Effects of Lignophenols on Mechanical Performance of Biocomposites Based on Polyhydroxybutyrate (PHB) and Polypropylene (PP) Reinforced with Pulp Fibers

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The effects of lignophenols and pulp fibers as reinforcing elements in biocomposites were studied with poly-(3-hydroxybutyrate) (PHB) biopolymers and polystyrene (PS) matrix materials. Lignophenols and ($NH_2(CH_2)_3Si(OC_2H_5)_3$) were compared as plasticizing or compatibilizing additives in tests of composite properties. PHB and PP were blended with pulp fiber cellulose and lignophenol by torque rheometer, and the test specimens were processed via injection moulding. Various testing methods, including tensile and impact tests, SEM, XRD, TGA, and ART-FTIR were used to investigate the properties of the composites. PHB and PP-cellulose fiber composites with strong mechanical properties could be created by using a torque rheometer as a mixer at 190 ºC with very short mixing times. The ($NH_2(CH_2)_3Si(OC_2H_5)_3$) was found to improve the mechanical features of the PP, but not very obviously for both tensile and impact strengths of PHB. However, the lignophenols positively affected the PHB-pulp fiber composites. In summary, a novel method has been demonstrated for creating biodegradable composites with pulp fibers in the absence of a coupling agent, and lignophenols may be applicable as an additive in the cases described in this study.

Keywords: Pulp fibers; Lignophenols; Poly-(3-hydroxybutyrate); Polypropylene; Mechanical properties

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INTRODUCTION

Wood fiber-reinforced plastics have gained a major share in the consumer market. Wood fiber-reinforced plastics account for the fastest growing segment of the plastic industry with an annual growth of 25%, which indicates a strong market demand for wood fiber-reinforced plastics in the near future (Wei *et al.* 2013). The market for wood plastic composites (WPC) was 545 million pounds in 2009 (Singh and Mohanty 2007). Wide acceptance of WPC by the global market has resulted from their relatively low cost and weight, superior properties relative to wood or plastic alone, recyclability, and adaptability to existing plastic processing techniques as well as the desire of the industry to produce eco-friendly products. WPC is primarily utilized in structural materials for decking, railings, automotive interiors, and housing. Polyethylene (PE), polyvinylchloride (PVC), and polypropylene (PP) are the primary resins that are used to prepare WPC. Several types of WPCs that use wood fiber and conventional polymers have been developed (Harper and Wolcott 2004; Li and Wolcott 2004; Selke and Wichman 2004; Schirp *et al.* 2014). The polymers that are currently used in conventional WPC are derived from petroleum, which is non-renewable and which is becoming depleted. As the demand for crude oil increases, the reduced cost of WPC will no longer be an advantage. The next generation of renewable, bio-based, and eco-friendly WPCs represents a potential alternative to conventional WPCs in the global market.

The UPM-Kymmene Corporation is one of several well-known multinational corporations that uses forest resources and has access to significant natural fiber reserves (*e.g.*, 930,000 hectares of private forests producing 3.2 million tons of pulp from an annual output of 9.7 million tons). As the global demand for paper decreases, the use of natural fiber raw materials for developing new products could provide an alternative source of revenue for some companies.

Natural fibers are an emerging reinforcing agent for polymer matrices due to their availability, low cost, low density, and compatibility with other materials (Mohanty *et al.* 2002). The mechanical properties of PHBV were improved by reinforcing them with cellulosic natural fibers (Luo and Netravali 1999; Dufresne *et al.* 2003; Bhardwaj *et al.* 2006). In addition, PHB can be reinforced by wood fibers with a high cellulosic content to enhance its mechanical properties and reduce the cost of molded products. Although relatively few hydroxyl and carboxylic acid groups are present at the ends of PHB molecular chains, it is possible that dipolar interactions occur among the moderately polar (-C=O) and polar groups (-OH and –COOH) of PHBV and the hydroxyl group (-OH) of cellulosic wood fiber. Thus, interfacial interactions could take place between the fiber and the matrix (Jotier *et al.* 1988; Fei *et al.* 2004).

The objectives of this study were to fabricate pulp fiber-reinforced PHB or PP composites and evaluate their mechanical and thermo-mechanical properties as a function of pulp fiber weight and the contents of PHB and PP. The morphological aspects of the composites, such as fiber dispersion and fiber-matrix interface, were investigated with scanning electron microscopy (SEM). Lignophenols are members of a class of lignin-based polymer synthesized using a phase separation system. Thus, as an additional goal, the effects of the lignophenols on the composite properties were studied when they were added to pulp fiber and plastics.

EXPERIMENTAL

Materials

Matrix (PP): The PP powder was supplied by DEBASUHUA Co. LTD (NanJing, China), under code PP550 and had a melt flow rate (MFR) of 4.0 g/10 min.

Matrix (PHB): PHB was supplied by Nanjing Advanced Polymer, Jiangsu, China. The MFI for the PHB was between 2 and 3 g/10 min (170 ºC, 2.16 kg).

Additive: KH550 was obtained from Sigma-Aldrich and had a molecular formula of $NH_2(CH_2)_3Si(OC_2H_5)_3$, a molecular weight of 221 and a density of 0.941-0.950. KH550 was evaluated as a plasticizer or compatibilizing agent for PHB.

Pulp Fiber Reinforcements: Oven dried bleached Eucalyptus pulp (short fiber, SF) and oven dried bleached Botnia-90 pulps fiber (long fiber, LF) were obtained from UPM (Changshu Mill).

Lignophenols (Lps): Lignophenols were synthesized using poplar wood meal samples in a phase separation system (Funaoka and Fukatsu 1996). Dried pulp fiber was immersed in a lignophenol-acetone solution for 24 h to allow the lignophenol to become evenly dispersed in the pulp fiber surface. After the solvent was completely evaporated, the lignophenol-treated pulp fibers were used to reinforce the composites. The weight percentage of the lignophenol to pulp fiber was 5%.

Methods

Compounding the composite materials

The composite materials were manufactured by employing a torque rheometer (RJL-200, ShenZhen NewSans Materials Co. Ltd.) as a mixer. Pulp fiber contents of 20, 30, and 40 wt% were used. The lignophenols were mixed with pulp fiber in acetone at a lignophenol to cellulose ratio of 1:15. After soaking for a sufficient period, the acetone was volatilized. The lignophenols-treated fibers and the plastic particles were simultaneously fed into the mixing tank. The fiber content in the composite was calculated based on the oven-dried weight of the pulp. The moisture content in the pulp was reduced due to the evaporation caused by the high mixing temperature. The following processing parameters were used: a machine speed of 50 rpm; temperatures of 190 ºC, 200 ºC, and 190 ºC in zones 1, 2, and 3, respectively; and feeding and mixing times of 10 min.

Compression moulding

The test samples for mechanical testing were injection using a conventional injection moulding press (Mini Injection Machine SZ-15, WuHan RuiMing Machinery Manufacturing Co. Ltd.) with a maximum injection capacity of 15 g. The mould temperature was 190 ºC, and the pressure was 0.3 MPa.

Mechanical testing

Tensile testing was performed according to the ASTM 3039 standard for tensile testing on a WDW-1 Electronic Tensile Testing Machine (ShenZhen NewSans Materials Co. Ltd.). Charpy impact testing was performed on a JB-300 Pendulum Lamented Impact Testing Machine (ShenZhen NewSans Materials Co. Ltd.) according to ISO 179. At least 5 specimens were tested for each material.

Electron microscopy

Fractured surfaces of the materials were studied using a JEOL (JSM-6490A) scanning electron microscope (SEM) with an acceleration voltage of 30 kV. The sample surfaces that were cut were sputter coated with gold to avoid charging.

X-Ray diffraction and thermogravimetric analysis (TGA)

Diffraction patterns were obtained using copper radiation from a Rigaku Ultima IV X-ray diffraction system (Rigaku Corporation, Japan) set at 40 kV and 30 mA and with the detector placed on a goniometer. Data was acquired at a scale of 2θ from 5º to 70º.

Thermogravimetric analysis (TGA) of the PLA, PHB and their composites were conducted using a Mettler-Toledo TGA/SDTA 851e machine at a heating rate of 10ºC/min over a temperature range of 30 to 600 ºC. A plot of weight percentage against temperature was prepared for each specimen.

Fourier Transform Infrared Spectroscopy Analysis (FTIR)

A Perkin Elmer system 2000 FTIR Spectrometer was used to analyze the PHB, 30 wt% pulp fiber-PHB, 30% Lp treated pulp fiber-PHB, PP, 30 wt% pulp fiber-PP and 30% Lp treated pulp fiber-PP specimens. IR spectra were obtained using an attenuated total reflectance (ATR) accessory.

Dynamic mechanical analysis (Henriksson and Lundmark)

The dynamic mechanical properties of the composites were evaluated using a Perkin-Elmer DMA Diamond system. A 15 mm knife-edge, three-point platform with a 5 mm probe tip was used and DMA tests were performed from 30 to 130 ºC with a heating rate of 4 ºC/min. Nitrogen was used as the purge gas. All measurements were conducted at physiological frequency of 1 Hz. The dimensions of DMA specimens were 22×5×1.5 mm.

RESULTS AND DISCUSSION

Mechanical Testing

The mechanical properties of the PHB/SF, PHB/LF, PP/SF, and PP/LF composites were compared to mechanical properties of the ($NH_2(CH_2)_3Si(OC_2H_5)_3$) or Lps additives.

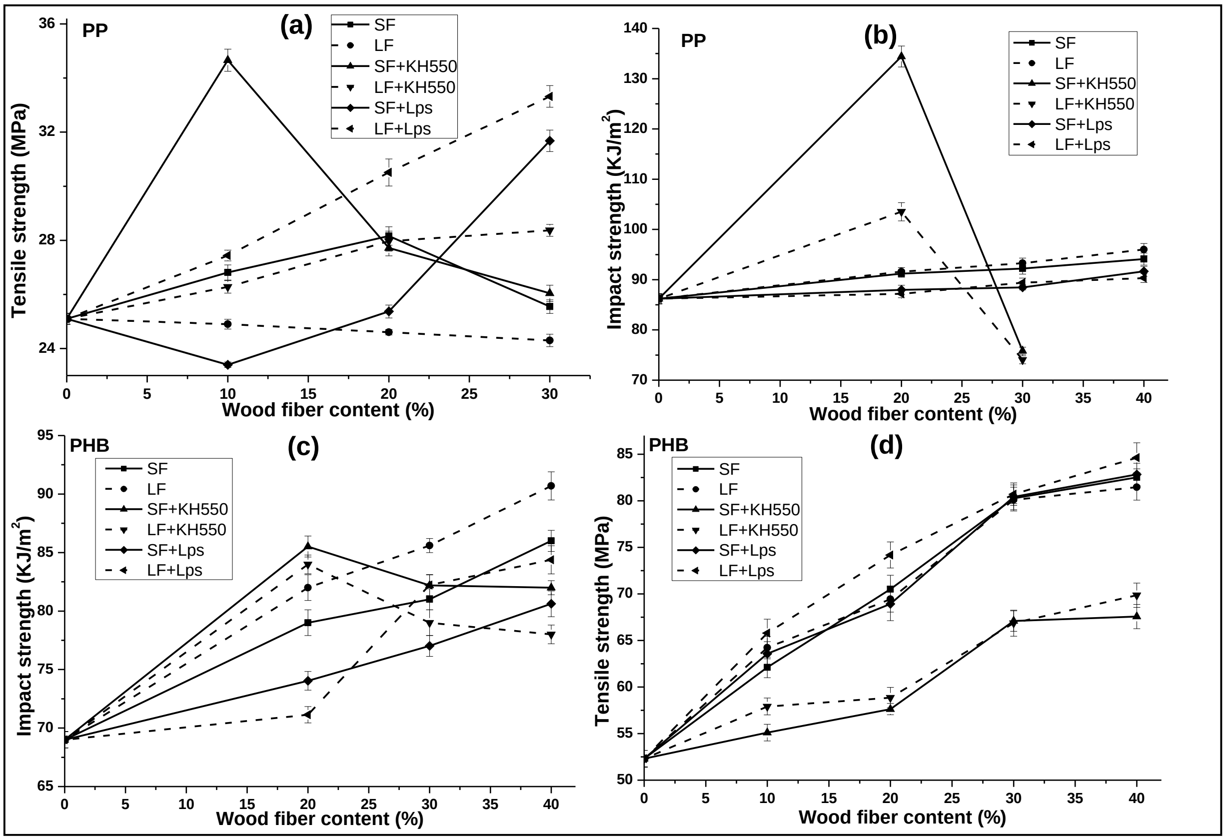

Fig. 1. Mechanical properties of composites relative to the percentage of fiber content; the term KH550 represents ($NH_2(CH_2)_3Si(OC_2H_5)_3$).

Figure 1(a,b) shows the tensile strength and Charpy unnotched impact strength results for the PP reinforced with short and long fibers with and without additives. The tensile strength was relatively low when no additives were used. However, when 2% of ($NH_2(CH_2)_3Si(OC_2H_5)_3$) was added, the tensile strength indicated greater changes in the case of short fibers than for long fibers. A wood fiber content of 10% resulted in the highest tensile strength. However, a wood fiber content of 20% produced the highest impact strength for both the short and long fibers. The impact strength decreased sharply as the fiber content was further increased. When Lps was used as an additive, the tensile and impact strengths increased slowly as the fiber content increased. The tensile strength was greater and the impact strength was lower when the additives were used.

Figure 1(c,d) shows the tensile strengths and the Charpy unnotched impact strengths for the PHB that was reinforced with short and long fibers with or without additives. The short and long fiber-reinforced PHB composites showed greater tensile strengths as the fiber content was increased to 40 wt%. Although the tensile strength increased with fiber content when ($NH_2(CH_2)_3Si(OC_2H_5)_3$) was added, the absolute value was lower. In addition, the impact strength showed variability, and the highest value was observed at a wood fiber content of 20%. After reaching its peak, the impact strength decreased. However, the lowest value was still greater than the original PHB value. When Lps was used as an additive, the tensile strength and impact strength increased as the fiber content increased. Although the tensile strength was greater in the presence of additives, the impact strength was lower.

In the findings described above, the addition of ($NH_2(CH_2)_3Si(OC_2H_5)_3$) decreased the tensile strength of PHB composites. Meanwhile, the impact strength rose moderately with the addition of fiber within the range 0 to 20% fiber. The addition of Lps did not have obvious effects on the tensile strength; however it partly decreased the impact strength of PHB composites. This result implies that the pulp fibers were adequately dispersed into PHB matrix. The ($NH_2(CH_2)_3Si(OC_2H_5)_3$) additive was not necessary for PHB composites. When Lps was used, negative effects on mechanical properties were not observed. Most natural fibers are composed of "fiber bundles" that have different properties depending on the fiber bundle geometry (Bledzki and Jaszkiewicz 2010). Here, long and short fibers were formed from pure cellulose fiber, which is used for papermaking. Thus, the bundles had relatively constant aspect ratios (fiber length/fiber width) (Bax and Müssig 2008). Lps has a high solvent solubility and is evenly wrapped around the pulp during pretreatment. The addition of Lps resulted in decreased impact strengths for PP and PHB composites, but the resulting impact strength was no smaller than the impact strength of plastics themselves. This result occurred because the fibers were well dispersed in the polymers before the addition of a compatibilizing agent. In addition, the compatibility between the pulp fibers and the PHB polymers contributed to this result. It was found that the addition of Lps reduced the compatibility of fibers and PHB. Lps has an affinity for both pulp and polymer matrices, but it might not form an effective hard bridge between them due to the low amount of Lps being used. Additionally, Fig. 1(a,b) shows that short fibers were blending effectively and sufficiently in PP-fiber composites, such that both the tensile strength and the impact strength of short fiber composites were higher than long fiber ones. By contrast, Fig. 1(c,d) shows that long fiber-PHB composites had greater tensile strength and impact strength than short fiber ones. These results indicated that PHB is more suitable for mixing with pulp fibers compared with PP when using a torque rheometer as the mixer.

Scanning Electron Microscopy Analysis

Scanning electron microscope (SEM) images of the fracture faces of PP-fiber composite without a coupling agent are shown in Fig. 2. The SEM photos of the PP-fiber composite fracture faces with the ($NH_2(CH_2)_3Si(OC_2H_5)_3$) compatibilizing agent are shown in Fig. 3. Finally, SEM photos of the PP-lignophenol-fiber composite fracture faces are shown in Fig. 4.

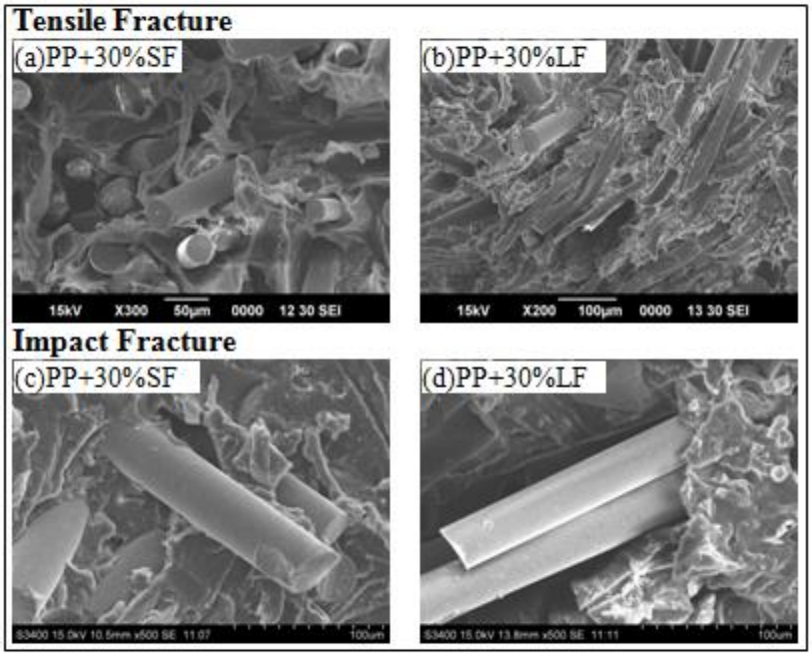

Fig. 2. Scanning Electron Microscope photos about fracture face of PP-fiber composites without coupling agent

Without a compatibilizing agent, the interface between the pulp fiber and polymer matrix was poor, because larger pores affected the tensile and impact fracture results (Fig. 2). Following the addition of ($NH_2(CH_2)_3Si(OC_2H_5)_3$) or Lps to the composites, the pores were no longer visible in the SEM images. In addition, there was no connection between the pulp fibers and polymer matrix (Figs. 3, 4). The PHB composites and manufactured PHBV cellulose exhibited similar interphasial adhesion (Bledzki *et al.* 2009). In both the presence and absence of the compatibilizing agent, the fiber and polymer matrix were too close to have pores (Fig. 5). This absence of pores was related to the high viscosity and toughness of the PHB. As previously discussed (Ren *et al.* 2014), relatively good interphasial adhesion occurs between the fibers and the matrix in PHB.

Organic acids, such as crotonic acid (Gatenholm and Mathiasson 1994), may form because the component chains in these materials were partly degraded during the mixing process at elevated temperatures. For PP, the degradation features were less clear than the PHB degradation features. In addition, the pore sites become filled with the compatibilizing agent when the additives were included because the interactions between the pulp fibers and polymers were poor.

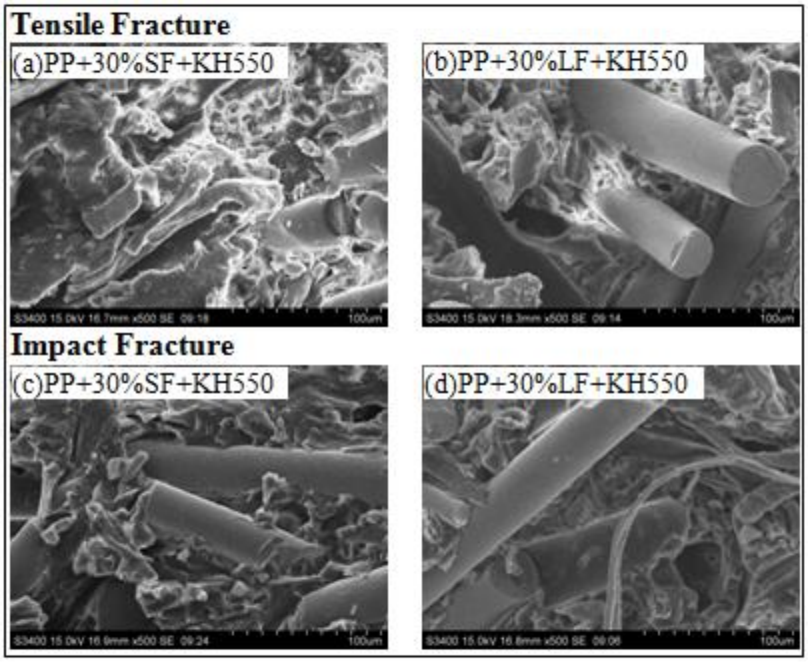

Fig. 3. Scanning Electron Microscope photos about fracture face of PP-fiber composites with KH550 compatibilizing agent

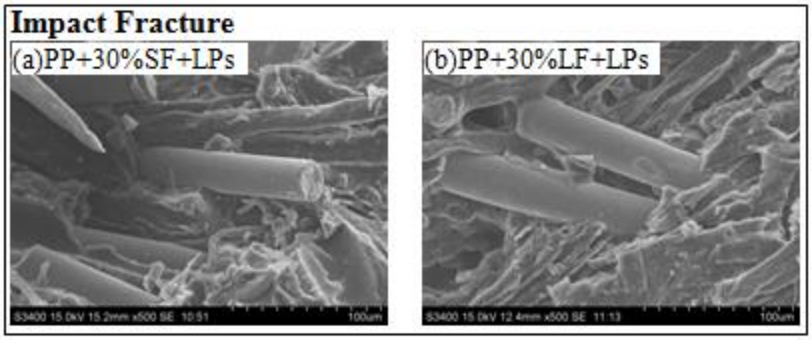

Fig. 4. Scanning Electron Microscope photos about fracture face of PP-Lignophenols-fiber composites

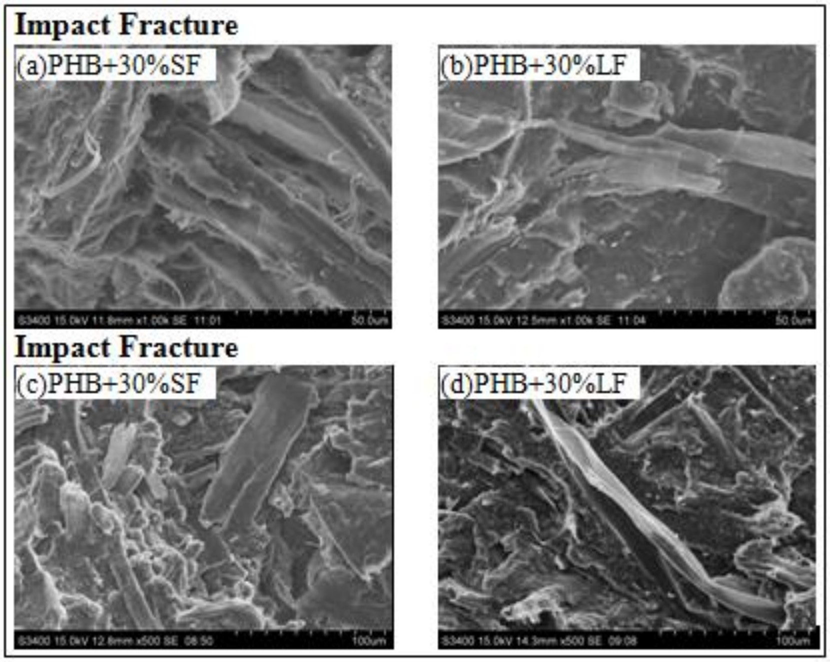

Fig. 5. Scanning Electron Microscope photos about fracture face of PHB-Lignophenols-fiber composites

The compatibilizing agents were more effective for the PP composites than for the PHB composites as a result of the presence of a chemical interaction between the fiber and PP and because ($NH_2(CH_2)_3Si(OC_2H_5)_3$) is not compatible with PHB. In addition, PHB has a high viscosity and is well dispersed around the fibers. The positive effects of compatibilizing agents have not been previously observed in PHB-fiber composites.

X-Ray Diffraction Analysis

X-ray diffraction (XRD) analysis was used to determine the presence of crystalline structures and the degree of crystallinity in the blends. PHB is a highly ordered polymer that crystallizes in orthorhombic cells and produces strong reflection peaks at 13.5º and 16.8º with three weaker peaks at 19.1º, 22.2º, and 25.5º. The first two peaks are typical of orthorhombic structures. Figure 6(a) shows the XRD spectra of the PHB-fiber composites. Reflection peaks were observed at 13.5º and 16.8º. However, the three weaker peaks were not observed, most likely because injection molding was used to obtain the control samples, which result in fewer changes during the injection process. The patterns of the composites that were mixed using a torque rheometer differed from the composites that were composed of pure PHB. In addition, the diffraction at 2θ=13.5º and 16.9º showed a decreased intensity, as the two sharp peaks became a single shoulder, and a new peak appeared at 2θ=22.5º. These data are discussed in a previous report (Ren *et al.* 2014).

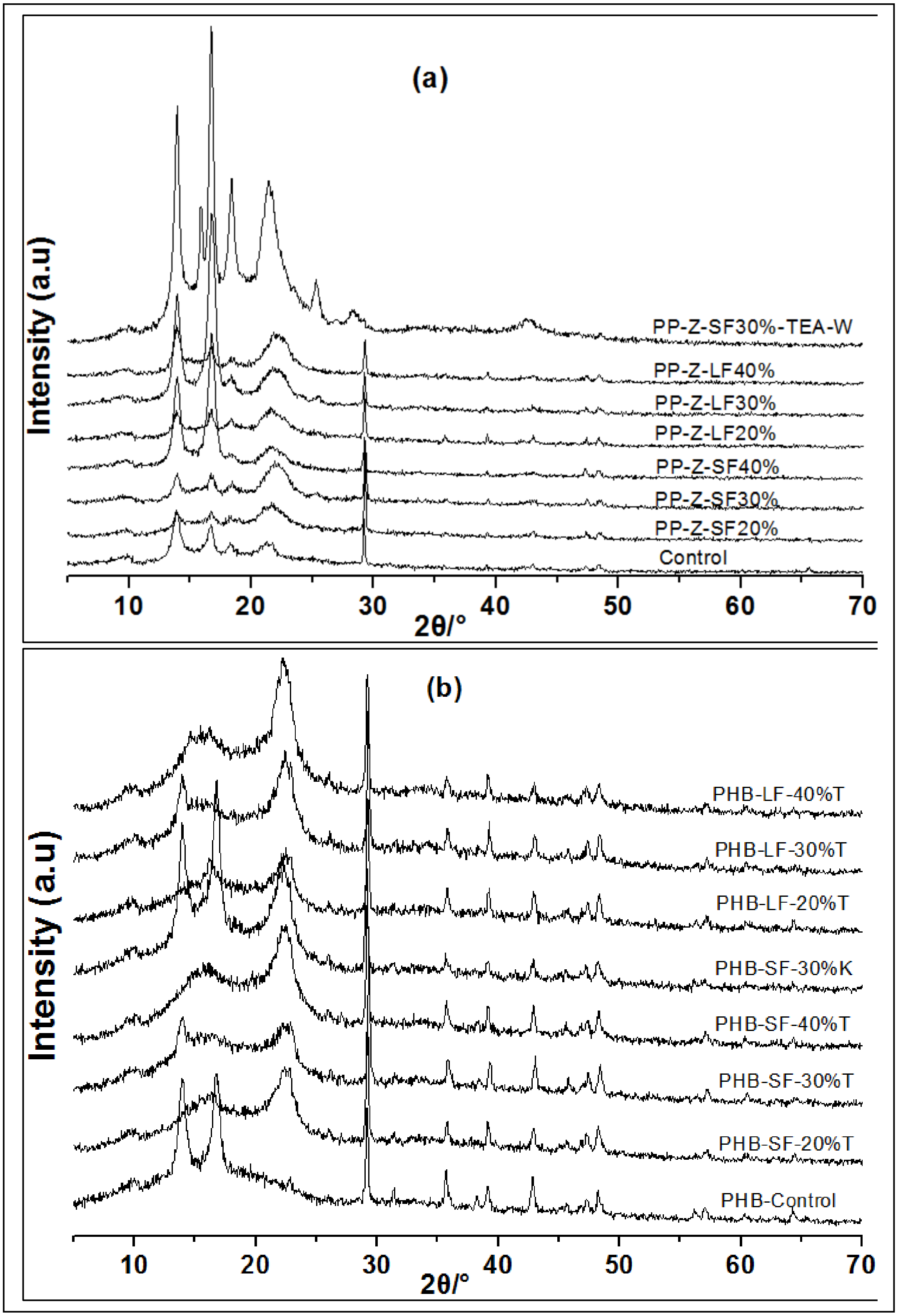

Fig. 6. X-ray diffraction patterns of PHB and PLA composites.
[a] K: Composites were mixed using kneader; T: Composites were mixed using torque rheometer.

The XRD spectra of the PP-composites are shown in Fig. 6(b). Here, the PP resulted in three main peaks at 2θ=14º, 16º, and 22º. The crystal structure did not change when the long or short fibers were mixed with other components. However, when the long fiber content was increased to 40%, the components became difficult to blend and the peak patterns changed sharply. This change suggested that a fiber content of 40% may be the upper limit for blending pulp with PP.

Thermogravimetric Analysis

PP has a greater thermal stability with a greater T_0 (400 °C) and $T_{\max}$ (430 °C) temperature (Park *et al.* 2011). In contrast, PHB has lower T_0 (268 °C) and $T_{\max}$ (285 °C) temperatures (Arrieta *et al.* 2014). Because cellulose has a T_0 of 325 °C and a $T_{\max}$ of 350 °C (Shen *et al.* 2013), the TG curves for the PP-pulp composites exhibited a two-stage weight loss profile. In Fig. 7, the first stage resulted from cellulose degradation, and the second stage resulted from polymer degradation.

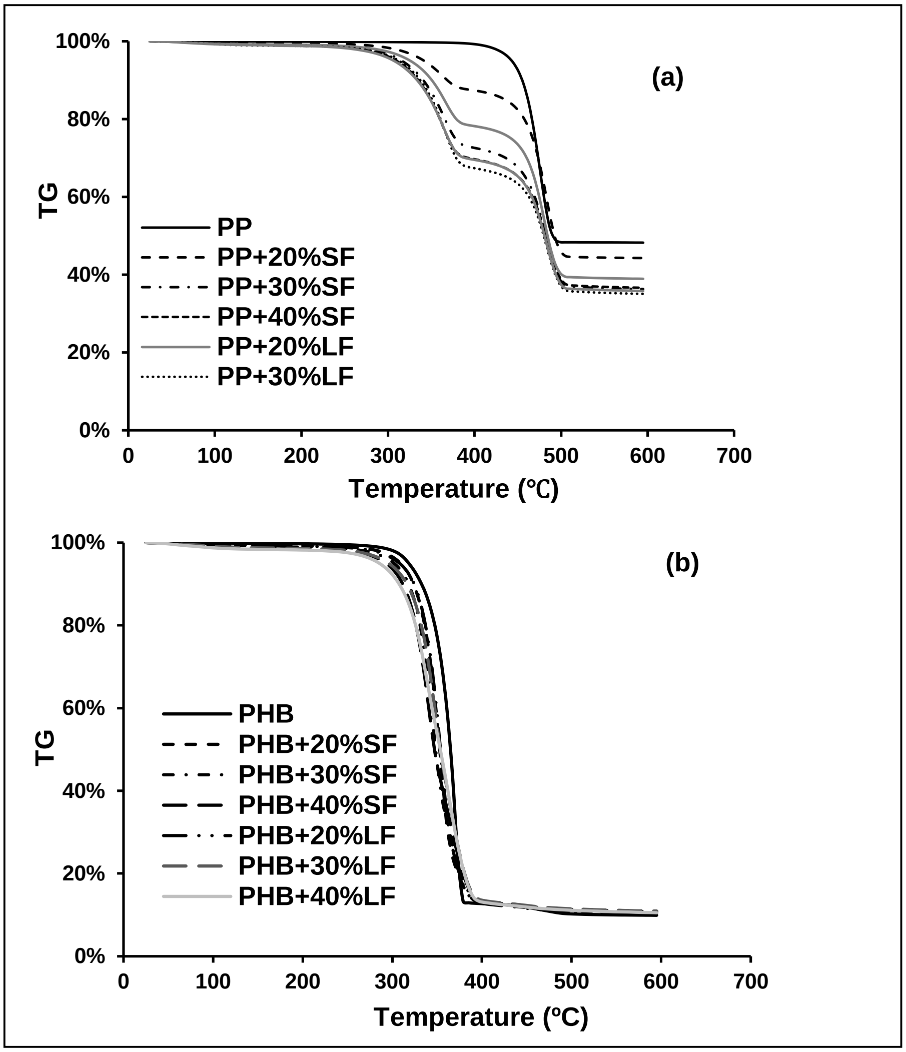

Fig. 7. Thermogravimetry charts of PHB and PLA composites

As the fiber content increased, the percent weight loss increased. In the PHB-fiber composites, the weight loss profile included a single stage, which occurred because the thermal degradation temperature of PHB was similar to the thermal degradation temperature of cellulose.

FT-IR Analysis

Figure 8(a) shows the FTIR spectra of processed neat PHB and the PHB-30%SF and PHB-30%SF-Lps composites. In addition, Fig. 8(b) shows the FTIR spectra for the processed neat PP and the PP-30%SF and PP-30%SF-Lps composites. The bands at 1267 and 1180 cm^{-1} in the FTIR spectra of the PHB (Fig. 8a) can be used as an indication of changes in the degree of crystallization (Bloembergen *et al.* 1986). When comparing the intensities of the neat PHB bands at 1267 and 1180 cm^{-1} with the 30 wt% wood fiber loaded PHB bands, the intensity of the band at 1267 cm^{-1} decreased as the intensity of the band at 1180 cm^{-1} increased. This result indicated that the degree of crystallinity in PHB decreased with the addition of pulp fiber and is consistent with the decreasing sharpness of the XRD peaks. In addition, a shoulder was observed at 2750 to 2800 cm^{-1} in the spectrum of the pulp fiber loaded with PHB. This shoulder likely resulted from the carboxylic acid groups in the PHB that were generated when the ester groups were cleaved.

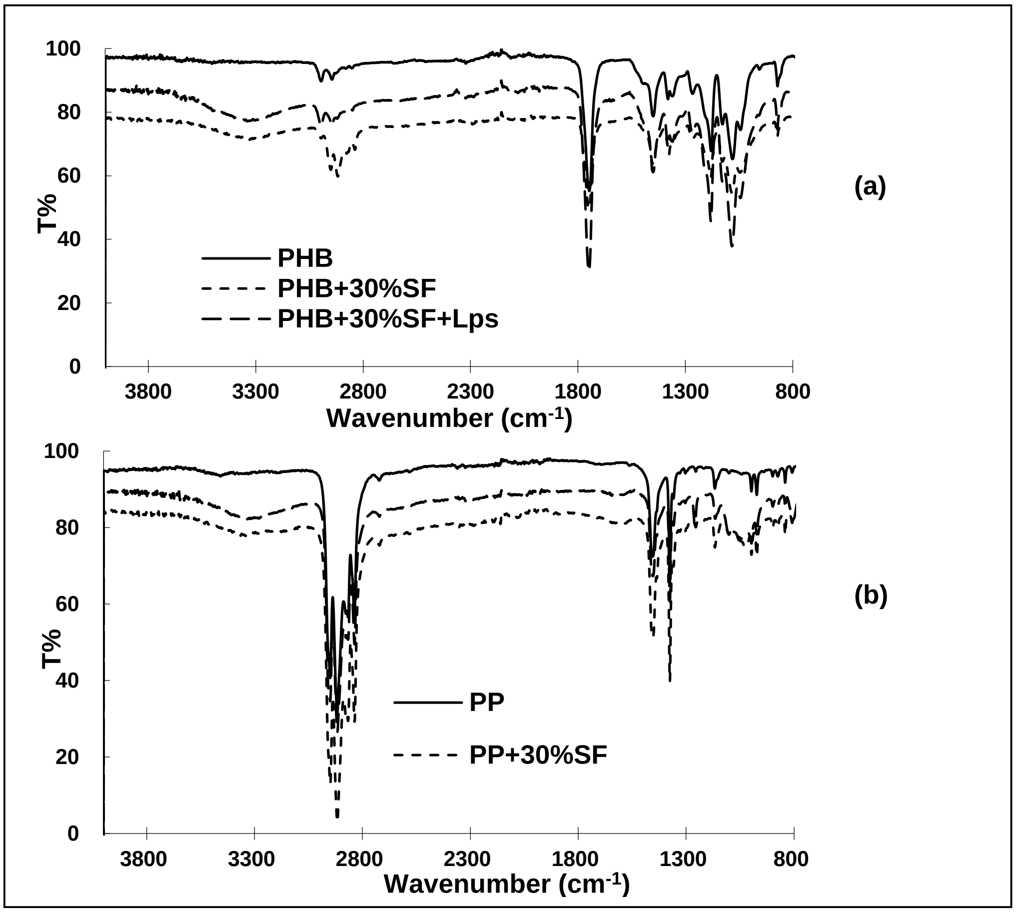

Fig. 8. FT-IR Spectra of different pulp fiber contents reinforced PHB and PP composites compared with Lps modified pulp fiber reinforced PHB and PP

In Fig. 8(b), the absorptions bands observed at 2949, 2916, and 2837 cm^{-1} are attributed to –CH$_2$- and –CH$_3$ groups and the absorption bands at 1454 and 1375 cm^{-1} result from -CH- and –CH$_2$- groups, respectively. No significant differences were observed among the neat PP and the PP-SF30% and PP-30%SF-Lps composites, which suggested that there were no chemical interactions between the polymer matrix and the pulp fibers. In the PP-30%SF-Lps spectrum, bands were observed at 1260 and 1027 cm^{-1} that originated from hardwood lignophenols. No chemical interactions were evident between the polymer matrix, pulp fiber and lignophenols. Therefore, the mechanical characteristics of the PP-fiber composites were inferior to those of the PHB-fiber composites.

Dynamic mechanical analysis (Henriksson and Lundmark)

Dynamic mechanical tests were performed to characterize the composites. Figure 9 shows the dynamic modulus and tan delta curves for the PHB and its composites. The results suggest that the addition of pulp fiber at 40 to 80 ºC increases the mobility of the amorphous phase of the matrix polymer and reduces damping in the composites (the extent of damping depends upon the pulp fiber weight percentage). The addition of lignophenols increased the peak temperatures of *E*’ and *E*” from 50 to 70 ºC, which indicated that the thermal stability of the lignophenol composites was greater than their stability in the absence of lignophenols. After the addition of lignophenols, the absolute values of *E*’ and *E*” increased, which demonstrated that the addition of lignophenols positively affected the composites. The tan delta (loss factor) curves are based on the ratio of storage modulus (*E*’) and loss modulus (*E*”); this ratio is an index for material’s mention stability. The loss factor did not change relative to the PHB-fiber modulus curves (Fig. 9 (c)); it decreased when the contents of fiber were increased. The smaller the loss factor, the better was the dimensional stability. For this reason, the dimensional stability of composites is increased with increasing fiber content. These results demonstrated that the addition of lignophenols significantly affected the dynamic mechanical features of these composites.

In summary, this study compared PP-fiber and PHB-fiber composites. The additions of ($NH_2(CH_2)_3Si(OC_2H_5)_3$) and lignophenols to PHB and PP did not improve their mechanical properties. However, the addition of lignophenols significantly improved the dynamic mechanical features of PHB. These results indicate that PHB is the preferred polymer to add to pulp fiber due to its high viscosity and unique fiber dispersion features in the PHB polymer matrix. Lignophenols are lignin-based biodegradable polymers that mixed readily with pulp fiber due to their linear structure. However, the addition of lignophenols did not negatively affect the mechanical and thermal characteristics. Thus, our work demonstrates that PHB and PP can be mixed with pulp fibers at high rates, even without the use of a petroleum-derived coupling agent. These composites exhibited favorable industrial features and can be completely biodegraded. Consequently, these composites should have great potential for green chemical applications.

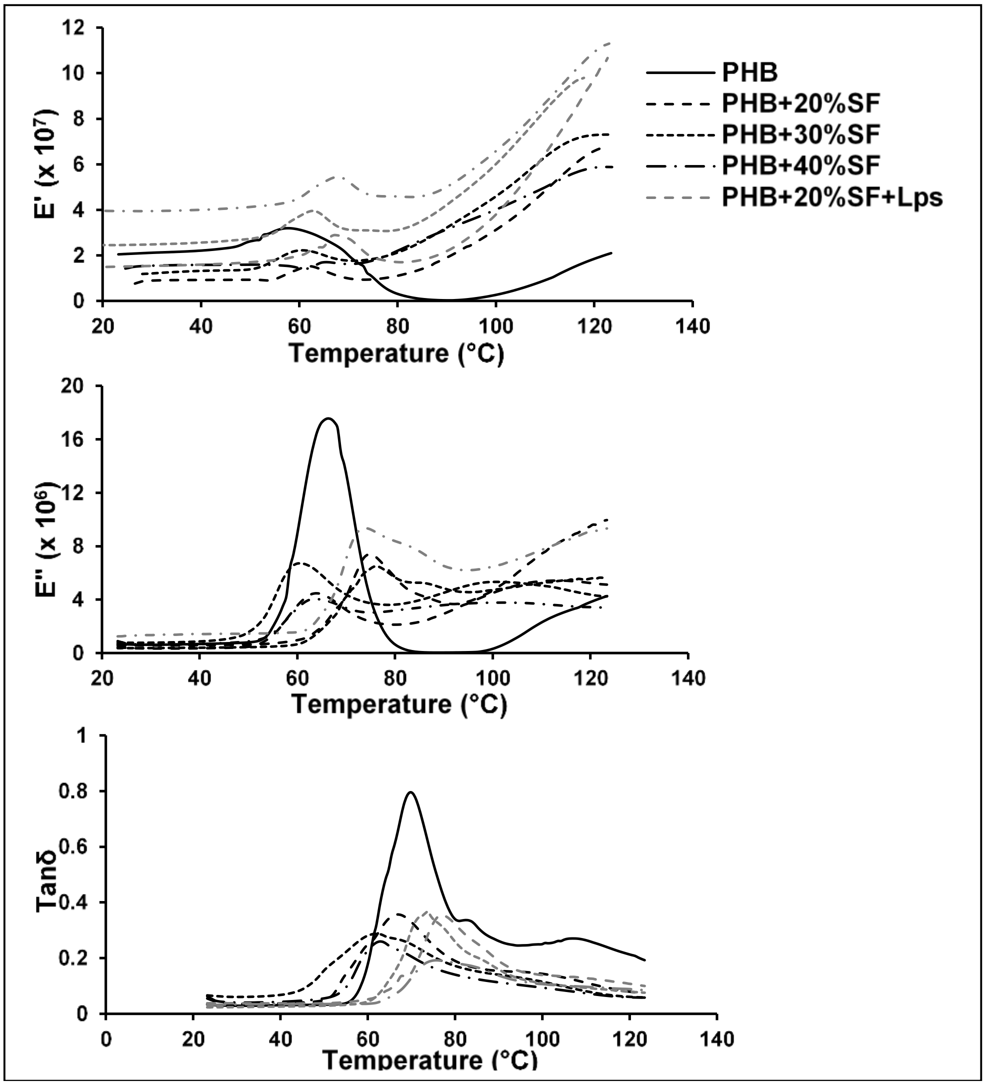

Fig. 9. Dynamic mechanical analysis runs for PHB-fiber-Lps composites: (a) Storage Modulus, (b) Loss Modulus, (c) Tan delta

CONCLUSIONS

1. Polypropylene (PP)- and polyhydroxybutyrate (PHB)-cellulose fiber composites with strong mechanical properties could be created using a torque rheometer as a mixer at 190 ºC with very short mixing times.
2. The tensile and impact strength features of the PP were slightly improved after the addition of the plasticizer or compatibilizing agent ($NH_2(CH_2)_3Si(OC_2H_5)_3$). However, no significant improvement was observed for tensile strength of PHB. The impact strength of PHB was slightly improved.
3. The short and long fiber-reinforced PHB composites showed greater tensile and impact strengths as the fiber content was increased to 40 wt%; the mechanical features of the

same fiber-reinforced PP composites were not as favourable as those of PHB. The addition of lignophenols had relatively minor negative effects on the mechanical characteristics of both PHB and PP. Using dynamic mechanical analysis, positive effects were observed after including lignophenols in the PHB-pulp fiber composites.

4. This study demonstrates a novel method for creating biodegradable composites with pulp fibers in the absence of a coupling agent.

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