



De-polymerization of industrial lignins to improve the thermo-oxidative stability of polyolefins

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ABSTRACT

De-polymerized lignins with greatly reduced molecular weight (< 1700 g/mol based on GPC-UV) and increased reactivity were prepared from two types of technical lignin, kraft and hydrolysis, using a proprietary de-polymerization technique. The resulting de-polymerized kraft and hydrolysis lignins (DKL and DHL) have increased aromatic hydroxyl content and decreased aliphatic content, and thus decreased total hydroxyl content and decreased polarity compared to the original lignins. Both types of de-polymerized lignin tested showed significant improvement in the thermo-oxidative stability of the polyolefins as measured by oxidation induction time, activation energy, initial degradation temperature and maximum degradation temperature. The de-polymerized lignins had up to five times more antioxidant activity than the crude lignins as a result of their higher phenolic content, improved hydrophobicity, and lower molecular weight. De-polymerized KL (DKL) had the strongest antioxidant effects, followed by de-polymerized HL (DHL), KL and HL: this correlates with their phenolic content. Mechanical tests show that incorporating de-polymerized lignins did not degrade the mechanical properties of the polymers. These properties are to be investigated further.

1. Introduction

Lignin is the largest renewable resource for aromatic compounds (Ragauskas et al., 2014). One of the primary constituents of plant cell walls, lignin is an amorphous polymer of three main phenyl propanoid units connected dominantly by ether linkages (Chakar and Ragauskas, 2004; Xu et al., 2014). As of 2013, global production of kraft lignin (commonly abbreviated as KL) in black liquor—a waste product from the kraft pulping process—was approximately 50 million tonnes per annum. Most KL is used as a low-cost fuel for chemical recovery and heat generation in pulp mills, with less than 5% utilized in chemicals or other products (Laurichesse and Avérous, 2014). Hydrolysis lignin (abbreviated HL) is a by-product of the hydrolysis of lignocellulosic biomass for cellulosic ethanol production, and is used mainly as a low-cost fuel for heat generation.

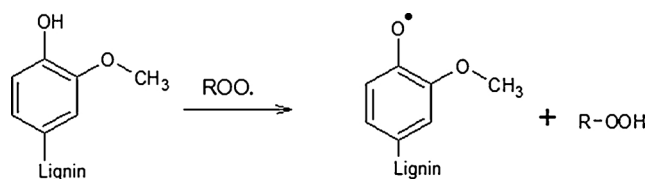
With the growth of pulp and paper mills, and biorefineries for biomass-derived fuels and chemicals, the production of lignin in downstream will further increase (Ragauskas et al., 2014). As a result, there is a growing need to develop value-added products from lignin, thus diversifying the product portfolios of the mills, biorefineries and cellulosic ethanol plants, and helping make the processes more competitive economically.

Due to its high aliphatic hydroxyl, aromatic hydroxyl and carboxyl content, lignin has been investigated as an alternative to commercial reactants in the production of polyurethane foam, adhesive, epoxy resins and adipic acid (Ferdosian et al., 2014; Huang et al., 2014; Mahmood et al., 2015; Vardon et al., 2015). In the field of polymers or polymer composites, lignin has been incorporated in UV and thermal stabilizers, plasticizers, fillers, and fire retardants (Laurichesse and Avérous, 2014; Stewart, 2008). A number of studies have suggested that lignin could be a promising resource for bio-based antioxidants, due to its structural similarity to the hindered phenolic antioxidants traditionally used in polymer stabilization (Dizhbite et al., 2004; Egüés et al., 2012; García et al., 2010; Lu et al., 2012).

Industrial antioxidants are additives used in polymers to prevent thermo-oxidative degradation during the polymers' processing and lifetime. Commercial stabilizing packages include a combination of hindered phenol-based antioxidants and phosphorous-based melt stabilizers. These phenolic antioxidants are called "hindered" because the reactive hydroxyl group is shielded by hydrocarbon units connected to each neighboring atom in the benzene ring. The bulky groups in ortho positions push the OH group to donate the H, trapping the initial free radicals derived from the oxidation reactions. The antioxidant molecule resonance stabilizes itself into stable phenoxy radicals, preventing the

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Scheme 1. Trapping of peroxy radicals by lignin.

Table 1
Mass fraction of different constituent of the crude lignins.

Component	Mass fraction (wt%)	
	KL	HL
Lignin	97–98	56.7
Carbohydrates	0	29.8
Ash	0.57	1.2
Others	1–2	12.3

initiation of new radicals (Preedy and Watson, 2007; Tolinski, 2015). Similarly, as shown in Scheme 1, lignin's inherent hindered phenolic structure enables it to work as a free radical scavenging antioxidant, as demonstrated by the 2, 2-diphenyl-1-picrylhydrazyl (DPPH) method (Dizhbite et al., 2004; Egüés et al., 2012; García et al., 2010; Lu et al., 2012).

Most previous works concerning the effects of lignin on polymer stabilization (Alexy et al., 2000; Canetti et al., 2006; Gregorová et al., 2005; Szalay and Johnson, n.d.; Levon et al., 1987; Pouteau et al., 2003; Pucciariello et al., 2004; Yue et al., 2012) utilized high purity lignin extracted from plants through organic solvents or steam explosion. The properties and structures of lignins vary greatly on the source, though, and there is a scarcity of literature on the effects of technical lignins as a thermo-oxidative stabilizer, particularly at a low level. The benefits of adding lignins to polymers are twofold: (1) lignins are less expensive than commercial antioxidants and neat polymers, and (2) it is expected that a polymer-lignin bio-blend would be more biodegradable than a neat polymer (Domenek et al., 2013; Kosikova et al., 1993; Mikulasova et al., 2001).

However, the large molecular weight and polar molecular structure of lignin leads to low reactivity and poor compatibility with the non-polar polymer matrix and would result in the deterioration of the polymer's mechanical properties (Alexy et al., 2000; Duval and Lawoko, 2014; Piña et al., 2015; Pouteau et al., 2003; Pucciariello et al., 2004).

Table 2
Weight and number average molecular weight and polydispersity index (PDI) of DKL and DHL.

Type of lignin (acetylated)	M _w (g/mol)	M _n (g/mol)	PDI ^a
DKL	1517	965	1.57
DHL	1639	502	3.26

^a Polydispersity index (=M_w/M_n).

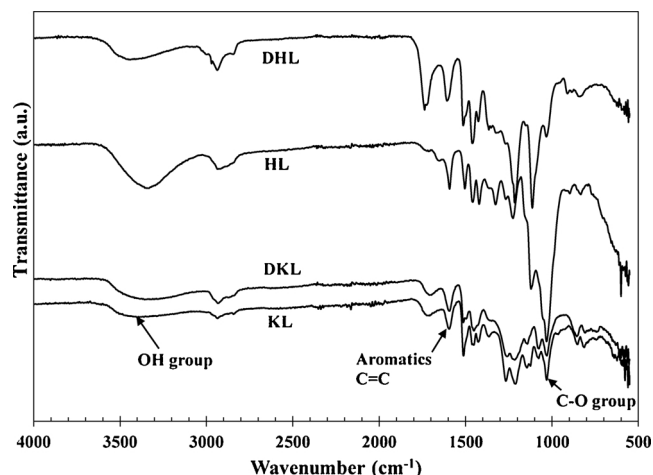
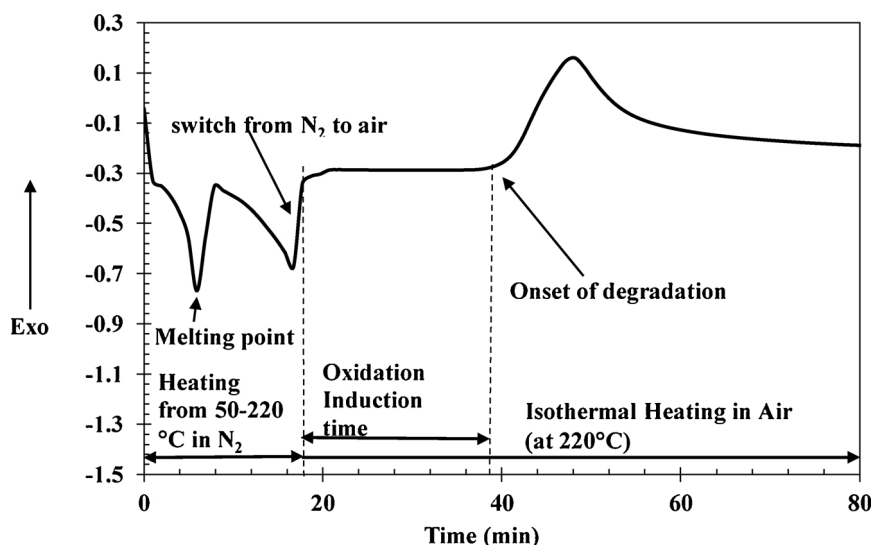


Fig. 1. FTIR spectra of 4 kinds of lignins.

The compatibility of lignin with the polymer matrix could be enhanced through esterification or grafting techniques (Dehne et al., 2016; Sailaja, 2005; Sailaja and Deepthi, 2010; Ye et al., 2016), but esterification decreases the phenolic content of lignin and grafting adds cost to the process of lignin valorization.

Since the phenyl propanoid units in lignin are connected by ether linkages, a different method from those previously mentioned is possible: the breakdown of these ether linkages between the phenyl propanoid units in lignin through de-polymerization. This could be a low cost way of increasing the phenolic content of the lignin, potentially improving its antioxidant property. De-polymerization also has the potential of reducing the hydrophilicity of crude lignins by decreasing the aliphatic hydroxyl content. Past research comparing the antioxidant activity of lignin from various sources indicated that the antioxidant activity of the lignin increased with decreasing molecular weight,



Scheme 2. Schematic illustration of a typical DSC thermogram of oxidation induction time measurement of polymer-lignin samples.

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