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Can all lignins act as an antioxidant for polypropylene?

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ABSTRACT

Lignin, a high-volume byproduct of the pulp and paper industry, contains sterically hindered phenolic hydroxyl groups that enable antioxidant activity in polymer systems. This study investigates the potential of three eucalyptus-derived lignins, referred to as L1, L2, and L3, extracted from black liquor via acid precipitation under varying conditions, as primary antioxidants in polypropylene (PP). The lignins exhibited distinct pH values: L1 (3.35), L2 (3.68), and L3 (7.97). A comprehensive characterization, combining structural, chemical, and molecular analyses, was performed to correlate intrinsic features with antioxidant efficiency in PP. Although extraction conditions influenced purity and functionality, only detailed characterization allowed reliable prediction of stabilization performance. Lignins with acidic pH values (L1 and L2) showed higher purity and a greater concentration of sterically hindered phenolic groups, correlating with enhanced antioxidant activity. Oxidative induction time (OIT), rotational rheometry, and size exclusion chromatography (SEC) confirmed the superior performance of L1 and L2. At 2000 ppm, PP-lignin formulations containing L1 or L2 exhibited significantly higher OIT values, viscosities, and molar masses compared to PP with conventional synthetic antioxidants. Structural differences between syringyl and guaiacyl units in L1 and L2 further influenced stabilization during high-temperature processing, with L2 demonstrating exceptional performance under elevated temperature, oxygen, and shear. This work highlights the importance of combining extraction strategies with advanced lignin characterization to predict antioxidant efficiency, while introducing methodologies that correlate rheological behavior with molar mass distribution. These findings support lignin's application as a cost-effective, bio-based, and high-performance antioxidant additive for recycled polypropylene.

1. Introduction

Lignin is the most abundant aromatic macromolecule in nature [1,2]. It is generated by reactions of coumaryl, coniferyl, and sinapyl alcohols that give rise to p-hydroxyphenyl (H units), guaiacyl (G-units), and syringyl (S-units), respectively [3]. This natural compound contains varying amounts of methoxyl and hydroxyl groups in its structure, and its heterogeneity increases further depending on the extraction process, potentially leading to the formation of multiple structures with different monomeric linkages [1–8].

Lignin is industrially obtained as a by-product of the pulp and paper manufacturing process. Currently, global lignin production is estimated at approximately 100 million tons per year. Despite its abundance, the vast majority of lignin is combusted on-site for energy recovery, with only 1–2 % being utilized in high-value applications such as advanced materials, chemicals, and polymer additives [4,9]. Lignin extraction from plant biomass during the delignification stage can be performed through various pulping methods, including the widely adopted Kraft process. Each pulping technique yields lignins with distinct physicochemical properties, such as variations in molar mass, functional group content, and degree of condensation, which directly influence their reactivity and potential applications [3,10].

Comparative analysis of lignin substructures generated during delignification processes indicates that an increased concentration of phenolic hydroxyl groups, coupled with a reduction in aliphatic hydroxyl content, enhances the antioxidant activity of lignin. These

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structural modifications improve the radical scavenging capacity, making lignin a more effective stabilizing agent in polymeric matrices [2,8]. Due to their complex and heterogeneous structure, lignins may contain sterically hindered phenolic moieties capable of acting as hydrogen donors. This antioxidant mechanism is analogous to that observed in synthetic primary antioxidants, which rely on the presence of hydroxyl and methoxyl functional groups to neutralize free radicals [2,10–12]. Hindered phenolic antioxidants represent the most widely used class of stabilizers in polymer systems, accounting for approximately 56 % of total antioxidant consumption in the plastics industry. Among these, polypropylene is the primary consumer, due to its high susceptibility to thermo-oxidative degradation [13,14]. These stabilizers work by donating hydrogen atoms from phenolic groups to polymeric free radicals, resulting in the formation of stable phenoxy radicals and hydroperoxides bound to the polymer. During polypropylene processing, the material is subjected to elevated shear rates and temperatures, which promote structural degradation and compromise its functional performance. Consequently, the incorporation of antioxidant additives is essential to mitigate thermo-oxidative degradation and preserve material integrity [15–17]. Given this context, the potential of lignin as a natural antioxidant for polypropylene has garnered increasing scientific interest. Lignin's phenolic structure and its availability as a renewable by-product position it as a promising alternative to synthetic stabilizers in polymer formulations. Studies have demonstrated its efficacy in mitigating polypropylene degradation through antioxidant mechanisms, supported by evidence from Refs. [12,18–20].

The substantial volume of lignin generated as a by-product, along with emerging trends promoting the use of renewable and sustainable resources in chemical processes, has stimulated research aimed at improving its extraction, recovery, and chemical modification. These advancements seek to enhance lignin's value and broaden its applicability across various industrial sectors [21,22].

Therefore, this study investigated the replacement of conventional synthetic phenolic antioxidants, commonly used in polypropylene, with lignins obtained from the Kraft pulping process under distinct precipitation conditions. These procedures yielded three lignin samples with varied structural characteristics, enabling a comparative evaluation of their antioxidant performance in polymer stabilization.

2. Materials and methods

The lignins used in this study, L1, L2, and L3 (Fig. 1), were supplied by the pulp and paper industry and were obtained from the Kraft pulping of eucalyptus wood under three distinct precipitation conditions. Precipitation from black liquor was carried out using carbon dioxide and sulfuric acid. Due to confidentiality agreements, the supplier did not disclose specific details and parameters of the precipitation processes. Homopolymer polypropylene (PP) powder (DP 5000 SCPV), free of antioxidant additives and produced via Spheripol technology, was provided by Braskem. To evaluate the replacement of conventional synthetic primary antioxidants in polypropylene, the sterically hindered phenolic antioxidant Evernox-10 GF [Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate)] from Everspring Chemical Inc., and the secondary phosphite antioxidant Alkanox 240 [Tris(2,4-di-tert-butylphenyl) phosphite] from Addivant were used.

2.1. Lignin characterization

The pH of the lignin samples was measured using a potentiometric method with a combined glass electrode. The ash content was determined according to the TAPPI T 211 standard procedure [23] at two temperatures. Dry lignin samples (105 °C, 1 h) were subjected to thermal treatment in a muffle furnace at 525 ± 25 °C and 900 ± 25 °C for 1 h to determine ash content. Moisture content was measured using a vacuum oven at 60 °C until constant mass. The lignin content was determined following the TAPPI T 222 standard methodology. Elemental analysis was performed using a Bruker S8 TIGER X-ray fluorescence (XRF) spectrometer. Total phenolic content in the lignin samples was quantified using the Folin–Ciocalteu reagent method (Sigma-Aldrich) [24,25]. Initially, lignin solutions were prepared in methanol and diluted with distilled water at various concentrations. A calibration curve was constructed using a standard solution of gallic acid. The samples were kept in the dark for 30 min before spectrophotometric analysis. Absorbance measurements were performed at 760 nm using a Quimis spectrophotometer (Brazil). The total phenolic content was expressed as grams of gallic acid equivalent per 100 g of dry lignin.

To evaluate antioxidant activity, the DPPH (2,2 Diphenyl-1-picrylhydrazyl) free radical method was used [26]. Methanol solutions of DPPH (0.2 mg/mL), of each lignin, and of quercetin used as standard antioxidants (1, 0.5, 0.25, 0.125, 0.0625, and 0.03125 mg/mL) were prepared. Afterward, 2 mL of each lignin solution at different concentrations was mixed with 2 mL of the DPPH solution and kept in the absence of light for 30 min to allow the stabilization reaction of the DPPH radicals by lignins and quercetin to occur. Subsequently, the absorbances were read on a Quimis UV/VIS spectrophotometer (Brazil) at a wavelength of 517 nm to evaluate the remaining concentration of DPPH radicals. The absorbance curve was prepared as a function of the lignin concentration. From the curve equation, the inhibitory concentration (IC50) was determined, which refers to the minimum concentration of antioxidant required to inhibit 50 % of a given DPPH concentration.

Volatile compounds were identified by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7000 Series Triple Quadrupole system, comprising a gas chromatograph (GC) coupled to a triple quadrupole mass spectrometer (MS). Chromatographic peaks were identified either by direct interpretation of the mass spectra or by comparison with the NIST/EPA/NIH Mass Spectral Library (Version 2.0g, 2011). The GC was equipped with an Agilent HP-5MS column (19091S-433: 812.83871, 5 % phenylmethylsiloxane). Lignin samples were placed in sealed headspace vials and heated at 200 °C for 15 min. Sample introduction was performed in split mode (10:1) with an injection volume of 500 µL. The headspace temperature was selected to

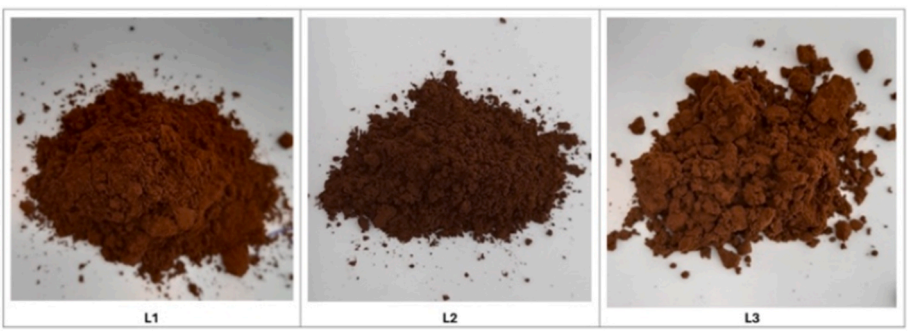

Fig. 1. L1, L2 and L3 lignins.

simulate the thermal conditions of the extrusion process, enabling the identification of potential volatile compounds released under processing conditions.

The FT-IR spectra were obtained by Total Attenuated Reflectance (ATR) in the range of 4000–525 cm^{-1} with a resolution of 4 cm^{-1} and 256 scans per sample, using a Thermo Scientific Nicolet IS50 FT-IR spectrophotometer (USA).

The lignins were previously dried for 4 h at 60 °C. Proton Nuclear Magnetic Resonance spectra (^{1}H NMR) and Carbon Magnetic Resonance spectra (^{13}C NMR) from the lignin samples were obtained with a Bruker spectrometer operating at 500 MHz for ^{1}H and 128.4 MHz for ^{13}C, at 26.0 °C, with chemical shifts referenced to the solvent dimethyl sulfoxide deuteride (DMSO-d6) with 99.8 % of the Deuterium (ppm) or 0.03 % tetramethylsilane (TMS) and deuterium oxide (D_2O).

2.2. Polymer processing

Polypropylene (PP) was added with lignins (L: L1, L2, L3), synthetic primary (AO1) and synthetic secondary (AO2) antioxidants. The compositions (Table 1) were obtained in a twin-screw extruder from Thermo Scientific Haake PTW16. The screw speed was 80 rpm, and the processing temperature was 180 °C in zone 1 (feed) and 200 °C in the other zones (2–6).

The secondary antioxidant (AO2) was added to all formulations except PP (as received), and PP that was extruded. PP AO2 is the formulation that analyzed the efficiency of the secondary antioxidant during the processing, and PP AO1AO2 is the typical formulation for basic commercial stabilization. Based on the characterization results of the formulations produced by extrusion with the three lignins (500, 1,000, 3,000, and 5000 ppm), two more formulations were produced under the same extrusion conditions, only with the L1 and L2 lignins at a content of 2000 ppm.

The PP granules with 500 to 5000 ppm of L1 lignin are shown (Fig. 2). The formulations PP, PPAO1AO2, PP2000L1AO2, PP3000L1AO2, PP2000L2AO2, and PP3000L2AO2 were subjected to the degradative process in a Haake Polylab OS Rheomix torque rheometer 600 OS, at 240 °C and 100 rpm. This procedure was applied to evaluate the difference in performance of L1 and L2 lignins as antioxidants.

2.3. PP with synthetic antioxidant and lignins characterization

The compositions were analyzed by Oxidative Induction Time (OIT) obtained by differential scanning calorimetry (DSC), molar mass by size exclusion chromatography (SEC), and viscosity by parallel plate rheometry in the stationary phase. The OIT analyses were carried out using TA Instruments Q100 DSC (USA) with uncovered aluminum crucibles containing 8–9 mg of sample. The heating ramp during the analyses varied from room temperature to 180 °C, presenting a heating rate of 20 °C/min with an inert nitrogen atmosphere. After 5 min in this condition (180 °C, N_2), the gas was changed to an oxidative atmosphere. The time needed to start the oxidation was measured between the gas exchange time and the beginning of the oxidation (start of the exothermal variation). The molar mass measurements by size exclusion chromatography (SEC) of the PP formulations were performed using the Viscotek high temperature gel permeation chromatograph, model GPC5351US (Viscotek Automated Conventional HT-GPC System) with a refractive index (RI) detector. In the SEC analyses, the trichlorobenzene solvent (TCB) was used at a temperature of 150 °C and a flow rate in the main and auxiliary pumps of 1 mL/min. The solvent was pre-stabilized with 1 % 2,6-di-tert-butyl-4-methylphenol (BHT). The pellets were used to measure the rheological properties in the Anton Paar MCR 102 at 180 °C in an inert atmosphere (N_2) using parallel plate geometry (diameter 25 mm). The sample loading gap was 1 mm. The tests were carried out in a steady state and occurred in the range of 0.01 s^{-1} to 10 s^{-1} shear rates.

Table 1
Formulations used to obtain the evaluated materials.

Formulations	(ppm)		
	AO1	AO2	L
PP	0	0	0
PP extruded	0	0	0
PPAO2	0	1000	0
PPAO1AO2	500	1000	0
PP500LAO2	0	1000	500
PP1000LAO2	0	1000	1000
PP2000LAO2	0	1000	2000
PP3000LAO2	0	1000	3000
PP5000LAO2	0	1000	5000

3. Results and discussion

Table 2 presents the characterization results of lignins L1, L2, and L3 obtained through various analytical techniques. Lignins L1 and L2 exhibited lower pH values compared to L3, which is attributed to differences in the precipitation conditions during black liquor processing. Literature reports indicate that lignins precipitated under more acidic conditions tend to exhibit higher purity and reduced hemicellulose content [23,27,28]. The ash content in the lignin samples was identified as comprising predominantly inorganic elements such as sodium, sulfur, and potassium. Among the samples, L3 lignin exhibited the highest ash content and the lowest lignin content. Notably, the combined total of lignin and ash in L3 was approximately 55.56 %, indicating that the remaining 44.44 % likely consists of organic impurities, including residual cellulose and hemicellulose [23,27,28].

Syringyl and guaiacyl compounds were identified by gas chromatography–mass spectrometry (GC–MS) based on peak area intensity (counts). These compounds possess sterically hindered phenolic structures capable of acting as hydrogen donors, contributing to antioxidant activity. Among the samples, L2 lignin exhibited the highest concentrations of syringyl and guaiacyl. Additionally, lignins L1 and L2 showed higher polyphenol content and greater structural purity compared to L3, which contained elevated levels of inorganic constituents and residual cellulose and hemicellulose.

L1 lignin presented the lowest inhibitory concentration value (IC50), indicating that a lower concentration of L1 lignin can inhibit 50 % of a given concentration of DPPH radicals, thereby demonstrating greater antioxidant performance using this methodology [29,30].

The infrared spectra (Fig. 3) showed differences in the range relating to the OH bond of hydroxyls (~3400 cm^{-1}) and between the absorption bands from 1800 cm^{-1} to 600 cm^{-1}. Lignins L1 and L2 show absorption at 3400 cm^{-1}, and L3 lignin around 3250 cm^{-1}. These bands are characteristic of axial deformation of the O-H bond of phenolic and aliphatic hydroxyls. The bands 2936 cm^{-1} and 2840 cm^{-1} in lignins L1 and L2 are associated with the C-H bond present in methoxyl linked to the ring of syringyl and guaiacyl structures [3,31,32]. The double peak at ~2350 cm^{-1} in the spectra of L2 and L3 lignins represents the antisymmetric stretching mode of gaseous CO_2 present in the environment and is irrelevant to the analysis. The bands at 1597 cm^{-1} and 1421 cm^{-1} of the spectra of L1 and L2 lignins, and around 1571 cm^{-1} for L3 lignin, and also at 1511 cm^{-1} in all lignins, are related to the bonds C=C and C-C present in the aromatic ring of guaiacyl and syringyl groups [32,33]. The band 1383 cm^{-1} of the L3 lignin spectrum, which may be associated with aldehydic C-H bending present in hemicelluloses [34,35]. The absorption around 1209 cm^{-1} and 1030 cm^{-1} can be attributed to vibrations of the guaiacyl group [33,36]. Lignins L1 and L2 exhibit strong absorption at 1150 cm^{-1}, while this band is softer in L3 lignin, associated with C=O vibrations of the guaiacyl structure [27]. At 826 cm^{-1}, there is the C-H deformation bend of the syringyl ring [33,37].

The hydrogen ^{1}H NMR and carbon ^{13}C NMR, nuclear magnetic resonance spectra, are shown in Fig. 4. Chemical shifts between 4.2 and

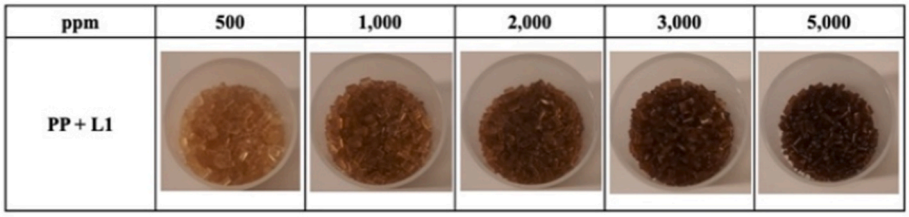

Fig. 2. PP and L1 formulations.

Table 2
Characterization of lignins.

Properties	L1	L2	L3
pH	3.35 ± 0.02	3.68 ± 0.02	7.97 ± 0.03
Total phenolics (g of gallic acid/100g of Lignin)	146.43 ± 0.50	108.60 ± 3.58	83.01 ± 0.75
IC50 (mg/L)	0.232	0.263	0.294
	y = 24.886ln (x) + 86.034	y = 20.818ln (x) + 85.615	y = 22.501ln (x) + 83.592
	R^2 = 0.979	R^2 = 0.9855	R^2 = 0.9448
	Quercetin: 0.013 y = 14.651ln(x) + 113.72 R^2 = 0.9238		
Ash content (%)			
525 °C	15.08 ± 4.00	9.85 ± 6.83	46.81 ± 5.62
900 °C	0.76 ± 0.03	1.37 ± 0.38	16.39 ± 0.42
Elements (%)			
Na	0.08	0.18	9.75
S	0.60	1.04	4.07
K	0.02	0.05	1.93
Cl	0.007	0.01	0.27
Si	0.02	0.04	0.17
Ca	0.02	0.04	0.07
Fe	0.005	0.01	0.03
Al	0.004	0.007	0.02
Others	–	0.015	0.069
Moisture (%)	2.4	1.5	4.8
Soluble lignin (%)	8.47 ± 0.004	8.4 ± 0.136	21.12 ± 0.155
Insoluble lignin (%)	86.69 ± 0.161	86.82 ± 1.021	18.05 ± 0.034
Total lignin (%)	95.16 ± 0.157	95.22 ± 0.885	39.17 ± 0.121
Area of the peaks (counts) at 200°C			
Guaiacyl	1.44 x 10^6	1.79 x 10^6	4.64 x 10^5
Syringyl	3.63 x 10^5	1.07 x 10^6	4.63 x 10^5

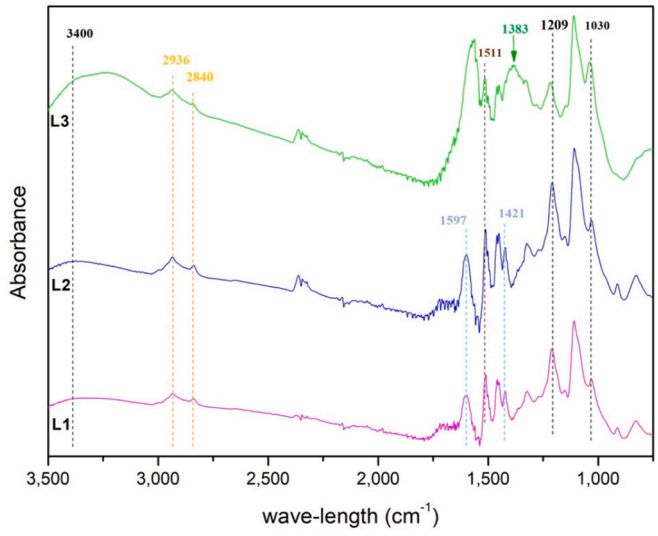

Fig. 3. FTIR spectra of L1, L2, and L3 lignins.

3.1 ppm have greater intensity in the L1 and L2 lignins' spectra, attributed to the methoxyl of syringyl and guaiacyl groups of lignin in several studies of lignin structures [1,27,32]. For L3, these signals are also present in its proton NMR spectrum at a smaller and less defined intensity. For the aromatic region, the L3 signals are almost imperceptive despite having been made under the same conditions as samples L1 and L2. All these issues are related to the fact that sample L3 shows low solubility in d6-DMSO. The lignin bonds that show condensed aromatic structures are β-O-4, β-β, and β-5, whose protons are associated with peaks from 4 to 6.3 ppm [2,39] (Fig. 4A). In Fig. 4B, the region associated with aromatic ring carbons (C1 and C6) is between 100 and 150 ppm [32,33,38]. L3 lignin shows no chemical shifts with sufficient intensities to characterize aromatic structures, similar to L1 and L2 lignins when analyzed in d6-DMSO. However, when exchanging the d6-DMSO solvent for D_2O, it is possible to observe hydrogen signs attributed to the aromatic region and the signals attributed to methoxyl groups became more defined and noticeable (Fig. 4C). In the ^{13}C NMR spectra, the presence of methoxyl is evidenced by the peak at 53.8 ppm, as confirmed by authors who used ^{13}C NMR analyses for lignin analysis [33,38]. However, when performing the analysis in D_2O, it is possible to observe such carbon signs with their respective attributions (Fig. 4D). The chemical shifts of hydrogens in 7.5; 7.0 and 6.5 ppm evidenced in L1 and L2 lignins are attributed to aromatic ring hydrogens of p-hydroxycoumaryl (H), guaiacyl (G) and syringyl (S) groups (Fig. 5), respectively [2,32,33,38].

Fig. 6 shows the HSQC spectra of lignins L1, L2, and L3. In the region of 3.45–4.02 ppm, attributed to the methoxyl group, correlations are observed with the peaks of this group for carbon at 57.03 ppm. In the aromatic region, correlations are also seen with hydrogens at approximately 6.59, 6.74, and 6.69 ppm, with carbons at 103, 104, and 106 ppm. The aromatic signals of the quaternary carbons around 148 ppm (G) are confirmed in the HSQC spectrum by the absence of corresponding hydrogen signals. This corroborates the assignments made for the hydrogen and carbon NMR analyses. In this context, lignins L1 and L2 present evidence of similar chemical structures associated mainly with the guaiacyl (G) and syringyl (S) groups, as observed in both FT-IR and NMR analyses. These groups have phenolic hydroxyls with steric hindrance and, therefore, the potential to act as a primary antioxidant for polypropylene.

According to Table 3, formulations containing L1 and L2 lignins at concentrations between 3000 and 5000 ppm exhibited oxidation induction time (OIT) values higher than those of polypropylene stabilized with conventional synthetic antioxidants (PPAO1AO2). This suggests that the free radicals generated under high temperatures and an oxidizing atmosphere during the tests were effectively eliminated by the hydrogen atoms of the phenolic groups in lignin, a mechanism analogous to that of synthetic primary antioxidants [40–43]. The lower stabilization performance observed for L3 lignin may be attributed to its structural characteristics, including the presence of inorganic residues, cellulose, and hemicellulose, as well as a reduced content of phenolic moieties.

Fig. 7 indicates a consistent rheological profile across all polypropylene (PP) formulations, characterized by a Newtonian plateau at low shear rates and a viscosity reduction with increasing shear rate, typical of pseudoplastic materials. Notably, formulations incorporating

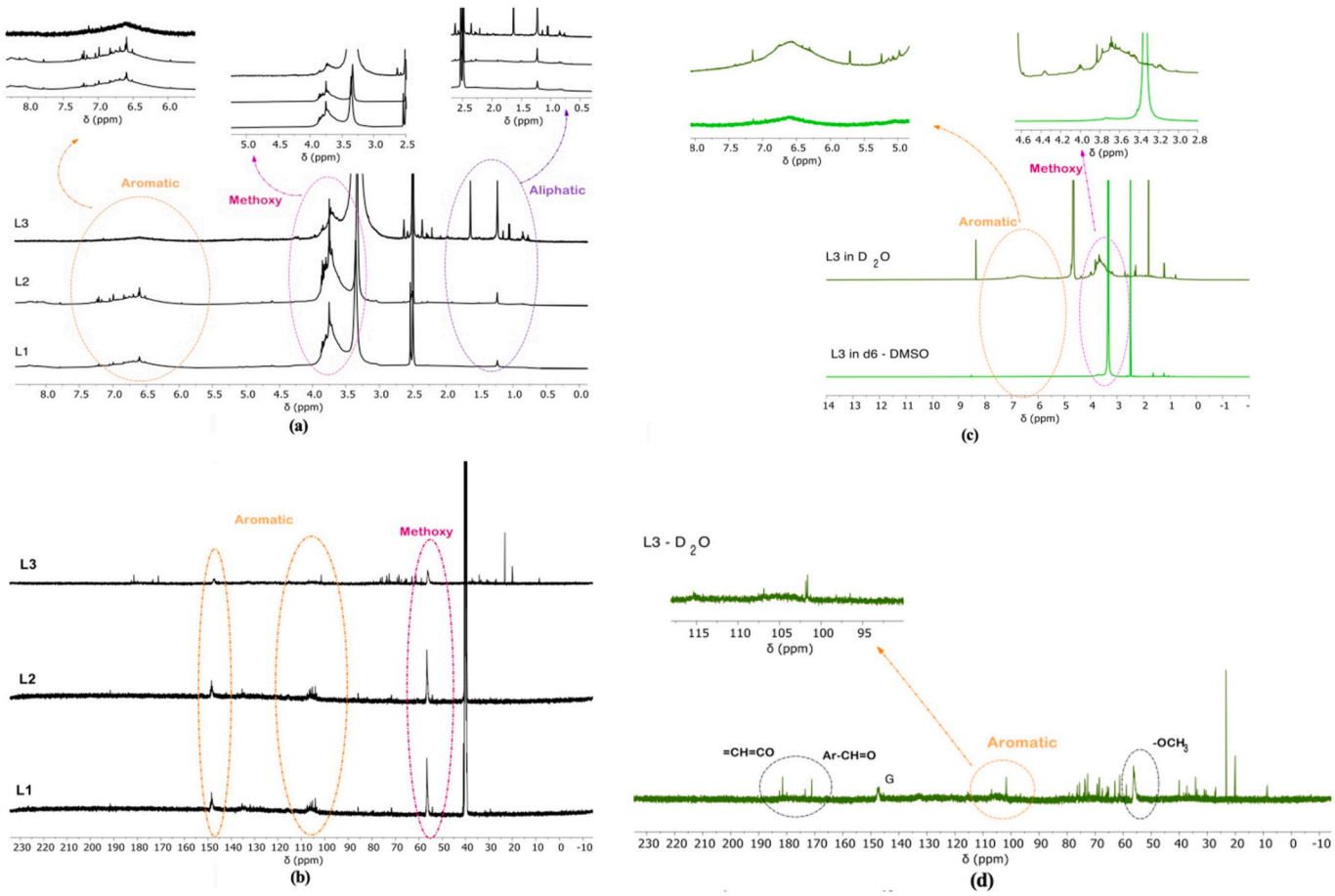

Fig. 4. 1H NMR (A; C) and 13C NMR (B; D) spectra of L1, L2, and L3 Lignins.

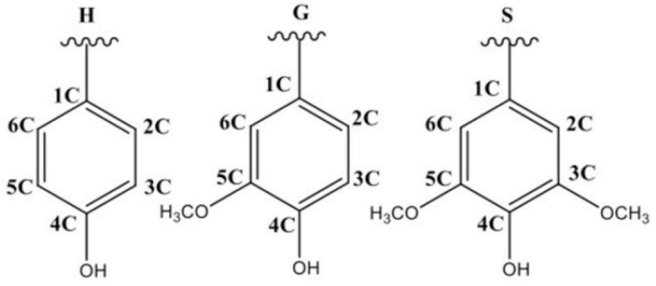

Fig. 5. P-hydroxycoumaryl (H), guaiacyl (G), and syringyl (S) aromatic groups.

lignins L1 and L2 exhibit higher viscosities at a shear rate tending toward zero (η_0) than the synthetically stabilized reference (PPAO1AO2) at concentrations equal to or exceeding 1000 ppm. A similar trend is observed for the formulation containing lignin L3, although only from 3000 ppm onwards.

According to the results related to molar mass, polypropylene (extruded PP) without an antioxidant and polypropylene with a secondary antioxidant (PPAO2) showed a reduction compared to PP as received (PP). In this context, extrusion processing caused degradation. The stabilized PP (PPAO1AO2) had a lower molar mass than PP; that is, even with the synthetic stabilization system, there was degradation.

Formulations containing lignins L1 and L2 at concentrations above 1000 ppm exhibit higher molar masses compared to the synthetically stabilized reference (PPAO1AO2) and tend to approximate the molar mass values of the as-received polypropylene (PP). In contrast, formulations incorporating lignin L3 show molar mass values comparable to those of PPAO1AO2 at concentrations of 3000 and 5000 ppm. These results suggest that lignins L1 and L2 contribute to the preservation of the polymer's molecular structure, potentially through antioxidant mechanisms that inhibit chain scission during processing.

To better evaluate the performance of lignins L1 and L2 as primary antioxidants, a test was conducted using a torque rheometer at 240 °C and 100 rpm for 10 min. These conditions are considered severe due to the high temperature, elevated shear rate, and the oxygen availability provided by the rheometer's mixing chamber. Formulations containing 2000 ppm and 3000 ppm of L1 and L2 were selected, as these concentrations demonstrated performance levels comparable to synthetic stabilization, according to the previously obtained data. The viscosity values at the Newtonian plateau for formulations with L2 lignin were higher at both concentrations studied. They exceeded those of the PP formulation with synthetic additives in both processing methods, extrusion and torque rheometry, with the latter showing a more pronounced effect. These results reinforce the potential of L2 as an effective antioxidant, particularly under oxidative and thermomechanical stress Table 4.

The highest viscosity values correlate with increased molar mass and a shift in the molar mass distribution toward higher molar mass, as shown in (Fig. 8). These findings indicate that L2 lignin was more effective in donating hydrogen atoms to stabilize polypropylene free radicals generated during thermo-oxidative degradation, both in the extrusion process and under the intensified thermo-mechanical and oxidative environment provided by the torque rheometer. Although L2 lignin exhibited a lower total phenolic content, it contained higher concentrations of syringyl and guaiacyl moieties. These functional groups are known for their steric hindrance, which contributes to greater stability during hydrogen donation to free radicals.

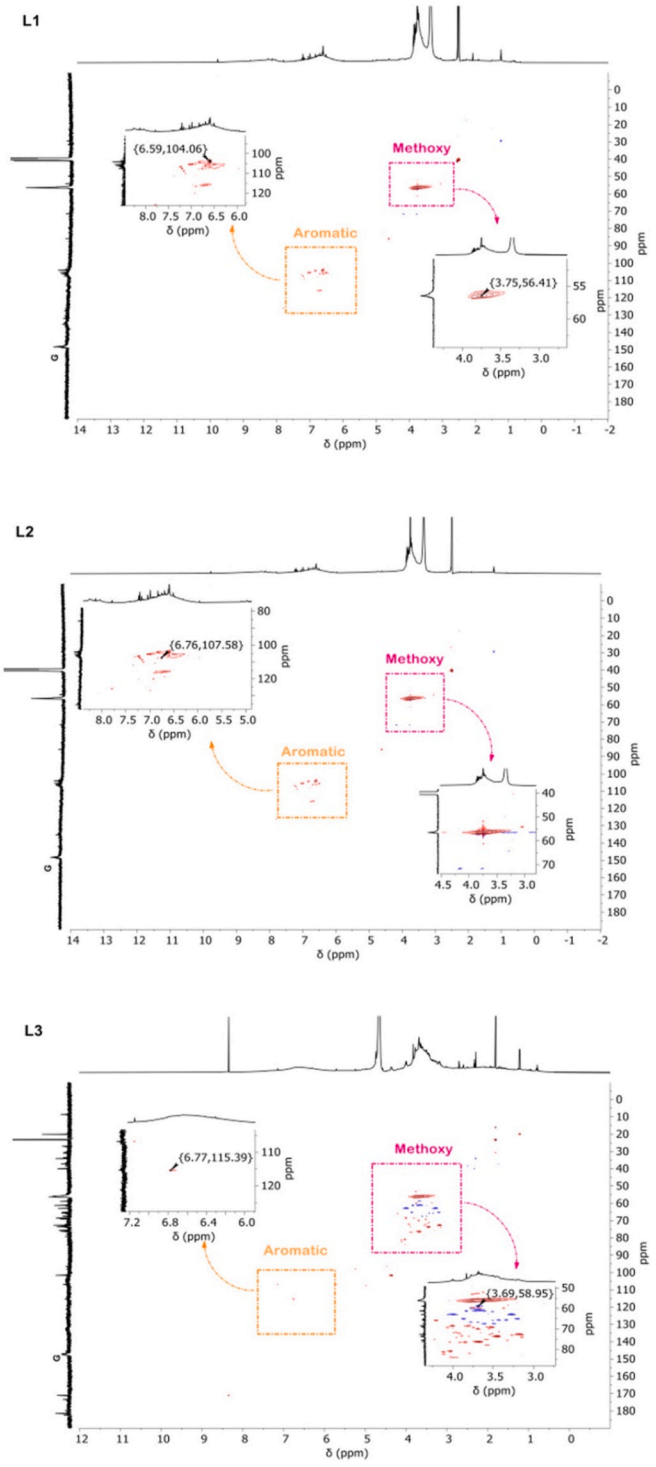

Fig. 6. HSQC NMR spectra of L1, L2, and L3 Lignins.

Consequently, under intensified thermo-oxidative stress, L2 lignin demonstrated superior effectiveness in preserving the molecular integrity of polypropylene. The stability of the phenoxyl radical at high temperatures can explain the better antioxidant performance of lignin L2 relative to L1. The higher the temperature, the lower the stability of this radical, which is dependent on groups 2 and 6 of the aromatic ring. Syringyl has methoxy groups in positions 2 and 6, while guaiacyl has methoxy groups only in position 2, which gives the former greater stability of the phenoxyl group. Since lignin L2 has higher syringyl group content and a higher syringyl to guaiacyl ratio (0.6 for L2 and 0.25 for L1), the stability of the phenoxyl groups when hydrogen is donated is greater, resulting in higher antioxidant potential at high temperatures.

Table 3
Oxidative induction time, viscosity at zero shear rate, molar mass, and polydispersity.

Formulations	Oxidative induction time (min)	η_0 (Pa. s)	$\overline{M}_n$ (Da)	$\overline{M}_w$ (Da)	$\overline{M}_w/\overline{M}_n$
PP	0.63 ± 0.05	14,425	179,000	583,000	3.25
PP extruded	0.27 ± 0.06	6398	122,000	363,000	2.97
PPAO2	0.22 ± 0.01	6565	125,000	385,000	3.06
PPAO1AO2	35.56 ± 4.55	12,033	137,000	453,000	3.29
PP500L1AO2	1.86 ± 0.36	10,101	134,000	434,000	3.23
PP500L2AO2	1.62 ± 0.20	11,434	133,000	441,000	3.30
PP500L3AO2	1.88 ± 0.66	10,945	162,000	474,000	2.92
PP1000L1AO2	6.85 ± 1.46	13,155	162,000	577,000	3.54
PP1000L2AO2	12.18 ± 1.21	13,736	160,000	534,000	3.33
PP1000L3AO2	1.22 ± 0.01	9442	144,000	421,000	2.91
PP2000L1AO2	38.76 ± 2.89	14,006	147,391	427,371	2.90
PP2000L2AO2	68.62 ± 5.91	14,197	161,243	454,398	2.82
PP3000L1AO2	56.99 ± 8.32	14,323	160,000	547,000	3.42
PP3000L2AO2	27.41 ± 8.61	14,398	141,000	539,000	3.81
PP3000L3AO2	1.61 ± 0.32	12,091	115,000	480,000	4.16
PP5000L1AO2	72.08 ± 1.45	14,189	158,000	615,000	3.88
PP5000L2AO2	53.26 ± 6.27	14,489	167,000	560,000	3.36
PP5000L3AO2	2.94 ± 0.77	13.788	131,000	462,000	3.52

Several studies demonstrated the antioxidant properties of lignin in polypropylene, achieving better results in mechanical and oxidative stabilization properties compared to commercial antioxidants. The main kind of lignin was obtained by the Kraft and Organosolve fractionation processes [16,31,41,44,45].

In this study, rheological and molar mass analyses provided clear evidence for the preservation of the polypropylene molecular structure, as well as the superior thermo-oxidative stabilization conferred by lignin-based additives when compared to a commercial antioxidant system. It is essential to consider the presence of phenolic hydroxyl groups exhibiting steric hindrance within the lignin structure, as well as a high overall lignin content accompanied by reduced levels of impurities—such as inorganic constituents and residual cellulosic materials—originating from the lignin extraction process. These structural and compositional attributes are critical for enhancing the antioxidant efficiency and stabilizing performance of lignin in polypropylene formulations.

4. Conclusion

Lignins L1, L2, and L3 exhibit distinct chemical compositions and purities, which directly influence their potential as primary antioxidants. L1 and L2 demonstrated favorable characteristics for this function. For lignin to act effectively as a primary antioxidant, its molecular structure must include phenolic hydroxyl groups with steric hindrance, such as those present in guaiacyl and syringyl units, as well as a low level of impurities. These impurities, including inorganic components and residual cellulosic materials, are largely determined by the conditions of the black liquor precipitation process used during lignin extraction.

Using oxidative induction time (OIT) measurements, parallel plate rotational rheometry, and size exclusion chromatography (SEC), it was demonstrated that lignins L1 and L2 function as effective primary antioxidants in polypropylene at concentrations starting from 2000 ppm. Among them, L2 lignin exhibited superior performance under the high-temperature and high-shear conditions imposed by the torque rheometer. This enhanced activity is likely associated with its higher content of guaiacyl and syringyl units, which provide sterically hindered phenolic hydroxyl groups capable of efficiently donating hydrogen atoms to stabilize free radicals generated during thermo-oxidative degradation.

The results of this study suggest that lignin is a viable antioxidant for polypropylene, especially in applications involving recycled materials.

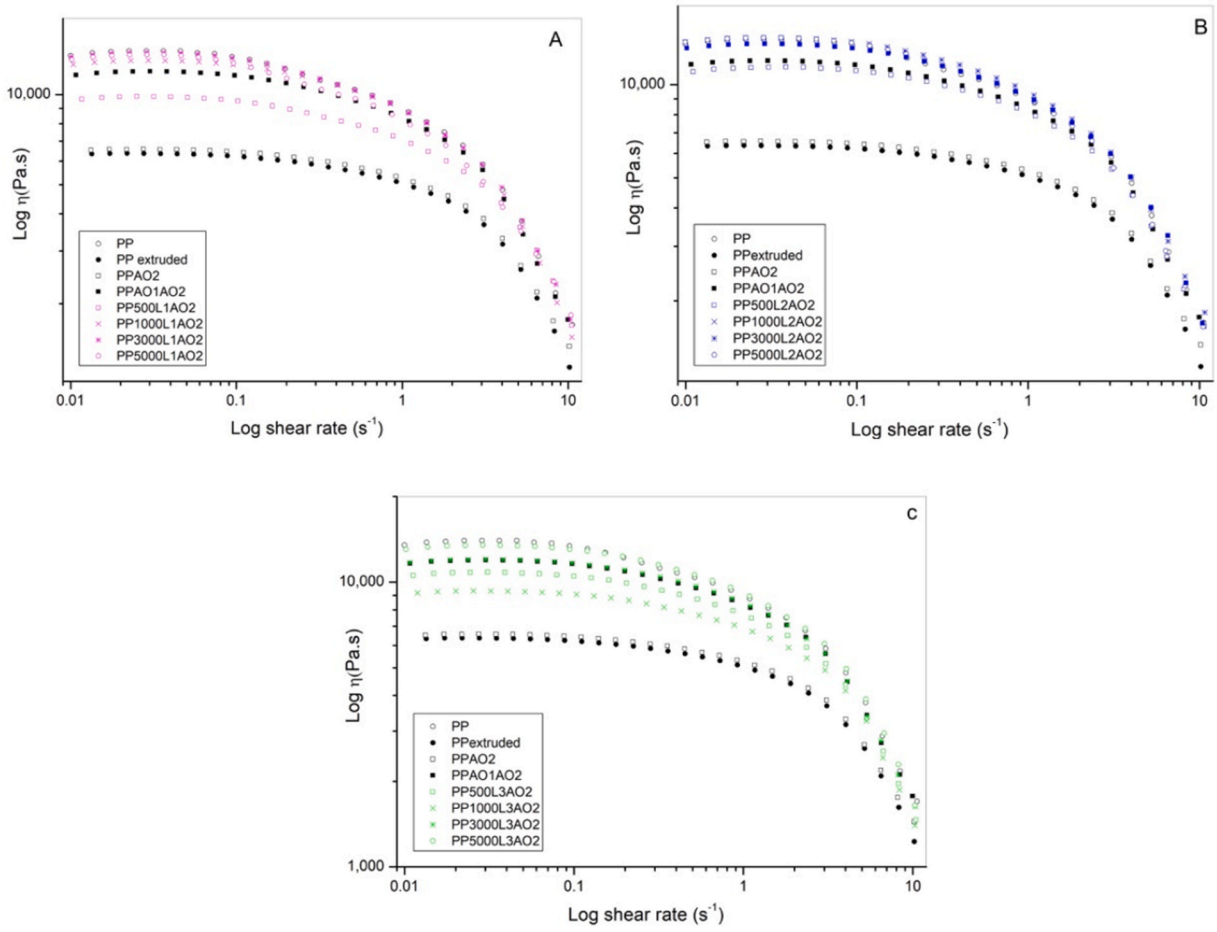

Fig. 7. Viscosity depending on the shear rate (A) PP - L1 (B) PP – L2 (C) PP – L3.

Table 4
Viscosity at zero shear rate (η_0) and numerical and weight-average molar mass of formulations processed by extrusion and in a torque rheometer at 240 °C for 10 min (PP, PPAO1AO2, PP2000L1AO2, PP3000L1AO2, PP2000L2AO2, PP3000L2AO2).

Formulations		η_0 (Pa.s)	$\overline{M}_n$ (Da)	$\overline{M}_w$ (Da)	$\overline{M}_w/\overline{M}_n$
PP	Neat	14,425	179,518	550,838	3.07
	Extruded	12,313	103,322	324,422	3.14
	240 °C, 10min	428	20,675	69,472	3.36
PP AO1AO2	Extruded	13,934	184,029	541,941	2.94
	240 °C, 10min	1574	45,783	132,375	2.89
PP2000L1AO2	Extruded	14,006	147,391	427,371	2.90
	240 °C, 10min	2583	77,349	148,370	1.92
PP3000L1AO2	Extruded	13,982	173,812	440,662	2.54
	240 °C, 10min	3849	85,119	258,442	3.04
PP2000L2AO2	Extruded	14,197	161,243	454,398	2.82
	240 °C, 10min	3621	89,487	179,915	2.01
PP3000L2AO2	Extruded	14,074	173,360	460,745	2.66
	240 °C, 10min	4432	126,061	303,776	2.41

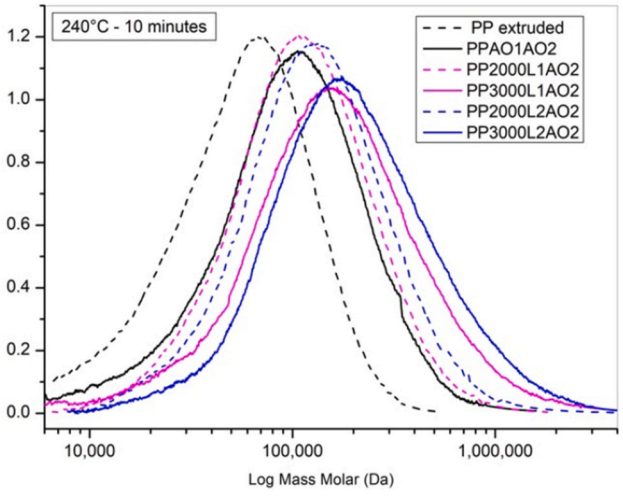

Fig. 8. Molar mass distribution curve of formulations processed in a torque rheometer at 240 °C for 10 min (PP reactor, AO1, AO2, PP2000L1AO2, PP3000L1AO2, PP2000L2AO2, PP3000L2AO2).

In these cases, the brown coloration imparted by lignin may not be a limitation, as color changes are already expected or tolerated in such materials.

CRediT authorship contribution statement

Ana Clelia Babetto: Writing – original draft, Validation, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Lívia Maria Garcia Gonçalves:** Methodology, Formal analysis. **Eliada Andrade Silva:** Methodology, Formal analysis. **Benedito Santos Lima Neto:** Investigation, Formal analysis, Conceptualization. **Andreia de Araújo Morandim-Giannetti:** Writing – review & editing, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Sílvia Helena Prado Bettini:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Formal

analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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