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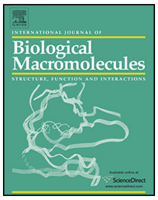

Thermal-oxidative effect of Kraft lignin antioxidant in polypropylene: Uncovering the key factor using correlation analysis model

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ABSTRACT

Which factors are crucial to improving lignin antioxidant ability in polymers has been debated over years. Here, the structural effect of natural antioxidant from technical Kraft lignin (KL) on the oxidation induction time (OIT) of KL/polypropylene (PP) was quantitatively investigated using correlation analysis model instead of traditional linear fitting model. The correlation coefficient and significance value of their relationship clearly demonstrated the dominating role of non-condensed Phenolic —OH (Ph-OH) in improving KL/PP thermal-oxidation stability, subsequently followed by $\bar{M}_n$, aliphatic —OH/total Ph-OH, condensed Ph-OH and polydispersity. OIT is positive with non-condensed and total Ph-OH, while it declines with increase of the above other factors. Remarkably, the longest OIT (~90 min) was obtained even at extreme loading (0.5 wt%), almost ~911% and ~201% huge increase in contrast to that of pure PP and crude KL/PP composite, respectively. Meanwhile, the mechanical properties of KL fractions/PP blends can be maintained at the same or better level than that of pure PP, due to strong interfacial adhesion strength.

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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 is very huge, approximate to 2.25 billion USD per year [1]. Recently, potential health issues and environmental challenges have been confronted by synthetic antioxidants, including the migration of them from polymer surface which caused unknown cytotoxicity [2]. Thus, great interest has been attracted on the novel phenol-based natural antioxidant, for example ascorbic acid (vitamin C) [3], curcumin [4], quercetin [5] and tannic acid [6], etc. Compared with other renewable poly-phenols, the tremendous advantages of low cost, good biological compatibility [7] and renewability (about 70 million tons per year) make lignin could be the most practical natural antioxidant.

Until now, most of studies on lignin antioxidant activity have been concerned on the correlation between the lignin inherent structures and its radical capturing ability (determined by DPPH method) [8–15], in which linear regression model was widely adopted for describing their relationship. Given the biodiversity of lignin, variability in performance as an antioxidant is expected, for example, depending on the lignin source, extraction methods, structure, molecular weight, functional groups, etc. Overall, it has been indicated that its antioxidant activity is positive with the total phenolic hydroxyl content, but it is reduced with that of aliphatic hydroxyls. Also, a lower molecular mass and narrower molecular weight distribution seem to be beneficial.

When comes to lignin antioxidant performances in polymers [16–20], there have been few detailed and systematic studies to illustrate the relationship between lignin structures and lignin/polymer blends thermal stability. Another question is, even if in the related publication, some disagreements over the years as to which factors are crucial to improving lignin antioxidant ability in polymers were still pendent. For example, Pouteau et al. concluded that classically important factors such as phenol content and intrinsic reactivity of the molecule are less important than

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Abbreviations: KL, Kraft lignin; OIT, oxidation induction time; PP, polypropylene; Ph-OH, phenolic -OH; CC, correlation coefficient; p, two-tailed significance; THF, tetrahydrofuran; CH, cyclohexane; $\bar{M}_n$, the number-average; $\bar{M}_w$, weight-average molecular weights; MWD, molecular weight distribution; B, interfacial interaction parameter; ϕ_f, volumetric filler fraction; σ_{yc}, the yield stress of the composite; σ_{ym}, the yield stress of the matrix.

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factors making easier solubility, which depends on the low molecular weight and total OH content [21]. In contrast, Sadeghifar and Argyropoulos reported that the role of the phenolic OH was found to be extremely important toward to improve the thermal oxidative characteristics of kraft lignin/PE blends [22]. It is not surprised to come to this discrepancy because of the improper linear fitting model which is a plot of oxidation induction time/temperature as a function of lignin group's content. Obviously, traditional analysis model like linear fitting was helpless for the importance ranking of influence factors from lignin structures. Considering the lignin heterogeneous and complex structures, it was expected to find a new model to figure out which one is the most crucial parameter in controlling the antioxidant activity of lignin in polymers. Correlation analysis is the process of studying the strength of that relationship with available statistical data [23]. A correlation coefficient (CC) of +1 represents a perfect positive relationship, meaning that as one variable increases in value, so does the other; −1 indicates an opposite trend; A value of 0 means that there is no relationship between the variables being tested [24]. From the CC value and two-tailed significance (p), it is clearly to provide a quantitative index to solve the above problems.

In this work, softwood Kraft lignin (Domtar Corporation) fractions with various solubility parameters were obtained by fractional precipitation of mixed solvent from tetrahydrofuran ($\delta = 19.4\,\mathrm{MPa}^{1/2}$) and cyclohexane ($\delta = 16.8\,\mathrm{MPa}^{1/2}$). The relationship among the lignin features and its antioxidant behaviors in PP was established by correlation analysis instead of linear regression model. The main objective of this study was to confirm the most crucial structural features of the lignin as thermal oxidation stabilizer in PP and obtain high performance of renewable polymer stabilizer.

2. Experimental

2.1. Materials

Industrial pine kraft lignin ($\bar{M}_w = 5784$, $\bar{M}_w/\bar{M}_n = 7.03$, 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, 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. Polypropylene (PP) was a commercial grade (PPH-T03, Sinopec Beihai Refining Corporation) with a melt flow rate of 2.94 g/10 min. Tetrahydrofuran (THF) and cyclohexane (CH) solvents 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. Softwood Kraft lignin fractions preparation

The procedure for preparing Softwood Kraft Lignin fractions was referred to the method described by Cui et al. [25]. Here, the solvent was rechosen in order to obtain high yield of fractional lignin with various solubility parameters. Briefly, 100 g KL was dissolved into THF (1 L) under vigorous stir for 6 h at room temperature, the insoluble precipitation (0.97 wt% of KL) was removed by vacuum filtration. Then the filter liquor was collected and adjusted to 1.0 L with THF again. An aliquot of CH (0.25 L) was added into the dissolved KL solution (supernatant I), and then stirred for about an hour to allow the lignin fraction to coagulate. Finally, this precipitate was separated and referred as 4T1C-IKL. The suspension II was transferred to a clean 3L glass bottle and 0.75 L CH was slowly added into it to form a gummy residue designated as 1T1C-IKL. The resulting supernatant (III) was concentrated on a rotary evaporator and vacuum dried; finally it was re-dissolved with 200 mL of THF. In this step, 400 mL CH was slowly dropped to generation precipitation recorded as 1T2C-IKL. Finally, amount of 400 mL CH was added into the above resulting supernatant (IV) to get lignin fractions referred to 1T4C-IKL. Finally, 1T4C-SKL powder was obtained by concentrating the residual suspension on a rotary evaporator and dried in vacuum oven. The whole fractional procedure was showed as Fig. 1.

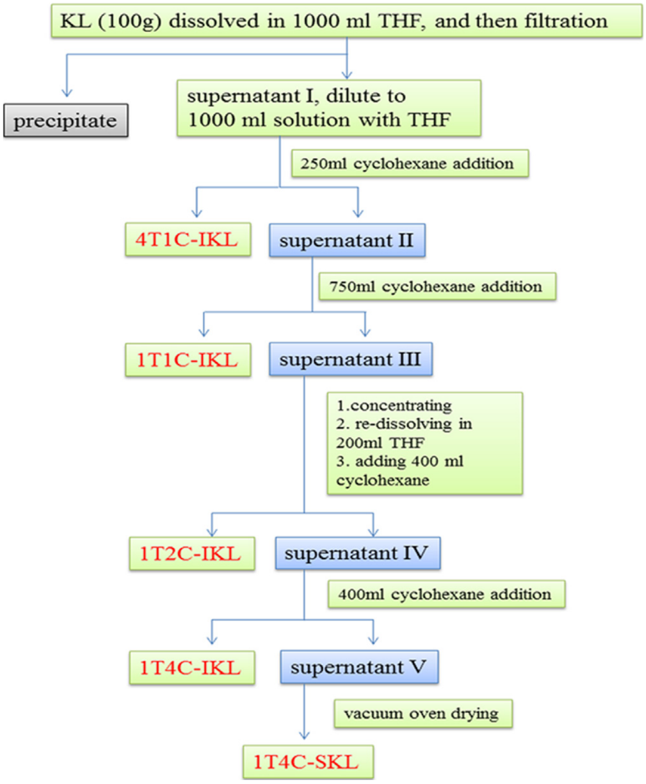

Fig. 1. Flow chart illustrating the fractional precipitation of KL with cyclohexane/tetrahydrofuran mixture.

2.3. Compounding and film preparation

KL fractions 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). Another cooling press procedure was conducted at room temperature for 10 min under 10 MPa. Films of neat PP was obtained under the same conditions.

2.4. Characterization of lignin samples

The crude and fractional lignins were 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 [11]. All spectra were automatic baseline corrected and normalized at the standard peak.

The number-average, weight-average molecular weights and molecular weight distribution ($\bar{M}_n$, $\bar{M}_w$ and MWD, respectively) of the acetylated lignin fractions samples were estimated by gel permeation chromatography (GPC) equipped with two linear columns (Styragel HR 1, Styragel HR 2) and differential refractive index detector. Prior to GPC analyses, all samples examined in this work were subjected to acetylation as previously described [11]. The acetylated lignin (25.0 ul, concentration in THF 1 mg/mL) was

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