

Characterization of Polypropylene Fiber and Lignocresol Enhanced Poly(3-hydroxybutyrate) Composite Films

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The depletion of fossil resources and the environmental impact of petroleum-based plastic materials have driven a strong global interest in renewable biobased polymers and composites derived from natural resources. Since biodegradable polymers have their own drawbacks, it is often combined as a composite with other fillers. Polypropylene (PP)/Poly(3-hydroxybutyrate) (PHB) composite films and lignocresol (LC)/PP/PHB composite films were cast by blending methods. This study investigated the effects of the amounts of added PP fiber and LC on the mechanical and thermal properties in the corresponding composite films. The overall properties of LC/PP/PHB composite films were best with 8 wt.% PP fiber content and 3 wt.% LC content. The tensile strength (13.00 MPa) was up to 1.25 times that of the original PHB film (10.44 MPa), and the thermal properties of the composite films were improved by adding 3 wt.% LC. Thermogravimetry (TG) analysis indicated that the onset temperature (382.0 °C) rose by 50.7 °C compared with PP/PHB film (331.3 °C), and the residual mass was close to 0%.

Keywords: Polypropylene (PP) fiber; Poly(3-hydroxybutyrate) (PHB); Lignocresol (LC); Composite film; Mechanical properties; Thermal properties

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INTRODUCTION

Due to the shortage of fossil fuel resources and “white” or plastic pollution, renewable and biodegradable polymers and composites derived from natural resources have attracted attention (Thakur *et al.* 2014). Poly(3-hydroxybutyrate) (PHB) is one of these environment-friendly polymeric materials. Its application, however, has often been limited by its brittleness caused by its high crystallinity (Mousavioun *et al.* 2012). Recently, fillers from renewable sources have been used in the preparation of PHB-based biocomposites (Johana and Mei 2002; Pinto *et al.* 2009; Bledzki and Jaskiewicz 2010; Wei *et al.* 2015).

Lignins are complex phenolic polymers that exist in higher plant tissues and are the second most abundant terrestrial polymer after cellulose, the only aromatic compound in the cell wall of plants. Recently, biorefinery appears to be a promising alternative to utilize biomass. Lignin, however, as a third of the components found in the cell wall, is often used as a burning fuel, which has constrained the development of biorefinery technology. Thus, exploring and utilizing lignin has received increasing attention and has been investigated extensively by both academic and industrial researchers.

Lignin has been used as a filler in composite materials, and it has potential for material applications. The physical properties of PHB-lignin biocomposites have been

examined (Bertini *et al.* 2012; Mousavioun *et al.* 2012). In papermaking and biorefinery industries, however, active groups in lignin decrease, and its properties become unstable. The overall performances of PHB-lignin composites are unfavorable. The compatibility between PHB and lignin needs to be improved.

Lignophenol, a kind of modified lignin, has several structural characteristics that vary from conventional lignin; for example, it is highly phenolic, very light colored (pinkish white), highly homogeneous, and stable (Funaoka 1998; Funaoka 2013). Adding lignophenol as a substitute for lignin into composite films could improve the compatibility between PHB and the lignin-derived component without a sacrifice in mechanical properties. In previous research, the mechanical strength and thermal properties of PHB-lignocresol biocomposite films show good results at a less than 10% addition of lignocresol (Qian *et al.* 2015). However, the flexibility of composite films was still poor.

Since fibers enable considerable improvement in both strength and flexibility of composite materials, the concerns about the addition of fibers into composites have been raised currently. Polypropylene (PP) fiber possesses good strengthening and toughening features and is often filled into reinforced concrete to improve its mechanical performance (Murahari and Rao 2013; Shen *et al.* 2012; Zhang *et al.* 2016). Polypropylene fiber reinforced concrete (PFRC) has been widely used in engineering construction. Currently, the research on adding PP fiber into other composites has attracted more attention (Mercado-Cabrera *et al.* 2013; Yap *et al.* 2013). In this paper, PP fiber was filled into PHB-lignocresol composite films with attention focused on the effect of PP fiber on the mechanical and thermal properties of composites.

EXPERIMENTAL

Materials and Chemical Reagents

Lignocresol (LC) was derived from native bamboo (Shaoxing, Zhejiang, China) lignin through a phase separation system (Funaoka and Abe 1989) by using *p*-cresol as a derivative and 72% concentrated sulfuric acid as a catalyst. The *p*-cresol was supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Polyhydroxybutyrate (PHB) was from Nanjing Advanced Polymer (Nanjing, China). The melt flow rate (MFR) for PHB was between 2 and 3 g/10 min (170 °C, 2.16 kg). PP fiber was supplied by W. R. Grace & Co (Shanghai, China).

Preparation of Composite Films

PP/PHB composite films were prepared as follows. PP fiber and PHB were dissolved in chloroform at 90 °C by distillation and stirring. Next, the solution was cast on a Teflon plate, and the solvent was evaporated at room temperature. PP fiber content in the film was 0, 4, 8, 12, or 18 wt.%.

LC/PP/PHB composite films were prepared as follows. First, 0.35 g of PP fiber and 4.00 g of PHB were dissolved in chloroform at 90 °C by distillation and stirring. LC was dissolved in acetone at room temperature. These two solutions were mixed uniformly and cast on a Teflon mold (100 mm × 130 mm × 6 mm). After solvents were volatilized completely, the physical characteristics of the composite films were ready for measurement. LC content in the film was 0, 1, 3, 6, 9, or 12 wt.%.

Mechanical Properties of Composite Films

Test specimens with a thickness of 1.0 to 1.5 mm, length of 33.0 mm, and width of 6.0 mm were prepared from the composite films in accordance with the GB ISO 527-3 (1995) standard. The tensile strength and elongation ratio were measured at the rate of 20 mm/min using an EZ Test (CMT4303, Qingtong Instrument Development Co. Ltd., Hangzhou, China) at room temperature. The values to be reported represent the average of 6 separate measurements.

Scanning Electron Microscopy (SEM)

The overall structure and the tensile fracture images of PP/PHB film were characterized using a FEI Quanta 200 environmental scanning electron microscope (Suzhou, China) at 10.00 kV under vacuum.

Characterization of Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were obtained on a Bruker VERTEX 80 spectrometer (Saarbrücken, Germany) using KBr discs. The spectra were recorded in the range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} over 32 scans.

Thermal Properties of Composite Films

Thermogravimetry (TG) of the composite films was investigated using TG/DTA 6200 (SEIKO Instruments Inc., Shanghai, China). TG was run at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen, with a heating temperature range from 0 to 600 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Effect of PP Fiber on Mechanical Properties of PP/PHB Composite Films

Tensile strength

The tensile strength of PP/PHB composite films changed with the PP fiber contents (Fig. 1). The tensile strength of composite films first increased and subsequently decreased.

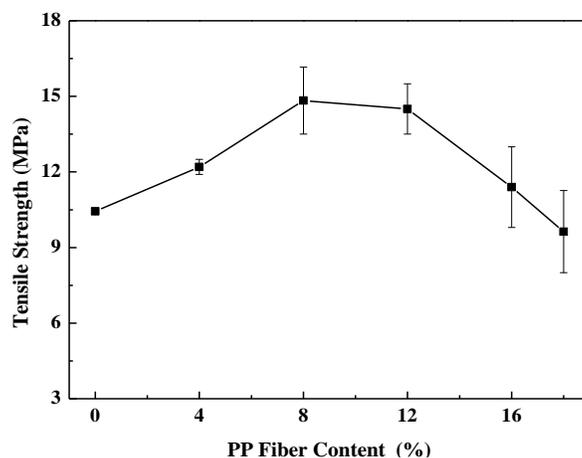


Fig. 1. Relationship between PP fiber content and tensile strength

When the PP fiber content was 8 wt.%, the tensile strength of composite film was strongest and was nearly 1.5 times that of the tensile strength of neat PHB film. The PP fiber, which possessed a relatively high tensile strength compared with PHB, contributed to the increased tensile strength of composite films. However, excess addition of PP fiber resulted in decreased homogeneity of the resultant composite films. Thus, the composite films weakened with the further addition of PP fiber. In fact, when the PP fiber content was over 18 wt.%, the PP fiber flocculated during the casting of films. In conclusion, the optimum amount of PP fiber added should be less than 8 wt.%.

Elongation at break

The elongation at break of PP/PHB composite films also changed with the PP fiber contents (Fig. 2). The elongation at the break of composite films initially decreased. The minimum elongation at break occurred with 8 wt.% PP fiber content and was stable with the further addition of PP fiber. Because the elongation at break of PP fiber was lower than that of PHB, adding PP fiber into PHB films decreased the elongation at break of composite films. Furthermore, adding PP fiber destroyed the continuous phase of PHB. At 8 wt.% PP fiber content, the continuous phase of PHB was destroyed completely, which resulted in the elongation at break in cross-linked state between PHB and PP fiber (Chung *et al.* 2013). Thus, the elongation at break of composite films was stable upon further addition of PP fiber. Therefore, the follow-up experiments were based on PP/PHB composite films with 8 wt.% PP fiber content.

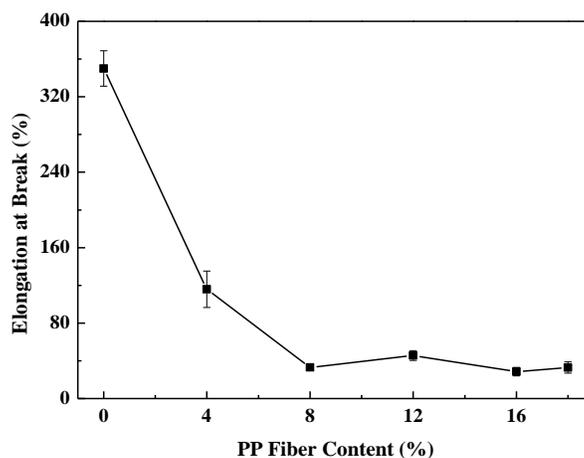


Fig. 2. Relationship between the PP fiber content and elongation at break

Effect of Lignocresol on Mechanical Properties of LC/PP/PHB Composites

Tensile strength

The tensile strength of LC/PP/PHB composite films is shown in Fig. 3. The tensile strength of LC/PP/PHB composite films initially decreased, increased, and then remained stable. Adding LC into PP/PHB composite films had a weak influence on the tensile strength. Compared with PP/PHB composite films, the tensile strength of LC/PP/PHB composite films decreased less than 19 wt.%. When a low percentage of LC was added, no intermolecular hydrogen bonding interactions occurred between PHB and LC due to the low content of hydroxyl groups (Chung *et al.* 2013). At this time, the molecular arrangement was disordered. Therefore, the tensile strength of LC/PP/PHB composite films decreased compared with PP/PHB composite films. When the content of

LC was increased in composite films, intermolecular hydrogen bonding interactions between PHB and LC formed and strengthened. Thus, the tensile strength of LC/PP/PHB composite films increased within a narrow range. When LC content reached 3 wt.%, intermolecular hydrogen bonding interactions were strongest and were no longer strengthened by the further addition of LC due to the limited hydroxyl groups of PHB. Therefore, the tensile strength of LC/PP/PHB composite films tended to be stable after a 3 wt.% addition of LC.

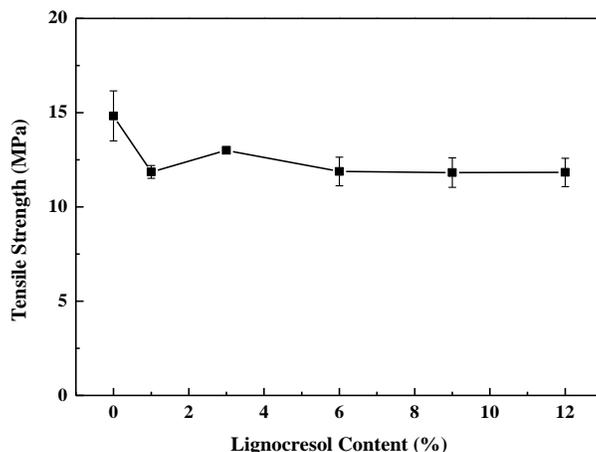


Fig. 3. Relationship between lignocresol content and tensile strength

Elongation at break

The elongation at break of LC/PP/PHB composite films is shown in Fig. 4. The elongation at break of LC/PP/PHB composite films initially decreased and subsequently increased. When the LC content was 3 wt.%, the D-value on the elongation at break between PP/PHB composite films and LC/PP/PHB composite films was minimal. The lower elongation at break of LC compared with PHB contributed to the decreased elongation at break of composite films. In addition, the continuous phase of PHB could be destroyed by adding LC. Therefore, the elongation at break of LC/PP/PHB composites decreased until the LC content reached 6 wt.%.

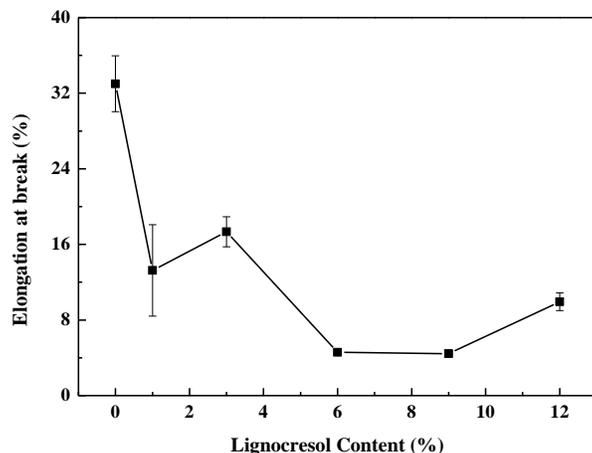


Fig. 4. Relationship between lignocresol content and elongation at break

After the LC content reached 6 wt.%, the elongation at break stabilized due to intermolecular forces of all of the components. When the LC content was 12 wt.%, the elongation at break increased within a narrow range, which was caused by the self-assembling of LC (Chung *et al.* 2013). Therefore, the follow-up experiments were based on LC/PP/PHB composite films in which the LC content was 8 wt.%.

SEM Analysis of the Composite Films

Representative SEM micrographs of the overall surface and the tensile fracture surface of PP/PHB composites with 12 wt.% PP fiber loadings are shown in Figs. 5 and 6. In Fig. 5, the SEM image of PP/PHB composite film shows a number of pullout traces of PP fiber with rough surfaces and micro-voids between the PP and PHB matrix, as well as an agglomeration of the PP fiber in the PHB matrix. There were many PP fibers scattered outside of the PHB matrix in the tensile fracture surface of the PP/PHB composites and gaps caused by the PP fiber. In addition, the matrix and the PP fiber were clearly distinguishable in Fig. 6. These data indicated that the compatibility between PP fiber and the PHB matrix was poor. Therefore, the tensile strength of PP/PHB composites decreased with increased PP fiber in composites.

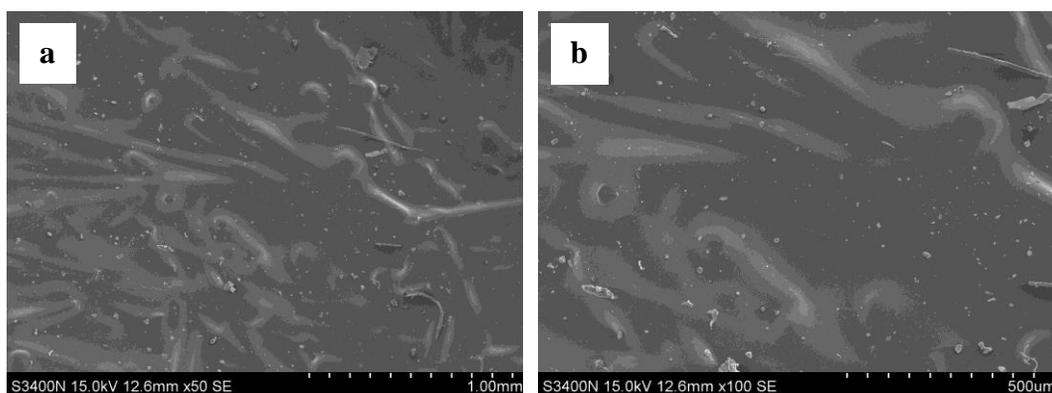


Fig. 5. SEM micrographs of the overall surface of PP/PHB composites

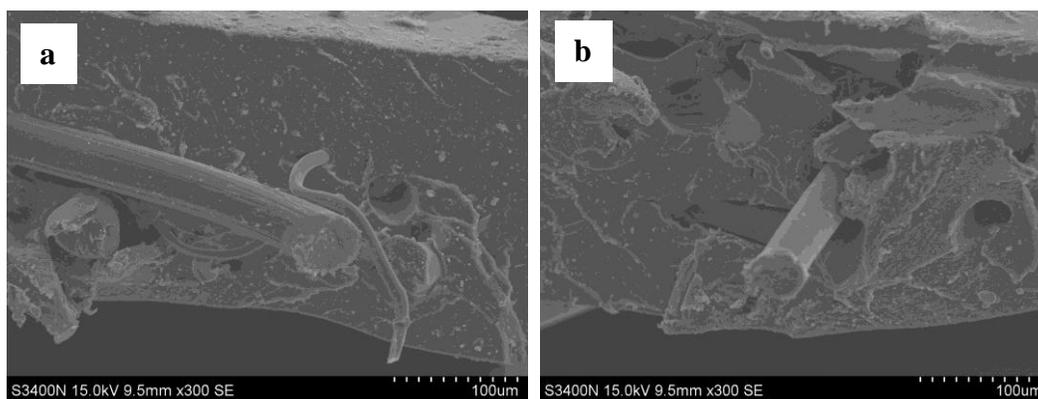


Fig. 6. SEM micrographs of the tensile fracture surface of PP/PHB composites

FT-IR Analysis of Composite Films

The neat PHB film, PP fiber, and PP/PHB composite film were compared by FT-IR analysis (Fig. 7). There were four consecutive peaks between 2962 and 2800 cm^{-1} signaling the stretching vibrations of methylene. Two kinds of single absorption peaks

occurred at 1460 cm^{-1} and 1305 cm^{-1} signaling the deformation vibrations of methylene. Two kinds of double absorption peaks at 973 cm^{-1} and 955 cm^{-1} signaled the rocking vibration of methyl in the spectra of the PP fiber. The characteristic absorption peaks of hydrogen bonding at approximately 3000 cm^{-1} , carbonyl group bonding at 1664 cm^{-1} , and hydroxyl bonding at 675 cm^{-1} were observed in the spectra of the PHB film. There were no new bonds, only weakened vibrations of methylene and hydrogen bonding in PP/PHB film that indicated no chemical bonds between PP and PHB formed.

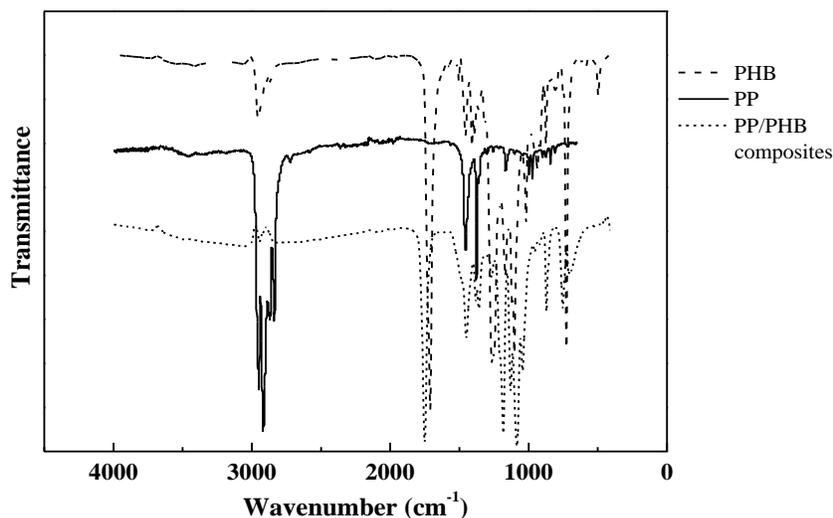


Fig. 7. FT-IR spectra of pure PP film, neat PHB film, and PP/PHB composite film

LC, PP/PHB film, and LC/PP/PHB composite film are compared by FT-IR analysis (Fig. 8). There were peaks at 1325 , 1220 , and 1130 cm^{-1} (vibrations of the syringyl group), peaks at 1270 and 1040 cm^{-1} (vibrations of the guaiacyl group), a broad peak at approximately 3400 cm^{-1} (vibration of the hydroxyl group), and a peak at 1300 to 900 cm^{-1} (signaling the of vibration of phenolic hydroxyl).

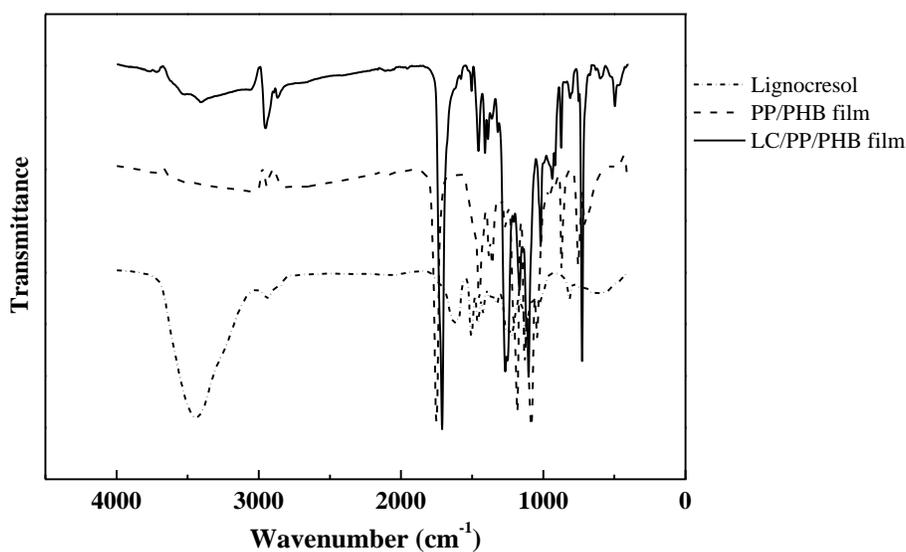


Fig. 8. FT-IR spectra of LC, PP/PHB film, and LC/PP/PHB film

In addition, a distinct C=O vibration belonging to a carboxyl or ester group at 1730 cm^{-1} was found in the spectra of LC, which is attributed the esterified coumaric acid in bamboo lignin (Ren and Funaoka 2007). In the FT-IR spectra of LC/PP/PHB composite film, the broad peak at approximately 3400 cm^{-1} signaled that the hydroxyl group weakened compared with LC, and the absorption peak of hydrogen bonding at approximately 3000 cm^{-1} strengthened as compared to the PP/PHB composite film, which may have been caused by new hydrogen bonding between PHB and LC.

TG Analysis of the Composite Films

The thermal behaviors of neat PHB film, PP/PHB film, and LC/PP/PHB film are shown in Fig. 9. The onset temperature of neat PHB film was $382.2\text{ }^{\circ}\text{C}$. The onset temperature of PP/PHB composites decreased to $331.1\text{ }^{\circ}\text{C}$ after the addition of PP fiber. However, with further addition of LC, the onset temperature of LC/PP/PHB composites increased to $382\text{ }^{\circ}\text{C}$. The residual mass value of LC/PP/PHB composites was close to 0%. These data indicated that LC played a bridging role between PP fiber and PHB so that the degree of damage caused by PP fiber in the PHB matrix was weakened by adding LC. Considering all the data, LC can be used as a natural additive to LC/PP/PHB composites, as it improved their thermal and physical characteristics. Further related research is necessary to develop a new kind of composite without coupling agents, which is expected to lower the cost and improve cyclic utilization in the future.

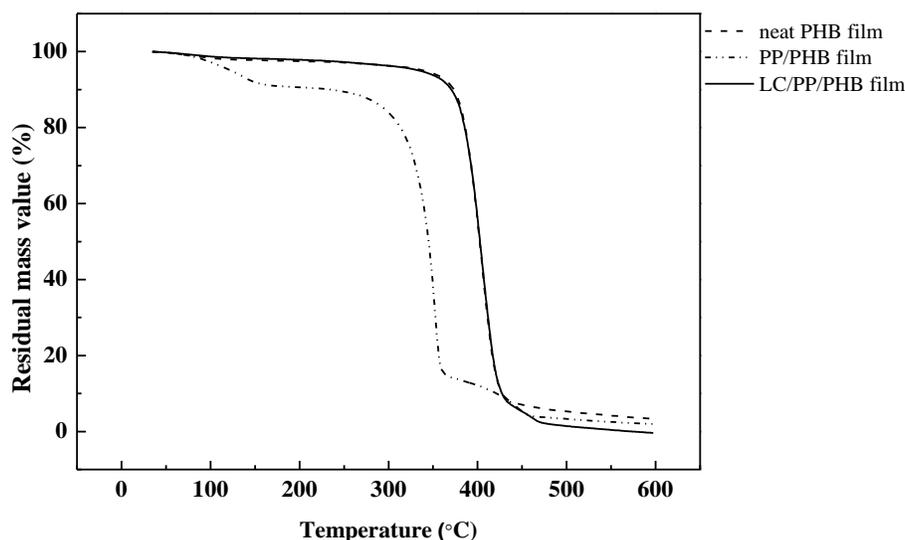


Fig. 9. TG curves of neat PHB film, PP/PHB film, and LC/PP/PHB film

CONCLUSIONS

1. The elongation at break of PP/PHB composites decreased, but the tensile strength increased with the addition of PP fiber. When adding 8 wt.% PP fiber, the tensile strength was nearly 1.5 times that of the tensile strength of neat PHB film. The addition of PP fiber into the PHB matrix was limited to within 8 wt.%.

2. The SEM images of the overall surface and the tensile fracture surface of PP/PHB composites at 12 wt.% PP fiber loadings showed that the compatibility between PP fiber and PHB matrix was poor.
3. The addition of LC to the PP/PHB composites had little influence on the tensile strength of the composite membrane, but much influence on the elongation at the break of LC/PP/PHB composites. FT-IR spectra revealed that there was hydrogen bonding between PHB and LC.
4. TG analysis showed that adding PP fiber to PHB films weakened their thermal stability. Compared with PP/PHB composites, LC may play a bridging role between PP fiber and PHB in LC/PP/PHB composites, which improved the thermal stability of composites. The LC/PP/PHB composites were fully biodegraded at 450 °C.

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