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Preparation and properties of short natural fiber reinforced poly(lactic acid) composites

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Abstract: The natural fiber/poly(lactic acid) (PLA) composites were prepared with ramie and jute short fiber as reinforcement and PLA as matrix. The mechanical and thermal properties of the composites were investigated. The results show that the properties of the composites are better than those of plain PLA. When the content of the fiber is 30%, the composites can get the best mechanical properties. The dynamic mechanical analysis results show that the storage moduli of the PLA/ramie and PLA/jute composites increase with respect to the plain PLA. The Vicat softening temperature of the composites is greatly higher than that of PLA. The results of thermogravimetric analysis show that adding fiber to the PLA matrix can improve the degradation temperature of PLA.

Key words: poly(lactic acid); ramie; jute; composite

1 Introduction

Recently, with growing pressure on the world's resources as well as concerns about disposal of plastics intensifying interest and commercial activity, biodegradable polymers have received much attention[1]. Biopolymers offer environmental benefits such as biodegradability, greenhouse gas emissions, and renewability of the base material[2]. Poly(lactic acid)(PLA) has received much attention of biodegradable polymers[3−5]. PLA is a linear aliphatic thermoplastic polyester, produced from renewable resources[6]. PLA has properties that are comparable to many commodity polymers (e.g. PP, PE, PVC, PS) such as high stiffness, clarity, gloss, and UV stability[7]. PLA is commonly produced by two methods[8]. It can be commonly synthesized by ring-opening polymerization of lactide. PLA may also be produced by direct polycondensation of lactic acid. Lactic acid, the starting material for PLA synthesis, can be produced by fermentation from a number of different renewable resources. Because PLA has high strength, thermal plasticity, and biocompatibility, it has been used as package materials and other products[9]. However, the physical properties of PLA such as brittleness limit the PLA polymer application[10]. A way to improve the mechanical and thermal properties of PLA is the addition of fibers or filler materials[11].

For many applications, natural fibers provide reinforcement properties at lower cost, lower density, and higher strength and stiffness[12]. The potential advantages of natural fiber have been well documented and are generally based on environmental friendliness as well as health and safety factors[13−14]. Most researches concentrate on natural fibre/nondegradable polymer composites but research reports on natural/biodegradable polymer composites are rather limited[15−16]. The performance of natural fiber including recycled newspaper fiber, bamboo and hemp fiber, etc, reinforced PLA composites has been investigated[17−19]. DAVID et al[20] determined the mechanical properties of the PLA/jute fiber composites and showed that the tensile strength of composites was significantly higher than that of PLA. But the elongation at break of the composites is still very low as about 2%. And most of the fiber used was the fabric, it may decrease the productive efficiency.

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In this study, ramie fiber and jute fiber reinforced PLA composites were prepared by a two-roll mill with the ramie fiber and jute fiber as reinforcement and PLA as the matrix. The mechanical and thermal properties of the composites were studied.

2 Experimental

2.1 Materials

PLA (M_w=160 000) was supplied by Shanghai Tong-Jie-Liang Biomaterial Co. Ltd., China. Ramie fiber and jute fiber were purchased from Jinlan Fiber Co. Ltd., China.

2.2 Composite preparation

Ramie fiber and jute fiber were cut to 10 mm in average length. Then ramie fibers or jute fiber (10%−50%) and PLA were blended using a two-roll plastics mill at 140 ℃ for 5 min. The composites obtained were then molded into sheets by hot pressing at 170 ℃ and 20 MPa for 4 min, followed by cooling to room temperature at 5 MPa. The sheets were prepared for structure characterization and properties measurements.

2.3 Characterization

Specimens of neat PLA and composites were tested for tensile strength according to GB 13022—91 standard, using a CMT5105 machine (Shenzhen Sansi Material Instruments Ltd., China). Crosshead speed was set at 20 mm/min.

The neat PLA and composites were tested for flexural strength under three-point bending in a DXLL-5000 machine (Shanghai Jiedeng Instruments Ltd., China) in accordance with GB 1449—83. The size of the flexural testing samples used was 65 mm×10 mm ×3.5 mm. The machine was operated at a crosshead speed of 1.2 mm/min and a span length of 60 mm. The flexural strength (S) was measured using the following equation:

$$S=8FL/(\pi d^3)$$

where F denotes the load, L is the span and d is the diameter of the specimen.

The impact strength of composites in comparison to neat PLA was determined from the specimens having dimensions of 65 mm×10 mm×3.5 mm. The test was carried out in an XCJ-50 test machine (Chengde Test Instruments Ltd., China) according to GB 1451—83.

Dynamic mechanical analysis (DMA) was performed in three-point bending mode using a DMA Q800 dynamic mechanical analyzer. The samples were cut from the sheets with dimensions of 60 mm×13 mm ×2.4 mm. The test specimen dimensions were kept as similar as possible in order to obtain an accurate comparison.

Thermogravimetric analysis(TGA) was performed on Q100 thermogravimetric analyzer (Tainstsh, USA) at a heating rate of 20 ℃/min. Samples were examined under the presence of nitrogen (80 mL/min) over a temperature range from room temperature to 700 ℃.

The Vicat softening temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. The Vicat softening temperature was tested according to the ASTM D1525 standard. A test specimen was placed in the testing apparatus so that the penetrating needle rested on its surface for at least 1 mm from the edge. A load of 10 N was applied to the specimen. The specimen was then lowered into an oil bath at room temperature. The bath was raised at a rate of 120 ℃/h until the needle penetrated 1 mm.

3 Results and discussion

3.1 Tensile properties of composites

The tensile properties of neat PLA were compared with the PLA/Ramie and PLA/jute composites. Fig.1(a) shows the tensile strength of PLA and PLA-based composites. Neat PLA has a lower tensile strength than

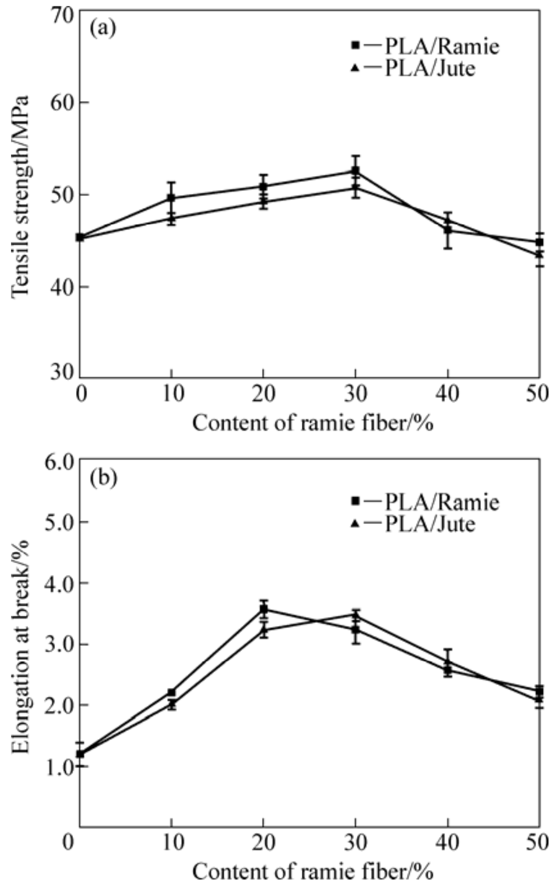

Fig.1 Tensile properties of neat PLA and PLA-based composites: (a) Tensile strength; (b) Elongation at break

PLA-based composites. Firstly, the increase in tensile strength with addition of ramie fiber or jute fiber to PLA matrix is suggested that the stress is expected to transfer from the matrix to the strong fiber. But when the addition of fibers is more than 30%, the tensile strength of composites decreases even is lower than that of neat PLA. This is because the dissipation of fiber in the PLA matrix becomes bad. The tensile strength of PLA/ramie composites is higher than that of PLA/jute composites. The strength of ramie is higher than that of jute. Elongation at break of the samples is also tested and shown in Fig.1(b). Elongation at break of the neat PLA or PLA-based composites increases slightly by addition of the fiber firstly due to that the addition of the natural fiber limits the mobility of the polymer matrix. Then elongation at break of the neat PLA or PLA-based composites decreases due to the bad dispersion of fiber in the matrix.

3.2 Flexural properties of composites

Fig.2 shows the flexural properties of both neat PLA and PLA-based composites. According to the results, the flexural strength of the composites increases compared with the neat PLA matrix due to the addition of ramie fiber and jute fiber, and an efficient stress transfer between PLA and natural fiber. When the content of fibers is over 30%, the flexural strength of composites decreases even is lower than that of neat PLA due to the bad dispersion in the matrix. The flexural strength of PLA/ramie composites is also higher than that of PLA/jute composites.

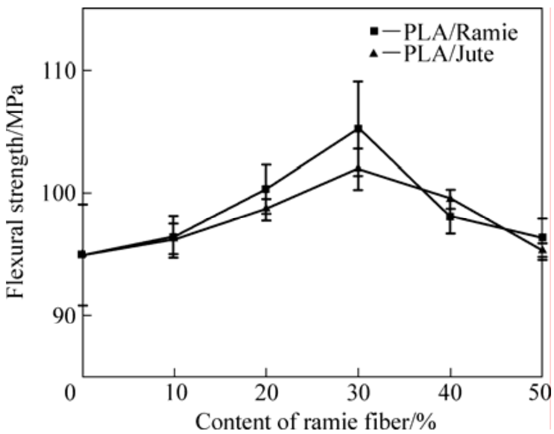

Fig.2 Flexural properties of neat PLA and PLA-based composites

3.3 Impact strength of composites

The notched Izod impact strength results for the tested materials are shown in Fig.3. By comparing with the neat PLA, the impact properties of PLA-based composites are improved. The reason is that the ramie can increase the amount of energy required for pulling it out. Toughness is the major factor controlling the impact strength. Generally, the toughness of fiber reinforced polymer composites is dependent on the fiber, the polymer matrix and the interfacial bond strength[11]. The impact strength of PLA/ramie composites is also higher than that of PLA/jute composites due to the strength of ramie higher than jute.

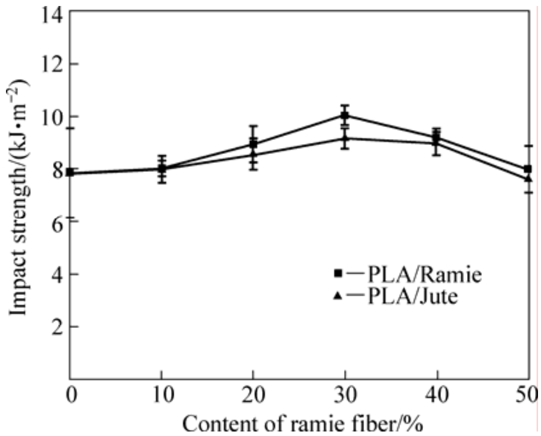

Fig.3 Impact strength of neat PLA and PLA-based composites

3.4 Dynamic mechanical properties of composites

Fig.4 shows the temperature dependence of dynamic storage modulus, loss modulus, and tan δ of the PLA and PLA-based composites. The DMA data were performed to show how the microcomposites exposed to elevated temperatures affect the stiffness of the composite material.

The storage modulus is closely related to the load bearing capacity of the material. From Fig.4(a), the storage modulus of PLA-based composites is higher than that of PLA matrix. This might be due to increase in the stiffness of the reinforcement imparted by the fibers, which allows a greater degree of stress transfer from the matrix to the fiber. The storage modulus of all samples decreases with increasing temperature, and there is a significant fall in the region of 50−70 ℃. However, the softening temperature of composites by surface treatment is higher than that of PLA. It might be due to the addition of ramie fiber of jute fiber, resulting in a decrease of chain mobility and a regular reinforcing effect.

Loss modulus of the PLA matrix and PLA-based composites is shown in Fig.4(b). The maximum heat dissipation occurs at the temperature where loss modulus is the maximum, indicating the glass transition temperature (T_g) of the system. The T_g of all the composites shifts to higher temperatures due to the fiber in the PLA matrix. This can be associated with the decreased mobility of the matrix chains, due to the addition of fibers.

The ratio of loss modulus to storage modulus is measured as the mechanical loss factor or tan δ. The damping properties of the material are affected through the incorporation of fibers in a composite system due to shear stress concentrations at the fiber ends in association with the additional viscoelastic energy dissipation in the matrix material. Here, tan δ peak can be related to the impact resistance of material. As shown in Fig.4(c), the damping peak in the PLA-based composites decreases in comparison to neat PLA.

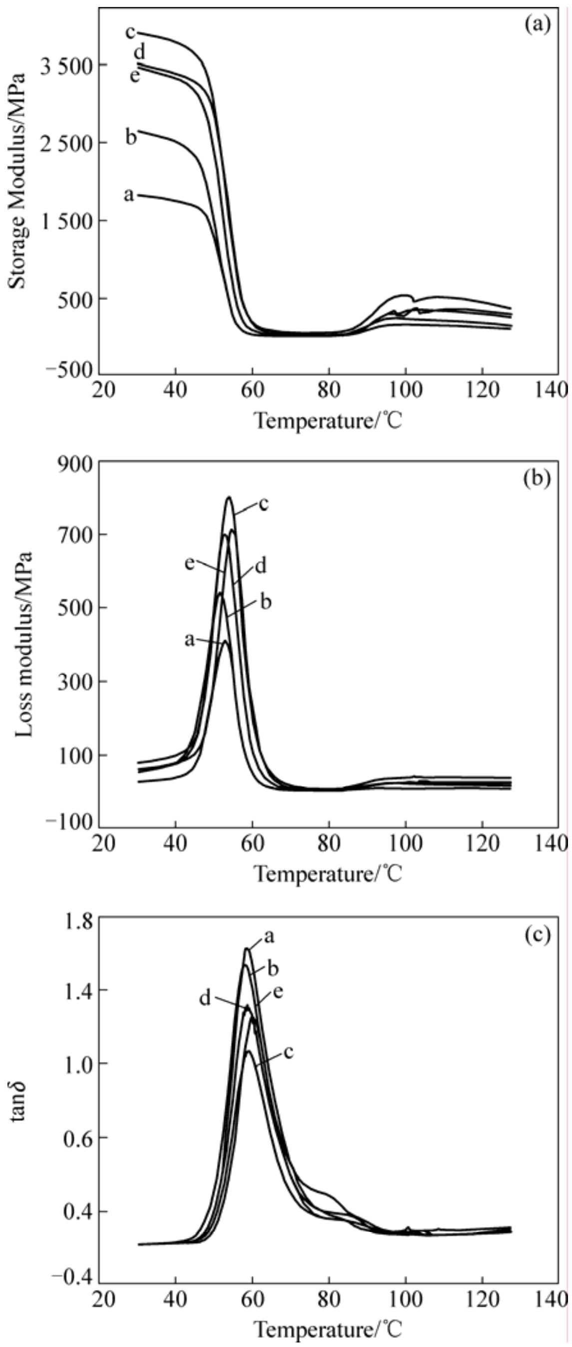

Fig.4 Temperature dependence of storage modulus (a), loss modulus (b) and tanδ of PLA and PLA-based composites (c)

3.5 Thermogravimetry analysis

The thermal stability of neat PLA and PLA-based composites was investigated with thermal analysis, and the results are shown in Fig.5. Thermal degradation of PLA shows completely in a single stage and occurs at 356.3 ℃. From Fig.5, the composites show a lower degradation temperature than PLA. It might be due to the decrease of relative molecular mass of PLA. When the composites are mixed by the two rolls, the incorporation of ramie fiber and jute fiber in PLA matrix has also effect on the thermal degradation temperature.

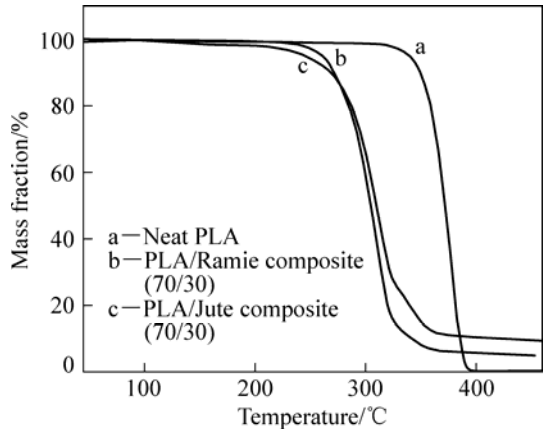

Fig.5 Thermogravimetric curves of PLA and PLA-based composites

3.6 Vicat softening temperature of composites

Vicat softening temperatures of the PLA resin and PLA-based composites are listed in Table 1. As seen in Table 1, Vicat softening temperature of PLA-based composites increases significantly compared with neat PLA resin. In general, there are three options to increase the heat resistance of a polymer: increasing the T_g, increasing the crystallinity, and reinforcing. The heat resistance improvement might be due to that natural fiber reinforcement prevents the deformation of the PLA-based composites. From Table 1, Vicat softening temperature of PLA/Ramie composites is higher than that of PLA/jute composites. This improvement mainly derived from the strength of ramie fiber is higher than that of jute fiber.

Table 1 Vicat softening temperature of neat PLA and PLA-based composites

Composite	Vicat softening temperature/℃
Neat PLA	60.4±43.3
PLA/Ramie(70/30)	103.5±2.5
PLA/Jute(70/30)	93.5±1.7

4 Conclusions

1) The mechanical properties of PLA-based composites increase with the addition of the fiber firstly, and then decrease when the content of fibers is over 30%. The mechanical properties and the thermo-mechanical

properties of the composites (PLA/fiber=70/30) are higher than those of neat PLA. The improvements are due to the efficient of the fiber as the reinforcement.

2) The mechanical properties of PLA/ramie are higher than those of PLA/jute because the strength of ramie is higher than that of jute.

3) The Vicat softening temperature of the composites also increases with the addition of the fiber. But the degradation temperature of the PLA-based composites decreases with the addition of the fiber. Future work will concentrate on the efforts to the compatibility of the fiber and the matrix.

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