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Thermal stability and miscibility of poly(hydroxybutyrate) and soda lignin blends

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ABSTRACT

The thermal properties and miscibility of poly(hydroxybutyrate) (PHB) and soda lignin blends were investigated by thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and Fourier transform infra-red spectroscopy (FTIR) over the entire range of composition. Although the addition of soda lignin shifts the onset of PHB decomposition to lower temperatures, the PHB/lignin blends are thermally more stable than PHB over a wider temperature range. The thermal behaviour of these blends as measured by TGA suggests compatibility for the blends containing up to 40 wt% soda lignin. These results correlate well with the glass transition temperature (T_g) data where a single T_g was obtained for these blends. At higher lignin to PHB ratios, two T_gs depicting immiscibility were obtained. The infra-red data show that the miscibility of the blends containing up to 40 wt% soda lignin is associated with specific hydrogen bonding interactions between the reactive functional groups in lignin with the carbonyl groups of PHB.

1. Introduction

The negative impact of petrochemical-based platform chemicals and industrial commodities has led to the use of "green" materials to reduce greenhouse gas and toxic emissions, reduce energy demand, and reduce the use of non-renewable resources. As a consequence, there has been focus on the use of environmentally friendly natural polymers and biopolymers. These polymers include cellulose, hemicellulose, lignin, starch, proteins, fats, polynucleotides, glycolide/lactide-based linear aliphatic polyesters, non-glycolide/lactic linear aliphatic polyesters and aliphatic and aromatic polycarbonates. Of particular interest is a class of microbially produced polymers known as polyhydroxyalkanoates (PHAs). PHAs serve as intracellular carbon and energy storage materials for the algae and bacteria that produce them (Verhoogt et al., 1994). Polyhydroxybutyrate (PHB) is a member of this class of polymers. PHB is insoluble in many solvents and has good barrier properties towards water, oxygen and carbon dioxide (Ghaffar, 2002). It is readily broken down, with the aid of enzymes, to water and carbon dioxide. These properties combined with PHB's potential for sustainable usage, makes it a potential commodity material in the packaging industry.

The reasons why the potential of PHB has not been fully utilised, apart from prohibitive of its cost, are its stiff and brittle nature and its thermal instability during processing. The crystal structure and crystallization conditions are responsible for these thermo-mechanical properties. PHB undergoes secondary nucleation at ambient temperature because of its low glass transition temperature (T_g) and it possesses a low nucleation density resulting in the formation of large spherulites (Barham and Keller, 1986). The spherulites contain crazes, and splitting occurs around the centre of these crazes, hence producing a significant structural weak point (Mahendrasingam et al., 1995). PHB undergoes thermal degradation and depolymerisation at temperatures close to its melting point and degradation is further enhanced by high shear rates during melt processing and extrusion.

As a result of these limitations, research efforts have concentrated to modify PHB by (a) changing its bulk properties without changing its physical form, (b) changing its microstructure, (c) making it more resistant to thermal degradation, (d) changing its chemical properties, (e) modifying its solubility so that less toxic chemicals are used, (f) improving its processability, and (g) lowering production costs without sacrificing properties. One approach to improve PHB's properties is through blending. Polymer blending is a less expensive way of producing materials with desired properties. Literature contains several investigations of blends of PHB and other polymers such as poly(ξ-caprolactone) (Antunes and Felisberti, 2005), poly(vinylidene fluoride) (Chiu et al., 2001), poly(viny alcohol), poly(lactic acid), poly(vinyl acetate), poly(vinylphenol), poly(DL-lactide)-co-poly(ethylene glycol), and cellulose esters. These polymers, depending on proportion, result in good miscibility with PHB. Many of these compounds have been found to be miscible or partially miscible on the basis of specific

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hydrogen bonding interactions (Kuo et al., 2002; Kuo and Chang, 2001; Sixun et al., 2003; Yong et al., 2001; Yoshie et al., 1995; Zheng and Mi, 2003). The main factors affecting the miscibility of polymers are the chemical nature of the polymer constituents and their molecular weight. The chemical nature of the polymers accounts for the existence of strong interactions (i.e. negative enthalpy) between the polymers. Thus, polymers with interacting functional groups that result in hydrogen bond formation and ionic interaction would enhance miscibility between polymer systems (Viswanathan and Dadmun, 2002).

Lignin is an amorphous macromolecule composed of phenylpropane repeat units and possesses aliphatic and aromatic hydroxyl groups as well as carboxylic acid groups. These interacting functional groups, as well as its amorphous nature make lignin a good candidate for blending with aliphatic polyesters, such as PHB. The amorphous nature of lignin may reduce the formation of large spherulites, retard crystallisation (Ghosh, 1998) and reduce secondary nucleation, all of which impact on PHB brittleness. Limited studies have been carried out on PHB and lignin blends. Ghosh (1998), Ghosh et al. (1999, 2000a,b) prepared blends (from the melt and solution) of PHB, polyhydroxybutyrate-hydroxyvalerate (PHBV), cellulose acetate butyrate with organosolv lignin and organosolv lignin ester. The organosolv lignin and its butyrate derivative were found to have a high degree of miscibility with PHB, and that lignin inhibits and retards PHB crystallisation. Ghosh et al. (2000b) reported that the T_g of the blends increased from that of pure PHB towards that of lignin/lignin butyrate further confirming some compatibility between PHB and lignin. The organosolv lignin used in these studies was obtained through extraction of hardwood with aqueous ethanol. The source from which lignin is obtained and the method of extraction has a strong bearing on its properties (Lora and Glasser, 2002). Thus, in this work the miscibility between PHB and soda lignin was examined using thermal and spectroscopic methods. The soda lignin was obtained from sugarcane fibre (i.e. bagasse) with sodium hydroxide as solvent used in the extraction process.

2. Materials and methods

2.1. PHB

Bacterial PHB was obtained from Sigma Aldrich. The weight average molecular weight, M_w as determined by gel permeation chromatography is 440,000 g mol^{-1} while the number average molecular weight, M_n is 260,000 g mol^{-1}. The T_g of the PHB is −4 °C and the melting point is 173 °C.

2.2. Soda lignin extraction

Bagasse was obtained from a Mackay Sugar Mill, Queensland, Australia. It was wet depithed (through a 4.2 mm screen) and then air dried. Soda lignin was extracted from bagasse by the soda process using a 20 L Parr reactor. In this method, 1 kg of bagasse is cooked with about 10.5 L of 0.7–1 M NaOH. Once the reactor reached the operating temperature of 170 °C, it was maintained at that temperature for 1.5 h. After cooling, the liquid (black liquor) was removed from the bottom of the reactor and sieved to remove fibrous material. To the black liquor, dilute H_2SO_4 (0.1 M) was slowly added with stirring to pH 5.5. Near pH 5.5 an obvious change in the appearance of the solution occurs; from black to murky brown. This change is due to the initial stages of lignin precipitation. The mixture was stirred for 10–15 min after which acidification is continued to pH 3. It was then transferred to a 65 °C water bath and stirred using an overhead stirrer for 30–45 min. The mixture was then vacuum filtered to recover the soda lignin. The soda lignin was repeatedly washed with hot water until all signs of foaming have subsided. It was then left to air-dry before being further dried in a vacuum oven at 45 °C overnight. This procedure increases the purity of soda lignin by reducing the inclusion of ash and carbohydrate components. It is different from other procedures reported in the literature because it is based on a two-stage acid precipitation process. We posit that the initial precipitation process at pH 5.5 produces lignin particles of high purity which were then allowed to grow to larger sizes before proceeding to the second precipitation stage where the proportion of impurities is highest. The extraction process and recovery procedure resulted in the recovery of 89% of the starting lignin content (22.2 wt%) in the bagasse.

2.3. Lignin characterisation method

2.3.1. Elemental analysis

Elemental analysis was performed on the soda lignin sample using a FLASHEA 1112 Elemental analyser instrument. In preparing the sample for analysis it was dried at 100 °C overnight, to remove any moisture. To measure carbon, hydrogen and nitrogen contents, 2–4 mg of sample was encapsulated in a tin container, and for measuring oxygen content the same quantity of soda lignin was encapsulated in a silver container. The results were obtained gas chromatography, and compared with those of standard materials.

2.3.2. Ash analysis

Crucibles were pre-dried to constant weight in a muffle furnace at 575 °C. Lignin samples (0.5–2 g) were weighed into the crucibles and heated to 105 °C to remove moisture. The crucibles were then heated at 575 °C to constant weight. The weight of ash remaining was calculated as a percentage of the original dry weight of sample (Sluiter et al., 2008a). An internal reference bagasse material in which the ash content is known was used as a standard.

2.3.3. Sugar analysis

Analytical grade glucose was supplied by B.D.H. D-(+) Xylose and D-(+) arabinose with purity > 99% were supplied by Sigma. D-Cellobiose with purity ≥99% was supplied by Fluka. Standard stock solutions were prepared with degassed deionised water. Analytical grade concentrated H_2SO_4 (98%) was supplied by Merck.

Aliquots of 3 mL of 72% H_2SO_4 were added to 0.3 g samples of soda lignin in pressure tubes. The tubes were placed in a water bath at 30 °C for 1 h and stirred intermittently to completely wet the lignin sample. The acid was then diluted to 4% through the addition of water and the samples were autoclaved in pressure tubes at 121 °C for 1 h (Sluiter et al., 2008b). The samples were filtered with porcelain crucibles to remove solids and the liquid fraction was analysed by high performance liquid chromatography (HPLC) for glucose, xylose and arabinose. This was performed on a Waters system equipped with a Waters 590 pump and a Waters 410 RI detector. The HPLC configuration included a Shodex KS-801 column with guard KS-G. The column was operated at 85 °C. The standard sugar solutions were also subjected to acid hydrolysis prior to HPLC analysis in order to obtain the standard recoverable sugars.

2.3.4. Characterisation of functional groups

Lignin possesses different functional groups. The functional groups quantified were the methoxyl group (Abreu and Freire, 1995), carboxylic acid (Dence, 1992), phenolic hydroxyl group (Dence, 1992) and total hydroxyl group contents (Gosselink et al., 2004).

2.3.5. Molecular weight determination

The soda lignin sample was prepared in 0.1 M NaOH eluent at 0.2 mg mL^{-1} just prior to analysis and filtered through a 0.45 μm syringe filter before running. The analysis was

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Table 1
Molecular weight of soda lignin and lignin components (wt%).

Ash*	Glucan*	Xylan*	Arabinan*	Purity	
2.0	0.2	1.6	<0.1	96.1	
M_n (g mol^{-1})	M_w (g mol^{-1})	Methoxy**	Phenolic OH**	RCOOH**	Total OH**
2160	2410	10.9	5.1	13.6	14.5

* Error in analysis (% ±2).
** Error in analysis (% ±5).

performed on a Waters system equipped with a Waters 2487 UV detector set at 280 nm. The column used was a Shodex Asahipak GS-320 HQ with guard Asahipak GS-2G 7B. Sodium polystyrene sulphonate standards of molecular weights 4950 g mol^{-1}, 16,600 g mol^{-1}, 57,500 g mol^{-1}, 127,000 g mol^{-1}, 505,100 g mol^{-1} and 1,188,400 g mol^{-1} used to prepare a standard calibration curve. Lignin weight average molecular weight (M_w) and number average molecular weight (M_n) were calculated using the equation obtained from the trend line of the standard curve.

2.4. Blend preparation

Soda lignin and PHB were dried at 100 °C for 12 h and then stored in desiccators under vacuum prior to use. Lignin–PHB blends with lignin contents from 10 wt% to 90 wt% were mixed in a Haake mini lab twin screw using the procedure reported by Ghaffar (2002). To minimise PHB degradation, the temperature of the extruder was maintained at 175 °C for 2 min. The polymer blends were extruded as strands then cooled and pelletised. The pellets were stored in a desiccator to avoid moisture absorption. Similar processing conditions were carried out for soda lignin and PHB.

2.5. Characterisation of blend samples

2.5.1. Thermogravimetric analysis (TGA)

The thermal decomposition studies were carried out in a TA Instruments Q500. Approximately 10 mg of sample was weighed into an aluminium pan and analysed by thermogravimetric analysis (TGA). Heating was at a rate of 10 °C min^{-1} and was performed from room temperature to approximately 800 °C. The test was performed in an atmosphere of nitrogen, which was injected at a flow rate of 15 mL min^{-1}. A curve of weight loss against temperature was constructed from the data obtained by the instrument. A derivative of this curve (DTG) was produced to indicate the temperatures at which maximum rates of weight loss occurred.

2.5.2. Differential scanning calorimetry (DSC)

Approximately 10–15 mg of sample was precisely weighed and then encapsulated in an aluminium pan. The pan was then placed in a DSC-Q100 instrument and heated from 0 °C to 200 °C at a heating rate of 10 °C min^{-1} (cycle 1). The test was performed in an atmosphere of nitrogen, which was injected at a flow rate of 15 mL min^{-1}. Samples were then cooled down at a rate of 30 °C min^{-1}, to −10 °C (cycle 2). Samples were then reheated to 200 °C at a rate of 10 °C min^{-1} (cycle 3). The plot obtained from this second heating run shows the T_g as a step transition.

2.5.3. Scanning electron microscopy (SEM)

The morphology of the PHB/soda lignin blends was examined using a scanning electron microscope, type FEI Quanta 200 Environmental SEM at an accelerating voltage of 15 kV. For this examination the pellets were compression moulded between two sheets of Teflon using an established procedure (Ghosh et al., 1999).

2.5.4. Fourier transform infra-red spectroscopy (FTIR)

IR spectra were collected using a Nicolet 870 Nexus Fourier transform infra-red (FTIR) spectrometer equipped with a Smart Endurance single bounce diamond ATR accessory (Nicolet Instrument Corp., Madison, WI). Spectra were manipulated and plotted with the use of the GRAMS/32 software package (Galactic Corp., Salem, NH). The spectrometer incorporated a KBr beam splitter and a deuterated triglycine sulphate room temperature detector. Spectra were collected in the spectral range 4000–525 cm^{-1}, using 64 scans at 4 cm^{-1} resolution with a mirror velocity of 0.6329 cm s^{-1}. The measurement time for each spectrum was around 60 s.

3. Results and discussion

The molecular weight and the percentage composition of the soda lignin used in this work are given in Table 1. The purity (determined from the sum of the ash and sugars) is comparable to organosolv lignin obtained from a previous study in our laboratory (Mousavioun and Doherty, 2010). The polydispersity (i.e. ratio of M_w to M_n) of the soda lignin is 1.1 indicating that the lignin polymer consists of molecules of similar chain length.

The integral thermogravimetric curves for PHB, soda lignin and PHB/soda lignin blends are given in Fig. 1. PHB appears to have two main overall degradation steps while soda lignin degradation is complex constituting of several processes (Mousavioun and Doherty, 2010). For PHB/soda lignin blends, degradation occurs in several more stages (Fig. 1) suggesting that blending PHB with soda lignin completely changes the decomposition behaviour of PHB. As shown in Fig. 1, the decomposition temperature at which the material has reached 5% degradation (T_0) of PHB decreases with the addition of soda lignin. For example, T_0 for pure PHB is 212 °C, whereas it is 162 °C for PHB/lignin blend with a composition of 60/40. Also, the temperature at the maximum rate of weight loss of PHB decreases with soda lignin addition (Fig. 1). Whilst these results are suggestive that the addition of soda lignin promotes PHB

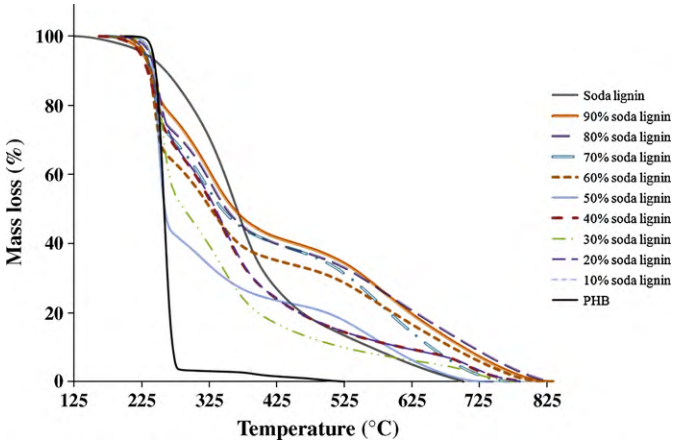

Fig. 1. The integral thermogravimetric curves for PHB, soda lignin and PHB/soda lignin blends.

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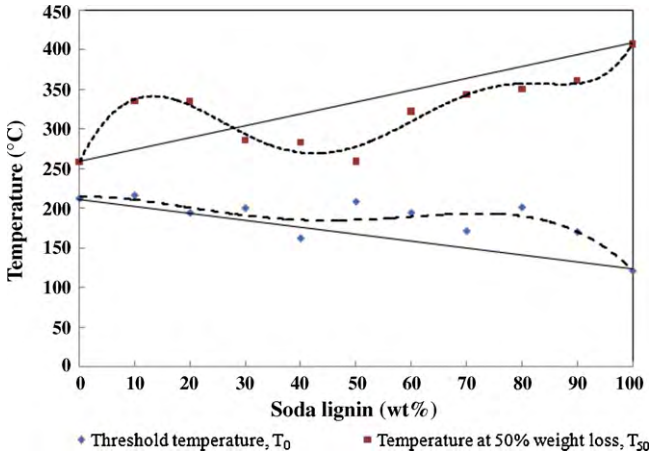

Fig. 2. Plots of T_0 and T_{50} of PHB/soda lignin blends versus soda lignin content.

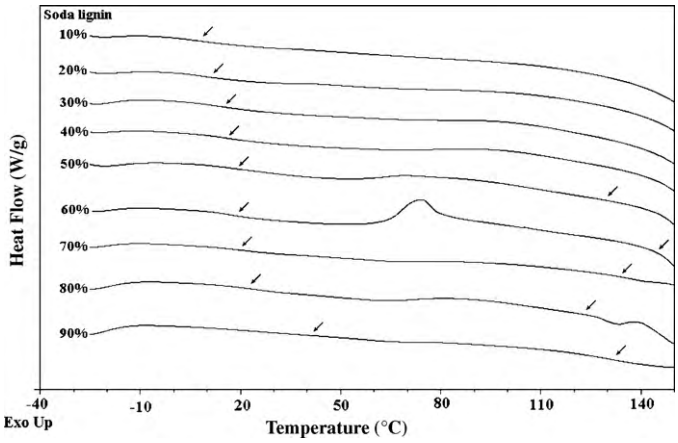

Fig. 3. DSC curves of PHB/soda lignin.

degradation, it does not, however, give a quantitative assessment of the overall thermal stability of the blends. As shown in Figure 1, degradation of pure PHB is almost complete by ~260 °C, whereas the weight loss for the blends at this temperature is less than 60 wt%. The lower weight loss is an indication that the blends are thermally more stable than PHB over a wider temperature range.

Lizymol and Thomas (1993) used TGA to study the thermal properties of miscible and immiscible polymer blends. For the miscible poly(vinyl chloride)/poly(ethylene-co-vinyl acetate) blends, they found that increasing the proportion of poly(ethylene-co-vinyl acetate) in the blend effectively increased T_0 and the temperature at 50% weight loss (T_{50}) more than in proportion to the proportion of poly(ethylene-co-vinyl acetate) in the blend. For the immiscible poly(ethylene-co-vinyl acetate/poly(styrene-co-acrylonitrile) systems, the T_0 values of the blends were lower than the proportion of poly(ethylene-co-vinyl acetate) in the blend, while T_{50} values were virtually unaffected. Based on this approach, plots of T_0 and T_{50} of PHB/soda lignin blends versus soda lignin content were constructed and the results are presented in Fig. 2.

As the soda lignin content increases T_0 decreases, but the decrease does not correspond to the proportional amount of soda lignin added to the blend. However, at low lignin contents (up to 20 wt%), T_{50} values increases more than in proportion to the proportion of soda lignin added (i.e. well above the tie line) possibly suggesting some degree of miscibility between soda lignin and PHB at these compositions. At soda lignin concentrations > 20 wt%, the results may suggest incompatibility between the components. As the PHB/soda lignin systems are not similar to those of Lizymol and Thomas (1993), the results shown in Fig. 2 may simply be an indication of lignin degradation products reacting with PHB degradation products to form stable species.

The most accepted parameter to assess polymer miscibility is the T_g. A single T_g of a blend implies complete miscibility between the polymer pairs in their amorphous fractions, whose value is an average of the individual component's T_g. Two or more T_gs suggest that the degree of miscibility is restricted. Fig. 3 shows the DSC curves of the blends where the T_gs were obtained. The exothermic peak at ~80 °C (for 50 wt% and 60 wt% lignin) is associated with cold crystallisation temperature of PHB. Ghaffar (2002) obtained similar cold crystallisation temperatures for PHB and polyvinyl acetate blends. Why the peak is prominent in some blends and not in others is not known and is worth for future investigation.

Most miscible polymers display a single T_g whose value is dependent on the proportion of the individual components (Fox, 1956). Fig. 4 illustrates the T_gs of PHB and the blends. A single T_g is obtained up to a soda lignin content of 40 wt%, thereafter there are two T_gs. The T_g's results therefore give a further indication of miscibility between PHB and soda lignin at soda lignin contents up to 40 wt%.

Fig. 3 also shows that the T_g of the PHB component of the blends increases with increase in soda lignin content. Similar results were obtained by Ghosh et al. (1999, 2000a,b) for organosolv lignin/PHB blends, though the values obtained in the present study were slightly higher (Fig. 4). This could be related to the method of preparation, differences in the PHB source, or the lignin type as soda pulping generally increases the carboxylic acid and hydroxyl contents of lignins relative to organosolv pulping (Gosselink et al., 2004).

To obtain a better idea of interactions between PHB and soda lignin, we evaluated the T_g data using the well-known Fox, Gordon–Taylor and Kwei equations. These are:

Fox equation:

$$\frac{1}{T_g(\text{blend})} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

Gordon–Taylor equation:

$$T_g(\text{blend}) = \frac{W_1 T_{g,1} + K_{GT} W_2 T_{g,2}}{W_1 + K_{GT} W_2} \quad (2)$$

Kwei equation:

$$T_g(\text{blend}) = \frac{W_1 T_{g,1} + K_W W_2 T_{g,2}}{W_1 + K_W W_2} + q w_1 w_2 \quad (3)$$

where $T_{g,1 \text{ or } 2}$ and $w_{1 \text{ or } 2}$ are glass transition temperatures of the pure components and their corresponding weight fractions, respectively. K_{GT}, K_w and q are adjustable parameters. As can be seen in

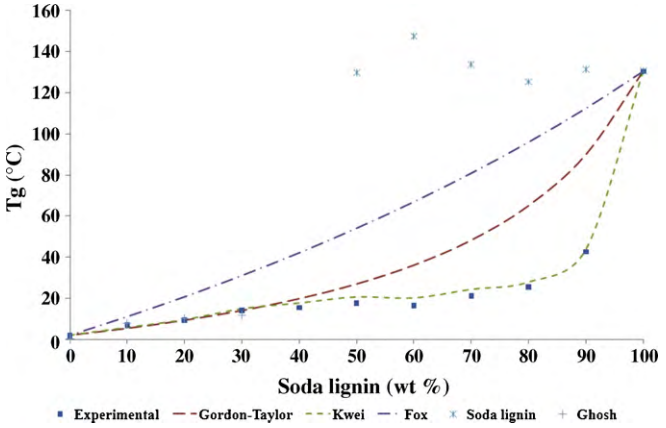

Fig. 4. T_gs of PHB and the blends versus soda lignin content.

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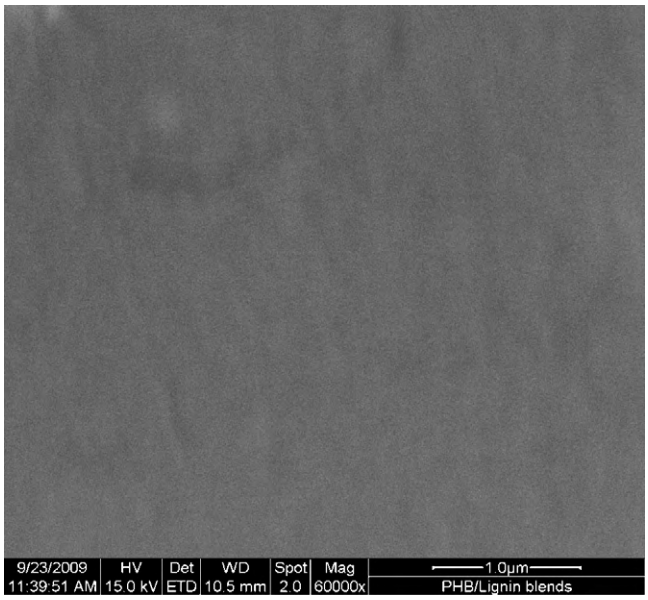

Fig. 5. SEM image of PHB/soda lignin containing 10 wt%.

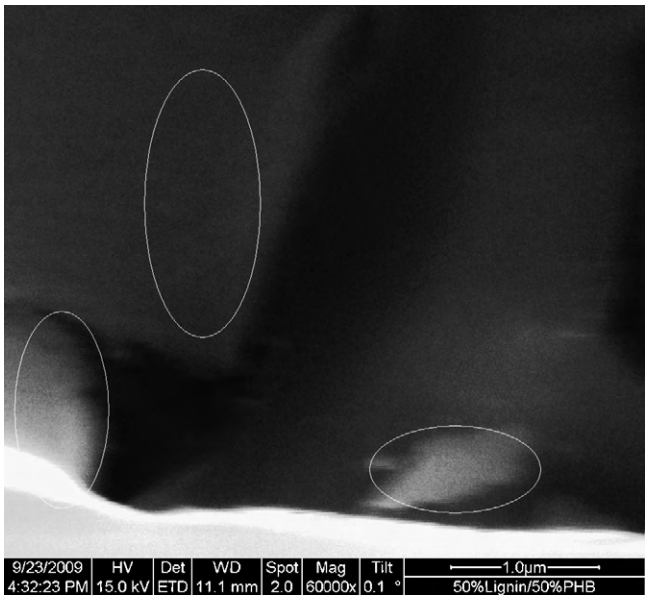

Fig. 7. SEM image of PHB/soda lignin containing 50 wt%.

Fig. 4, the PHB/soda lignin blends up to 40 wt% lignin fit nicely to the Gordon–Taylor with a K_{GT} value of 4.15. It also fitted the Kwei equation with K_w value of 0.2 and q having a value of 22. The positive value of q and a relatively high value of K_{GT} indicate that strong interactions (ElMiloudi et al., 2009) exist between OH groups of lignin and the carbonyl groups of PHB for the blends containing up to 40 wt% lignin.

Figs. 5–7 illustrate typical SEM images of blends. For blends of PHB/soda lignin containing 10 wt% and 30 wt% lignin, there was no apparent phase separation, whereas for the blend with a 50/50 composition in weight, phase separation is observed. For other compositions higher than 50 wt% soda lignin, phase separation between the components was detected. Thus, the SEM data follow similar trends as the data obtained from the T_g of the blends.

Attempts in understanding the miscibility of the PHB/soda lignin blends have been made using FTIR as have been undertaken by previous workers with similar polymer systems (Dong and Ozaki, 1997). Infra-red spectroscopy provides information on hydrogen bond formation (and other interactions) and the strength of H-bonds through wavenumber shift, band intensity and band width of specific signals. Fig. 8 shows the FTIR spectra from 1800 cm^{-1} to 1620 cm^{-1} of the carbonyl stretching region of PHB and PHB/soda lignin blends. PHB spectrum exhibits three peaks, these are at 1742 cm^{-1}, 1722 cm^{-1} and 1709 cm^{-1}, though the first peak at 1742 cm^{-1} is more of a shoulder to the main peak at 1722 cm^{-1}. The peak at 1742 cm^{-1} is associated with the amorphous component of PHB, the peak at 1724 cm^{-1} is associated with the crystalline component of PHB (in its preferred conformation), and the peak at 1709 cm^{-1} is associated to hydrogen bonded carbonyl (Guo et al., 2010). The band at 1685 cm^{-1} has been reported to be a crystalline band, although its origin is not known (Guo et al., 2010).

Fig. 8 also shows that for blends containing 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% soda lignin, there is a small but definite shift (2 cm^{-1}) to a lower wavenumber for the main PHB peak. The shift to a lower wavenumber is indicative of hydrogen bonding interactions because the stretching frequencies of participating groups usually move towards lower wavenumbers (Barsbay and Güner, 2007). Barsbay and Güner (2007) obtained such small shifts for blends of dextran and poly(ethylene glycol) cast in water. The present results therefore indicate that the reactive functional

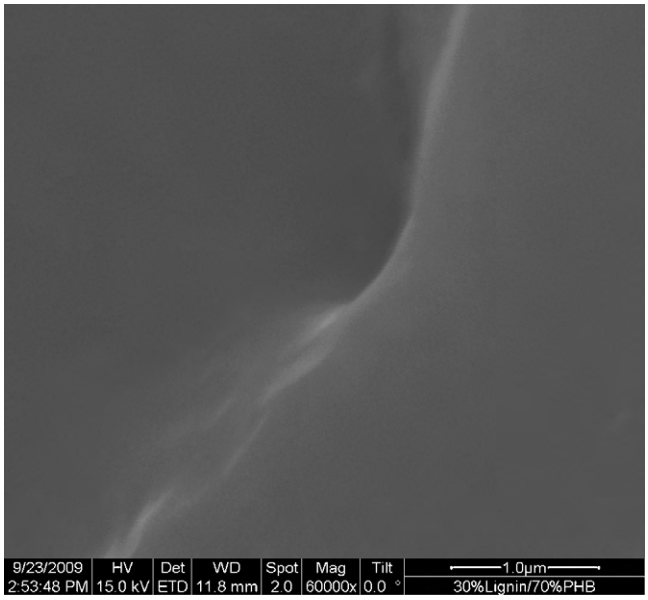

Fig. 6. SEM image of PHB/soda lignin containing 30 wt%.

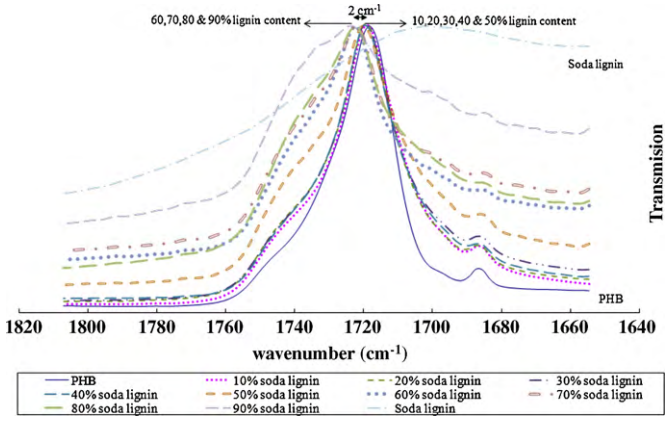

Fig. 8. FTIR spectra of the carbonyl stretching region of PHB and PHB/soda lignin blends.

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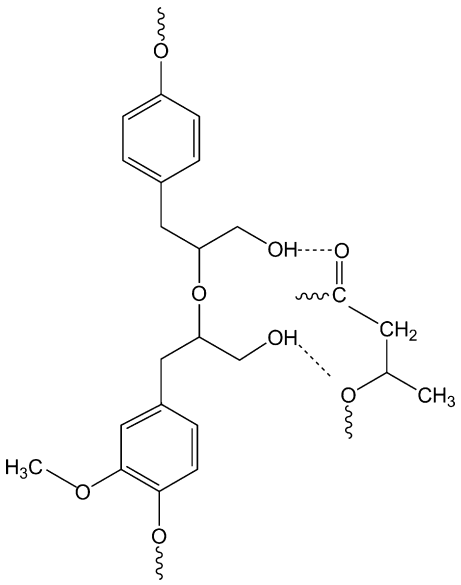

Fig. 9. Hydrogen bonding interactions between the reactive functional groups in soda lignin and the carbonyl groups of PHB.

groups of lignin are engaged in hydrogen bonding interactions with the carbonyl oxygen in PHB (Fig. 9).

The reason why there were no differences in the wavenumber shifts between these blends containing different proportions of lignin is not known. Fig. 8 also shows that there are no shift observable for PHB blends containing 60–90 wt% of lignin relative to the PHB band at 1724 cm^{-1}, confirming previous observations about immiscibility of PHB/lignin blends containing these compositions. It should however, be noted (as shown in Fig. 8), there are noticeable shifts to lower wavenumbers for all the blends for the PHB band at1742 cm^{-1}. As this band is of far less intensity compared to the main band at 1722 cm^{-1}, and so takes less prominence, it may be concluded that there are some favourable weak interactions between amorphous part of PHB and lignin at all lignin proportions.

4. Conclusion

Soda lignin was found to improve the overall thermal stability of PHB, though it reduced the initial temperature of decomposition of PHB. The TGA, DSC and SEM of the PHB/soda lignin blends suggest that intermolecular interactions between PHB and soda lignin were favoured at soda lignin content of up to 40 wt%. These intermolecular interactions were found to be due to hydrogen bonding formation between the reactive functional groups of lignin and the carbonyl groups of PHB.

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