistent with the results from the palmitoylation of wood.[30] Strong signals at 132.5 ppm corresponded to the benzene ring carbons and confirmed the substitution of hydroxyl groups by carboxybenzoyl groups. After esterification, the blunt peaks at 74.7 and 77.2 ppm indicated that esterification also occurred at the C2 position.

Dynamic Mechanical Analysis

Dynamic mechanical analysis is an effective method for studying the viscoelastic behavior of polymeric composites under a dynamic load.[31] Figure 5 shows the storage modulus – temperature curves of plastics derived from the three lignocellulosic biomass materials. When the temperature increased from far below 0 °C, the storage modulus initially remained stable at a high value, as the polymer chains in the lignocellulosic biomass were frozen and unable to move. As the temperature increased above 0 °C, the storage modulus gradually decreased with the increasing temperature. Specifically, the values of the storage moduli from 20 °C to 80 °C for the three esterified products were mulberry wood > wheat straw > poplar wood, in accordance with the results of the flexural strengths, as tested at room temperature.

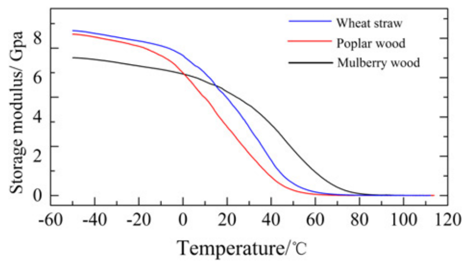


FIGURE 5. Storage modulus – temperature curve.

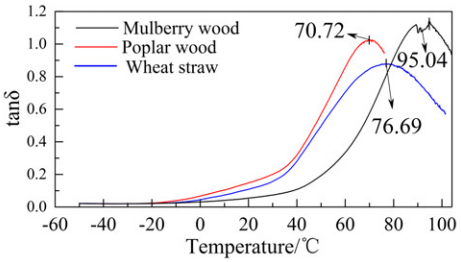


FIGURE 6. Damping factor – temperature curve.

Tanδ is called damping factor and was used to characterize the damping behavior of the tested materials, which was calculated as the ratio of the loss modulus to the storage modulus. When the temperature increased to the glass transition temperature (Tg), a glass transition in the non-crystalline region of the material occurred. Consequently, the mechanical strength changed substantially. The temperature at which the damping factor in the tanδ curve reaches its peak can be regarded as Tg.[32] Figure 6 shows the damping factor – temperature curves of the three esterified lignocellulosic biomasses. From the damping factor curves in Figure 6, the Tg values can be estimated at 70.72 °C, 76.69 °C, and 95.04 °C for their respective bio-based plastics. There was a close relationship between the WPG and the Tg value because a low extent of modification resulted in a higher rotational energy barrier in the esterified products, which requires high energy to overcome. Based on Tg, the extent of esterification can be deduced (poplar wood > wheat straw > mulberry wood), which is in good agreement with the WPG results. In addition, the height of the damping peak corresponded to the difficulty of segmental relaxation occurrence in the polymers. The strongest damping

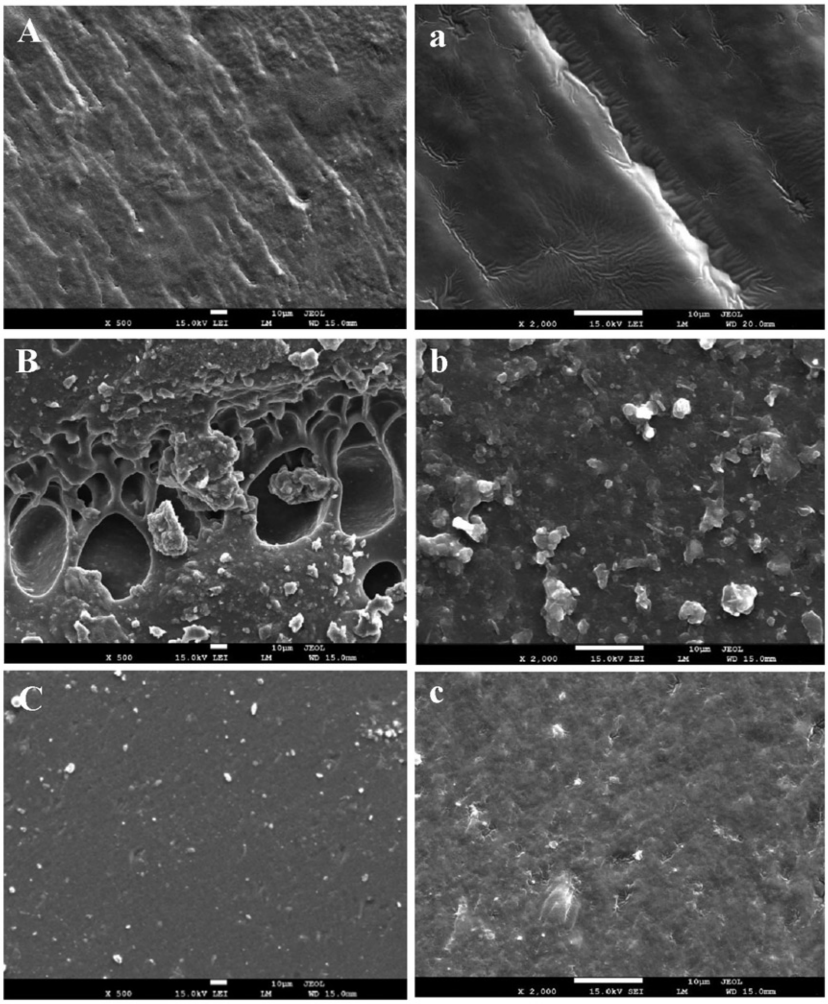


FIGURE 7. Morphologies of the fractured surfaces of the injection-molded specimens (A/a: Poplar wood; B/b: Wheat straw; C/c: Mulberry wood).

peak was observed for mulberry wood-based plastics, which indicated good mechanical stability at high temperature.

SEM Analysis

Figure 7 shows the cross-sectional images of all the tested samples and shows the brittle fracture of the materials, which indicated poor toughness in the esterified products. In the zoomed-in images, the morphological results showed a large difference between the three esterified products. For the poplar wood-based plastics, the cross-sectional images showed a very smooth and continuous morphology (Figure 7(A)) without any fibrillar structures (Figure 7(a)), indicating a thorough extent of esterification. The total modification of the lignocellulosic structure led to the inferior flexural strength. For wheat straw-based plastics, many cavities were present in the inner layers of the specimens (Figure 7(B)), possibly because of severe degradation of the cellulose during esterification. Meanwhile, particles that were likely degraded cellulosic components were visible and were anchored in the loose matrix (Figure 7(b)). However, these inhomogeneous particles could hardly enhance the mechanical performance of the specimen. In contrast, the homogeneous morphology in the cross-sectional images of the mulberry wood-based plastics (Figure 7(C)) was similar to that of the esterified poplar wood, but fibrillar fillers were uniformly embedded in the matrix (Figure 7(c)). Such fibrillar fillers may be microfibrillated cellulose, which would play an important role in the reinforcement of the plastics. Therefore, mulberry wood-based plastics exhibited better mechanical properties than the other two bio-based plastics.

CONCLUSIONS

Bio-based plastics derived from poplar wood, mulberry wood, and wheat straw were successfully prepared by highly efficient esterification with PA in NMI. The WPG results revealed that under the same conditions, poplar wood had the highest extent of esterification due to its soft and loose structure, whereas the tight texture of the mulberry wood caused the lowest WPG. Notably, an esterification time of 0.5 h resulted in lighter colored plastics. In terms of mechanical performance, the mulberry wood-based plastics exhibited the best performance in both flexural and tensile strength. FT-IR revealed the chemical structures of the esterified products. Solid-state ^{13}C NMR spectra chemically confirmed the successful esterification in addition to the effects of the ball-milling treatment. DMA analysis of the storage modulus and the damping factor reflected the detailed viscoelastic behavior of the injection-molded specimens. The SEM results demonstrated different morphologies of the bio-based plastics, which has a large impact on the mechanical performance of the bio-based plastics.

FUNDING

This work was supported by the National Natural Science Foundation of China (51603104), the Natural Science Foundation of the Jiangsu Province (BK20160921), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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