

Polylactic Acid-based Wood-plastic 3D Printing Composite and its Properties

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Wood-plastic composites for 3D printing from plant fiber (bleached pulp powder, mechanical pulp powder, newspaper pulp powder, eucalyptus powder, pine powder, and lignin) and polylactic acid (PLA), with silane coupling agent (KH550) as plasticizer, were prepared *via* melt extrusion. The physical properties, such as surface morphology, apparent density, tensile strength, melt flow rate, compatibility, and thermal stability were measured. Moreover, the effects of the content of various types of plant fiber powder in PLA on the properties of the prepared composites were investigated. The results showed that the modified lignin/PLA composite exhibited a superior performance under the same added amount. In particular, when the amount of lignin added was 15%, the tensile strength of the composite was 74.0% higher than that of pure PLA, and the melt flow rate was reduced by 17.8% compared with pure PLA. The density of the composite increased 15.8% compared with pure PLA when the lignin content was 20%. The scanning electron microscopy cross-sectional morphology and differential scanning calorimetry analyses showed that the optimal addition amount of lignin was 15%. Finally, the prepared lignin/PLA composite material was used in 3D printing with a smooth silky property and an excellent printing performance.

Keywords: 3D printing; Polylactic acid; Wood-plastic composite

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INTRODUCTION

In recent years, 3D printing has gradually appeared in people's field of vision. Various types of technologies have been used in 3D printing, such as fused deposition type (FDM), selective laser sintering (SLS), three-dimensional printing (3DP), and so on. Among them, FDM has been widely used due to its simple operation (Credi *et al.* 2016). The FDM technology is also continuously being developed in the 3D printing field, and printing materials are extremely important for the sustainable development of 3D printing. It has been confirmed that to a certain extent the properties of 3D printing materials directly determine the future development of the 3D printing field (Lee *et al.* 2014).

Generally, most of materials used in FDM are mainly plastics, such as PLA and polycarbonate (PC). Among them, PLA has attracted much attention by academic researchers because of its complete biodegradability (Chia and Wu 2015). The PLA is produced by natural microorganisms. After being discarded, it can be completely degraded into carbon dioxide by bacteria in soil and decomposed, which avoids the pollution of the surrounding environment. It has been said that "because of nature, return to nature" by Letcher and Waytashek (2014). However, the application of PLA is limited in 3D printing

due to its high production cost, high brittleness, poor heat resistance, and poor tensile properties (Inzana *et al.* 2014).

Therefore, researchers have begun to add various modifying substances to PLA to improve its performance. Among these modified substances, plant fibers have become an attractive material because of their relatively light weight, low cost, and their excellent renewability (Sitthi-Amorn *et al.* 2015; Stansbury and Idacavage 2016). Adding a certain amount of plant fiber into PLA to prepare 3D printed wood-plastic composite material not only reduces the production cost, but also makes the 3D printed product have a natural woody feeling, which partly offsets the disadvantages of pure PLA materials.

The wood-plastic composite material not only combines the advantages of various substrates, but it also makes up for the shortcomings of individual materials, achieving complementary advantages and a good market prospect (Bhattacharjee *et al.* 2016; Afrose *et al.* 2016). Many scientists have conducted research on improving the performance of PLA-based wood-plastic composites for 3D printing, and it has been shown that the type and content of plant fibers in composites significantly affect the performance of wood-plastic composites (Standau *et al.* 2019). For example, Mirko Kariz *et al.* (2018) investigated the effects of wood power content on the performance of 3D printed wood-plastic composites, and found that the tensile strength of printed filaments increased from 55 MPa to 57 MPa after adding 10% wood materials. However, as the wood content increased, the tensile strength significantly decreased. When the wood materials content increased to 50%, a lower tensile strength of 30 MPa was found. Daniel Filgueira *et al.* (2017) used thermomechanical pulp (TMP) fibers to mix with PLA to prepare materials for 3D printing. From the measurement of the contact angle and mechanical properties, it was found that the prepared composite material has good hydrophobicity and mechanical strength and was suitable for use in 3D printing. Tao *et al.* (2017) prepared a PLA-based wood-plastic composite for 3D printing with a better printing performance when using a wood powder content of 5%. Fernández-Cervantes *et al.* (2019) obtained PLA polymeric scaffolds with bone tissue morphology by 3D printing, which should later be functionalized for reinforcement of the scaffold with hydroxyapatite.

At present, although PLA-based wood-plastic composite materials for 3D printing have made some progress in preparation, there are still many shortcomings. Not only can a few species of PLA-based wood-plastic composite materials be used for 3D printing, but also minimal doses of plant fibers were added in the composite material. In response to this issue, this study considered different kinds of plant fibers that were melt-blended with PLA to prepare different species of PLA-based wood-plastic composite materials. Because the compatibility between plant fiber and PLA is poor, the plant fiber was modified with KH550 before making the wood-plastic composite material, so that the fiber is more evenly dispersed in the PLA to improve its compatibility with PLA. Then, through testing the apparent density, water absorption, tensile strength, melt flow rate, compatibility, and thermal stability of composite materials, the effects of plant fiber types and contents on the properties of PLA-based wood-plastic composites were analyzed. An optimum formulation to produce the best environmentally friendly 3D printed wood-plastic composite will be found. Finally, the prepared wood-plastic composite material will be applied in 3D printing to observe its printing performance.

EXPERIMENTAL

Materials

The materials used were PLA (4032D; Dongguan Xingwang Plastic Materials Co., Ltd., Dongguan, China), bleached pulp board, mechanical pulp board, newspaper powder, eucalyptus powder, pine powder, and lignin (Yatai Senbo Shandong Pulp & Paper Co., Ltd., Shandong, China). The experimental reagents used were a silane coupling agent (KH550; Qingdao Yousuo Chemical Technology Co., Ltd., Qingdao, China), absolute ethanol (Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin, China), and silicone oil (Jiande Polymer New Material Co., Ltd., Jiande, China).

Preparation of modified fiber

The bleached pulp board, the mechanical pulp board, and the newspaper were cut into thin strips and pulverized by a micro-plant pulverizer (Shanghai Keheng Industrial Development Co., Ltd., Shanghai, China), and this was repeated until it became fine fibers. The milled fiber powder was sieved with wood powder and lignin powder through 300-mesh, soaked in 3% concentration of KH550 aqueous solution, stirred uniformly, soaked at room temperature for 24 h, repeatedly rinsed with ethanol through a suction filter device (Gongyi Yingying Gaoke Instrument Factory, Gongyi, China), and then it was placed in a forced air oven for 8 h at 100 °C. The dried fiber powder was finely pulverized by an ultrafine pulverizer (IKA, Königswinter, Germany), sieved through 300-mesh, and dried until use. The main components of the six plant fibers are shown in Table 1.

Table 1. Analysis of Chemical Components of Plant Fibers

Fiber Type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Other (%)
Bleached pulp	89.70	7.30	1.20	0.27	1.53
Mechanical pulp	59.20	21.20	12.20	0.21	7.19
Newspaper pulp	64.39	14.94	12.11	0.36	8.20
Eucalyptus powder	41.80	27.90	27.40	0.29	2.61
Pine powder	48.80	22.70	24.90	0.33	3.27
Lignin	—	—	97.60	0.46	1.94

Table 2. Ratio of Plant Fiber/PLA Wood-plastic Composites with Different Components and Contents

Sample Name	Modified Fiber Content (%)	PLA Content (%)	Total Amount (g)	Silicone Oil (%)
Sample 1	—	100	100	3
Sample 2	4	96	100	3
Sample 3	6	94	100	3
Sample 4	10	90	100	3
Sample 5	15	85	100	3
Sample 6	20	80	100	3

Preparation of modified fiber/PLA wood-plastic composite

Six modified fiber powders and the PLA were dried prior to the experiment to remove any surface free water. The fiber powder and the PLA drying temperature were 60 °C and 50 °C, respectively, and the drying time was 4 h. The dried six fibers were hand blended with PLA. The proportions of plant fibers in the composite are shown in Table 2.

The mixed samples were separately added to a torque rheometer (XSS-300; Shanghai Kechuang Rubber & Plastic Machinery Equipment Co., Ltd., Shanghai, China) and a single screw extruder (LSJ20; Shanghai Kechuang Rubber & Plastic Machinery Equipment Co., Ltd., Shanghai, China) for melt extrusion drawing. The temperature of each zone of the extruder was set to 150 °C, 160 °C, 170 °C, and 175 °C, and the uniform splines were slowly removed. Then, it was passed through a plastic granulator (Shanghai Kechuang Rubber & Plastic Machinery Equipment Co., Ltd., Shanghai, China) for granulation, and the prepared granules were dried and then placed in an extruder for melt extrusion drawing, and then repeated until the thickness of the wood-plastic composite wires was uniform and the diameter was 1.75 mm, which was suitable for 3D printing. These wires were dried at 50 °C for 24 h to remove free water from the surface. A picture of the torque plastic extrusion device is shown in Fig. 1.



Fig. 1. Torque rheometer + single screw extruder + granulator system

3D printing performance test

The prepared wood-plastic composite was used in a 3D printer (Beijing 3D Bote Technology Co., Ltd., Beijing, China) for the printing test. The experimental parameters of the 3D printing were: 60 °C hot bed temperature, 200 °C printing temperature, 60 mm/s printing speed, 80% filling rate, 0.3 mm printing layer thickness, and 0.4-mm nozzle diameter.

Methods

Apparent density

When the apparent density of the samples was measured, their quality was first measured using the high-precision electronic balance, and then the volume of each sample was measured using the method of drainage. Samples were fully dried in the oven at 105 °C for 4 h before measurement. Each group of five samples' average value was taken as the density value of the sample. The sample density value was obtained by Eq. 1,

$$\rho = \frac{m}{V} \quad (1)$$

where “ p ” is the density of the sample (g/cm³), “ m ” is the mass of the sample (g), and “ v ” is the volume of the sample (cm³).

Tensile strength performance characterization

The tensile strength of each test piece (L150mm, Φ 1.75 mm) was tested five times using a universal tensile machine (XWN-20; Changchun Xinke Testing Instrument and Equipment Research Institute, Changchun, China), and the average value was recorded. The tensile load of the test was 50 mm/min during the experiment. The tensile strength test calculation formula is shown in Eq. 2,

$$\alpha = \frac{P}{\pi r^2} \quad (2)$$

where “ α ” is the tensile strength of the sample (MPa), “ P ” is the maximum tensile load the specimen is subjected to (N), “ r ” is the sample radius (mm).

Melt flow rate test

The melt flow rate (MFR) of the composite material was tested by a melt flow rate meter (Chengde Precision Testing Machine Co., Ltd., Chengde, China), and 4 g of the sample was taken. The set temperature was 190 °C, the cutting time was 30 s, and the number of cuts was 5 (Väisänen *et al.* 2018). The MFR calculation formula is shown in Eq. 3,

$$MFR = \frac{600 \times W}{t} \quad (3)$$

where “ W ” is the average mass of the sample (g) and “ t ” is the sampling interval (s).

Scanning electron microscopy (SEM)

A scanning electron microscope (Hitachi Regulus 8220; Hitachi, Ltd., Tokyo, Japan) was used to observe the morphology of the sample section, and the modification mechanism was considered. Prior to the SEM scan, the sample section was subjected to vacuum metallurgy. The purpose of this was to make the sample electrically conductive, and then observe the cross-sectional surface morphology with a scanning electron microscope. The scanning speed was 500 times and 3000 times, and each sample was scanned 5 times.

Differential scanning calorimetry (DSC)

Approximately 4 g of the sample were placed in an aluminum crucible and warmed from room temperature to 200 °C at a rate of 10 °C/min. After the temperature reached 200 °C, the temperature was stopped for 5 min to eliminate the heat influence, and then the temperature was lowered to room temperature at a rate of 5 °C/min, and the temperature was kept for 5 min after the completion of the temperature reduction. The crystallization behavior of the sample under different conditions was studied through analyzing the DSC curve during the cooling process.

RESULTS AND DISCUSSION

Effect of Modified Plant Fiber on Apparent Density of PLA-based Wood-plastic Composites

Density is an important indicator to examine the 3D printed performance of materials. The densities of PLA-based wood-plastic composites with the addition of different modified plant fiber types and contents are shown in Fig. 2.

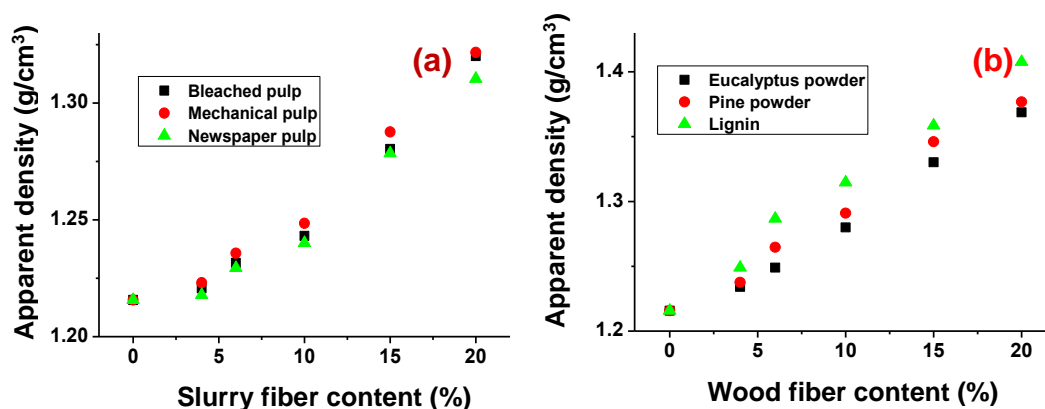


Fig. 2. Effect of modified plant fiber type and content on apparent density of composites: (a) pulp fibers and (b) wood fibers

The density of the PLA-based wood-plastic composite material gradually increased with the increase of the modified fiber content (Fig. 2), especially when the content of the modified fiber in the composite material increased from 10% to 20%. This was mainly attributable to the fact that the density of the modified fiber (1.30g/cm^3 to 1.50g/cm^3) was greater than that of the PLA (1.22 g/cm^3) (González-López *et al.* 2019). During the preparation of the composite material, the fibers were tightly wrapped inside the PLA, and the density of the composite increased through the tight combination between them. Therefore, a larger proportion of modified fibers resulted in a greater density of the prepared composite.

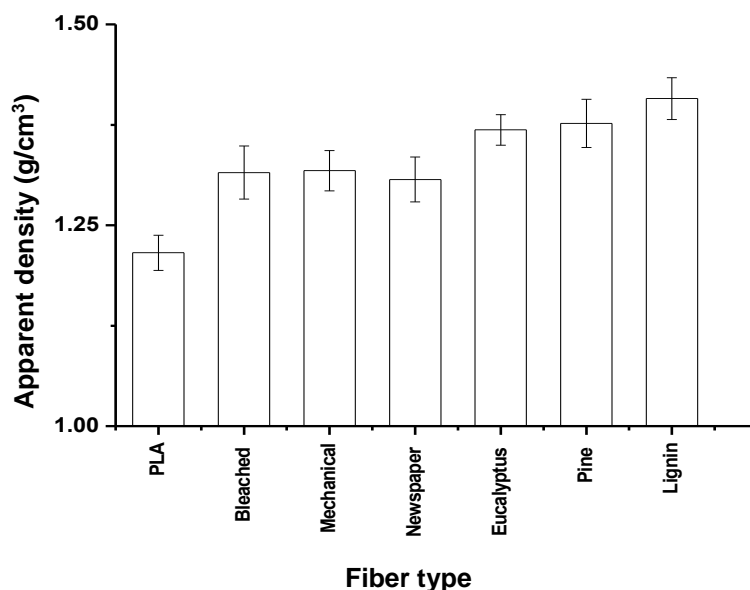


Fig. 3. Effect of modified plant fiber type on apparent density of composites

For wood-plastic composites, the density ought to be as high as possible. Therefore, PLA-based wood-plastic composites with a modified plant fiber addition amount of 20% were selected, and the effects of different modified plant fiber types on their apparent density were compared and analyzed.

In Fig. 3, the type of modified fiber had a negligible effect on the density of the composite. When the amount of modified fiber added reached 20%, the apparent density of the newspaper pulp/PLA composite was relatively low because the newspaper fiber is made of newspaper with a low density. In contrast, the apparent density of the lignin/PLA composites was relatively high, *i.e.* 15.8% higher than that of pure PLA. This was because the density of lignin is higher than that of other materials. After fusion with PLA, the density of composites noticeably increased.

Effect of Modified Plant Fiber on Strength Properties of PLA-based Wood-plastic Composites

Strength performance is one of the most important indicators of wood-plastic composites, and it could affect the application of composite materials to a certain extent. A higher tensile strength could make the performance of wood-plastic composites become better (Oguz *et al.* 2019). The tensile strength of wood-plastic composites with different modified plant fiber types and contents are shown in Fig. 4. The tensile strength of PLA-based wood-plastic composites first showed an increasing trend and then a subsequent decrease with the increase of modified fibers addition. When the amount of modified fiber reached 15%, the tensile strength of the composite reached a maximum value, the lignin/PLA composite exhibited a maximum tensile strength of 20.7 MPa compared with pure PLA (11.9 MPa), representing an increase of 74.0%. The amount of modified fiber had an obvious influence on the tensile strength of the composite. The small amount of the modified fiber resulted in an insufficient dispersion in the interior of the composite material, and a discontinuous strong reinforcement, thereby failing to enhance the effect. When the addition amount of the modified fiber was gradually increased, it became intertwined in the interior of the composite to form a 3D reinforcement that penetrated the inside of the material, thereby improving the tensile strength of the PLA-based wood-plastic composite. When the content of the modified fiber continued to increase, the fiber could not be completely covered by the PLA, and it was easily agglomerated inside the composite material. There was space between the powder particles, which contributed to low tensile strength of the composite material.

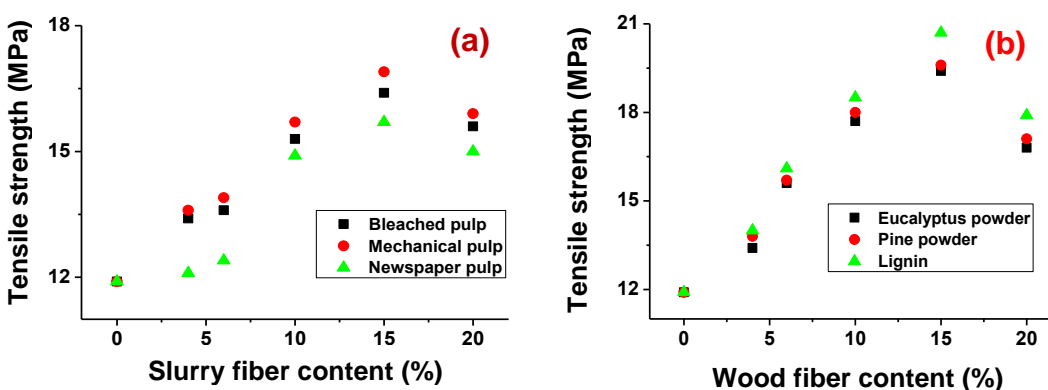


Fig. 4. Effect of modified plant fiber type and content on tensile strength of composites: (a) pulp fibers and (b) wood fibers

Comprehensively, PLA-based wood-plastic composites with 15% plant fiber had the best tensile strength. Therefore, PLA-based wood-plastic composites with 15% plant fiber addition were selected, and the effects of different plant fiber types on tensile strength were compared and analyzed.

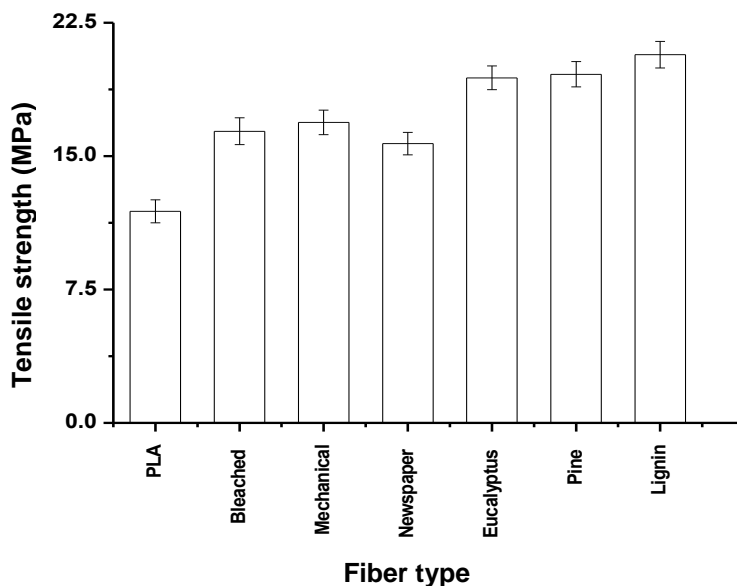


Fig. 5. Effect of modified plant fiber type on tensile strength of composites

Figure 5 shows a relationship between the tensile strength of the composite and the type of used reinforcement. Among all of the PLA-based wood-plastic composites, the lignin/PLA composites presented the highest tensile strength, and the newspaper pulp/PLA composites showed the lowest tensile strength. This was attributed to the fact that lignin-containing fiber has strong supporting properties, which plays a certain role in supporting the matrix and increasing the mechanical properties in the composite material. For the newspaper pulp, the soft recycled fiber could not support the PLA and led to a low tensile strength of the composite material. When the fiber addition amount was 15%, the tensile strength of the newspaper pulp/PLA composite reached 15.7 MPa, which was only 31.9% higher than the tensile strength of pure PLA (11.9 MPa).

Effect of Modified Plant Fiber on Melt Flow Rate of PLA-based Wood-plastic Composites

In the 3D printing process, a high fluidity of the printed materials is often required. The low flowability of the printing material usually causes difficulty in squeeze forming during printing, which is not conducive to filling. When a high fluidity of the printing material tends to be difficult to form sufficient pressing pressure, it is also not conducive to product molding (Tran *et al.* 2017).

The melt flow rate of wood-plastic composites with different modified plant fiber type and content are shown in Fig. 6. The melt flow rate of the PLA-based wood-plastic composite material tended to decrease with increasing amount of modified fiber. The good fluidity of PLA could improve the melt reaction with the modified fiber and form a complex rheological system in a molten state, because a large amount of carboxyl groups in the fiber will recombine with PLA. Therefore, the melt flow rate of PLA-based composites was clearly reduced.

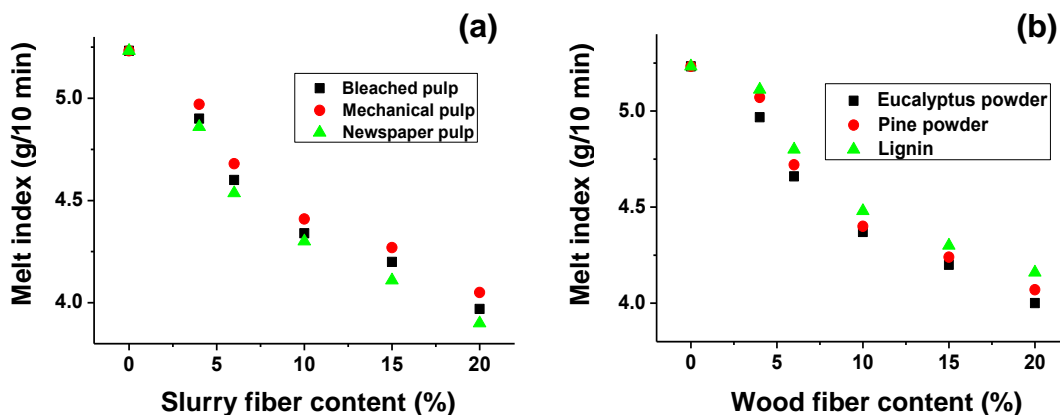


Fig. 6. Effect of modified plant fiber type and content on melt flow rate of composites: (a) pulp fibers and (b) wood fibers

In combination with density and tensile strength, a wood-plastic composite with a plant fiber addition of 15% was selected for comparison. The effects of different modified plant fiber type on the melt flow rate of the composites were compared and analyzed and are shown in Fig. 7.

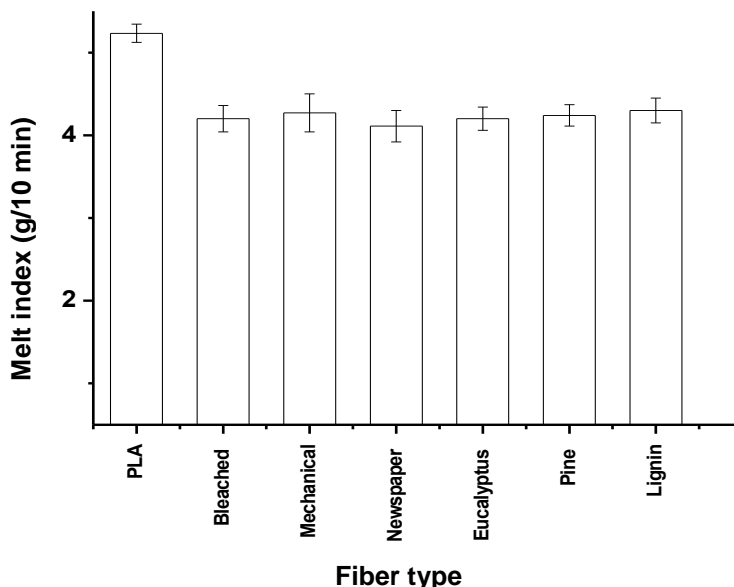


Fig. 7. Effect of modified plant fiber type on melt flow rate of composites

In Fig. 7, under the same amount of the added modified fiber (15%), the melt flow rate of the PLA-based wood-plastic composite material prepared from the six materials, specifically the bleaching pulp, mechanical pulp, newspaper pulp, eucalyptus powder, pine powder, and lignin, decreased from the pure PLA: 5.23 g/10 min to 4.20 g/10 min, 4.27 g/10 min, 4.11 g/10 min, 4.20 g/10 min, 4.24 g/10 min, and 4.30 g/10 min, respectively. The melt flow rate of the lignin/PLA composite was 17.8% lower than that of pure PLA. The melt flow rate of the newspaper pulp/PLA composite was 21.4% lower than that of pure PLA.

SEM Characterization of Modified Lignin/PLA Wood-plastic Composite

Through analyzing and comparing the apparent density, tensile strength, and melt flow rate of the composite, it was concluded that the performance of modified lignin/PLA composites under the same conditions were superior to other composite materials. To further explore the compatibility between lignin and PLA and find the optimal dosage of modified lignin, SEM imaging was used to scan the cross-section of composites with different lignin content to observe the dispersion of lignin in the PLA matrix.

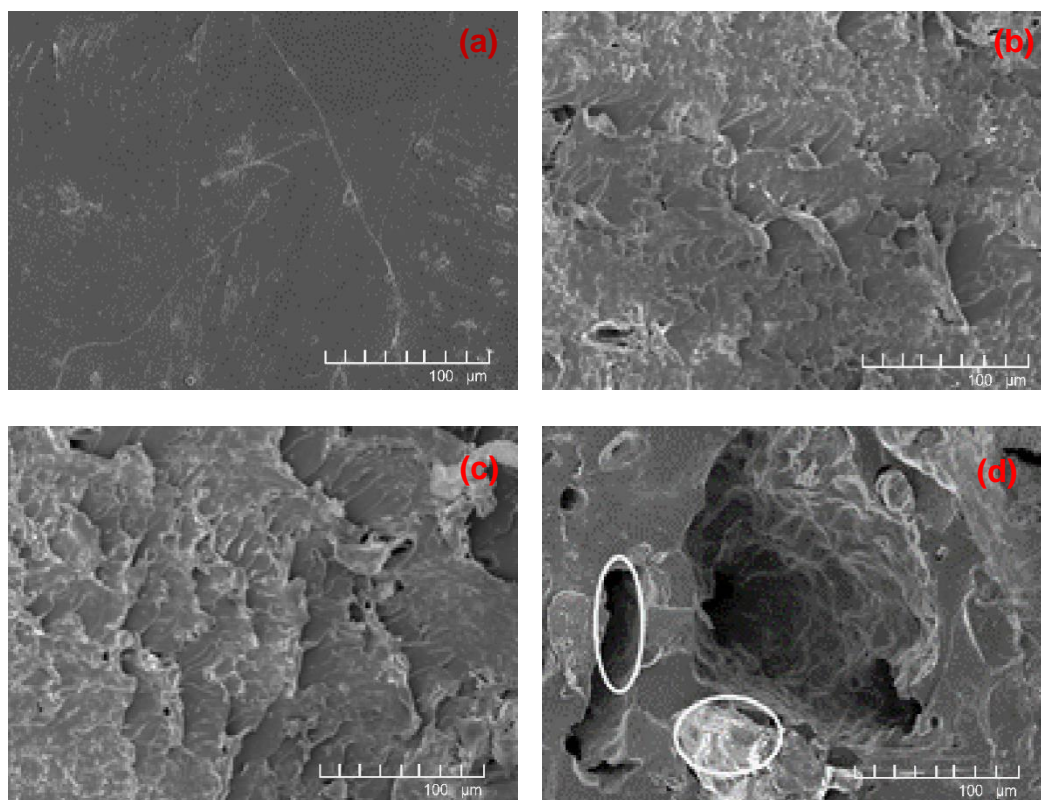


Fig. 8. SEM analysis of composites with different modified lignin content: (a) pure PLA, (b) 10% lignin fiber, (c) 15% lignin fiber, and (d) 20% lignin fiber

The SEM images of the cross-sectional structure of PLA-based wood-plastic composites with different modified lignin additions (0%, 10%, 15%, and 20%) are shown in Fig. 8. The surface of pure PLA was smooth and flat. When a small amount of lignin was added (10%), the composite displayed a good fusion property and dense cross-sectional structure, and the lignin was uniformly distributed in the PLA. When the amount of lignin added was 15%, the lignin was encapsulated well by PLA. A 3D reinforcing system formed with uniform dispersion inside. When the amount of lignin addition reached 20%, agglomerates of lignin were present in the PLA, revealing the rough cross-section of the composite, and many large holes appeared inside the material, as shown in Fig. 8(d).

The SEM images of a lignin/PLA wood-plastic composite material with a 3,000-fold lignin content of 15% and 20% are shown in Fig. 9. In Fig. 9(a), when the amount of added modified lignin increased to 15%, the lignin was uniformly dispersed in the PLA and wrapped in the PLA. When the amount of modified lignin increased to 20%, the lignin was not well dispersed in PLA. A clear agglomeration in PLA, and some gaps between lignin and PLA, were observed as shown in Fig. 9(b).

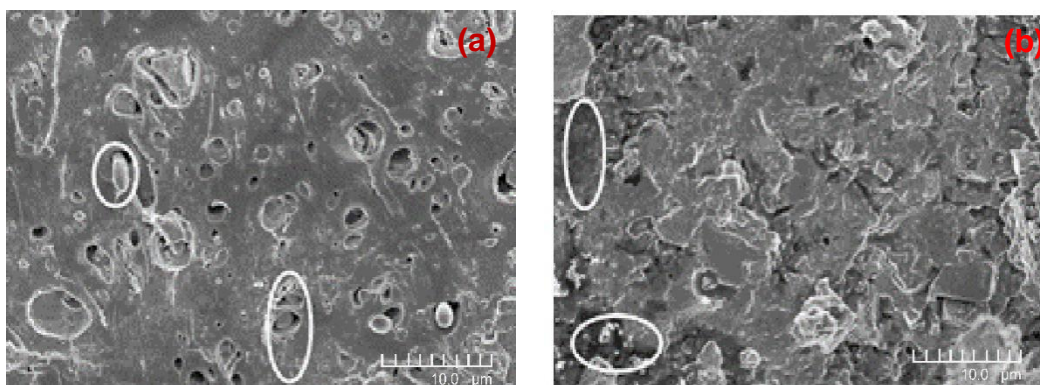


Fig. 9. SEM analysis of composites with different modified lignin content: (a) 15% lignin fiber and (b) 20% lignin fiber

Effect of Modified Lignin on Thermal Properties of Composites

The PLA is a substance that is easy to crystallize, and its crystallinity could affect the thermal and mechanical properties of the composite. The modified lignin fiber was selected to enhance the PLA, and the effects of different contents of modified lignin on the thermal properties of the lignin/PLA composite during cooling were investigated.

Figure 10 shows the cooling DSC curve of PLA composites with different contents of modified lignin, and Table 3 concludes the thermal performance data of the composite. As shown in Fig. 10 and Table 3, the crystallization temperature of pure PLA was 67.5 °C. The addition of lignin enhanced the crystallization temperature of the PLA composite, and the crystallization temperature of the lignin/PLA composite was obviously higher than that of pure PLA. When the content of lignin in the composite was 10%, secondary crystallization appeared. When the amount of added lignin was 15%, the first crystallization temperature of the composite increased to 102.4 °C, which was 34.9 °C higher than the crystallization temperature of pure PLA (67.5 °C).

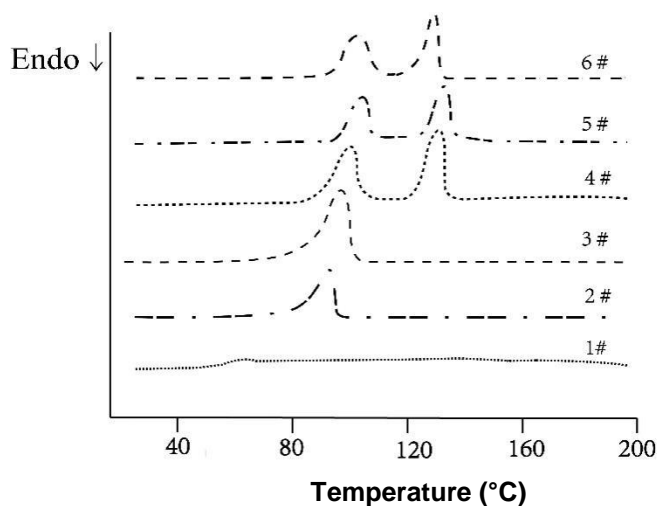


Fig. 10. Cooling DSC curve of the effect of different contents of modified lignin on the properties of composites (1# pure PLA, 2# lignin content 4%, 3# lignin content 6%, 4# lignin content 10%, 5# lignin content 15%, and 6# lignin content 20%)

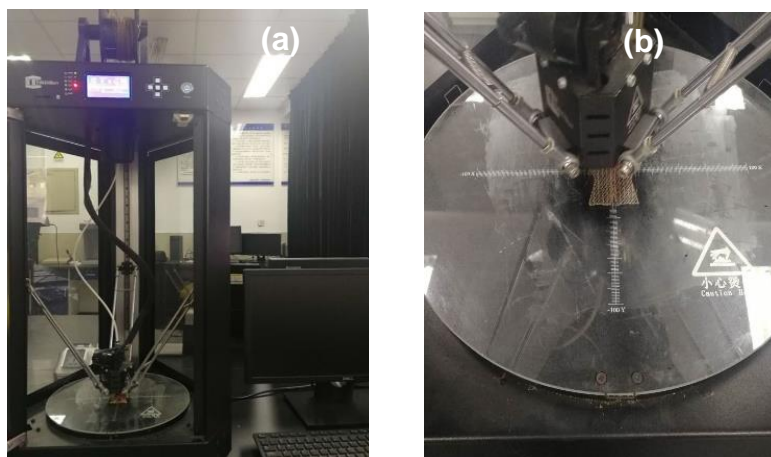
Table 3. Effect of Different Content of Lignin on the Cooling Performance of Wood-plastic Composites

Lignin Fiber Content (%)	Tc1 (°C)	Tc2 (°C)
0	67.47	—
4	97.02	—
6	98.79	—
10	100.06	131.34
15	102.36	133.75
20	101.71	131.08
* Tc1 is the first crystallization temperature during the cooling process; Tc2 is the second crystallization temperature during the cooling process		

The composite had a higher crystallization temperature, indicating its good mechanical properties and thermal properties. However, when the lignin content reached 15% and continued to increase its amount to 20%, the crystallization temperature of the lignin/PLA composite began to decrease. This was because after lignin was added to PLA, it formed a crystallization point in the PLA and acted as a crystal nucleating agent, which made the PLA crystal more perfect. The chain arrangement was more regular, the crystal size was smaller, and thus the crystallinity could be improved. However, the continued increase of lignin content will make the viscosity of the system become larger and make the lignin difficult to disperse. Furthermore, the small-sized particles will agglomerate together to form larger-sized particles, which can no longer function as a nucleating agent (Fortunati *et al.* 2012). During the crystallization process, the movement of the molecular segment was hindered, and the crystallinity of the molecule was lowered so that the crystallization temperature of the composite material was gradually lowered (Wendi *et al.* 2016). Figure 10 and Table 3 show that when 15% lignin was added, its effect on PLA crystallization performance and thermal properties was particularly remarkable.

3D Printing Performance Test of Lignin/PLA Wood-plastic Composite

After a series of experiments and tests, it was concluded that the PLA-based wood-plastic composite prepared with the addition of 15% modified lignin had the best comprehensive performance. A lignin/PLA wood-plastic composite material with better properties was prepared for the printing test in a 3D printer (Chao *et al.* 2018).

**Fig. 11.** 3D printer working diagram

It was found that the smoothness and silky texture achieved during the 3D printing process was good, the printing effect was good, and there was no occurrence of broken wire or warpage, which satisfied the requirements of 3D printing, and could be applied to 3D printing. A 3D printer working process is shown in Fig. 11, a 3D printed wire is shown in Fig. 12(a) and a 3D printed article of lignin/PLA wood-plastic composite is shown in Fig. 12(b).

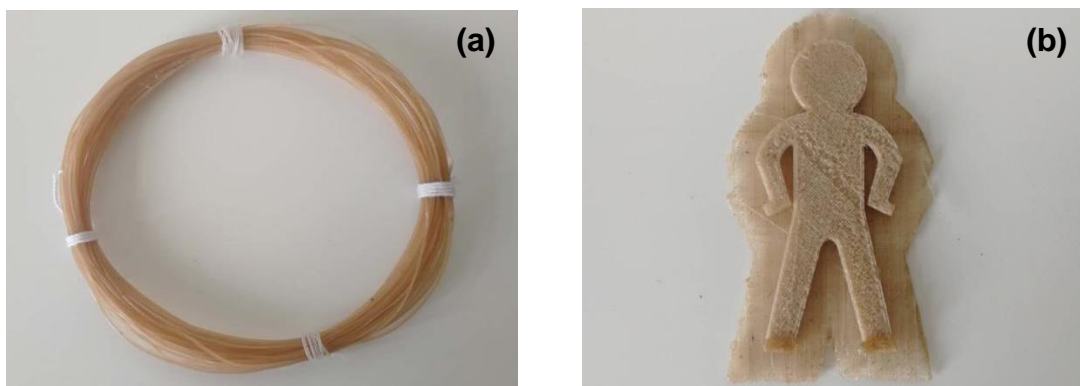


Fig. 12. (a) 3D printing material and (b) 3D printed product

CONCLUSIONS

1. Modified plant fiber was found to be compatible with poly-(lactic acid) (PLA). With an increased amount of modified plant fiber, the PLA-based wood-plastic composite material had an overall upward trend in apparent density compared with pure PLA. In terms of tensile strength, the tensile strength of PLA-based wood-plastic composite material first increased and then decreased, while its melt flow rate showed an overall downward trend.
2. The modified lignin/PLA composite had the best overall performance when the amount of modified plant fiber was the same. When the amount of lignin added was 15%, the tensile strength of the lignin/PLA composite reached 20.7 MPa, which was 74.0% higher than that of pure PLA, and the melt flow rate decreased 17.8% compared with pure PLA. When the amount of lignin added was 20%, the density of lignin/PLA composite increased 15.8% compared with pure PLA. The SEM scan of the cross-sectional morphology and the DSC analysis showed that the optimal addition amount of lignin was 15%.
3. The prepared lignin/PLA wood-plastic composite material was used in 3D printing, and it was found to be smooth with a silky texture, the printing effect was good, and there was no occurrence of broken wires or warpage, which satisfies the requirements of 3D printing, and can be applied in 3D printing.

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REFERENCES CITED

- Afrose, M. F., Masood, S. H., Iovenitti, P., Nikzad, M., and Sbarski, I. (2016). "Effects of part build orientations on fatigue behaviour of FDM-processed PLA material," *Progress in Additive Manufacturing* 1(1-2), 21-28. DOI: 10.1007/s40964-015-0002-3
- Bhattacharjee, N., Urrios, A., Kang, S., and Folch, A. (2016). "The upcoming 3d-printing revolution in microfluidics," *Lab on a Chip* 2016(10), 1720-1742. DOI: 10.1039/C6LC00163G
- Chao, L. J., Jun, W., Xiong, W., Wen, Y., Xu, Z. R., and Ming, B. (2018). "Effect of processing parameters on 3d printing of cement - based materials," *E3S Web of Conferences* 38, Article Number 03008. DOI: 10.1051/e3sconf/20183803008
- Chia, H. N., and Wu, B. M. (2015). "Recent advances in 3D printing of biomaterials," *Journal of Biological Engineering* 2015(9), Article Number 4. DOI: 10.1186/s13036-015-0001-4
- Credi, C., Fiorese, A., Tironi, M., Bernasconi, R., Magagnin, L., and Levi, M. (2016). "3D printing of cantilever-type microstructures by stereolithography of ferromagnetic photopolymers," *ACS Applied Materials & Interfaces* 2016(8), 26332-26342. DOI: 10.1021/acsami.6b08880
- Fernández-Cervantes, I., Morales, M. A., Agustín-Serrano, R., Cardenas-García, M., Pérez-Luna, P. V., Arroyo-Reyes, B. L. (2019). "Polylactic acid/sodium alginate/hydroxyapatite composite scaffolds with trabecular tissue morphology designed by a bone remodeling model using 3D printing," *Journal of Materials Science*, 54(13) 9478-9496 DOI: 10.1007/s10853-019-03537-1
- Filgueira, D., Holmen, S., Melb, J. K., Moldes, D., Echtermeyer, A., and Chinga-Carrasco, G. (2017). "Enzymatic-assisted modification of TMP fibres for improving the interfacial adhesion with PLA for 3D printing," *ACS Sustainable Chemistry & Engineering* 2017(5), 9338-9346. DOI: 10.1021/acssuschemeng.7b02351
- Fortunati, E., Armentano, I., Zhou, Q., Puglia, D., Terenzi, A., and Berglund, L. A. (2012). "Microstructure and nonisothermal cold crystallization of PLA composites based on silver nanoparticles and nanocrystalline cellulose," *Polymer Degradation and Stability* 97(10), 2027-2036. DOI: 10.1016/j.polymdegradstab.2012.03.027
- González-López, M. E., Pérez-Fonseca, A. A., and Cisneros-López, E. O. (2019). "Effect of maleated PLA on the properties of rotomolded PLA-agave fiber biocomposites," *Journal of Polymers and the Environment* 27(1), 61-73. DOI: 10.1007/s10924-018-1308-2
- Inzana, J. A., Olvera, D., and Fuller, S. M. (2014). "3D printing of composite calcium phosphate and collagen scaffolds for bone regeneration," *Biomaterials* 35(13), 4026-4034. DOI: 10.1016/j.biomaterials.2014.01.064
- Kariz, M., Sernek, M., Ina, M., and Kuzman, M. K. (2018). "Effect of wood content in FDM filament on properties of 3D printed parts," *Materials Today Communications* 14, 135-140. DOI: 10.1016/j.mtcomm.2017.12.016
- Lee, J. S., Hong, J. M., Jung, J. W., Shim, J. H., Oh, J. H., and Cho, D. W. (2014). "3D printing of composite tissue with complex shape applied to ear regeneration," *Biofabrication* 6(2), Article ID 024103. DOI: 10.1088/1758-5082/6/2/024103
- Letcher, T., and Waytashek, M. (2014). "Material property testing of 3D-printed specimen in PLA on an entry-level 3D printer," in: *ASME 2014 International Mechanical Engineering Congress and Exposition*, Montreal, Quebec, Canada. DOI: 10.1115/IMECE2014-39379

- Oguz, H., Dogan, C., Ozen, T., Ovali, D., Nofar, M. R., and Kara, D. (2019). "Development of PLA-PBAT and PLA-PBSA bio-blends: Effects of processing type and PLA crystallinity on morphology and chemical properties," *AIP Conference Proceedings* 2055(1), Article ID 030003. DOI: 10.1063/1.5084813
- Sitthi-Amorn, P., Ramos, J. E., Wangy, Y., Kwan, J., Lan, J., and Wang, W. (2015). "Multifab: A machine vision assisted platform for multi-material 3D printing," *ACM Transactions on Graphics* 34(4), Article Number 129. DOI: 10.1145/2766962
- Standau, T., Zhao, C., Castellón, S. M., Bonten, C., and Altstädt, V. (2019). "Chemical modification and foam processing of polylactide (PLA)," *Polymers* 11(2), Article Number 306. DOI: 10.3390/polym11020306
- Stansbury, J. W., and Idacavage, M. J. (2016). "3D printing with polymers: Challenges among expanding options and opportunities," *Dental Materials* 32(1), 54-64. DOI: 10.1016/j.dental.2015.09.018
- Tao, Y., Wang, H., and Li, Z. (2017). "Development and application of wood flour-filled polylactic acid composite filament for 3D printing," *Materials* 10(4), Article Number 339. DOI: 10.3390/ma10040339
- Tran, T. N., Bayer, I. S., Heredia-Guerrero, J. A., Frugone, M., Lagomarsino, M., Maggio, F., and Athanassiou, A. (2017). "Cocoa shell waste biofilaments for 3D printing applications," *Macromolecular Materials and Engineering* 302(11), Article ID 1700219. DOI: 10.1002/mame.201700219
- Väisänen, T., Batello, P., Lappalainen, R., and Tomppo, L. (2018). "Modification of hemp fibers (*Cannabis sativa* L.) for composite applications," *Industrial Crops and Products* 111, 422-429. DOI: 10.1016/j.indcrop.2017.10.049
- Wendi, W., Zhen, Z., Guangfeng, W., and Huixuan, Z. (2016). "Effect of WF on non-isothermal cold crystallization of PLA/WF composites," *China Synthetic Resin and Plastics* 33(6): 23-28.

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