Performance Comparison of Four Kinds of Straw/PLA/PBAT Wood Plastic Composites

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Utilizing four kinds of straw fibers (sorghum, rice, corn, and soybean) as filling fibers, polylactic acid (PLA) and poly (adipic acid)/polybutylene terephthalate (PBAT) in a mixture (7:3) were used as matrix to prepare composite materials by a hot pressing molding process. The mechanical properties, and thermal stability of the four fiber-filled composites were evaluated. The composites had high interfacial quality and no obvious voids. The soybean straw/PLA/PBAT composite had the best interfacial quality. PLA/PBAT-based composite materials were examined. The experimental results show that the soybean straw/PLA/PBAT composite had the best tensile strength, bending strength, and impact strength (14.3 MPa, 19.5 MPa and 3.23 KJ·m⁻², respectively), which was 25.3%, 14.6%, and 27.8% higher than that of the corn straw/PLA/PBAT composite. The thermal stability of the corn straw/PLA/PBAT composite was the best, with an initial decomposition temperature of 286 °C, and the residual amount was 7.3%.

Keywords: Crop straw; PLA; Microstructure; FTIR; Thermal stability

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INTRODUCTION

With the gradual shortage of petroleum energy and the environmental crisis in recent years, there is much research on biomass fully degradable composites. Polylactic acid (PLA) is currently the most promising biomass polymer material. Its main raw material is lactic acid, which can be formed by fermentation of corn starch, rice, etc. (Lee et al. 2016; Murariu and Dubois 2016). It can also be extracted from the cellulose of agricultural wastes. Polylactic acid (PLA) can be 100% degraded. The main products of combustion are CO₂ and H₂O (Dharmalingam et al. 2015). It is environmentally friendly, non-toxic, and harmless to humans. Polylactic acid has good thermoplasticity and is suitable for processing. However, the impact strength and heat resistance of PLA are poor. At present, researches have mostly mixed poly (adipic acid)/butyl terephthalate (PBAT) with PLA, and modified PLA with PBAT's high toughness and good heat resistance to improve the application range of PLA composites (Cardoso et al. 2017). Crop straw is agricultural waste that is available in large quantities, low in price, and renewable. Research on straw fiber composite materials is of great significance for the reuse of agricultural waste.

In recent years, the main research directions of polylactic acid (PLA) biomass composites are FDM molding and impact modification of polylactic acid. Torres et al. (2015) studied the influence of changing FDM's three technological parameters on the torsional properties of PLA materials, demonstrating the ability to produce parts with mechanical properties at or near those of bulk PLA. Wach et al. (2018) investigated the
possibility of enhancing mechanical properties of PLA samples processed by a rapid manufacturing (RM) technique by increasing PLA crystallinity degree via thermal annealing, finding that polymer processed at 215 °C increases the degree of crystallinity to the maximum attainable level. Rasselet et al. (2019) studied the properties of the PLA/PA11 blends compatibilized with Joncryl. The results showed that samples only show strong rigidity, whereas their reinforcement and elongation at break are poor. In the research of plant fiber reinforced PLA composites, hemp fibers are mostly used. Xu et al. (2019) used a new composite lamination process to improve the mechanical properties of hemp fiber reinforced polylactic acid composites, and the results showed that the adhesion between fiber and matrix is enhanced and the mechanical properties are obviously improved by this composite process. Zhu et al. (2018) studied the effects of cellulose, hemicellulose, and lignin contents on the tensile strength of sisal fiber and the interfacial strength between SFS and polylactic acid (PLA) matrix. The appropriate cellulose, hemicellulose, and lignin contents had good effects on the tensile strength of SFS and the interfacial quality between SFS and PLA matrix.

In the related research, the PLA composites filler mainly uses hemp fibers or PLA is used as matrix of composites alone. In this paper, a PLA/PBAT blend is used as matrix, and then alkali treatment, silane and PLA-gMAH interface modification are carried out in parallel. Four common crop straws are used as filling materials. Various properties of different filled straw fiber composite are compared. The purpose of this study was to lay a foundation for further research.

EXPERIMENTAL

Materials

Straw powder from four crops (rice, corn, sorghum, and soybean), size 100 mesh, were procured from Lianyungang, Jiangsu Province, China. Polylactic acid (PLA, 4032D), size 100 mesh, was procured from Zhonglian Plastic Raw Materials, Dongguan, Guangdong Province, China; poly(adipic acid)/butyl terephthalate (PBAT), size 100 mesh, was procured from prudential plastic additives, Dongguan, Guangdong Province, China. Anhydrous ethanol (95%, liquid) was procured from Wuxi Yatai United Chemical Co., Ltd., Wuxi, Jiangsu Province, China; silane coupling agent (KH-590, liquid) was procured from Huai'an Heyuan Chemical Co., Ltd., Huaian, Jiangsu Province, China. PLA-gMAH(5568-K), size 100 mesh, Shenzhen ShengBang Plastic Raw Material, Shenzhen, Guangdong Province, China.

Preparation of straw fiber/PLA/PBAT composites

The straw powder was sieved through a 100-mesh size and placed into a 10 wt% NaOH aqueous solution for 12 h. After filtering the straw powder and washing it to neutrality, it was oven-dried at 80 °C for 12 h. Straw powder was modified with 5 wt% silane ethanol solution and dried in an oven at 80 °C. Matrix ratio: PLA(size 100 mesh) and PBAT(size 100 mesh) were mixed in a ratio of 7:3. The ratio of the composite to the plant fiber to the matrix was 7:3. The specific composition percentage by dry mass of the composite is shown in Table 1. Then these materials were put into a mixer to be evenly mixed for 10 min. The uniformly mixed materials were filled into a mold and hot pressed at 160 °C and 10 MPa for 15 min.
Microscopic Morphology of Tensile Section
The surface to be measured was treated by spraying gold with an ion sputtering instrument (E-1010, Hitachi, Japan) for 1 min, and the microscopic morphology of tensile section and wear surface of the sample was observed with a field emission scanning electron microscope (S-4800, Hitachi, Tokyo, Japan).

Mechanical Properties
Dimensions of samples prepared for the mechanical test were 100mm*10mm*7mm. Referring to GB/T 1040.1—2006 and GB/T9341-2008, respectively, the tensile strength and bending strength of composites were tested by a universal testing machine (CMT6104, Metz Industrial System (China) Co., Ltd., Shanghai, China). The test rate was set at 2 mm/min. According to GB/T 1043.1-2008, the impact strength of composites was tested by an impact testing machine (XJJ-5, Chengde Jinjian Testing Instrument Co., Ltd., Chengde, China). The experiment was repeated 3 times to obtain the mean value.

FTIR
The samples were oven-dried at 80 °C for 6 h. A total of 0.002 g of sample powder was mixed with 0.2 g of potassium bromide and compacted into tablets. The samples were tested with a Fourier transform infrared spectrometer (Nicoleis10, Shanghai DM Chemical Technology Co., Ltd., Shanghai, China) over a range from 400 to 4000 cm⁻¹, with a resolution of 4 cm⁻¹ and 16 scans.

Thermogravimetry
The thermogravimetric curve (TG) of the composite material was determined by a chip analyzer (STA449 F3, Netzsch, Shanghai, China). The sample mass was 10 to 20 mg, and the heating rate was 20 °C/min. The purge gas and protective gas rate was 20 mL/min, and the temperature range was 30 to 800 °C.

RESULTS AND DISCUSSION

FTIR Analysis
Figure 1 shows the infrared spectrum of straw fiber. The figures show that all fibers have strong absorption peaks in the range 3300 to 3000 cm⁻¹, and the waveband corresponds to the telescopic vibration absorption peak of the hydroxyl groups (−OH). The hydroxyl groups mainly are present in cellulose, hemicellulose, and other components in straw fibers (Xu et al. 2009); The double peaks near 2900 cm⁻¹ are absorption peaks of methyl -CH3 and methylene -CH2, which are also characteristic absorption peaks of cellulose (Wang and Liu 2015). From 1750 cm⁻¹ to 1650 cm⁻¹ is the stretching vibration peak of carbonyl in the fiber (Kolling 1992), which mainly comes from hemicellulose and grease on the fiber surface.
Taking sorghum straw (Fig. 1c) as an example, the permeability of the treated fiber at 3300 to 3000 cm\(^{-1}\) was significantly enhanced. The reason was that alkali treatment dissolved out the cementing matter in the fiber and destroyed the hydroxyl groups in the cellulose molecules at the same time (Chen et al. 1998). The opening of some hydrogen bonds made the fiber swell. The hydrolyzed silane was easier to combine with the hydroxyl groups in the fiber to form new hydrogen bonds, thus improving fibers binding ability and hydrophobicity. There was no obvious change in the bimodal around 2900 cm\(^{-1}\). Except for corn straw fiber, the absorption intensity of the other three fibers in this waveband slightly increased, which shows that the cellulose content in the modified fiber increases. The absorption intensity of carbonyl group at 1750 to 1650 cm\(^{-1}\) was lower than that before treatment; the reason was that alkali treatment can wash away the oily layer on the fiber surface. Si-O-Si has antisymmetric and symmetrical two stretching vibration peaks in 1100 to 1000 cm\(^{-1}\) and 880 to 780 cm\(^{-1}\), and the vibration absorption peaks of Si-C at 870 to 690 cm\(^{-1}\) showed little change. Although KH590 adds Si-containing groups, alkali treatment also washes away Si-containing impurities such as silt on the surface of straw. The characteristic group -SH of KH590 is difficult to be observed in the spectrogram due to its weak absorbance peak.

**Physico-mechanical Properties**

The mechanical properties of the straw/PLA/PBAT composites are shown in Fig. 2. The tensile strength, flexural strength, and impact strength of soybean straw/PLA/PBAT...
composites were better than those of the other three composites, reaching 14.3 MPa, 19.5 MPa, and 3.2 KJ·m$^{-2}$, respectively. With the same matrix condition, the strength of the fiber had a significant impact on the composite. The mechanical properties of straw fiber mainly depend on the contents of cellulose and lignin. Cellulose mainly improves the strength of fiber, while lignin is negatively correlated with tensile strength (Ge et al. 2016). Soybean straw fiber has the highest contents of cellulose (47.8%) among the four straw components (Li et al. 2011; Jiang et al. 2017). The strength values of soybean straw fiber were the best, which can effectively enhance the mechanical properties of composites, as shown in Fig. 2. In addition soybean straw/PLA/PBAT composite had the best interfacial quality. The external force can be uniformly transmitted between the fiber and the matrix, while stress concentration is effectively avoided. Corn straw/PLA/PBAT composites had the worst mechanical properties because the corn straw inner core layer is soft, low in strength and loose in fiber structure. Sorghum straw/PLA/PBAT composite and rice straw/PLA/PBAT composite had little difference in mechanical properties; both had high impact strength and good tensile and bending resistance. Sorghum straw/PLA/PBAT composite and rice straw/PLA/PBAT composite had little difference in mechanical properties; both had high impact strength and good tensile and bending resistance.

**Fig. 2.** Mechanical properties of straw fiber/PLA/PBAT wood plastic composites

**Microstructure Analysis**

Figure 3 shows the tensile section microstructure of four kinds of straw fiber/PLA/PBAT wood-plastic composites. The straw fibers were tightly combined with the matrix material, and the tensile section had no obvious void defects. With PLA-gMAH being used to enhance the compatibilization of PLA, there was no obvious delamination between PLA and PBAT. The best interfacial quality of fiber and matrix material was soybean straw/PLA/PBAT composite; the worst combination was corn straw. The inner layer of corn straw had low tissue strength, and it easily absorbed water, as shown in Fig. 1c. The fiber structure of corn straw was very loose, which affects the mechanical properties of the composite and causes the formation of fine cracks due to water vapor in the hot-press molding process. The loose structure makes it difficult for the matrix and fiber to come into close contact, resulting in poor interfacial quality of the tensile section.
The physical properties of soybean straw are similar to sawdust, and its strength is high. After modification treatment, the surface roughness of soybean straw fiber is increased, and it is easy to be infiltrated by PLA/PBAT matrix in molten state (Chandrasekar et al. 2017). The interfacial friction between fiber and matrix is higher after the composite material is solidified, and it is still tightly combined with the matrix at the tensile section, thus improving its mechanical properties. The cross-sectional interfacial quality of the composite filled with sorghum straw and rice straw was similar, second only to that of the composite filled with soybean straw, but the interfacial quality was much higher than that of the composite filled with corn straw. These two kinds of fibers have compact structures and are easily wrapped by the matrix during hot pressing. Thus, the interfacial quality of the four kinds of straw fiber reinforced polylactic acid/PBAT composites is directly proportional to the surface roughness, stiffness, and structural compactness of the straw fibers.

**Thermal Properties Analysis**

The TG/DTG curves of four kinds of straw/PLA/PBAT composites and four kinds of straw fibers after treatment are shown in Fig. 4. The weight loss process was mainly divided into three parts. From 100 °C to 200 °C, there was a slight decline in mass due to the evaporation of water and volatilization of a few small molecular compounds. Between 200 °C and 450 °C, all curves exhibited an extremely fast decline rate. During this process, the mass loss was mainly caused by decomposition of straw fiber and matrix. In fiber, cellulose (180 to 240 °C), hemicellulose (230 to 310 °C), and lignin (300 to 400 °C) (Ramiah 1970; Zeriouh and Belkbir 1995; Yang et al. 2007) are decomposed in sequence. The pyrolysis temperature of PLA is also between 260 °C and 400 °C (Arrieta et al. 2013; Wojtyła et al. 2017).

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**Fig. 3.** Microscopic tensile sections of straw fiber/PLA/PBAT composites using (a) sorghum, (b) rice, (c) corn, (d) soybean

**Fig. 4.** TG/DTG of composites (a) and TG/DTG of straw (b)
When the temperature rises to 500 °C, the third stage starts. A few non-pyrolyzed components continue to decompose and the pyrolysis residues are further carbonized, and the continuous decline in quality is not severe and gradually tends to be stable. It can be seen from the figure that the corn straw /PLA/PBAT composite was superior to the other three materials in terms of initial thermal degradation temperature (286.1 °C), pyrolysis speed, and pyrolysis residue (7.27%), so its thermal stability can be regarded as the best.

Comparing Fig. 4a with 4b, the main mass loss temperature range of the composite was 250 to 450 °C, and the main mass loss temperature range of the fiber was 200 to 380 °C; The residual amount of composites was lower than 10%, while that of fibers was higher than 15%. It can be seen from TG that the mass loss rate of the composite in the main mass loss interval was more severe than that of the fiber. The lowest pyrolysis temperature of PLA was 260 °C. Straw fibers in the composite were wrapped by the matrix, and it was difficult for the fibers to reach the surface temperature of the material through the matrix wrapping them, resulting in the initial pyrolysis temperature of the composite being slightly higher than that of pure fibers and the pyrolysis temperature span of the composite material is longer than that of pure fibers. The PLA/PBAT content in the composite material was the highest, and its pyrolysis mainly produces H₂O and CO₂ (Wang et al. 2009), which is lower than that of pure fiber residue, i.e. the residual rate is lower.

CONCLUSIONS

1. The mechanical properties of soybean straw/PLA/PBAT composites were the best, with tensile strength, flexural strength, and impact strength of 14.3 MPa, 19.3 MPa, and 3.23 KJ·m⁻², respectively. The mechanical properties of corn straw/PLA/PBAT composites were the worst, with the three properties decreased by 25.3%, 14.6%, and 27.8 %, respectively.

2. Due to the loose structure of the corn straw inner core, it is difficult to be completely soaked by the matrix. The kind of composite interface filled with corn straw exhibited the worst interfacial quality.

3. The TG curves of the four kinds of straw/PLA/PBAT composites were similar. The thermal stability of corn straw/PLA/PBAT composites was the best. The initial decomposition temperature was 286.1 °C, and the residual rate was 7.27% for the corn straw/PLA/PBAT composites.

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