

Biodegradable Composites: Ramie Fibre Reinforced PLLA-PCL Composite Prepared by in Situ Polymerization Process

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Summary

Thermoplastic biodegradable composites based on ramie fibre (RF) and a poly(l-lactic acid)-poly(ϵ -caprolactone) (PLLA-PCL) matrix was manufactured using the in situ polymerization method. In order to improve the compatibility and strengthen the interface in natural fibre composite materials, the RF was firstly treated by coupling agents. Then the RF reinforced thermoplastic PLLA-PCL composite was prepared by in situ polymerization of PLLA oligomer with NCO-terminated PCL prepolymer. The effect of fibre length and fibre content on tensile strength and impact strength of this natural-fibre-reinforced biodegradable composite (PLLA-PCL/RF) was discussed, including the influence of the use of silane coupling agent (KH550) for improved interfacial adhesion. The results showed that the tensile strength and impact strength of PLLA-PCL/RF were highest when the RF length was 5-6mm, RF content was 45% and with KH550 as surface treatment agent of RF.

Introduction

In the past decade, new environmental and economic concerns have led to a renewed interest for natural fibre in the composite industry[1-3]. The use of natural fibres in combination with biodegradable polymers and/or petrochemical polymers has been shown to yield properties suitable for low stress applications such as automotive door panels and rear-parcel shelf panels. The natural fibres in place of glass or carbon fibres as reinforcement in composite offers the advantages of high specific stiffness and strength, desirable fibre aspect ratio, low density, biodegradability, lower cost per unit volume, and sound absorption[4,5]. Several reports have devoted the use of natural fibres as reinforcement for thermoplastics such as polyethylene[6–8], poly(propylene)[9–12], polystyrene[13–15], and thermosets[16]. Green composites that are biodegradable and positive environmental benefit can be obtained. This kind of eco-friendly biocomposites from plant-derived fibres and

biodegradable plastics are novel materials that are presently developed[17-21]. These biocomposites can be completely degraded in the environment at the end of their service life. Of the many biodegradable thermoplastics available, poly(L-lactic acid) (PLLA) has been the most popular due to its high mechanical strength[22]. PLLA is an aliphatic polyester derived from corn and sugar beets[23] and degrades to nontoxic compounds in landfill. It is a brittle materials. As we know, toughness in composites is important to ensure that during use delamination and crack propagation within the composite is minimized. To overcome the brittleness of PLLA, a large range of plasticizers has been used with some success[24-27]. These small molecules plasticizers can cause significant changes to the thermal and mechanical properties of PLLA. Susan Wong, Robert A. Shanks and Alma Hodzic[28] reported that they had successfully used hyperbranched polymers as toughening modifiers for PLLA in place of commercial tougheners.

In this study, RF reinforced thermoplastic PLLA-PCL composite was prepared by in situ polymerization of PLLA oligomer with NCO-terminated PCL prepolymer. PCL reacted as toughening component. The main drawback of natural fibre-polymer composites is the weak interfacial bond between highly polar cellulose fibres and the essentially hydrophobic polymers forming the continuous phase. In this process, RF was firstly treated by coupling agents for improved interfacial adhesion before the composite was prepared. The influence of coupling agents, fibre length and fibre content on the composite mechanical properties was analyzed. The results indicated that the biodegradable composite with good mechanical properties was prepared by in situ polymerization process.

Experimental

Materials and sample preparation

Ramie fibres were purchased from Shanghai Red Lion Ramie Co. Ltd (China). Silane KH550 was supplied by Nanjing Shuguang Chemical Group Co., Ltd (China). L-Lactic acid (L-LA) purchased from Jiangxi Musashino Bio-chem. Co. Ltd (China) was 90wt% aqueous solution of the monomer, 99% optically pure according to the manufacturer. Poly(ϵ -caprolactone)diols with an Mn of 1000g/mol were supplied by Daicel Chemical Co., Ltd. (Japan). 1,6-Hexamethylene diisocyanate (HDI) was supplied by Nippon Polyurethane Industry Co., Ltd. Chloroform purchased from Shanghai Chemical Reagent Company, China Medicine (Group) was analytical-grade. The little water in which was removed prior to use by distillation.

PLLA oligomers and NCO-terminated PCL prepolymer were synthesized as we described previously[29]. The weight average molecular weight of synthesized PLLA was about 2.5×10^4 g/mol.

Surface Treatment of RF

Appropriate amount of KH550 was dissolved in the mixed solvent of 1:9v/v distilled water to ethanol to obtain a concentration of 1wt%. Dried ramie fibres were soaked in it for 30min. The fibre:KH550 solution ratio was kept constant at 1:1. Then the blends were cast onto glass plates and the solvents were evaporated. Residual solvent was eliminated by drying in a vacuum oven at 100°C for 4 h.

Preparation of Composite

NCO-terminated PCL prepolymer was dissolved in chloroform to obtain a concentration of 0.1g/ml. The same concentration of PLLA solution was prepared by dissolving in chloroform. Surface treated and dried ramie fibres were soaked in the PCL chloroform solution in a polymerization flask equipped with a mechanical stirrer and a water bath. Then, the appropriate volume of PLLA chloroform solution was added to this polymerization flask to give blends of 30:70 w/w PCL to PLLA. The experimental length of ramie fibre was 1-2mm, 5-6mm and 10-12mm; the ramie fibre content was 15wt%, 25wt%, 35wt%, 45wt% and 60wt%, respectively. The reaction was conducted with a stirrer rotation speed of approximately 30 rpm in a constant temperature water bath of 80°C for 4h. Then the blends were cast onto glass plates and the solvents were evaporated. Residual solvent was eliminated by drying in a vacuum oven at 50°C for 4 h. Finally the composite was obtained by hot pressing in a mould for 5 min under a pressure of 5 MPa at 180°C.

Mechanical testing

The mechanical properties testing were performed at room temperature (24°C) and at a relative humidity of 50%. The tensile testing was performed according to ASTM D-638 standard for tensile testing on an Instron. Izod impact testing was performed according to ASTM D-256-02 using the Ceast Resil impactor.

Scanning Electron Microscopy (SEM)

The impact fracture surfaces of the composite samples and the reinforcing ramie fibre surface with removing weakly adhered PLLA-PCL were directly observed with JSM-5600LV SEM (JEOL Electronic Co., Tokyo, Japan).

Results and Discussion

Influence of coupling agent

Although natural fibres possess many advantages over glass fibres, such as lower density, lower cost and recycle ability, they are not totally free of problems. Natural fibres are comprised mostly of cellulose, a highly hydrophilic macromolecule with strong polarity and, as a result, problems of compatibility with very apolar matrices almost certainly arise. Surface treatments, although having a negative impact on economics, may improve the compatibility and strengthen the interface in natural fibre composite materials.

In order to get good interfacial adhesion between matrix and ramie fibre, KH550 was used to treat the ramie fibre. Ramie fibre has many hydroxyl groups that are inactive. The $-OC_2H_5$ groups in KH550 can react with the hydroxyl groups of ramie fibre so that the treated ramie fibre was grafted $-NH_2$ functional groups which can easily react with $-NCO$ end groups of PCL to form acylamino. Then the RF reinforced thermoplastic PLLA-PCL composite was further prepared by in situ polymerization between $-NCO$ groups at the end of PCL and hydroxyl end groups of PLLA oligomer (Figure 1).

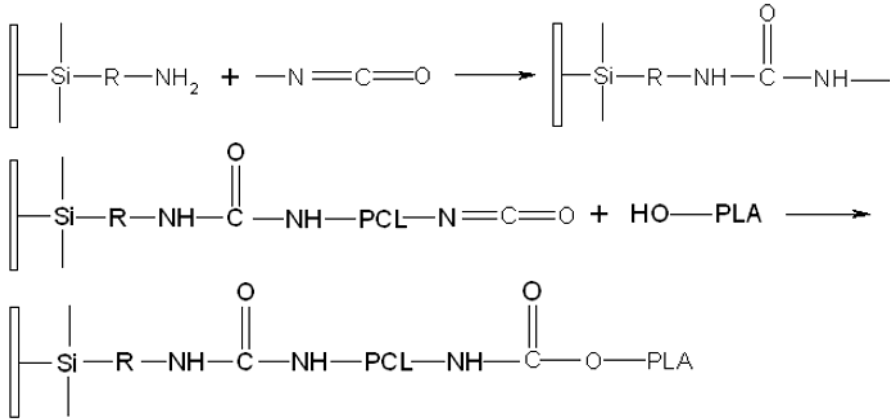


Figure 1. The synthesis schemes of RF reinforced PLLA-PCL composite

The effect of KH550 coupling agent on the mechanical properties of PLLA-PCL/RF composite is shown in Table 1. From Table 1, it could be seen that the mechanical properties of PLA-PCL /RF-KH550 composites were improved sharply. The tensile strength of composite in the presence of KH550 was increased by 11.31MPa compared with the RF without KH550 treating and the impact strength was increased by 58.9J/m. The results of those studies are also indicative of poor interfacial adhesion between PLLA-PCL copolymer and pure ramie fibre for their immiscible characteristics.

Table 1. The mechanical properties of PLLA-PCL/RF and PLLA-PCL/RF-KH550 composites

Sample	Fibre length mm	Fibre content %	Tensile strength MPa	Impact strength J/m	Elastic moulding MPa
PLLA-PCL/RF	5–6	15	12.14	30.0	420.8
PLLA-PCL/RF-KH550	5–6	15	23.45	88.9	775.3

Figure 2 and 3 show the fracture surface of the PLLA-PCL/RF (Figure 2) and PLLA-PCL/RF-KH550 (Figure 3) composites, respectively. It could be obviously observed that the interfacial adhesion between PLLA-PCL matrix and ramie fibre was improved when the ramie was treated by KH550. From Figure 2(a) and (b), it could be clearly found that the interface between ramie fibre and PLLA-PCL copolymer was very poor and the ramie fibres were almost separate from the matrix. There was no matrix adhering to the ramie fibre and some ramie fibres not be fractured but be pulled out from the matrix. All these representations indicated that pure ramie fibre was immiscible with PLLA-PCL copolymer. Compared with Figure 2, the interface between ramie fibres treated by KH550 and PLLA-PCL matrix were improved greatly. (Figure 3a, b) At the roots of ramie fibres the matrix held the fibre tightly and there was matrix adhering to the fracture ramie fibres. As a result it was believable that there was reaction between ramie fibres and PLA-PCL matrix.

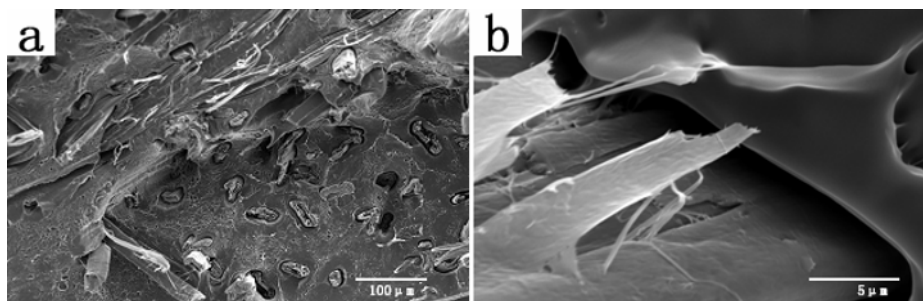


Figure 2. The impact fracture surface of pure ramie reinforced PLLA-PCL composites: (a) overview, (b) detailed picture

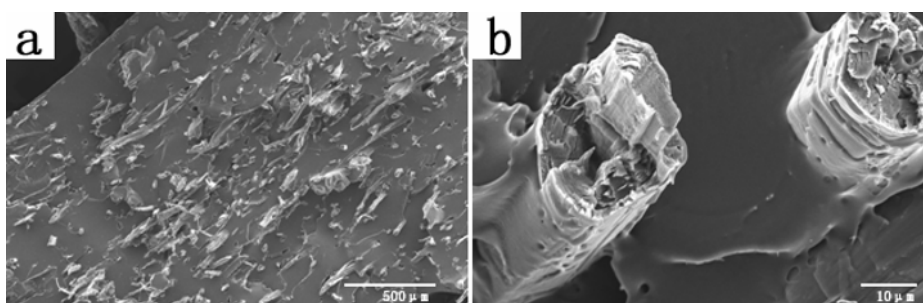


Figure 3. The impact fracture surface of RF-KH550 reinforced PLLA-PCL composites: (a) overview, (b) detailed picture

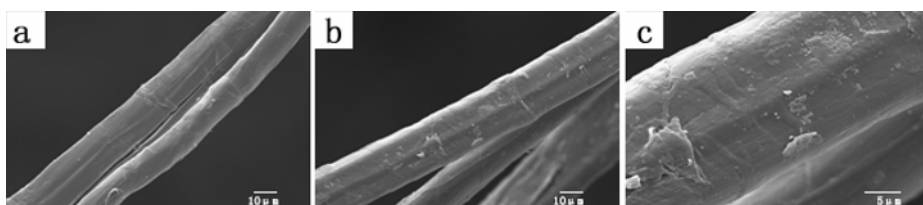


Figure 4. The surface of ramie fibres extracted in chloroform for 48h: (a) pure RF reinforced PLLA-PCL composite, (b) RF-KH550 reinforced PLLA-PCL composite, (c) the detailed picture of (b)

In order to prove this in situ grafting, the matrix PLLA-PCL copolymer was removed from the ramie fibre reinforcing PLLA-PCL composites by being extracted in chloroform for 48h. The ramie fibres surface chemically adhered with PLLA-PCL copolymer were obtained. Figure 4(a) is the SEM micrographs of pure ramie fibre reinforced PLLA-PCL after extracted in chloroform for 48 h. Obviously the fibre surface was smooth and without any matrix on it. However, the ramie-KH550 fibre reinforced PLLA-PCL were extracted in chloroform for 48 h as the same (Figure 4b), it could be distinctly observed that there was matrix adhering to the ramie fibre. Consequently it was further proved that PLLA-PCL copolymer had reacted with KH550 in the ramie fibre and the hydroxyl groups in the ramie fibre were not reactive.

It was known that isocyanate is much more reactive to $-NH_2$ than $-OH$ which explained why $-OH$ groups were not reactive, and the purpose of the coupling agent.

Influence of ramie fibre length

In short fibre strengthening matrices there is a critical fibre length. When the fibre length is above the critical fibre length, the fibre in composites would absorb energy by fibre fracture mechanism. When the fibre get more longer, the fibre would bear more the weight of force of the composite. But if the fibre length is under the critical length the fibre would absorb energy by fibre pull-out mechanism. And here good interface can not make impact energy increasing, but poor interface is beneficial to improve impact energy.

The effects of RF length on the mechanical properties of PLLA-PCL/RF-KH550 are summarized in Table 2. It can be seen that in the case of PLLA-PCL/RF-KH550 the impact energy increases with increasing fibre length until a plateau level is reached. According to above theory we can obviously find that ramie fibre length of 1-2mm still do not reach the critical length. However when the ramie fibre length is 5-6mm, the composite impact energy get maximum. So it could be concluded that 5-6mm was the critical length. We can observe that the tensile strength is continuous increasing with increase of the fibre length. However the impact energy decline by 27.9 J/m compared with 5-6mm of fibre length when the fibres are long as 10-12mm.

Table 2. The effect of RF length on the mechanical properties of PLLA-PCL/RF-KH550

Sample	Fibre length mm	Fibre content %	Tensile strength MPa	Impact strength J/m	Elastic moulding MPa
PLLA-PCL/RF-KH550	1—2	15	16.18	27.3	409.5
PLLA-PCL/RF-KH550	5—6	15	23.45	88.9	775.3
PLLA-PCL/RF-KH550	10—12	15	25.73	61.0	820.3

Impact energy just reflects the ability of unit width of composite absorbing energy at fracture according to ASTM D-256. Obviously when the ramie fibres fully exerted its ability to bear the weight of force, the impact energy would reduce with fewer fibres in the unit width. When the fibre length increased from 5-6mm to 10-12mm, the fibre amount in unit width sure got fewer at a definite fibre content. As a result when the fibres were long as 10-12mm, the impact energy declined by 27.9 J/m compared with fibre length of 5-6mm. During tensile test all the fibres in the composite bear the weight of force so as to the tensile strength is continuous increasing with increase of the fibre length based on above theory. And it also could be observed that the tensile strength was increased by 7.27MPa when the fibre length was increased from 1-2mm to 5-6mm. However the tensile strength was only increased by 2.28MPa when the fibre length was increased from 5-6mm to 10-12mm. So the fibre with length of 5-6mm was optimal choice to reinforce PLA-PCL copolymer.

Influence of ramie fibre content

Figure 5(a) and (b) shows the tensile strength and impact strength of the manufactured PLLA-PCL/RF-KH550 composites as a function of the ramie fiber content,

respectively. As shown in Figure 5(a), the tensile strength of the composites increased with the ramie fiber content increased when the fiber content was less than 45 wt.%. However, if the fiber content was more than 45 wt.%, the reduction of tensile strength occurred. The same trend was also found in the notched impact strength of the composites (Figure 5 b).

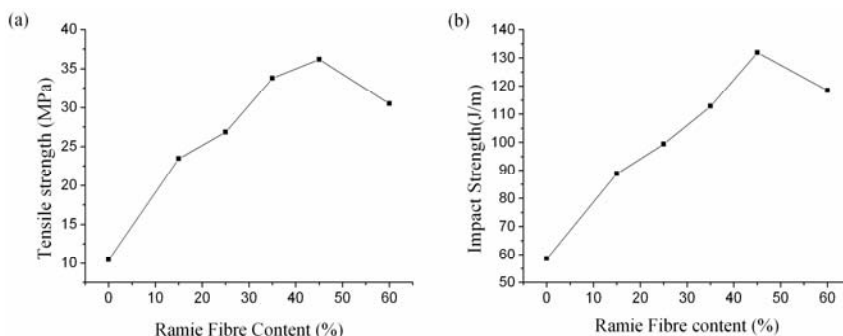


Figure 5. Effect of ramie fiber content on the mechanical properties of PLLA-PCL/RF-KH550 with fibre length of 5-6mm: (a) the effect of fibre content on tensile strength, (b) the effect of fibre on impact strength

As we described previously[30], fiber reinforced composites absorb impact energy via three major mechanisms: fiber breakage, fiber pullout, and matrix crack propagation. The end of each fiber acts as a Griffin flaw and is a crack initiation site. For ramie fiber reinforced PLLA-PCL composites, the increase of fiber content corresponds to the increased surface area, which can provide higher pullout forces. But, if the fiber content reached a critical amount, the crack initiation sites increased and induced excessive defects, which would result in the decreased of mechanical properties of composites.

Conclusion

The ramie fiber reinforced PLLA-PCL composite was prepared by in situ polymerization. PLLA-PCL copolymer could be grafted to the RF-KH550 so that the interface between ramie fibre and PLLA-PCL copolymer was improved greatly. Mechanical testing and SEM micrographs analysis indicated that the mechanical properties of synthesized composite was well when the ramie fibre was pretreated by KH550, ramie fibre length was 5-6mm and the content of ramie fibre was 45%.

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