



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



Shupin Luo<sup>a,b</sup>, Jinzhen Cao<sup>a</sup>, Armando G. McDonald<sup>b,\*</sup>

<sup>a</sup> MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Qinghua East Road 35, Haidian, 100083 Beijing, China

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

## ARTICLE INFO

### Article history:

Received 31 August 2016

Received in revised form

17 November 2016

Accepted 18 December 2016

### Keywords:

Lignin

Esterification

Blend

Tensile property

Thermal transition

Rheology

## 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 C<sub>2</sub>–C<sub>6</sub> anhydrides esterified lignins (molar mass, glass transition temperature (T<sub>g</sub>), 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 behaviour. 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<sub>g</sub> depression and smaller dynamic elastic and viscous moduli than the other lignin esters, suggesting that it acted as a plasticizer.

© 2016 Elsevier B.V. All rights reserved.

## 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

\* Corresponding author.

E-mail address: [armandm@uidaho.edu](mailto:armandm@uidaho.edu) (A.G. McDonald).

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

The compatibility between lignin and polymers can be enhanced by several strategies, such as addition of a compatibilizer (Reza Barzegari et al., 2012), derivatizing the OH groups by esterification or etherification (Laurichesse and Averous, 2014), cross-linking or grafting (Luo et al., 2016), or using low molecular weight lignin (Pouteau et al., 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, Montiel-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, physicochemical 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 ( $\epsilon$ -caprolactone) (PCL) systems, among which  $C_4$  and  $C_5$  anhydrides esterified lignin exhibited better miscibility with PCL compared to  $C_3$  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 Mead-Westvaco 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/cm<sup>3</sup> and a melt flow index of 4.0 g/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

Download English Version:

<https://daneshyari.com/en/article/5762291>

Download Persian Version:

<https://daneshyari.com/article/5762291>

[Daneshyari.com](https://daneshyari.com)