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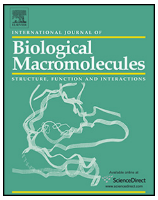

Selective aminolysis of acetylated lignin: Toward simultaneously improving thermal-oxidative stability and maintaining mechanical properties of polypropylene

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ABSTRACT

Even with outstanding radical capturing ability, the utilization of lignin as a natural antioxidant in polypropylene (PP) still has been pended. Usually, the compatibility of its blends is improved based on the reaction of hydroxyl content, thus leading to the decreasing content of phenolic hydroxyl (Ph-OH) group and inferior thermal-oxidative stability of lignin blends. Here, the selective aminolysis of acetylated Kraft lignin (pyr-KL) was investigated, which structures were characterized using FTIR, ^{31}P-NMR and GPC. The Ph-OH group of acetylated KL could be released by the addition of pyrrolidine; however the aliphatic hydroxyl group is still blocked. With the control of reaction conditions, the highest oxidation induction time of pyr-KL/PP (0.5 wt% loading) reaches up to 22.6 min, almost 2.6 times than that of pure PP. More importantly, the mechanical properties of PP were also maintained under the loading of pyr-KL, which is much better than that of curde KL/PP.

1. Introduction

Steric hindered phenols are an important class of synthetic antioxidants for polymers, such as Irganox1010 is commonly incorporated into polymer matrix in order to inhibit polyolefines oxidation. The global demand for antioxidants would attain a value of 103.3 thousand tons by 2020 [1]. However, synthetic antioxidants have the potential of bringing about potential health issues and environmental problems [2]. Thus, great interest has been attracted on the novel phenol-based natural antioxidant, for example ascorbic acid (vitamin C), curcumin, quercetin and tannic acid, etc [3–6]. Compared with the above renewable poly-phenols, lignin, the most abundant of natural polyphenol with low cost, good biological compatibility and renewability (about 70 million tons per year) [7], shows tremendous prospect as natural antioxidant to partially replace petroleum antioxidant in polymer processing.

Due to the inhomogeneous and complex structures of Kraft lignin (KL), most of the literature on lignin antioxidant properties focuses on exploring the relationship between its radical capturing ability and chemical structures [8–11]. However, limited attention has been paid on the oxidation stability of lignin/polymers [12–16]. As practical antioxidant, it is widely acknowledged that the mechanical properties of neat polymer should not be impaired with the loading of fillers. However, the results from most of previous reports indicated that the mechanical behavior of lignin composites, especially the elongation is terribly decreased under even low loading of lignin [17–21]. Therefore, chemical modification of lignin is adopted for improving lignin compatibility with polymers. Several approaches are usually used, for example the grafting of lignin with nonpolar chains, alkylation as well as esterification [18,22–27]. All of the above methods are based on the reactivity of aliphatic —OH and phenolic hydroxyl (Ph-OH) groups. In this way, the compatibility of lignin blend could be improved; nevertheless the content of Ph-OH group is hugely decreased, lead-

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Abbreviations: KL, Kraft lignin; Ph-OH, Phenolic hydroxyl; PP, Polypropylene; KL-AC, Acetylated Kraft lignin; pyr-KL, Aminolysis of acetylated Kraft lignin; DPPH, 1,1-Diphenyl-2-picrylhydrazyl; OIT, Oxidation induction time.

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ing to the loss of thermal anti-oxidative effect of lignin in polymers. Here, we hypothesized that the above conflict could be resolved by obtaining lignin with high content of Ph-OH group but extreme low aliphatic —OH group content.

The first method is solvent fractional/precipitation, which is extensively studied for getting various molecular compositions of lignin fractions with narrow molecular weight distribution, controllable content of Ph-OH and aliphatic —OH groups [1,28,29]. For example, the dichloromethane extracted kraft lignin (KL) with low molecular weight and high content of Ph-OH group shows much better thermal stability for pure polypropylene (PP) than that of crude lignin [30]. Recently, the antioxidant properties of softwood KL fractions/polyethylene have also been reported, in which the oxidation induction temperature of polyethylene could be enhanced by 50 °C with 5 wt% loading of acetone soluble KL[15]. Nevertheless, the main problem of this approach is the extreme low yield of lignin fractions, only up to 6–15 wt%.

Aminolysis is a method used for characterizing the content of Ph-OH group of lignin, considering phenolic ester could be unblocked much faster than that of aliphatic ester with pyrrolidine [31–33]. To our best knowledge, there have been no reports about examining the structures of selective aminolysis of acetylated KL (pyr-KL) until now. Through this approach, we can get high free content of Ph-OH group of lignin, meanwhile its aliphatic —OH groups are highly blocked with acetate group. Therefore, it could be deduced that the dispersion of lignin particles in PP can be improved while its thermal anti-oxidation properties in polymer is also maintained. Compared with lignin fractions, this approach is based on crude lignin modification, which is a very fast reaction and high production yield. The novelty of this paper lies in the first use of aminolysis of acetylated lignin as natural antioxidant for improving PP thermal oxidation stability and without impairing blend's mechanical properties. In this paper, the crude and modified KL structures including functional group's content and molecular weight were studied with FTIR, ^{31}P NMR and GPC. In addition, the antioxidant performance of lignin in PP was studied using induction oxidation time (OIT) by DSC method. Finally, the compatibility and mechanical property of PP/lignin composites were also studied.

2. Experimental

2.1. Materials

Industrial pine kraft lignin ($\bar{M}_w$=5784, $\bar{M}_w/\bar{M}_n$=7.0, 11.5% methoxy group, KL) was supplied by Domtar Corporation and used as starting lignin source. The lignin was thoroughly mixed with distilled water at high shear rate, and then washed several times to remove dissolved salts. The washed lignin was freeze-dried under vacuum for at least two days to remove excess water. PP was a commercial grade (PPH-T03, Sinopec Beihai Refining Corporation) with a melt flow rate of 2.94 g/10 min. Pyrrolidine and dioxane are analytical reagents supplied by Aladdin Regent Company. Other chemicals used for GPC, ^{31}P NMR and other analyses were obtained from Sigma-Aldrich without further purification.

2.2. Acetylated kraft lignin (KL-AC) preparation

The detailed procedures were referred to the previous report [26]. Briefly, 5 g purified lignin was dissolved in 10 mL of acetic anhydride contained in a 100 mL three-necked bottle under low stirring speed. Following, the mixture was kept under nitrogen atmosphere for at least 30 min, and then the reaction was started by adding 0.25 mL 1-methylimidazole at 70 °C under vigorous stirring. After reacted 30 min, the reaction mixture was added dropwise to 120 mL distilled water containing 3 mL of concentrated HCl. Subsequently, KL-AC was washed with pure water several times and then vacuum filtrated, dried at 35 °C under vacuum oven for 24 h.

2.3. Selective aminolysis of acetylated kraft lignin

1.0 g KL-AC was firstly dissolved in 4 mL dioxane at a headspace bottle; subsequently predetermined amount of pyrrolidine was quickly added into the above mixture and then stirred at room temperature for 1 h [31]. After the determined time, the reaction solution was slowly dropped into 80 mL distilled water containing 2 mL of concentrated HCl. Crude products were washed by distilled water several times and vacuum-dried for overnight. The obtained samples were referred as 0.25pyr-KL and 1.5pry-KL, respectively according to the amount of pyrrolidine (0.25 and 1.5 times equal to total Ph-OH content of crude KL) added. The detailed reaction scheme is shown as Scheme 1.

2.4. Compounding and film preparation

Pure KL, KL-AC and pyr-KL were mixed with PP powder via Hakke rotation (180 °C, 4 min, 60 rpm/ min) at a loading of 0.5 wt% based on total blend's weight. Melting compounds were collected at room temperature and subsequently hot-pressed into films (180 °C, 10 MPa, 10 min) using a hollow square cooper plate (100 × 100 × 0.5 mm). Before hot processing, the covering plates were covered with tin foil paper. Another cooling press procedure was performed at room temperature for 10 min under 10 MPa. Films of neat PP was obtained under the same conditions.

2.5. Characterization of lignin samples

FTIR spectra of the samples were done on a Nicolet 560 FTIR spectrometer using KBr pellet technique. Each spectrum was recorded with 32 scans in the frequency range of 4000–400 cm $^{-1}$ with a resolution of 2 cm $^{-1}$.

The content of functional groups in KL samples was analyzed by quantitative NMR (Bruker 300 MHz spectrometer equipped with a Quad probe used for ^{31}P, ^{13}C, ^{19}F, and ^{1}HNMR acquisition) according to previous report [34]. All spectra were automatic baseline corrected and normalized at the standard peak.

The number-average, weight-average molecular weights and molecular weight distribution (recorded as $\bar{\mathrm{M}}_\mathrm{n}$, $\bar{\mathrm{M}}_\mathrm{w}$ and MWD, respectively) of the acetylated lignin samples were estimated by gel permeation chromatography (GPC) equipped with two linear columns (Styragel HR 1, Styragel HR 2) and differential refractive index detector. The columns were calibrated with a series of polystyrene standards. Due to the excellent solubility of 0.25pyr-KL and 1.5pyr-KL in tetrahydrofuran, therefore they were used without further acetylation. As for crude KL, it was subjected to acetylation as previously described in section 2.2. The acetylated lignin (25.0 ul, concentration in THF 1 mg/mL) was injected into the column; subsequently analysis was performed at 30 °C and eluted with THF at a flow rate of 1.0 ml/min.

The antioxidant activity of the lignin preparations was determined based on the radical scavenging capability according to the previous research [35]. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) was used as the radical generator. Briefly, various concentration of lignin solution (0.025, 0.05, 0.1, 0.2, 0.3 and 0.4 mg/ml. respectively) and 6.1 × 10^{-5} mol/L DPPH solution were prepared by dissolving them in 90% aqueous dioxane solvent, respectively. Then, 103.0 ul of lignin solution was mixed with 4 mL DPPH solution at room temperature for 1 h under dark condition. Immediately, the absorbance of maximum peak of DPPH radicals (around 517 nm) were monitored between 500 and 550 nm before and after added with lignin solution using UV spectrometer. The detailed procedures for calculating radical scavenging activity and IC50 (lignin concentration

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