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Correlations of the Antioxidant Properties of Softwood Kraft Lignin Fractions with the Thermal Stability of Its Blends with Polyethylene

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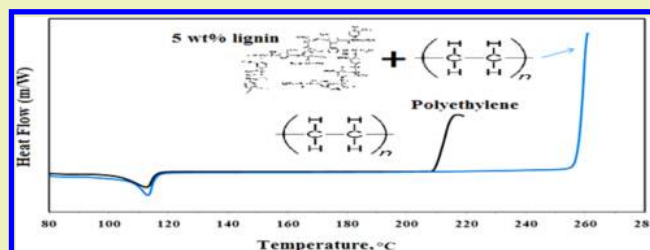
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ABSTRACT: Since technical lignins are increasingly considered as additives to polyolefins, an effort is made here to understand the fundamental antioxidant properties of softwood kraft lignin and its fractions on the thermal stability of its blends with polyethylene. Lower molecular weight acetone soluble kraft lignin (ASKL) fractions showed better antioxidant properties than unfractionated and acetone insoluble kraft lignin (AIKL). By selectively methylating the phenolic hydroxyl groups of the lignin and its fractions, it was shown that the lignin had no antioxidant ability. The phenolic OH groups in lignin, therefore, play a vital role toward imparting antioxidant characteristics in it. To further understand the role of lignin during the thermal processing of polyethylene, we measured the oxidation induction temperature (OIT_{temp}) of its blends with softwood kraft lignin and its fractions. Once again, the role of the phenolic OH was found to be extremely important toward the thermal oxidative characteristics of kraft lignin and its fractions. Since acetone soluble softwood kraft lignin contains 54% more phenolic units than its acetone insoluble counterpart, its blends (5 wt %) with polyethylene improved its OIT_{temp} by about 50 °C with no additional increases at higher lignin contents. At elevated processing temperatures, when polyethylene blends of lignin start to degrade, the aromatic nature of the created char reduces its rate of degradation, concomitantly increasing the thermal degradation temperature of polyethylene. This effect was further investigated and details of the relative contributions of the phenolic OH stabilization mechanism to the charring mechanism are discussed.

KEYWORDS: Softwood kraft, Lignin, Methylation, Polyethylene, Oxidative induction temperature, Lignin antioxidant, Thermal stability, DSC, Oxidation, Fractionation, Fractions, Phenolic hydroxyl, Antioxidant, Lignin–polyethylene blends, Thermal stability, OIT_{temp}



INTRODUCTION

Lignin as the second main component of wood is an aromatic biopolymer composed of phenyl propane units of p-hydroxyphenyl (H), Guaiacyl (G), and Syringyl (S). These precursor units are linked to each other in the lignin structure by various ether and C–C bonds.¹ The structure of kraft lignin, derived from the pulping process, is more heterogeneous than native lignin in the wood. Lignin structure and functional groups change during the delignification process.^{2,3} The use of lignin as a filler or reinforcements in thermoplastic materials is not new and dates back to 1960s.⁴ In recent years, lignin has been examined for use in many materials such as resins, adhesives, and polymer blends.^{4–10} Overall, there are significant economic and environmental factors that contribute to lignin's use as a component in synthetic polymer blends. As such, significant efforts are apparent in the literature over the span of the past decade. The availability of technical lignins such as kraft lignin offers more compelling reasons for its use as an alternative to fillers or as a reinforcement or extender component within a variety of synthetic polymer systems.

In general, the presence of the phenolic OH groups within the lignin structure has been documented as being responsible for beneficial effects toward oxidative, thermal, and light stability characteristics when present in polymer blends.^{11,12} These inhibition and UV stabilization effects of lignin have been attributed to its free radical scavenger abilities reducing oxygen radicals and stabilizing oxidation reactions.^{13–18} It is not surprising that such effects vary with the type and origin of the raw lignin, and the isolation and purification protocol as well as the molecular weight distribution, functional group content, its conjugation, heterogeneity, and presence of carbohydrates.^{16,19}

Many synthetic polymers are highly combustible and as such safety requirements are becoming increasingly stringent in terms of their fire resistance performance. For this reason a variety of diverse and efficient additives have been introduced for improving such characteristics. Typical classes of materials

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in use for these purposes are mineral flame retardants (metal hydroxides of aluminum, magnesium, hydroxycarbonates, and zinc borates), halogenated flame retardants, phosphorus-based flame retardants, nitrogen-based flame retardants, silicon-based flame retardants, and nanometric particles.^{20,21}

The effect of lignin-based additives on the thermal stability of polymers has been reported.^{22,23} For example, dioxane lignin has been shown to provide a high amount of char when heated at elevated temperatures under an inert atmosphere. This makes lignin suitable as a flame retardant additive because char is known to reduce the combustion rate of polymeric materials.^{6,24} The effect of lignin on the flame retardant characteristics of polymeric materials has been attempted to be quantified by the use of different methods such as cone calorimetry,²⁵ limiting oxygen index (LOI),⁵ and oxidation induction temperature (OIT_{temp}).²⁶

Due to the significance and complexity of these effects, an effort is made to further understand the underlying science of lignin in such applications. As such, during this work, we fractionated softwood kraft lignin into an acetone soluble (ASKL) and an acetone insoluble fraction (AIKL). The phenolic hydroxyl groups of each fraction and the original unfractionated material were completely and selectively methylated, and their antioxidant abilities were investigated using the DPPH (2,2-diphenyl-1-picrylhydrazyl) method.^{27–29} Furthermore, these materials were examined in detail for their effect on the thermal stability of lignin–polyethylene blends using the oxidative induction temperature (OIT_{temp}) protocol with the aim to correlate these data to the functional chemistry of the lignin.

MATERIALS AND METHODS

Softwood Kraft Lignin and Its Fractions. A sample of softwood (Southern Pine) kraft lignin isolated via the Lignoboost process (Per Tomani 2010)³⁰ was used as the starting material. A continuous delignification process was used (Kamyr digester), and the intensity of the delignification applied was of an approximate H factor ranging from 1000 to 1200. Molecular weights for all samples were measured after acetobromination³¹ using gel permeation chromatography equipped with the HR1 and HRSE columns. Functional groups were determined using quantitative ³¹P NMR. The molecular weight averages for the original sample were determined to be about $M_w = 6000$ g/mol and $M_n = 1500$ g/mol ($M_w/M_n = \text{PDI} = 4$), while the amounts of phenolic and aliphatic hydroxyl groups were determined to be 4.26 and 2.24 mmol/g, respectively. For this work, a medium density polyethylene was used as supplied by Equistar Corp. with a T_g , density, and melt index of 128 °C, 0.930 g/cm³, and 1.2 g/10 min, respectively. The following procedure for fractionating the lignin was followed as per our earlier effort.⁵³

The original dry and water washed kraft lignin was fractionated into two fractions using acetone (1 g/15 mL) at room temperature for 10 h. The dissolved lignin was separated from the residue by filtration. The acetone soluble fraction (ASKL) was then recovered by evaporating the solvent in a rotary evaporator followed by drying in a vacuum oven at room temperature for 12 h. The acetone insoluble fraction (AIKL) was washed with 10 mL/g acetone and then dried in a vacuum oven at room temperature in a manner similar to ASKL. The functional group contents, molecular weights (after acetobromination),³¹ and T_g values of all samples were determined by quantitative ³¹P NMR, gel permeation chromatography (GPC), and DSC, respectively, as described in earlier efforts.^{32,33}

Methylation of Lignin. The phenolic hydroxyl groups of all the original lignin and its fractions were selectively methylated using previously described methods.³⁴ More specifically, the sample was dissolved in 0.8 M NaOH solution (15 mL/g) at room temperature, and then, an appropriate amount of dimethyl sulfate (3 mmol/mmol

of total phenolic OH) was added. The solution was then stirred for 5 min at room temperature, and the mixture was heated to 75 °C for 2 h. The reaction mixture was then acidified (pH 2.5) with 2 M HCl, and the solid precipitate was washed with excess deionized water and freeze-dried. Quantitative ³¹P NMR was used to measure and verify nearly complete methylation. Notably, a green alternative to dimethyl sulfate, namely, dimethyl carbonate, was recently developed in our laboratory for the same purposes.³⁵

Lignin–Polyethylene blends. Lignin and polyethylene (Equistar Corp. with a T_g , density, and melt index of 128 °C, 0.930 g/cm³, and 1.2 g/10 min, respectively) were blended using a mini-extruder (DSM Xplore Micro 15 cm³ Twin Screw Compounder). Approximately 13 g of lignin–polyethylene blends was made at different lignin contents varying from 1% to 25%. The blending temperature of the twin-screw extruder was maintained at 170 °C, and the screw speed was 100 rpm. The mixture was heated and blended for 10 min.

Quantitative ³¹P NMR. ³¹P NMR was carried out using our published procedures.^{36,37} An accurately known amount (40 mg) of a thoroughly dry lignin sample was dissolved in 600 μL of an anhydrous pyridine/CDCl₃ mixture (1.6:1, v/v). A total of 200 μL of an endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide solution (9.23 mg/mL) was used as the internal standard, and 50 μL of a chromium(III) acetylacetonate solution (5.6 mg/mL) was added in the above pyridine/CDCl₃ solvent (the latter serving as the relaxation reagent). Finally, 100 μL of phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and transferred into a 5 mm NMR tube for subsequent ³¹P NMR acquisition with 256 scan for each sample. Quantitative ³¹P NMR was carried out using a Bruker 300 MHz spectrometer.

Oxidation Induction Temperature (OIT_{temp}). The oxidation induction temperature (OIT_{temp}) for each blend was determined using the following DSC protocol using a TA-Instrument model TA-Q100 at a temperature range of 40–300 °C. All samples were dried at 40 °C for 24 h in a vacuum oven prior to these analyses. Approximately 5 mg of a sample were weighed directly into a DSC hermetic aluminum pan, which was then covered with its lid and sealed by cold pressing. Three small holes were created on the lid. After being loaded into the TA-Q100, all samples were heated to 105 °C at a rate of 5 °C/min under a N₂ gas stream and then isothermally conditioned at this temperature for 20 min prior to being quenched to 40 °C where they were isothermally kept again for another 5 min. Finally, the DSC thermograms were recorded by increasing the temperature to 300 °C at a rate of 5 °C/min under an oxygen stream to derive the oxidation induction temperature (OIT_{temp}).

Antioxidant Activity. The antioxidant activity was determined by the radical scavenging activity method using 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) as described by a number of literature citations.^{18,38,39} The UV absorbance of a DPPH solution in dioxane:water (90:10, v/v) at a concentration range from 25 to 200 mg/L was measured thus forming a calibration curve. Different concentrations of lignin in the same dioxane–water solution were then prepared. A total of 0.1 mL of these lignin solutions was added to the dioxane–water mixture of DPPH (100 mg/L, 1.9 mL). After incubating them for 1 h at room temperature in the dark, the UV absorbance of the solutions was determined at 517 nm in triplicate. As a reference for our overall work, we used Trolox (a synthetic antioxidant). The radical scavenging activity was calculated as follows

$$\text{I\%} = [(Ab_0 - Ab_c)/Ab_0] \times 100$$

where Ab_0 is the absorbance of the control (DPPH solution in the absence of lignin), and Ab_c is the absorbance of DPPH solution in the presence of lignin sample. The IC₅₀ (concentration providing 50% inhibition) was calculated graphically using a calibration curve in the linear range by plotting the concentration vs the corresponding scavenging effect. The antioxidant activity expressed as the antioxidant activity index (AAI) was calculated as follows. This method provides a constant value, independent of DPPH and sample concentration.

Table 1. Functional Groups, Molecular Weights, and T_g Values of Original and Methylated Lignins Examined in This Work

sample identity	aliphatic–OH (mmol/g)	phenolic–OH (mmol/g)	COOH (mmol/g)	M_w (g/mol)	PDI	T_g °C
kraft lignin (KL)	2.24	4.25	0.42	6300	5.7	153
methylated KL	1.98	00.00	0.41			126
acetone soluble fraction (ASKL)	1.63	5.76	0.57	3500	3.7	112
methylated ASKL	1.59	00.00	0.48			95
acetone insoluble fraction (AIKL)	2.74	3.08	0.35	14000	7	173
methylated AIKL	2.71	00.00	0.33			146

$$AAI = \frac{(\text{Final concentration of DPPH in blank (mg/L)})}{IC_{50} \text{ (mg/L)}} \times 100$$

RESULTS AND DISCUSSION

Because the focus of this effort was to further comprehend the effect of the different fractional components of softwood kraft lignin in inducing antioxidant and thermal stabilization characteristics in polymer blends, we fractionated the kraft lignin using acetone as per our earlier effort.⁴⁰ The investigated lignin sample was found to contain about 65% of an acetone soluble fraction (ASKL), while its acetone insoluble fraction was about 35% (AIKL). The molecular weight of ASKL was around 3500 g/mol (M_w) with a relevant PDI of about 3.7 (Table 1). As already demonstrated,⁴⁰ the acetone insoluble fraction showed a considerably higher weight-average molecular weight ($M_w = 14,000$) with a much wider range of molecular weight distribution or polydispersity index (PDI = 7). It is important to mention here that the weight-average molecular weight and the PDI of the original unfractionated lignin was 6300 g/mol and PDI = 5.7, respectively (Table 1).

These significant variations in the molecular weights and species distributions observed among the two fractions and the initial lignin, set the foundations for our subsequent focused effort aimed at unraveling their role toward the antioxidant and polymer blend stabilization characteristics of lignin.^{41,42} Functional group distributions of the original kraft lignin and its fractions as well as its methylated analogues, their molecular weights and T_g values are presented in Table 1.

The functional group distribution data enumerated in Table 1 obtained by quantitative ³¹P NMR further demonstrates significant variations of these vital groups being present. The ASKL fraction contain about 85% more total phenolic OH compared to AIKL and about 60% less aliphatic OH. Literature accounts demonstrate that the presence of the phenolic OH within the lignin structure is responsible for its effect on oxidation, thermal, and UV light stability of polymer blends.^{11,12} As such, the data of Table 1 further demonstrates the value of examining these fractions toward such properties in further understanding their effect on the antioxidant and polymer blend thermal stabilization regimes.

Recent literature accounts have shown that such groups are vitally important in inducing thermal cross-linking reactions in lignin.^{5,34} However, their polar nature adds to factors that promotes its incompatibility with nonpolar synthetic polymers.^{4,10} Consequently, in an effort to delineate the effect of phenolic hydroxyl groups on the sought properties of lignin, their selective methylation was carried on the fractions and the original lignin. The data of Table 1 shows that the methylation reaction, carried out in accordance to previously published procedures,³³ was highly selective in targeting the phenolic hydroxyl groups. As such, the antioxidant activity and thermal stability data that follows may offer answers related to the role

of the lignin's phenolic OH because they are selectively masked while their aliphatic counterparts remain free.

Lignin Antioxidant Activity and Role of Phenolic OH.

The antioxidant activities of lignin have been extensively investigated.^{13,16–18} Overall, there is an abundance of information that relates radical scavenging activity of lignin with the type and origin of the raw material, isolation and purification methods used, molecular weight distribution, actual functionalization of the lignin, and its conjugation, heterogeneity, and presence of carbohydrates. During this work, the antioxidant activity of the original kraft lignin and two of its fractions were examined. In an effort to understand the role of the phenolic hydroxyl groups, all samples were selectively methylated.³³ The antioxidant activity of all six samples was assessed using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method.^{27,28} DPPH is a stable free radical with a maximum UV absorption at 517 nm, which is widely used for antioxidant measurements of plant extracts and food supplements, additives,³⁸ and lignin.^{15,43–45} The use of Trolox, a synthetic antioxidant, was used as a control antioxidant reagent offering a comparative measure for the efficacy of lignin as an antioxidant.

Figure 1 graphically displays the radical scavenging ability of the initial unfractionated kraft lignin sample, the two fractions

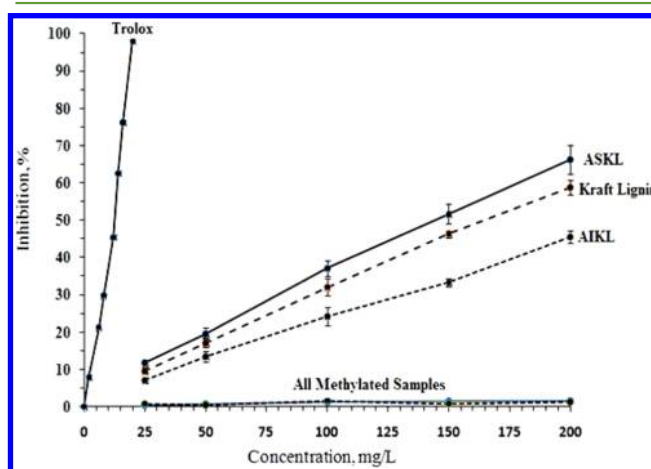


Figure 1. Antioxidant activity of original and methylated kraft lignin and its fractions as a function of sample concentration.

(ASKL and AIKL), and all three methylated samples as a function of concentration. The concentration to induce 50% inhibition (IC_{50}) and the antioxidant activity index (AAI) for this effort are tabulated in Table 2. Complete (100%) inhibitions for unfractionated, ASKL, and AIKL were determined to occur at 332, 291, and 446 mg/L concentrations, respectively.

Both sets of data (Figure 1 and Table 2) showed moderate antioxidant activity for the unmodified lignin and its fractions. Trolox showed very strong antioxidant activity. In comparison

Table 2. Antioxidant Activity of Unfractionated Kraft Lignin and Its Fractions

antioxidant factor	ASKL	unfractionated lignin	AIKL	Trolox
IC ₅₀ (mg/L)	145.7	166.1	223.2	14.1
antioxidant activity index (AAI)	0.68	0.6	0.448	7.1
antioxidant activity scale ^a	moderate	moderate	weak	very strong

^aWeak AAI < 0.5; moderate 0.5 < AAI < 1.0; strong 1.0 < AAI < 2.0; very strong AAI > 2.0⁵²

to Trolox, all lignin samples showed moderate antioxidant activity.

The role of phenolic OH on the antioxidant activity of lignin and its fractions was further investigated by selectively methylating all phenolic OH groups (forming their methoxy derivatives).³³ As anticipated, all samples whose phenolic OH were methylated showed no antioxidant activity in a dioxane–water (9:1 v/v) solution using DPPH (Figure 1). This in itself reveals that the phenolic OH within the lignin is the main functional group responsible for its antioxidant characteristics. Since all phenolic OH's were selectively methylated with no effect on the aliphatic OH, the role of the aliphatic OH on the radical scavenging activity of the lignin remains unclear.⁴⁶ Current efforts in our laboratory now focus on unraveling the role and nature of free radicals in kraft lignin and its fractions in anticipation to comprehend their salient role toward many lignin characteristics.

The accumulated data reveals that the presence of higher amounts of phenolic OH (Table 1) offers better antioxidant activity (Table 2). When the antioxidant activity index (AAI) of the samples was plotted as a function of their phenolic OH content (Figure 2A), it can be seen that the AAI is positively correlated to this group ($R^2 = 0.9721$) in agreement with earlier literature accounts.^{46,47} ASKL contains 35% more phenolic OH than its unfractionated counterpart and 85% more phenolic OH than the AIKL fraction. On the basis of the determined IC₅₀ indices, ASKL showed 15% more antioxidant activity than the unfractionated lignin and 50% more than the AIKL fraction. The antioxidant index activity (AAI) of ASKL was found to be about 11% and 34% greater than the antioxidant activity of the unfractionated lignin and its AIKL fraction, respectively.

Figure 2B shows the effect of molecular weight of the lignin and its fractions on the antioxidant activity. It is clear that lignin fractions of lower molecular weight possess higher antioxidant activity in accordance with earlier efforts^{48,49} that revealed negative effects of higher molecular weights on antioxidant activity. Low molecular weight kraft lignin fractions were determined to contain more phenolic OH than their high molecular weight counterparts (Table 1).³²

Polyethylene–Lignin Blend Thermal Stability (Oxidation Induction Temperature (OIT_{temp})). In tandem with the antioxidant character of kraft lignin, there are abundant citations in the literature that document it is free radical scavenging properties. Kraft lignin is thought to interfere with oxygen radicals and as such stabilize oxidation reactions in complex organic systems.^{13,15–18,19} The radical scavenging activity of lignin varies with the type, mode of preparation, chemical modification, and heterogeneity of a given lignin.¹⁹ Surprisingly, a large variety of functional groups have been held responsible for the free radical scavenging ability of lignin

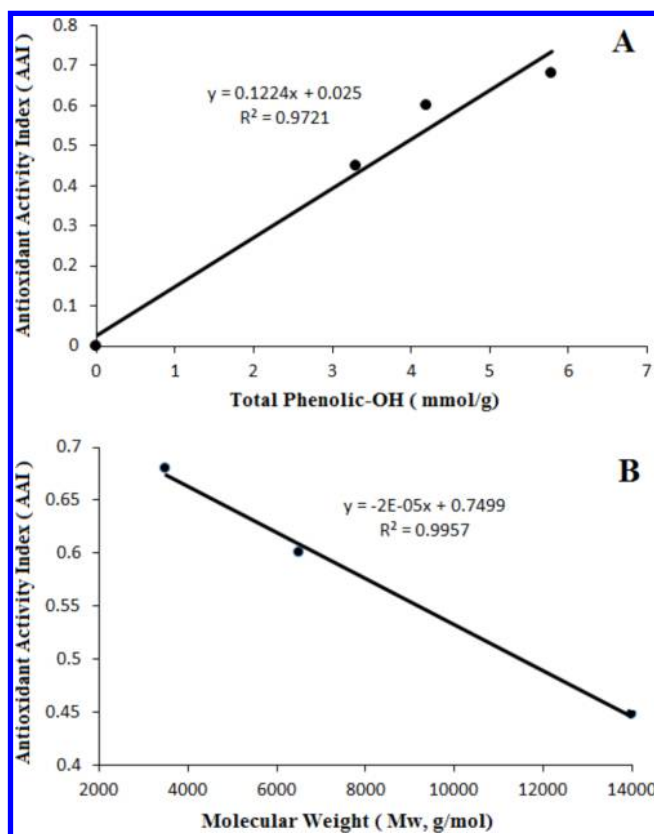


Figure 2. Plots of the antioxidant activity index (AAI) of kraft lignin and its fractions as a function of total phenolic hydroxyl group content (A) and molecular weight (B).

including its hydroxyl, methoxyl, carbonyl, and carboxyl groups.^{16,47}

The thermal stability of lignin and lignin–polyethylene blends can be evaluated by using the oxidation induction temperature (OIT_{temp}). The method utilizes a standardized heating protocol within the chamber of a differential scanning calorimeter (DSC) in open sample holders or holders with pierced lids.⁵⁰ More specifically, during the dynamic OIT_{temp} measurements, the sample is heated at a specific constant heating rate under oxidizing conditions until oxidation events start causing the evolution of heat as detected by the DSC. The oxidation induction temperature OIT_{temp} (also called oxidation onset temperature OOT) is the same as the extrapolated onset temperature that appears as an exothermic DSC signal and shows the temperature at which the materials starts to effectively burn.

Role of Phenolic OH on OIT_{temp} of PE–Lignin Blends.

On the basis of our quantitative ³¹P NMR data and the antioxidant activity previously determined (Figure 1 and Table 2), ASKL was shown to possess higher phenolic OH content and thus better antioxidant activity than its unfractionated counterpart and AIKL. In general, the addition of lignin offers improvements in the thermal stability of synthetic polymer, and the presence of the phenolic OH in them has been held responsible for these effects.^{5,17,51}

To further understand this effect, polyethylene blends of 5% kraft lignin and its fractions containing different amounts of phenolic OH were created, and their oxidation induction temperatures were determined. Figure 3 shows excellent linear correlations between the determined oxidation induction

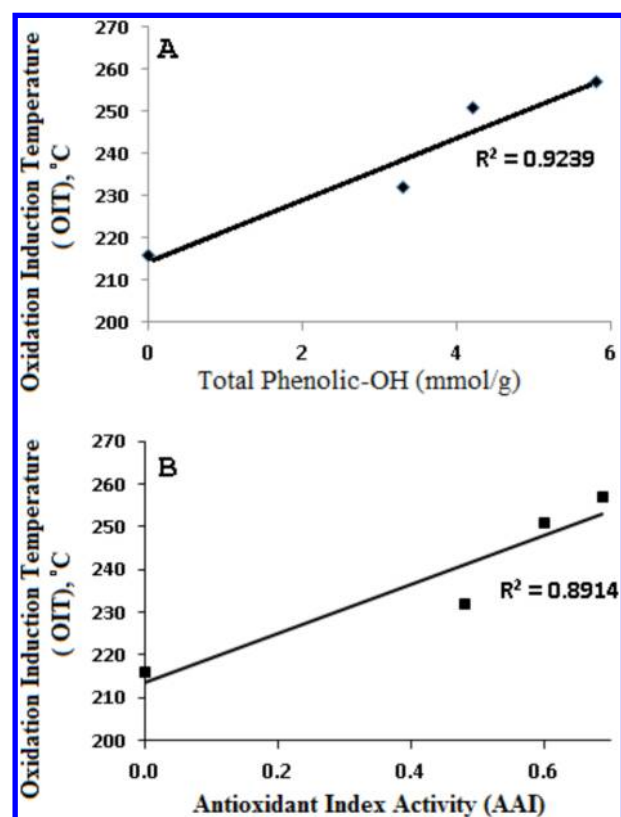


Figure 3. Effect of lignin phenolic OH (A) and AAI (B) on the OIT_{temp} of polyethylene in blends with lignin at 5% w/w.

temperatures for these blends with the lignin's phenolic OH content (Figure 3A) and antioxidant activity (Figure 3B). The 5% PE blends that contained ASKL (possessing the highest amounts of phenolic OH; Table 1) displayed the highest oxidation induction temperature and maximum antioxidant activity (AAI). In contrast, AIKL containing the lowest amounts of phenolic OH showed lower OIT and AAI values, while upon complete methylation of the phenolic OH, these values were the lowest.

Despite the best OIT_{temp} data obtained for the lower molecular weight sample (ASKL), the literature reveals that the relation between molecular weight, functional groups, and thermal stability of blends with various polymers is more complex, and there are other parameters that can affect the OIT_{temp} .¹⁷

Figure 4A shows the oxidation induction temperature DSC data profiles obtained for unmethylated and for methylated (Figure 4B) lignins and its fractions in 5% (w/w) blends with PE. The OIT_{temp} of neat medium density PE was determined to be around 206 °C (Figure 4). By adding unfractionated kraft lignin and/or ASKL, the OIT_{temp} values are shown to significantly increase. The highest OIT_{temp} value obtained was determined to be around 260 °C (nearly 55 °C more than neat PE) when 5% of original unfractionated lignin and/or ASKL was added. However, when the acetone insoluble fraction of kraft lignin was used to create a 5% PE blend, its stabilizing effect on the OIT_{temp} of the blend was significantly lower (OIT_{temp} was increased only by 23 °C). Therefore, the overall, stabilization action of lignin and its fractions as manifested in the OIT_{temp} measurements seems to correlate well with the phenolic OH content of the lignin (Figure 3A). Namely, ASKL containing 5.76 mmol/g of phenolic OH offers better

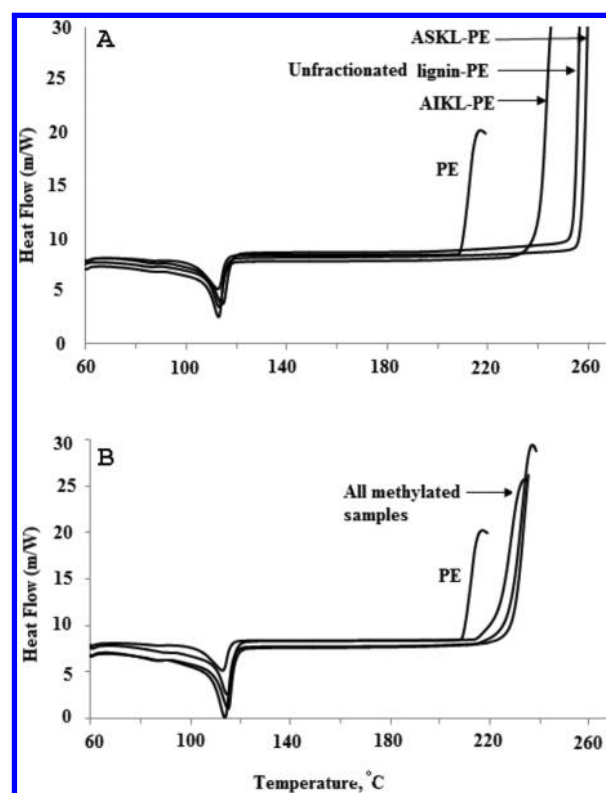


Figure 4. Oxidation induction temperature profiles of unfractionated, methylated, and fractionated (ASKL and AIKL) lignin in polyethylene blends (5%, w/w lignin content).

stabilization than AIKL that contains about 3.08 mmol/g of phenolic OH. Notably, the T_g of AIKL is significantly higher than either ASKL or the unfractionated lignin, and this could play a role in the data of Figure 4.

Role of Lignin Char on OIT_{temp} of PE–Lignin Blends. To further comprehend the details of the thermal oxidative stability of pure PE and PE–lignin blends, the oxidation induction temperature (OIT_{temp}) was determined as a function of lignin content in a series of such blends.

So far in this work, it was demonstrated that the presence of the phenolic OH groups within the lignin structure is responsible for beneficial effects toward oxidative, thermal, and light stability characteristics when present in polymer blends and supported by various literature citations.^{11,12} Scherer and Godoy,⁵² however, point out to the fact that when PE is blended with lignin and during elevated processing temperatures, the aromatic char originating from the lignin seems to reduce the PE degradation rate thus increasing its thermal degradation temperature.

While methylated lignin is shown to offer no antioxidant activity (Figure 2) when incorporated in PE blends, at levels ranging from 5% to 25% (w/w) (Figures 4B and 5), the OIT_{temp} of PE is shown to improve by about 10 and 29 °C, respectively. This data validates the earlier work of Canetti et al. that points to the nature of the char of lignin toward improving the thermal stability of its blends with synthetic polymers.

The data of Figures 4B and 5 offers an opportunity to at least qualitatively account and understand the relative contributions that phenolic OH and the charring effect play in increasing the thermal oxidative properties of PE–lignin blends. To do this, it is reasonable to assume that all the improvement in the OIT_{temp} values of the blends observed when using methylated samples is

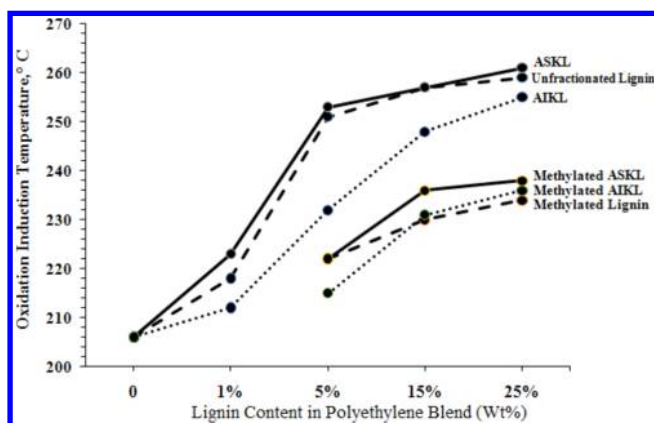


Figure 5. Effect of original and methylated lignin and its fractionated samples on the oxidation induction temperature (OIT_{temp}) of polyethylene blended with 1% to 25% (w/w) lignin.

due to the contribution of the lignin char mechanism. Furthermore, the improvements in the OIT_{temp} data (Figure 4) documented for the unfractionated and nonmethylated lignin samples are due to both the contribution of the phenolic OH/antioxidant property and the effect of the lignin char production. By subtracting the OIT_{temp} data obtained for the PE blends containing original unmodified lignin from the OIT_{temp} data obtained for the PE blends containing methylated lignin (in both cases at 5% w/w), one may arrive at an estimate of the relative contributions of the two mechanisms. For example, for the 5% w/w blends, the OIT_{temp} of neat PE was increased by about 50 °C when unfractionated and/or ASKL lignins were used. The OIT_{temp} improvement for the same blends created with methylated lignin was around 15 °C. This qualitatively indicates that the phenolic OH/antioxidant activity of lignin contributes more toward improving the OIT_{temp} of PE–lignin blends (at 5 wt % loading).

The data of Figure 6 attempts to further elaborate on the relative contributions of the two mechanisms of kraft lignin on the OIT_{temp} data of PE as a function of lignin loading.

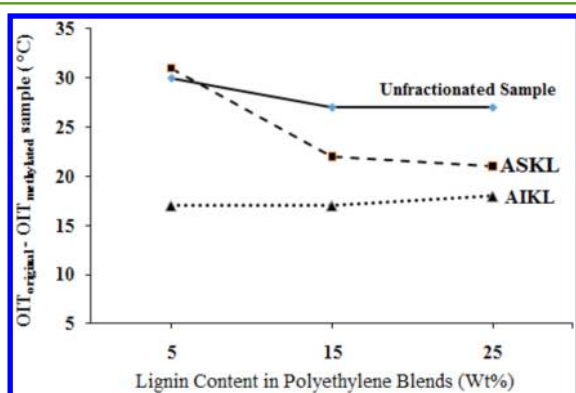


Figure 6. Differences of OIT_{temp} values between blends of lignin with PE (5 w/w) using original and methylated lignin.

The data overall shows that for unfractionated and/or ASKL samples when blended with PE at relatively low levels (about 1–5% w/w) the antioxidant/phenolic OH mechanism is the main contributor in increasing the PE OIT_{temp} . As the levels of lignin increase further, the contribution of the char mechanism becomes increasingly more important. This observation, however, does not apply when the acetone insoluble kraft

lignin fraction (AIKL) was used most likely because it has a significantly lower amount of phenolic OH than either the original unfractionated lignin of the ASKL.

CONCLUSIONS

The effect of lignin fractionation and methylation on its antioxidant properties and the thermal stability of its blends with polyethylene were investigated. While the unfractionated softwood kraft lignin showed moderate antioxidant activity, the lower molecular weight fraction of kraft lignin (ASKL) showed 55% better antioxidant activity than its acetone insoluble counterpart that only showed 15% better antioxidant activity. By selectively methylating all the phenolic OH groups of the lignin, the DPPH antioxidant method showed zero antioxidant activity, revealing the significance of the lignin's phenolic OH toward imparting in it antioxidant characteristics. Furthermore, oxidation induction temperature (OIT_{temp}) measurements were used to investigate the effects of softwood kraft lignin and its fractions on the thermal stability of polyethylene and its blends. Methylated lignin samples when blended with polyethylene showed inferior OIT_{temp} values when compared to its nonmethylated counterparts. When 5% (w/w) blends of the original unmodified kraft lignin and its ASKL were used, the OIT_{temp} values were improved by about 50 °C compared to the starting polyolefin, and further increases of the lignin amounts in the PE blends showed no additional improvements on the OIT_{temp} .

Despite the fact that the data shows that the phenolic–OH in kraft lignin and its antioxidant activity are related, methylated lignins in 5% and 25% (w/w) blends with PE did increase the OIT_{temp} values by 10 and 29 °C, respectively. It is likely that the aromatic nature of the char (originating from the lignin) that is created at elevated processing temperatures reduces the polyethylene degradation rate, which eventually increases the polyethylene thermal degradation temperature.

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Notes

The authors declare no competing financial interest.

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