**Esterification of industrial lignin and its effect on the resulting
poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or polypropylene blends**

Shupin Luo^{a,b}, Jinzhen Cao^a, and Armando G. McDonald^{b,*}

^a MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Qinghua East Road 35, Haidian 100083, Beijing, China.

^b Renewable Materials Program, Department of Forest, Rangeland and Fire Sciences, University of Idaho, 875 Perimeter Drive MS1132, Moscow, ID 83844-1132, USA

*Corresponding Author.

E-mail address: armandm@uidaho.edu. Tel.: +1 (208) 885 9454. Fax: +1 (208) 885 6564.

Abstract: Utilisation of lignin in plastic based blends offers a sustainable alternative to non-renewable materials as well as value-added use of technical lignin obtained from pulping operations. To overcome poor compatibility between lignin and plastic, in this study, two industrial lignins (softwood Kraft and agricultural fiber soda) were esterified (with acetic, propionic, butyric, and hexanoic anhydrides) and subsequently blended with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) or polypropylene (PP) at a weight ratio of 3:7. This paper systematically characterized C₂-C₆ anhydrides esterified lignins (molar mass, glass transition temperature (T_g), hydrophobicity, and polarity), and provides a comprehensive evaluation of the effect of different lignin esters in the blends on tensile properties, water absorption, thermal transitions, for the first time, spherulite morphology, and dynamic rheological behavior. Generally, compared to blends with unmodified lignin, a progressive increase of tensile strength (25%) and elongation at

break (26%) could be observed with increasing ester carbon chain length in PHBV based systems, while no improvement was seen in PP based systems. Water absorption of PHBV and PP blends decreased by about 50% after lignin esterification. The effect of lignin esterification on the crystallization process was matrix dependent: depression of melting crystallization and occurrence of cold crystallization was observed in PHBV based blends, while the melting crystallization shifted to higher temperature in PP based blends. The lignin acetate and propionate blends were partially miscible showing two-stage glass transitions by thermal mechanical analysis. Esterification led to more uniform dispersion of lignin in the plastic matrix. The frequency of PHBV spherulites increased and their size decreased from 700 μm to less than 100 μm with addition of lignin acetate and propionate. Lignin hexanoate blends showed a T_g depression and smaller dynamic elastic and viscous moduli than the other lignin esters, suggesting that it acted as a plasticizer.

Keywords: lignin; esterification; blend; tensile property; thermal transition; rheology

1. Introduction

Finite fossil fuel resources, pollution associated with discarded petroleum based plastic materials, and rising environmental awareness, have sparked a shift in the development of polymers and composites derived from natural resources (Chung et al., 2013). For example, 40% of plastic produced is used in packaging and short-term applications (throw-away cups, utensils, etc) and after being disposed the resulting

waste can end up in marine and terrestrial environments (PlasticsEurope, 2012). To overcome these negative impacts of plastic is to substitute with biobased and biodegradable plastics, such as polyhydroxyalkanoates (PHA), polylactic acid, cellulose derivatives and lignin (Flieger et al., 2003; Kai et al., 2016).

As an integral part of plants, lignin is the second most abundant natural polymer and accounts for around 25% of non-fossil organic molecules in the biosphere (Thakur et al., 2014). Technical lignin is generated as a byproduct from pulping or biomass pretreatment processes. Currently, an estimated 50 million tons of lignin is produced from the pulp and paper industry annually, and even larger amounts of lignin will be generated from the lignocellulosic biorefinery industry in the near future (Alekhina et al., 2015; Gellerstedt, 2015). However, only about 2% of lignin is commercially utilized for relatively low-value applications, such as dispersants or binders, and the majority is burnt for heat (Saito et al., 2012). Recently, considerable efforts are being made to investigate waste lignin as sustainable alternatives to nonrenewable products, such as macromonomers for synthesis of copolymers (e.g. polyurethanes, epoxy resins, lignin polyester-amides) (Arshanitsa et al., 2016; Ferdosian et al., 2016; Li et al., 2015), component for composite applications (e.g. surfactants, lubricants, coatings, plasticizers), reinforcing fillers for polymers, feedstock for chemicals (e.g. vanillin), and precursors for carbon materials (Duval and Lawoko, 2014; Stewart, 2008; Upton and Kasko, 2016).

In the field of polymer composites, lignin is a promising alternative to inorganic fillers as a low-cost renewable reinforcement or filler in polymer materials via

67 copolymerization or blending (Luo et al., 2016), which offers particular benefits such as
68 promoting nucleation (Wang et al., 2015), antioxidant activity (Gregorová et al., 2005),
69 thermal stability (Gordobil et al., 2015), and biodegradation (Cazacu et al., 2004) to the
70 polymer. Lignin hybrid materials such as silica/lignin (Bula et al., 2015;
71 Grzábka-Zasadzińska et al., 2016) and switchgrass/lignin (Sahoo et al., 2013, 2014)
72 have also been used as fillers in polypropylene or bioplastics, and silica/lignin was
73 found to be capable of an effective crystal nucleation due to its porous structure.
74 However, the incorporation of unmodified lignin in thermoplastics has been reported
75 and accompanied by a deterioration in mechanical properties (Alexy et al., 2000;
76 Camargo et al., 2011; Pucciariello et al., 2004). The main reason is that the lignin
77 molecule is relatively polar due to its numerous hydroxyl (OH) groups, presenting poor
78 compatibility or immiscibility with non-polar or weak-polar polymer matrix, which
79 results in poor stress transfer between the phases (Duval and Lawoko, 2014). Moreover,
80 as an irregular phenolic heteropolymer, lignin has a propensity to self-aggregate due to
81 strong inter- and intra-molecular hydrogen bonding between the carboxylic acid groups
82 and various ether oxygens and hydroxyl groups, causing defects that act as stress
83 concentration points in the matrices (Chung et al., 2013).

84 The compatibility between lignin and polymers can be enhanced by several strategies,
85 such as addition of a compatibilizer (Reza Barzegari et al., 2012), derivatizing the OH
86 groups by esterification or etherification (Laurichesse and Averous, 2014), cross-linking
87 or grafting (Luo et al., 2016), or using low molecular weight lignin (Pouteau et al.,
88 2003). Among all the reactions concerning OH groups of lignin, esterification is the

easiest to carry out considering the reaction parameters (Laurichesse and Averous, 2014). The advantage of using acid anhydrides is that they can be bio-derived (Hatti-Kaul et al., 2007). To alter lignin solubility in nonpolar solvents, Thielemans and Wool (2005) esterified Kraft lignin with several carboxylic acid anhydrides, in a solvent-free reaction using 1-methylimidazole as catalyst. The solubility of lignin in nonpolar solvents was observed to increase with increasing carbon chain length on the ester group. Similarly, a series of thermoplastic-like lignin derivatives including acetate, propionate, and butyrate were successfully synthesized via one-step esterification by Fox and McDonald (2010), presenting comparable flexural properties to common plastics (e.g. polypropylene (PP) and polyethyleneterephthalate). They also found the glass transition temperature (T_g) of softwood Kraft and corn stover lignin esters decreased linearly with the increasing carbon atoms (C_2 - C_4) in the ester substituent. Recently, Monteil-Rivera and Paquet (2015) successfully esterified lignin with various anhydrides (acetic, propionic, butyric, methacrylic, maleic) using a fast solvent-free, catalyst-free, microwave-assisted method. Esterification could also introduce vinyl groups into the lignin macromolecules to enhance reactivity towards crosslinking or polymerization with other polymeric systems (Gordobil et al., 2016).

Additionally, lignin esters with long carbon chain have been investigated for applications as lubricants or coating materials. Lignin stearate esters were applied as lubricants/processing aids in linear low density polyethylene processing (Nadji et al., 2009). Lignin palmitate and laurate were used to form a continuous film coating on paperboard, which provided good hydrophobicity and acted as an oxygen barrier (Hult

et al., 2013).

By attaching different sized substituents to lignin, physiochemical and thermal properties of lignin can be manipulated, which allows for tailoring the properties of resulting product for various applications. Regarding the use of esterified lignin in polymer blends, Teramoto et al. (2009) reported three miscible organosolv lignin ester/poly (ϵ -caprolactone) (PCL) systems, among which C₄ and C₅ anhydrides esterified lignin exhibited better miscibility with PCL compared to C₃ due to the higher structural similarity with the PCL repeating unit. Pawar et al.(2016) reported the synthesis of stable lignin stearates of controllable degrees of substitution (DS) by varying the degree of saturation of the fatty acid. The incorporation of 25 wt% lignin stearate (97% DS) into polystyrene (PS) blended films was found to lower the T_g by 22 °C, indicating that lignin stearates plasticize PS as well as other thermoplastics. A recent study by Dehne et al. (2016) studied five types of technical lignins which were esterified (acetate (Ac), propionate (Pr), and butyrate (Bu)) and blended with polyethylene (50%). The hardwood Kraft and soda lignin exhibited a progressive increase of tensile (up to 45%) and flexural (up to 30%) strength from unmodified to Pr based blend and decreased for Bu based blend. For softwood Kraft lignin the highest strength and modulus were observed for the Ac based blend.

In this study, two readily available technical lignins (softwood Kraft and agricultural fiber soda) were esterified with Ac, Pr, Bu, and hexanoic (He) anhydrides. The chemical features, molar mass, T_g, and hydrophobicity for the unmodified and esterified lignins were determined to obtain structure-property relationships. The unmodified and

esterified lignins were compounded with PHBV or PP and the blend properties (tensile, water soak, thermal, rheological, spherulite structure) were determined to establish critical factors influencing processing and end-use performance of these materials.

2. Materials and methods

2.1. Materials

Indulin AT (IN) softwood Kraft lignin was provided by MeadWestvaco Co. Protobind 1000 (PB) lignin from agricultural fiber soda pulping was supplied by ALM India Pvt. Ltd. The purity of IN and PB lignin (total content of Klason and acid soluble lignin) was determined by the previous study (Li and McDonald, 2014) to be 93.5% and 90.3%, respectively. Acetic anhydride (99%), propionic anhydride (97%), butyric anhydride (98%), hexanoic anhydride (97%), and 1-methylimidazole (1-MIM, 99%) were obtained from Acros Organics and used as received.

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) powder (ENMAT Y1000, HV = 8 mol %) with a weight-average molar mass (M_w) of 443 000 g/mol (Luo et al., 2016) was supplied by Tianan Biopolymer Inc., Ningbo, China. Polypropylene (PP, H04F-00) with a density of 0.90 g/cm³ and a melt flow index of 4.0g/10 min at 230 °C was obtained from Bamberger Polymers, USA.

2.2. Lignin esterification

The esterification procedure was revised from a previously reported esterification method (Fox and McDonald, 2010). Samples of each lignin type (5 g) were placed in a 100 mL round-bottomed flask to which the acid anhydride (25 mL) and 1-MIM (0.5 mL) were added. The reaction was kept for 24 h at 65 °C for Ac, 95 °C for Pr, 120 °C for Bu,

and 140 °C for He anhydrides with efficient stirring. To ensure complete esterification, the amount of anhydride used was in excess than an equimolar of OH groups in lignin, based on 5.10 mmol OH/g lignin (Chung et al., 2013). The esterified lignins (Ac, Pr and Bu) were recovered by adding the reaction mixture drop wise into ice water with stirring to allow for complete precipitation, while the lignin-He was recovered by precipitation in a mixture of ethanol and water (3:1 v/v), followed by centrifugation, and washed exhaustively with the respective precipitating media (until no strong odor of acid was smelled) to remove residual catalyst and carboxylic acids. The resulting products were freeze-dried and weighed to determine the weight percentage gain (WPG).

2.3. Characterization of lignin

Fourier transform infrared (FTIR) spectra of original and esterified lignin were collected using a ThermoScientific iS5 FTIR spectrometer equipped with a ZnSe attenuated total reflection (ATR) probe (iD5). The spectra for each sample (in duplicate) were baseline corrected, averaged, and normalized using Omnic v.9.2 software (Thermo scientific).

The weight average molar mass (M_w) of lignin esters was determined by size exclusion chromatography (SEC) with multi-angle light scattering (MALS, Post Nova PN3609, 658 nm), UV (Waters model 2487, 280 nm) and refractive index (RI, Waters model 2414) detection. Samples were dissolved in chloroform (CHCl_3) at a concentration of 2 mg/mL and filtered (0.45 μm , PTFE syringe filter) prior to analysis. The refractive index increment (DN/DC) value of each sample was determined by first injecting a PS standard (with a precisely known concentration and DN/DC for

calibration) and then the lignin ester samples directly injected through all the detectors with CHCl_3 at 0.5 mL/min. The DN/DC values were calculated using the RI traces with NovaMALS v.1.5 software. Then the samples were injected and separated using a Jordi DVB mixed bed column at 30 °C on elution with CHCl_3 at 0.5 mL/min. The calibration of the system was made using PS standards, and M_w analyzed with NovaMALS v.1.5 software using the obtained DN/DC values.

Thermal Mechanical Analysis (TMA) was carried out with Perkin Elmer TMA 7 instrument using a penetration probe at an applied static force of 10 mN. Lignin samples were pressed to small discs (1 mm × 10 mm Ø) using a hydraulic press (Carver) and analyzed from 40 to 200 °C at 5 °C /min. The T_g was determined from the onset point of softening (Li and McDonald, 2014).

For the contact angle (CA) determination, powdered lignin samples were pressed into thin discs (10 mm Ø) for measurement, as described above. In the case of plastic matrices, thin films from melt extrusion were used for the test. The CA of two test liquids (water and diiodomethane) on the samples were respectively measured using the sessile drop method on a Thwing-Albert PG-2 Pocket Goniometer at room temperature. Data were processed using the Pocket Goniometer v.3.3 software. Surface energies of the lignin and matrix were estimated using the equilibrium CA. Both the geometric (Owens-Wendt, Eq. (1)) (Tran et al., 2013) and Harmonic (Wu, Eq. (2)) (Shimizu and Demarquette, 2000) approaches were used to evaluate the surface energies and its polar and dispersive components as follows:

$$\gamma_L(1 + \cos \theta) = 2 \left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p} \right) \quad (1)$$

$$\gamma_L(1 + \cos \theta) = 4 \left(\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \right) \quad (2)$$

where θ is the equilibrium CA, γ_S is the solid surface energy, γ_L is the liquid surface tension, γ_S^d and γ_S^p are the dispersive and polar components of the surface energy of the solid, γ_L^d and γ_L^p are the dispersive and polar components of the surface tension of the liquid.

2.4. Preparation and characterization of the blends

The blends were made from PHBV (or PP) with original or esterified lignin in a Dynisco Lab Mixer Molder/Extruder. Lignin content was constant (30%) in all samples. Mixture of plastic matrix and lignin was melt compounded at 60 rpm for 5 min, and then injection molded into discs, dog-bones, or rectangular bars. Melt temperature was adjusted between 180 and 190 °C depending on the lignin ester and then injection molded into specimens at a mold temperature of 80 °C.

Tensile tests were conducted on injection molded dog-bone specimens (at least 6 replicates) according ASTM D1708, using an Instron 5500R-1132 universal test machine with load cell of 5 kN and crosshead speed of 1 mm/min. The strain was measured using a micro-extensometer (model 3542, Epsilon Technology Corp.).

Water absorption of the polymer blends was performed on discs (2 mm × 25 mm Ø, 4 replicates). The specimens were kept in distilled water (23 °C) for 45 days. Weight and dimensions were measured before and after water soaking and at constant time intervals. The diffusion coefficients (D_f) of samples were calculated using Eq. (3) (Fabiya et al., 2011):

$$D_f = \pi(h/4M_\infty)^2(\Delta M/\Delta t^{1/2})^2 \quad (3)$$

where M_{∞} is the maximum MC measured at the end of the test, h is the sample thickness corresponding to M_{∞} , t is time, and $\Delta M/\Delta t^{1/2}$ is the initial slope from the MC versus $t^{1/2}$ relation.

Differential scanning calorimetry (DSC) measurement was performed on PHBV, PP and blends using a model Q200 DSC (TA instruments) under nitrogen (50 mL/min). Approximately 5 mg of sample was precisely weighed and encapsulated in an aluminum pan. The samples were first equilibrated at 40 °C (3 min) then ramped to 190 °C at a rate of 10 °C/min, held isothermally for 5 min to erase residual thermal history (cycle 1); cooled down to -50 °C at -10 °C/min and held isothermally for 3 min (cycle 2); then reheated to 190 °C at 10 °C/min (cycle 3). Data were analyzed using the Universal Analysis 2000 v.4.5A software (TA Instruments). Melting point (T_m) was obtained from the second heating cycle, while crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) were obtained from the peak of the cooling cycle. The degree of crystallization (X_c %) was calculated by the following equation:

$$X_c \% = \frac{\Delta H_m}{\Delta H_0 \times W_f} \times 100 \quad (4)$$

where melting enthalpy (ΔH_m) was calculated from the area under the peak observed on second heating ramp, ΔH_0 is the theoretical fusion enthalpy of a 100% crystalline polymer (PHBV: 146 J/g (Berthet et al., 2015); PP: 209 J/g (Ayrilmis and Kaymakci, 2013)), and W_f is the mass fraction of plastic matrix in the composites (0.7).

TMA of the plastic and blend samples was performed, as described above, on small sections of molded material ($2 \times 1 \times 1 \text{ mm}^3$) from -30 to 200 °C at 5 °C /min.

Spherulite morphology of PHBV was observed using an Olympus BX51 microscope

(10× objective, 10× eyepiece, polarized light filters) equipped with a Mettler Toledo FP900 Thermosystem (FP90 central processor and FP84 DSC-hot stage). A thin film of blend sample was placed in a transparent glass crucible, first heated from room temperature to 190 °C at a rate of 20 °C/min and maintained for 3 min, then cooled at -20 °C/min to desired temperature and allowed to crystallize isothermally. Micrographs were captured using an Olympus DP70 digital camera.

Parallel plate rheometry was performed using a Bohlin CVO 100N rheometer equipped with an extended temperature control module, in an oscillating shear mode on molded disc samples (2 mm × 25 mm Ø). Dynamic frequency sweep (0.1-100 rad/s) was run at 1% strain amplitude in the linear viscoelastic region at 175 °C for PHBV based blends and 170 °C for PP based materials. Prior to testing, the molten samples were equilibrated for 5 min to erase any thermal and deformation history.

3. Results and discussion

3.1. Yield and chemical characterization of esterified lignin

Yields (WPG) of IN and PB lignin esters are given in Table 1. The yields of IN-Ac (24%), IN-Pr (29%), and IN-Bu (46%) were comparable to a previous study (Fox and McDonald, 2010). The WPG of the lignin (IN and PB) esters progressively increased from Ac to Bu, while a decrease was seen for the He ester. Based on the WPG and number of available OH groups present in lignin (1.08 OH/C₉OCH₃ for IN (McDonald and Ma, 2004) and 1.05 for PB (Malutan et al., 2008)), the degree of substitution (DS) for lignin esters was estimated. It was found that the DS of lignin-He was much lower than the other three types of ester. This is probably because the longer chain anhydride

shows much lower reactivity (Doczekalska et al., 2014). Besides, precipitation and washing using aqueous ethanol solution during the product recovery might lead to some weight loss of the lignin-He.

The M_w of the lignin esters was determined by SEC with MALS/UV/RI detection using the obtained DN/DC values (Table 1). Due to solubility issues, the M_w of the starting IN and PB lignin was not determined. According to previous research, PB lignin (210,000 g/mol) (Pohjanlehto et al., 2014) has a higher M_w than IN lignin (93,700 g/mol) (Luo et al., 2016). This probably accounts for the higher M_w of PB esters than IN esters. As expected, the M_w increased with the increasing length of the ester carbon chains for both IN and PB lignins. Similarly, Dehne et al. (2016) found the M_w was higher for lignin esters (C_2 - C_4) with longer substituent.

FTIR spectroscopy was performed to determine the functionality of the various lignins and lignin esters (Fig. 1). Both IN and PB lignin show a broad OH stretching vibration around 3400 cm^{-1} . Upon esterification, the OH band almost completely disappears. The intensity of bands at 2966 cm^{-1} (CH_3 -valence vibrations) and 2937 - 2876 cm^{-1} (CH_2 -valence vibrations) (Thielemans and Wool, 2005) increased as the alkanoate chain length increased. A major absorption band at 1762 - 1740 cm^{-1} ($\text{C}=\text{O}$ stretching vibration) appears. The bands at 1590 and 1510 cm^{-1} correspond to aromatic skeletal vibrations in lignin (Hult et al., 2013). These changes strongly support the fact that lignin esterification was successful.

3.2. Thermal analysis of esterified lignin

The T_g or softening temperature of all the lignin samples was determined by TMA

due to its sensitivity, especially for lignin, and ease of use. Changes of sample height as a function of temperature under compression mode are exhibited in Fig. 2, and the T_g was determined from the onset point of softening (indicated by arrow). Original IN and PB lignin show a T_g of 166 and 170 °C, respectively, which agrees with the T_g values detected for the same industrial lignins by TMA in previous study (Li and McDonald, 2014). Original lignin has a rather high T_g , probably because the condensed rigid phenolic moieties and strong intermolecular hydrogen bonding interactions restrict the thermal mobility of lignin molecules (Gordobil et al., 2015). Upon esterification, the T_g dramatically decreased to 124 and 142 °C for IN-Ac and PB-Ac, and further decreased with the increasing chain length, which is attributed to the reduction of hydrogen bonding and increase in free volume by introducing bulky alkanoate substituents and thus increasing molecular mobility. Work by Glasser and Jain (1993) as well as Fox and McDonald (2010) indicated the T_g of organosolv, softwood Kraft, and corn stover lignin esters decreased linearly as the number of carbon atoms in the ester substituent increases from C_2 to C_4 . A similar trend was recognized in this study with both lignin types from unmodified lignin to Bu (Fig. 3), and PB lignin showed a linear decreasing trend up to He, while the T_g of IN-He was just off this linear relationship.

3.3. Contact angle measurements of esterified lignin

The CA of the original and esterified lignins as well as the plastics in water were determined to estimate their hydrophobicity and polarity. It was found that after approximately 10 s the CA of all the samples reached equilibrium (Fig. S1), therefore the CA after 10 s was applied as equilibrium CA (Table 2) for comparison. The

equilibrium CA in water decreased in the following order: lignin-He > lignin-Bu > lignin-Pr > lignin-Ac > original lignin. The CA of lignin-He almost reached 90 °. Both IN and PB esters showed a similar trend. The results indicate the hydrophobicity of lignin was significantly promoted by esterification, and it was positively related to the carbon chain length attached. Previous study also showed the acetylated Kraft lignin presented higher hydrophobicity than Kraft lignin (Gordobil et al., 2015). Using the CA values of both water and diiodomethane, the surface energies of lignin esters and matrices were estimated (Table 2). According to the harmonic approach, it can be concluded that the original IN lignin has a total surface energy (γ) of 71 mJ/m² with a high polar fraction (γ^p , 24 mJ/m²). Acetylation resulted in a decrease of γ (55 mJ/m²) with a much lower γ^p (9 mJ/m²), and the γ^p was further reduced with longer carbon chain length substituents, as expected. The PB lignin shows the same trend. In a similar fashion, the geometric method also shows the γ^p of esterified lignin was much lower than the original lignin. The decrease in polarity of esterified lignin is expected to promote compatibility with the polymeric matrix. In terms of matrices, the γ of PP (41 mJ/m²) is consistent with reported literature values (36-40 mJ/m²) (Shimizu and Demarquette, 2000). The small γ^p (2 mJ/m²) for PP was probably caused by additives or contaminants present on the surface of film during processing. As expected, the γ of PHBV (47 mJ/m²) as well as its γ^p (6 mJ/m²) is higher than that of PP. In other words, PHBV is slightly more polar than PP.

3.4. Tensile properties of the blends

The tensile properties of the pure plastics and lignin/plastic blends were determined

and the results are shown in Fig. 4. The Young's modulus of both PHBV and PP matrices was enhanced by incorporation of 30% lignin, while tensile strength and elongation at break were impaired. For example, the addition of IN to PHBV gave a resulting decrease in strength and elongation by 28% and 40%, respectively. This could be related to the amorphous nature and inherent mechanical properties of lignin, bearing a high modulus and low toughness. The poor compatibility of unmodified lignin with the matrix polymer could explain the loss in strength (Pouteau et al., 2004).

PP based blends showed no significant change in tensile strength as a result of lignin esterification, except for a slight increase in IN-Ac/PP sample. Both the Young's modulus and elongation at break were shown to decrease upon esterification, indicating that esterification is not an effective strategy to amend the tensile properties of the IN/PP blends. As incorporation of IN esters into PP did not bring satisfying mechanical performance as expected, we decided to have a more detailed examination of PHBV based blends. A point to mention is that PHBV is slightly more polar than PP and thus expected to be more compatible with lignin and their esters.

The effect of lignin esterification on the tensile properties of resulting PHBV blends was quite different from that of PP. In the PHBV based blends, a gradual increase in tensile strength was observed from around 20 to 25 MPa from Ac to Bu substituents, except for PB-He/PHBV sample. Meanwhile, tensile elongation of esterified lignin/PHBV blends was shown to increase by approximately 26% from Ac to He substituents. This can probably be ascribed to an enhanced miscibility and better interaction between the lignin ester (less polar) particles within the PHBV matrix.

Moreover, it is conceivable that a better entanglement of the lignin with PHBV was achieved with increasing ester chain length. Altogether, these factors contributed to an enhanced stress-transfer between lignin and the matrix and therefore resulting in a higher tensile strength yield point. The PB-Ac/PHBV sample showed a higher Young's modulus (302 MPa) than the unmodified PB/PHBV (254 MPa). For the IN and PB esters, the Young's modulus decreased from Ac to He substituents. For example, Young's modulus for IN-Ac/PHBV (310 MPa) decreased by 25% for the IN-He/PHBV . The reduction in stiffness coincides with the results found by Dehne et al. (2016). Generally, esterification of lignin prior to blending with PHBV improved the miscibility and compatibility, however, the long chain lignin esters (Pr, Bu, and He) behaved as internal plasticizers leading to improved ductility and reduced stiffness.

3.5. Water absorption test of the blends

During 45 days of immersion, the water absorption (WA) of samples was evaluated by the percentage weight gain (Fig. S2). As expected, pure PHBV (0.58%) and PP (0.07%) as a reference showed a low WA after immersion (Table 3). In contrast to that, blends made from lignin display a higher WA (2.39%, 2.29% and 1.15% for IN/PHBV, PB/PHBV and IN/PP, respectively). This can be ascribed to the OH groups present in lignin rendering it more hydrophilic than pure PHBV or PP; moreover, the amorphous structure of lignin could be assumed to loosen the network structure of the blend in comparison to pure plastics (Dehne et al., 2016). Upon esterification, a significant reduction of WA can be observed for the esterified lignin/plastic blends. For example, the WA of both PHBV and PP based blends decreased by about 50% after acetylation of

lignin. WA decreased with increasing length of the lignin ester carbon chain, indicating a progressively more hydrophobic character of the lignin, which was also supported by the results of contact angle test. However, the IN-He was the exception, which was likely related to the lower density of IN-He based blends. Diffusion coefficients (D_f) was determined using Fick's law of diffusion model by plotting WA versus time^{1/2} with a 2nd order polynomial curve fit (Fabiya et al., 2011). An increase in D_f by lignin esterification (Table 3) indicated the time taken to reach the equilibrium MC was shorter for esterified lignin based blends.

3.6. DSC analysis of the blends

DSC thermograms of the cooling and second heating scans of pure PHBV and IN/PHBV blends are shown in Fig. 5, and the corresponding parameters of thermal transitions including melting and crystallization are summarized in Table 4. The melt crystallization peak temperature (T_c) of PHBV decreased from 91 °C to 71 °C with the addition of 30% lignin, suggesting lignin hindered the crystallization process of PHBV. A possible explanation is that lignin restricts the motion of PHBV chains due to the hydrogen-bonding interactions between the OH groups in lignin and ester groups in PHBV (Wang et al., 2015). Meanwhile, the cold crystallization (T_{cc}) peak of PHBV originating from the rearrangement of amorphous regions into a crystalline phase arose in second heating scan in lignin/PHBV composites. Compared to original IN lignin, the T_c peak of IN-Ac, IN-Pr, and IN-Bu based composites was suppressed and became much broader and less apparent, and the T_{cc} shifted to higher temperature, indicating a reduction in the crystallization kinetics. However, the IN-He/PHBV thermogram was a

little different from the other lignin ester blends, showing a higher T_c (77 °C). The enthalpy of PHBV during crystallization (ΔH_c) was reduced by the addition of lignin and further decreased by using the lignin esters.

In the subsequent reheating scan, only one single melting peak at 170 °C was observed in pure PHBV, while incorporation of 30% IN resulted in dual melting peaks, with a low-temperature peak (T_{m1} , 163 °C) that appeared on the shoulder of the high-temperature peak (T_{m2} , 172 °C). In a previous study, addition of 10% IN into PHBV showed that the low-temperature peak was the main peak (Luo et al., 2016). This means that the T_{m2} peak become larger with the addition of lignin, while the T_{m1} peak is suppressed. A similar phenomenon has been observed in alkaline lignin/PHBV blends by Wang et al. (2015), and explained as T_{m1} and T_{m2} are related to the homogeneous and heterogeneous nucleation of PHBV, respectively. Lignin enhanced the nucleation of PHBV. Comparing the ester substituents among each other, IN-Ac, IN-Pr, and IN-Bu based PHBV blends showed similar T_{m1} (158 °C) and T_{m2} (170 °C) values. While, IN-He/PHBV gave higher values of T_{m1} at 167 °C and T_{m2} at 174 °C. The degree of crystallinity (X_c %) was decreased slightly by the addition of lignin, however, there was no significant difference between adding lignin esters to PHBV and pure PHBV. Incorporation of original and esterified PB lignin into PHBV presented a similar effect on the thermal behaviours with IN lignin (Figure S3), whilst addition of IN lignin affected PP matrix in a different way. IN/PP blends showed a slight increase of 8 °C in T_c compared to pure PP (Fig. 6). This finding agrees with the literature, and most likely caused by the nucleating effect of lignin on PP resulting in a reduction of supercooling

for crystallization and thus the crystallization occurred at higher temperature (Maldhure et al., 2011). The decrease in ΔH_c of PP from 102 J/g to 72 J/g by lignin addition indicates that the regular mode of crystallization was interfered when lignin was present. Comparing the lignin ester blends among each other, the T_c increased marginally from IN-Ac/PP (121 °C) to IN-Pr/PP (123 °C), and then decreased to 119 °C at IN-He/PP.3.7. Glass transition of the composites by TMA

Although the T_g of PHBV is detectable in the DSC melting scan, the T_g of lignin is often difficult to detect due to the complex structure. Besides, the T_g for PP based blends is not visible in the DSC thermograms. Therefore, TMA was used to detect the T_g of lignin/PHBV and lignin/PP blends (Table 4) because of its higher sensitivity, especially for lignin, than DSC. The obtained TMA thermograms for blends from PHBV with original or esterified IN are given in Fig. 7. IN/PHBV showed a T_g of 40 °C, which is slightly higher than that of pure PHBV (35 °C). The T_g of IN in IN/PHBV could not be determined due to an overlapping PHBV melt endotherm. For IN-Ac/PHBV, a two-stage transition was observed before the melting of PHBV, with the low-temperature T_g around 54 °C and the high-temperature T_g around 124 °C that matched the softening point of IN-Ac. It is interesting to see in IN-Pr/PHBV and IN-Bu/PHBV, instead of a two-step transition, there was only one transition starting from slightly higher temperature than IN-Ac/PHBV. This was probably due to the T_g of IN-Pr (95 °C) and IN-Bu (79 °C) was in close proximity with that of PHBV, thus not exhibiting a clear boundary between the two transitions. IN-He/PHBV exhibited a one-step transition originating from an overlap of the respective component T_g values.

Compared to other lignin esters, the IN-He/PHBV blend showed a depression in T_g . Similarly, Pawar et al. (2016) observed a decrease in T_g in blend of lignin stearate (C_{18}) and PS compared to unmodified lignin blend, which was caused by the plasticization effect of long chain fatty acid substituted lignin.

Compared with esterified IN, incorporation of esterified PB into PHBV had similar effect on T_g but there were some differences. A small step around 180 °C was observed after the main transition of PHBV melting in PB/PHBV (Fig. S4), and probably caused by the softening of original PB. Additionally, the two-stage T_g appeared in PB-Pr/PHBV (Fig. S4), suggesting that the blend was not fully miscible in spite of an improved compatibility by lignin esterification. The depression of T_g in PB-He/PHBV again indicated the plasticization potential of long chain length substituents. For PP based blends, the effect of incorporating IN and IN esters on T_g was similar to that of PHBV. Two apparent T_g s (40 and 122 °C) were present in the IN-Ac/PP blend (Fig. 8). Compared to unmodified lignin blends, an increase in T_g and a depression in T_m for IN-Pr/PHBV, IN-Bu/PHBV, PB-Pr/PHBV and PB-Bu/PHBV were observed, suggesting that the lignin esters were closely associated with the plastic matrix, and exhibited partial miscibility. A similar phenomenon has been seen in lignin/poly(vinyl alcohol) polymer blends (Kadla and Kubo, 2004).

3.8. Spherulite morphology

To investigate further the effect of original and esterified lignin on the crystalline morphology of the plastics, HS-POM was applied to observe the structure of spherulites during the isothermal crystallization process. The PP spherulites were too small to be

observed at 100 $\times$ magnification and therefore only the PHBV based blends were subjected to HS-POM analysis (Fig. 9). PHBV spherulites clearly exhibited a typical Maltese cross birefringent crystal pattern (Wei and McDonald, 2015). Pure PHBV had a small number of rather large-sized spherulites (average radius about 700 μm) with clear straight boundaries, because there were large spaces for the spherulites to grow before impinging on each other (Wang et al., 2015). With the addition of 30% lignin, the lignin was embedded in the PHBV spherulites, which interfered with their integrity. It was noticeable that the agglomeration of lignin occurred in both IN/PHBV and PB/PHBV blends. By substituting the OH groups in lignin, an improved compatibility and a more uniform dispersion of IN-Ac and PB-Ac in the PHBV spherulite was observed. By adding PB-Ac, the number of spherulites increased and the radius of PHBV spherulites decreased to 74 μm , while the spherulites in IN-Ac/PHBV were large (430 μm). Incorporation of IN-Pr into PHBV obscured the boundary between spherulites (Fig. 9d), and the number of spherulites increased and their size was reduced to about 35 μm . Therefore, it could be expected that the IN-Pr/PHBV sample will be less brittle than the IN/PHBV due to smaller crystals which minimizes crack formation between the spherulites. Unexpectedly, the PB-Pr/PHBV sample showed no visible spherulite morphology (Fig. 9g) and the same phenomenon appeared in PB-Bu, PB-He, and IN-He composites. This was likely due to the long chain lignin esters were more evenly distributed within the plastic matrix, thus interfering with formation of PHBV spherulite crystals that could be observed. Analysis of the HS-POM and DSC data, suggests that the presence of lignin esters induced changes in the nucleation density and spherulite

growth geometry in PHBV but not in the degree of crystallinity.

3.9. Rheological properties of the composites

Studying the melt rheological properties of polymer blends is essential to understand the melt processing behaviour of these materials and if they can readily be processed (Mousavioun et al., 2013). Dynamic parallel plate rheometry is often used to study these systems. Figs. 10 and 11 shows the dynamic elastic (G') and viscous (or loss, G'') moduli of IN/PHBV and PB/PHBV blends under isothermal conditions at 175 °C, respectively. At low frequency (ω), the G'' was higher than G' for pure PHBV and PP, indicating a viscous response predominated in the molten state. Incorporation of 30% lignin in plastic increased G' and G'' and narrowed the gap between them at low ω , making the resulting blend melt more solid-like, due to the rigid character of lignin. Esterification of lignin had a distinct effect on the dynamic rheological behaviour of lignin/plastic melts. For PHBV based blends, acetylation of lignin apparently promoted both G' and G'' compared to original lignin/PHBV samples, probably attributed to the better interaction between lignin and PHBV. Comparing the lignin esters among each other, both G' and G'' decreased with an increase in ester chain length in the IN/PHBV blends (Fig. 10). This is very likely caused by the plasticizing effect of longer chain esters, reflected by the lower T_g values. It is interesting to see that unlike other samples which had higher G'' than G' at low ω , the G' of IN-Pr/PHBV was higher than G'' . This is likely due to the better compatibility between two phases in IN-Pr/PHBV compared to IN/PHBV and IN-Ac/PHBV, and the less plasticization effect as compared to the IN-Pr or IN-He. Thus the motion of polymer chains was restrained and the blend melt

exhibited a solid-like behaviour at low ω .

In terms of PB/PHBV blends (Fig. 11), lignin esterification resulted in slightly higher G' than G'' in the lower ω region, suggesting an improved elastic behaviour due to an increased interaction. The PB-Pr/PHBV melt gave the highest G' and G'' values. However, for IN/PP melts, all the samples showed a viscous behavior in low ω region with higher G'' than G' (Fig. S5). Lignin esterification led to a reduction in both G'' and G' in the blend melt, and were shown to decrease with an increasing ester chain length. This trend is consistent with the change in T_g of lignin esters, indicating that the reduced rigidity of lignin, rather than the increased interaction between two phases, dominated the rheological properties of the IN/PP blends. The frequency at the G' and G'' crossover point (ω_c) for IN/PHBV, PB/PHBV, and IN/PP was observed, respectively at 144, 134, and 12 rad/s, which indicates a transition from viscous to elastic behaviour. Beyond this intersection point, G' became larger than G'' , resulting in an insufficient time to allow polymer chains to fully relax and respond at higher ω . The ω_c shifted toward higher ω values of 209, 160, 48 rad/s for IN-Ac/PHBV, PB-Ac/PHBV and IN-Ac/PP samples, respectively. Comparing different lignin esters within each blend melt system, the highest ω_c appeared respectively in IN-Ac/PHBV, PB-Ac/PHBV, and IN-Pr/PP.

4. Conclusion

Two industrial lignins (IN and PB) were successfully esterified using carboxylic acid anhydrides with varying chain length from C_2 to C_6 . The T_g of lignin was found to decrease linearly as the number of carbon atoms in the ester substituent increases from

C₂ to C₆. The M_w and hydrophobicity of lignin tended to be higher for longer ester substituents while polarity tended to be lower. The lignin ester chain length was shown to influence the PHBV or PP blend tensile properties, water absorption, thermal and dynamic rheological behavior as well as spherulite morphology, while the effect of lignin source (IN and PB) was not significant. In lignin ester/PHBV blends, the tensile strength and elongation at break progressively increased with an increase in ester chain length, while no improvement was seen in the lignin ester/PP blends. The decrease in the polarity of esterified lignins promoted better interactions with PHBV. Esterification of lignin also reduced the water absorption of the blends and generally longer chain ester showed lower water absorption, which is consistent with the contact angle results. The presence of lignin esters in the blend melt induced suppression of the melt crystallization peak and occurrence of the cold crystallization in PHBV blends, increase of melt crystallization peak in PP based system, while not changing the degree of crystallinity. The addition of certain lignin esters (PB-Ac or IN-Pr) in PHBV increased the number of spherulites and reduced their size. Long chain lignin esters were more evenly dispersed in the plastic matrix and interfered with spherulite growth. Although esterified lignins exhibit better compatibility with the plastic matrix than unmodified lignin, the presence of two T_gs indicated that they were partially miscible. Lignin hexanoate esters were shown to behave as a plasticizer. These results clearly show that industrial lignins acylated with C₂-C₆ anhydrides can be applied as green fillers for thermoplastics with better compatibility .

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Figure Captions

Fig. 1. FTIR spectra of original and esterified (Ac, Pr, Bu, and He) (a) IN and (b) PB lignin.

Fig. 2. TMA thermograms of original and esterified (Ac, Pr, Bu and He) (a) IN and (b) PB lignins.

Fig. 3. Relationship between T_g and number of C atoms in ester substituent for the esterified IN and PB lignins.

Fig. 4. (a) Tensile strength, (b) Young's modulus, and (c) elongation at break of plastic (PHBV and PP), lignin/plastic, and esterified (Ac, Pr, Bu and He) lignin/plastic blends.

Fig. 5. DSC thermograms of PHBV, IN/PHBV, and esterified (Ac, Pr, Bu and He) IN/PHBV blends during the cooling (top set) and second heating (bottom set) scans.

Fig. 6. DSC thermograms of PP, IN/PP, and esterified (Ac, Pr, Bu and He) IN/PP blends during the cooling (top set) and second heating (bottom set) scans.

Fig. 7. TMA thermograms of PHBV, IN/PHBV, and esterified (Ac, Pr, Bu and He) IN/PHBV blends. Note: arrows point to softening temperature (T_g).

Fig. 8. TMA thermograms of PP, IN/PP, and esterified (Ac, Pr, Bu, He) IN/PP blends.

Fig. 9. HS-POM micrographs of (a) PHBV, (b) IN/PHBV, (c) IN-Ac/PHBV, (d) IN-Pr/PHBV, (e) PB/PHBV, (f) PB-Ac/PHBV, and (g) PB-Pr/PHBV crystallized at their respective T_c . Scale bar: 200 μm .

Fig. 10. Elastic (G') and viscous moduli (G'') of PHBV, IN/PHBV, and esterified (Ac, Pr, Bu, He) IN/PHBV blend melts with frequency (ω) at 175 °C.

Fig. 11. Elastic (G') and viscous moduli (G'') of PB/PHBV and esterified (Ac, Pr, Bu,

719 He) PB/PHBV blend melts with frequency (ω) at 175 °C.

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Table 1. Weight percentage gain (WPG), degree of substitution (DS), refractive index increment (DN/DC), and weight average molar mass (M_w) of IN and PB lignin esters.

	IN-Ac	IN-Pr	IN-Bu	IN-He	PB-Ac	PB-Pr	PB-Bu	PB-He
WPG (%)	24	29	46	33	17	28	34	30
DS	0.73	0.67	0.83	0.43	0.54	0.66	0.64	0.41
DN/DC	0.148	0.137	0.141	0.133	0.140	0.144	0.139	0.115
M_w (10^3 g/mol)	264	505	1,020	2,390	820	907	1,300	2,860

Table 2. Equilibrium contact angles of PP, PHBV, IN and PB lignins, and lignin esters in water (H₂O) and diiodomethane (DIM), and surface energies (γ) and its dispersive (γ^d) and polar (γ^p) components calculated with the Harmonic and Geometric approaches.

Sample	Equilibrium contact angle (°)		Surface energy (mJ/m ²)					
	H ₂ O DIM		Harmonic			Geometric		
			γ	γ^d	γ^p	γ	γ^d	γ^p
PHBV	85.8	38.0	47.0	41.1	5.9	41.3	39.4	1.9
PP	97.2	42.2	41.1	39.1	2.0	38.5	38.3	0.2
IN	44.1	21.7	71.4	47.3	24.1	62.6	42.3	20.3
IN-Ac	76.4	25.7	55.1	46.0	9.1	47.8	43.9	3.9
IN-Pr	80.4	25.0	53.6	46.3	7.3	47.1	44.6	2.5
IN-Bu	84.9	25.4	51.7	46.1	5.6	46.3	45.0	1.4
IN-He	88.6	30.6	48.6	44.2	4.4	44.1	43.2	0.9
PB	56.2	27.6	63.9	45.3	18.6	55.1	41.2	14.0
PB-Ac	67.2	25.9	59.1	45.9	13.2	50.7	42.9	7.8
PB-Pr	73.5	27.3	55.8	45.4	10.4	48.1	43.0	5.1
PB-Bu	80.5	32.9	51.0	43.3	7.7	44.3	41.3	3.0
PB-He	86.6	36.6	47.2	41.7	5.6	41.8	40.2	1.6

Table 3. Water absorption (WA), diffusion coefficient (D_f) and density of plastic (PHBV and PP), lignin/plastic, and esterified (Ac, Pr, Bu and He) lignin/plastic blends. Values in parentheses are standard deviations.

Sample	WA (%)	D_f ($10^{-13} \text{ m}^2/\text{s}$)	Density (g/cm^3)
PHBV	0.58 (0.03)	2.66	1.17 (0.01)
IN/PHBV	2.39 (0.05)	2.02	1.20 (0.02)
IN-Ac/PHBV	1.02 (0.05)	3.06	1.18 (0.02)
IN-Pr/PHBV	0.83 (0.02)	3.44	1.18 (0.00)
IN-Bu/PHBV	0.71 (0.04)	3.20	1.17 (0.02)
IN-He/PHBV	0.93 (0.08)	2.66	1.16 (0.00)
PB/PHBV	2.29 (0.45)	1.64	1.19 (0.01)
PB-Ac/PHBV	1.20 (0.09)	2.35	1.17 (0.01)
PB-Pr/PHBV	1.01 (0.13)	2.53	1.17 (0.00)
PB-Bu/PHBV	0.80 (0.01)	2.68	1.17 (0.01)
PB-He/PHBV	0.70 (0.00)	2.87	1.17 (0.02)
PP	0.07 (0.00)	1.45	0.88 (0.02)
IN/PP	1.15 (0.08)	2.43	0.97 (0.01)
IN-Ac/PP	0.56 (0.05)	2.85	0.97 (0.01)
IN-Pr/PP	0.53 (0.03)	4.05	0.96 (0.01)
IN-Bu/PP	0.41 (0.08)	3.16	0.95 (0.01)
IN-He/PP	0.68 (0.09)	2.68	0.94 (0.01)

Table 4. Calorimetric and TMA data for the plastics (PHBV and PP), lignin/plastic, and esterified (Ac, Pr, Bu and He) lignin/plastic blends.

Sample	DSC						TMA
	T _{m1} (°C)	T _{m2} (°C)	X _c (%)	T _c (°C)	T _{cc} (°C)	ΔH _c (J/g)	T _g (°C)
PHBV	—	170	64.3	91	—	74	35
IN/PHBV	163	172	62.3	71	53	47	40
IN-Ac/PHBV	160	170	64.2	60	58	34	54 (120)*
IN-Pr/PHBV	158	170	64.8	66	65	33	59
IN-Bu/PHBV	158	170	64.8	71	68	34	61
IN-He/PHBV	167	174	64.5	77	67	49	48
PB/PHBV	165	172	62.4	80 (62)	—	66	55 (180)
PB-Ac/PHBV	165	172	65.6	75	49	55	52
PB-Pr/PHBV	163	171	66.1	73	60	33	56 (105)
PB-Bu/PHBV	163	172	65.2	77	58	38	61
PB-He/PHBV	168	174	62.9	81	61	55	52
PP	161	—	48.4	113	—	102	42
IN/PP	163	—	49.9	123	—	72	48
IN-Ac/PP	163	—	50.2	121	—	72	40 (122)
IN-Pr/PP	163	—	51.0	123	—	74	55
IN-Bu/PP	162	—	48.2	119	—	70	57
IN-He/PP	162	—	49.5	119	—	71	44

*Values in parentheses refer to the other temperature in a dual transition.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11