STUDY ON THE STRUCTURE AND PROPERTIES OF POLY(3-HYDROXYBUTYRATE-CO-4-HYDROXYBUTYRATE)/ RUBBER WOOD FIBER COMPOSITES MODIFIED WITH TITANATE COUPLING AGENT

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(Received May 2020)

ABSTRACT

In this study, the biodegradable composites were prepared from rubber wood fibers (Hevea brasiliensis) and biopolymer poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB) via hot pressing process, using the titanate as the coupling agent. The morphological, chemical structure, mechanical properties and water absorption (WA) of the composites were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), mechanical properties and WA analysis. Results showed that a new absorption peak of Ti-O-C was formed due to the addition of titanate, indicating that it was successfully grafted on the surface of wood fibers. In addition, the mechanical properties of the composites first increased and then decreased with the increasing of the titanate content. The obvious improvement of WA of composites was attributed to the inclusion of P34HB by titanate modified wood fiber. Moreover, it was also found that the optimal condition of the titanate coupling agent content was 1 wt%.

KEYWORDS: Wood flour, P34HB, titanate, structure, mechanical properties.

INTRODUCTION

Currently, due to the shortage of raw materials and environmental problems caused by traditional petroleum-based polymers, biodegradable polymers with biocompatibility and...
sustainability have been paid more and more attention, of which poly (3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB), derived from polyhydroxyalkanoates (PHAs) product, exhibits numerous qualities such as lower crystallinity, higher elasticity and toughness, which is considered as the most promising representative of eco-friendly polymers. However, the poor crystallization rate, mechanical properties, narrow thermal processing window and high cost of P34HB impede its large-scale commercial application.

Compared with synthetic fibers, wood fibers possess many potential advantages, including wide source, degradability, heat filling, low cost and excellent physical and mechanical properties (Zhang et al. 2010, Chen et al. 2017, Joffre et al. 2017, Panaitescu et al. 2020). Some studies showed that the addition of plant fibers to biopolymer matrix can improve the mechanical strength of composite materials, make up for the defects of biopolymer matrix, and reduce the manufacturing cost of composite materials (Torres-Telloa et al. 2017, Kellersztein et al. 2019). However, wood fiber is hydrophilic and incompatible with the hydrophobic biopolymer such as P34HB (Han et al. 2012, An and Ma 2017). It was found that the addition of coupling agent to modify the raw materials was one of the most effective methods to improve the interfacial compatibility. The two-phase structure of the coupling agent can enhance the compatibility between two different materials and improve the properties of the composites. The molecular formula of titanate coupling agent is R-O-Ti-(OR)ₙ, in which the pro inorganic end RO- is bonded with the hydroxyl -OH on the surface of wood fiber, and at the other end, the pro organic -OR can be bound with the organic body to achieve bridging effect and improve the interfacial compatibility between wood fibers and P34HB.

In this paper, rubber wood fibers (Hevea brasiliensis) were used to enhance the biopolymer poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB), and titanate was used as the coupling agent, to prepare P34HB/T/WF composites. The effects of different contents of titanate (0.5 wt%, 1 wt%, 2 wt%, 4 wt%, 8 wt%) on the cross-section morphology, chemical structure, mechanical properties and water absorption (WA) of the composites were investigated by various experimental characterization methods.

MATERIAL AND METHODS

Rubber wood (80~100 mesh) used in this study was provided by Lichang Wood Industry Co., Ltd (Linying, Henan). P34HB powder was provided by Tianjin Guoyun Bio-Materials Co., Ltd. Prior to use, wood flour was dried in an oven at 103°C for 12 h and P34HB was dried under vacuum at 80°C for 6 h. All other chemicals in the study were reagent grade and they were used without further purification.

0.5 wt%, 1 wt%, 2 wt%, 4 wt%, 8 wt% of titanate coupling agent was added into 90 wt% aqueous alcohol solution, and then a small amount of dioctyl phthalate (DOP) was added into the mixed solution. Finally, the mixture was sprayed on wood flour for modification treatment. After the ethanol in the wood flour volatilized completely, the modified wood flour was dried at 103°C for 6 h, and then cooled to room temperature and sealed for standby.

The modified wood flour and P34HB with a total mass of 150 g were weighed (mass ratio of 1:1) and put into a high-speed mixer to blend at 1420 r.min⁻¹ for 4 min. Subsequently, the mixtures were evenly spread over a 250 × 250 × 2 mm molds, and thermoformed with a pressure of 17 t at 170°C for 10 min. After hot pressing, the molds were removed into a flat vulcanizer with a pressure of 1 MPa for cold pressing of 3 min. Finally, the P34HB/T/WF composites were obtained by removing samples from the molds.
Cross-section microstructure of the composites was examined by the scanning electron microscopy (JSM-IT300LV, JEOL, Japan) with an applied voltage of 30 kV. The sample was sprayed with gold before observation. Fourier transform infrared spectroscopy (FTIR) was taken on a ThermoFisher Scientific iS5 instrument (Thermo, USA) in the resolution of 4 cm\(^{-1}\) and scanning time of 32 s. The mechanical properties of P34HB/T/WF composites were tested by Instron 3369 universal testing machine (Instron, USA) according to GB/T 1040-2006 and GB/T 9341-2008. Five samples were measured and the average values and standard deviation were reported.

According to the relevant provisions of GB/T 1034-2008, after the sample was cut into a size of 60 × 60 × 2 mm, it was dried in a vacuum drying oven at 50°C for 24 h, and then cooled to room temperature. At this time, the weight of the sample was recorded as \(m_1\). Immerse the sample in container containing distilled water for 24 h, then take out and wipe the water on the surface of the sample with filter paper, and weigh again and record as \(m_2\). The WA of each sample was calculated using the following formula:

\[
WA = \frac{(m_2 - m_1)}{m_1} \times 100\%
\]  

(1)

For each sample, three replicates were performed and the mean and standard deviation were reported.

**RESULTS AND DISCUSSION**

Fig. 1 shows the cross-section of P34HB/T/WF composites with different titanate coupling agent contents. As shown in Fig. 1a, the cross-section of the composites prepared by unmodified wood fiber exhibited high roughness, obvious fiber pull-out phenomenon and clear interface gaps (Han et al. 2012, Singh et al. 2008). It was mainly attributed to the poor compatibility and interfacial adhesion between unmodified wood fiber and P34HB, resulting in incomplete morphology (Aydemir et al. 2015, Barczewski et al. 2018).

![Fig. 1: The impact cross-section SEM image of P34HB/T/WF composites with different titanate contents. (a) 0 wt% titanate; (b) 0.5 wt% titanate; (c) 1 wt% titanate; (d) 2 wt% titanate; (e) 4 wt% titanate; (f) 8 wt% titanate.](image)

After adding titanate coupling agent, the adhesion between wood fiber and P34HB matrix was improved, and the orientation was significantly enhanced, so that the wood fiber was evenly
dispersed in P34HB matrix without obvious gaps, forming a continuous homogeneous phase, as shown in Fig. 1b and c. When the titanate coupling agent content was more than 1 wt%, the cross-section structure of composites became uneven (Fig. 1d-f), the wood fiber presented fracture, and the holes were also increased, which indicated that the excessive titanate coupling agent covering the surface of wood fiber limited the role of "bridge". As a result, the compatibility between wood fiber and P34HB matrix was greatly weakened as the excessive titanate was added.

Fig. 2 shows FTIR spectra of P34HB/T/WF composites with different titanate coupling agent contents. The band at 3400 cm\(^{-1}\) as stretching vibration of the intermolecular hydrogen bond O-H, which was significantly broader in the curve of 2 wt% titanate content, indicating that new intermolecular hydrogen bonds were formed.

![Fig. 2: FTIR spectra of P34HB/T/WF composites with different titanate contents.](image)

When the titanate content was more than 2 wt%, the intensity of O-H vibration peak gradually decreased. The 2980 cm\(^{-1}\) band was the characteristic peak of the stretching vibrations of methyl -CH\(_3\), which was provided by wood fiber. The adsorption peaks at 1720 and 1740 cm\(^{-1}\) represented the stretching vibration of C=O in the fully crystallized and semi-crystallized states of P34HB molecular chain, respectively (Liu et al. 2016, Prado et al. 2019). With the increase of titanate content, the intensity of peaks at 1720 cm\(^{-1}\) increased first and then decreased, while the intensity change of peaks at 1740 cm\(^{-1}\) was reversed, indicating that the properties of the composite had changed because of adding the titanate. At the same time, the absorption peak at 1125 cm\(^{-1}\) exhibited more and more sharper due to the formation of Ti-O-C bond. It further revealed that the titanate could act as a bridge between the surfaces of wood fiber and P34HB, promoting the interfacial compatibility of the composites (Jin et al. 2019).

Fig. 3 represents the relationship between the tensile and flexural properties and the titanate contents of P34HB/T/WF composites.
It can be seen from Fig. 3a-c that with the increase of titanate content, the mechanical and flexural properties of the composites first increased and then decreased. When the titanate content was 1 wt%, the mechanical properties of P34HB/T/WF composites reached the maximum values (tensile strength of 17.51 MPa, elastic modulus of 808.14 MPa, elongation at break of 5.86%, flexural strength of 36.14 MPa and Young’s modulus of 4845.67 MPa), indicating that excessive titanate content had a negative role in the compatibility of wood fiber and P34HB. The increase of the mechanical properties of the composites was firstly attributed to the combination of alkoxy group (R-O-) in the titanate coupling agent with hydroxyl group on the surface of wood fiber through chemical bond to improve their compatibility. Meanwhile, the ester plasticizer DOP promoted the crosslinking of titanate, wood fiber and P34HB, which can effectively absorb the external force for composites (Liu et al. 2019, Hu et al. 2020, Pupure et al. 2020). In addition, due to the interaction between the molecular structure of titanate coupling agent and P34HB polymer, there was the closer bonding between composite substrates, improving the compatibility with P34HB, and finally resulting in the mechanical strength of the composites increasing (Gao et al. 2016, Nikpour and Rodrigue 2016). When excess titanate was added (more than 1 wt%), the monolayers formed between wood fiber and P34HB was destroyed because of self-agglomeration, resulting to form stress layer and uneven interface (Febrianto et al. 2017, Maslowski et al. 2018). Moreover, the redundant coupling agent molecules not involving in the reaction weakened the binding ability of wood fiber and biopolymer P34HB, and finally reduced the mechanical properties of composites (Jiang et al. 2019, Kuciel et al. 2020).
Fig. 3d shows the WA change curve of P34HB/T/WF composites with different titanate contents. WA of the unmodified composite was 3%. With the increase of titanate coupling agent content from 0.5 to 8 wt%, the WA decreased from 1.9 to 0.7%. The smaller the WA of the composites, the better the water resistance (Xu et al. 2016a, 2016b, Liu et al. 2019). In the process of hydrolysis reaction between alkoxy group of titanate coupling agent and hydroxyl group of wood fiber, Ti was connected to the surface of wood fiber through oxygen bridge, forming molecular layer of coupling agent. On the other hand, titanate coupling agent improved the interfacial compatibility between wood fiber and P34HB, enhancing the hydrophobic P34HB coating on the surface of wood fiber, which were beneficial to reduce the WA of the composites.

CONCLUSIONS

In this study, P34HB/T/WF composites were successfully prepared by using the titanate as the coupling agent to increase the interfacial adhesion. A new absorption peak of Ti-O-C was found by FTIR spectra, which indicated that titanate was successfully grafted on the surface of wood fiber to achieve an ideal modification effect. When the titanate content increased, the mechanical properties of the composites first increased and then decreased. The tensile and flexural properties reached the maximum values when the content of titanate was 1 wt%, including tensile strength of 17.51 MPa, elastic modulus of 808.14 MPa, elongation at break of 5.86%, flexural strength of 36.14 MPa and Young's modulus of 4845.67 MPa. The obvious improvement of WA of the composites was attributed to the inclusion of P34HB by titanate modified wood fiber. There was a positive correlation between the water resistance of the composites and titanate content, and the optimal value of WA was 0.7%. According to the comprehensive analysis, it was also found that the optimal condition of the titanate coupling agent content was 1 wt%.

ACKNOWLEDGMENTS

This research has been financially supported by Opening Project Fund of Key Laboratory of Rubber Biology and Genetic Resource Utilization, Ministry of Agriculture/ State Key Laboratory Breeding Base of Cultivation & Physiology for Tropical Crops/ Danzhou Investigation & Experiment Station of Tropical Crops, Ministry of Agriculture (RRI-KLOF202001), and Science Foundation of Tianjin Municipal Education Commission (2019ZD039).

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