Research on the preparation and properties of biodegradable wood-plastic composites

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Abstract. In this work, the PLA/PBS/straw powder wood-plastic composite were fabricated by injection molding process. Special attention was paid to the effects of different parameters of injection molding process on the mechanical properties of the wood-plastic composite. The optimum injection molding process parameters of wood-plastic composites were determined by orthogonal experiment. According to the optimal injection molding process parameters, biodegradable wood-plastic composites filled with different compatibilizers were produced. The effects of MAPLA, silane and combination treatment on the interface compatibility and mechanical properties of the wood-plastic composite were investigated by scanning electron microscope and mechanical properties test. The results showed that the combination of the two compatibilizer treatments can improve the interface compatibility of wood-plastic composites, but the improvement of it mechanical properties is not obvious. The mechanical properties of wood-plastic composites were optimiz when the content of MAPLA was less than 5%.

1. Introduction

Energy crisis and environmental pollution have become a growing concern in the world. The emergence of many new environmentally friendly materials can solve these problems. Among these materials, biodegradable wood-plastic composite is a promising new material. [1-2] PLA is fabricated from renewable raw materials and has the property of being completely degraded by microorganisms, which is regarded as one of the most promising biodegradable plastics. [3] However, due to its brittleness and poor heat resistance, the application of PLA has been limited. In recent years, in order to improve the comprehensive mechanical properties of PLA, researchers mixed inorganic fillers with biodegradable polymers, filled PLA with a large number of cheap and readily available plant fibers, and carried out a large number of experimental studies on wood-plastic composites based on PLA [4-11]. As the rise of 3D printing, researchers have taken a closer look at its extrusion process [12], but investigation on the injection molding process parameters of PLA is not thorough. And the injection molding process parameters have crucial effect on properties of composites, then elaborate study on the process of the composites is essential. Therefore, in this work we obtained the optimal injection molding process parameters of wood-plastic composite spline through orthogonal experiment.

On account of PLA and PBS are hydrophobic materials with almost no polarity between their interfaces. When the interface is subjected to external forces, the stress transfer between the interfaces is poor. In this situation, the comprehensive mechanical properties of the wood-plastic composites deteriorate significantly. [13-16]. To improve the interfacial compatibility of wood-plastic composites, In this work, MAPLA, silane and compound treatment schemes were used to determine the
compatibilizer content and composition of wood-plastic composites with optimal mechanical properties through comparative experiments.

2. Materials and methods

2.1. Materials

Matrix: Polylactic acid (PLA) was received from Shenzhen guanghua weiye industrial co. LTD with a molecular weight of $1.5 \times 10^5$, a density of 1.24 g/cm³ and processing temperature of 170-230°C.

Matrix(ref): Polybutylene succinate (PBS) was received from Showa 3001 Japan with a density of 1.26 g/cm³ and melting point of 114°C.

Additive: Styrene-butadiene-styrene (SBS) 1401 (YH-792) was received from Sinopec asset management co. LTD. Baling petrochemical branch. Maleic anhydride graft polylactic acid (MAPLA) was received from Dongguan shengbang engineering plastic material co. LTD and used as couplint agent with graft rate 0.8-1.2%, melt flow rate 8 g/10 min (210°C/2.16 kg under experimental conditions). Silane KH-560 was received from Jinan xingfeilong chemical co. LTD and used as couplint agent for PLA and PBS. DOP was received from KaiMa reagent and used as plasticizer for PLA. Superfine talcum powder was used as lubricant with 1500 mesh. And Zinc stearate was received from Teda haipin chemical reagent factory.

2.2. Preparation of the samples

Put the 120-mesh straw flour into a drying oven and dry in a vacuum for 2 hours at 80 degrees Celsius. Remove moisture and volatile matter and set aside. Take a part of dried straw powder without silane treatment with mass fractions of 20%, activate it at 80°C for 2 hours, then dry it at 100°C for later use. 50% PLA, 30% PBS were respectively crushed in a high-speed pulverizer, separated by a 120-mesh screen, and then dried in a drying oven for 2 hours at a temperature of 85°C.

The dried straw flour (untreated, silane treated), PLA powder, PBS powder, 3% DOP plasticizer, 3% lubricants, 15% SBS and 4% zinc stearate were put into the high speed reheat mixer and mixed evenly and dried. The mixer temperature was set at 80°C for 15 minutes.

The mixed materials 1# were shown in Table 1 and added into the injection molding machine to prepare the mechanical spline of PLA/PBS/straw powder biodegradable wood-plastic composite material. The parameters of injection molding machine are shown in Table 2.

**Table 1. Contents of wood-plastic composites with different compatibilizers.**

| Groups | Materials | PLA | PBS | DOP | SBS | ZnSt | Lubricant | MAPLA | KH-560 |
|--------|-----------|-----|-----|-----|-----|------|-----------|-------|--------|
| 1#     |           | 50  | 30  | 3   | 15  | 4    | 3         |       | /      |
| 2#     |           | 50  | 30  | 3   | 15  | 4    | 3         | 5     | /      |
| 3#     |           | 50  | 30  | 3   | 15  | 4    | 3         |       | 5      |
| 4#     |           | 50  | 30  | 3   | 15  | 4    | 3         | 5     | 5      |

**Table 2. Orthogonal experimental condition.**

| Part     | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|----------|---|---|---|---|---|---|---|---|---|
| Temperature A/°C | 173 | 173 | 173 | 175 | 175 | 175 | 178 | 178 | 178 |
| Pressure B/MPa    | 40 | 40 | 50 | 40 | 45 | 50 | 40 | 45 | 50 |
| Speed C/MPa       | 35 | 40 | 45 | 40 | 45 | 35 | 45 | 35 | 40 |
2.3. Characterization

According to GB 1040-79 standard, the samples were determined by tensile machine (CMT-5105) with a tensile speed (chuck moving speed) of 10 mm/min. The impact test was determined by a pendulum beam (XJU-22), according to GB 1043-79. The flexural strength of the specimen was tested by a flexural testing machine (CMT-5504) with a head speed of 2.0 mm/min. The morphology of the resultant samples was characterized by scanning electron microscopy (FEI Q445).

3. Result and discussion

3.1. Data analysis of orthogonal experiment

In order to investigate the influence of injection temperature, injection pressure and injection speed on the comprehensive properties of wood-plastic composite, the orthogonal experimental method was used. The experimental conditions and experimental data are shown in Table 1 and Table 3. Through the range method, the influence of three factors on the injection effect and mechanical properties of wood-plastic composite is comprehensively analysed, as shown in Table 4, 5, 6 and 7.

| Table 3. Orthogonal experimental data. |
|----------------------------------------|
| Part | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Density/(g/cm³) | 1.018 | 1.010 | 1.034 | 1.038 | 1.025 | 1.026 | 1.020 | 1.040 | 1.045 |
| Tensile strength/MPa | 8.694 | 9.912 | 15.723 | 12.828 | 15.951 | 13.340 | 19.030 | 15.962 | 12.959 |
| Impact strength/MPa | 13.347 | 16.808 | 16.538 | 9.965 | 7.948 | 16.087 | 7.831 | 15.850 | 17.676 |
| Flexural strength/MPa | 15.122 | 10.653 | 11.571 | 11.236 | 17.923 | 14.202 | 20.510 | 10.442 | 17.544 |

Available from range analysis, injection molding temperature has the most important effect on the density of PLA/PBS/straw powder wood-plastic composites. Injection molding speed is the most important factor affecting to tensile strength. The most important parameter to impact strength is injection pressure. And injection molding temperature has a relatively large influence on the flexural strength.

According to Table 3, 4 and 5, the optimal injection molding process can be selected, i.e., the injection molding temperature of 178°C, the injection molding pressure of 50MPa, and the injection molding speed of 45%. Under these conditions, PLA/PBS/straw powder wood-plastic composites with optimal mechanical properties can be obtained.

| Table 4. Density range analysis table. |
|----------------------------------------|
| Factor | Density/(g/cm³) |
| 1 | 3.062 | 3.076 | 3.084 |
| 2 | 3.089 | 3.075 | 3.093 |
| 3 | 3.105 | 3.105 | 3.079 |
| R | 0.043 | 0.030 | 0.014 |

Factors order: A>B>C. Better production conditions: A₃B₃C₂.
Table 5. Tensile strength range analysis table.

| Factor | Tensile strength / (MPa) |
|--------|--------------------------|
| 1      | 34.329                   |
| 2      | 42.119                   |
| 3      | 47.951                   |
| R      | 13.622                   |

Factors order: C>A>B. Better production conditions: C₃A₃B₃.

Table 6. Impact strength range analysis table.

| Factor | Impact strength / kJ/cm² |
|--------|--------------------------|
| 1      | 46.693                   |
| 2      | 34.000                   |
| 3      | 41.357                   |
| R      | 12.693                   |

Factors order: B>C>A. Better production conditions: B₃C₁A₁.

Table 7. Flexural strength range analysis table.

| Factor | Flexural strength / MPa |
|--------|--------------------------|
| 1      | 37.346                   |
| 2      | 43.361                   |
| 3      | 48.496                   |
| R      | 11.150                   |

Factors order: A>C>B. Better production conditions: A₃C₃B₁.

3.2. Effect of MAPLA content on mechanical properties of wood-plastic composites

According to the optimal injection molding process parameters, the experimental parameters of injection machine are determined as shown in Table 8 and 9. The biodegradable wood-plastic composite was prepared by using straw powder without silane treatment and mixed materials 1° in Table 1. The flexural property, tensile property and impact property of the composite material with the change of MAPLA content is shown in Figure 1.

Table 8. Temperature parameters of injection machine.

| Part | Nozzle 1 | 2 | 3 | 4 | 5 | Oil temperature |
|------|----------|---|---|---|---|-----------------|
|      | Temperature / °C | 175 | 178 | 178 | 170 | 25 | 25 | 25 |

Table 9. Speed and pressure parameters of the injection machine.

| Part | Injection speed / % | Injection pressure / MPa |
|------|----------------------|--------------------------|
|      | 1        | 2        | 3        | 4        |
|      | 45       | 45       | 45       | 45       |
|      | 50       | 50       | 50       | 50       |

Other process parameters: The clamping pressure is 150MPa. The injection time is 5s. The holding time is 7s. The cooling time is 5s.
The addition of 5% MAPLA in wood-plastic composite shows the best flexural strength and tensile strength. Compared with the Wood-plastic composites without compatibilizer, the flexural strength was enhanced by 146.72% and the tensile strength was enhanced by 118.07%. The addition of 3% MAPLA in wood-plastic composite shows the highest impact intensity, it is 20.36 kJ/m², which was 36.19% higher than it without MAPLA.

As is well known, the mechanical properties of the wood-plastic composites are closely related to the interface compatibility of matrix and reinforced phase. The maleic anhydride functional group in MAPLA reacts with a large number of hydroxyl groups on the surface of straw powder to form hydrogen bond, which allow the non-polar molecular chains to tangle with the plastic molecular chains, like a bridge, increasing the interfacial bonding force between straw powder and plastic.

Figure 1. Mechanical properties of the wood-plastic composites with different of MAPLA content.

However, the excessive amount of MAPLA did not show any positive effect. This is due to the straw powder was not fully plasticized during the injection molding process, larger fiber particles were formed, which resulted in the reaction of MAPLA with the hydroxyl group on the surface of the particles, but not with the inside particles, that affected the mechanical properties of wood-plastic composites.

At the same time, the melt flow rate of MAPLA is low, and the increase of it leads to the increase of its viscosity, reducing the opportunity of hydroxyl reaction with straw powder surface. This affects the combination of straw powder and plastic interface, which reduces the mechanical properties of wood-plastic composites [17-19]. Therefore, the rational selection of MAPLA content is also the main factors to improve the comprehensive mechanical properties of PLA/PBS/ straw powder wood-plastic composites.

3.3. Effects of different compatibilizers on mechanical properties and structural morphology of plastic composites

The mechanical properties and structural morphology of wood-plastic composites with different compatibilizers were compared. The formulations of each wood-plastic composite sample are shown in Table 1. The mechanical properties of PLA/PBS/ straw powder wood-plastic composite material are shown in Figure 2, and the section microstructure is shown in Figure 3.
Figure 2. Mechanical properties of the wood-plastic composites with different compatibilizers.

Figure 2 showed that the mechanical properties of PLA/PBS straw powder wood-plastic composites are significantly different when different types of compatibilizer with the same percentage content were added. When 5% MAPLA was added, the comprehensive mechanical properties of PLA/PBS straw powder wood-plastic composites were relatively optimal. The comprehensive mechanical properties of wood-plastic composite treated with both were not significantly different from that of wood-plastic composite treated with 5% silane or 5% MAPLA.

Figure 3. SEM for the cross section structure of PLA/PBS straw powder wood-plastic composite

Figure 3(a) shows that there is an obvious boundary between straw powder and plastic in wood-plastic composites without compatibilizer. Straw powder and plastic have severe phase separation and poor interfacial compatibility, which affects the mechanical properties of wood-plastic composites.

With the addition of 5% silane, the interfacial bonding ability of wood-plastic composites was improved, as shown in Figure 3(c). However, due to the effect of small holes in the broken section, the mechanical properties of wood-plastic composites were not greatly improved.

When both MAPLA and silane were added to the composite material, the interface between straw powder and plastic was significantly improved. The plastic was coated with evenly distributed straw powder and inconspicuous boundary on the fracture section. But this had little effect on the mechanical properties of wood-plastic composite material. This may be due to the uneven flow rate of the melted raw materials, so that the holes in the cross-section affect the mechanical strength of composite material.
4. Conclusions
Through orthogonal experiments, the optimum injection molding process parameters of wood-plastic composite material were determined, including injection temperature 178°C, injection pressure 50MPa and injection speed 45%. Under these conditions, the effect of mechanical properties of PLA/PBS/straw powder wood-plastic composites with different compatibilizers was analyzed. The major conclusions are as follows:

(1) The interface of PLA/PBS/straw powder wood-plastic composite treated with 5% silane and 5% MAPLA was improved significantly, but the effect on the mechanical properties of it was not obvious.

(2) When different kinds of compatibilizers were added, 5% MAPLA had a greater influence on the comprehensive mechanical properties of PLA/PBS straw powder wood plastic composite than 5% silane treatment. In addition, the combination of the two treatments had a certain improvement on the structure and morphology of the cross section.

(3) When the content of MAPLA is 3%, the impact strength of wood-plastic composite is 20.36 kJ/m², which is 36.19% higher than the composites without maleic anhydride. When the content of MAPLA is 5%, the flexural strength and tensile strength of wood-plastic composite material are 46.72% and 118.07% higher than those without addition.

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