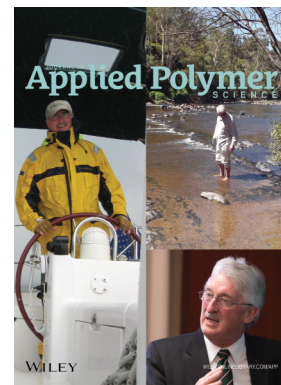


Special Issue: Sustainable Polymers and Polymer Science
Dedicated to the Life and Work of Richard P. Wool

Guest Editors: Dr Joseph F. Stanzione III (Rowan University, U.S.A.)
and Dr John J. La Scala (U.S. Army Research Laboratory, U.S.A.)



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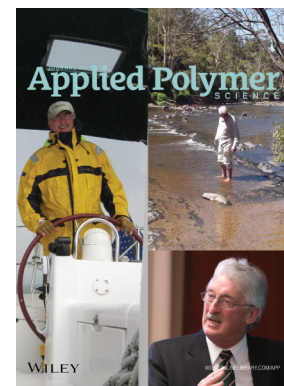
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Lignin as a green primary antioxidant for polypropylene

Renan Gadioli,¹ Walter Ruggeri Waldman,² Marco Aurelio De Paoli¹

¹Instituto de Química, Unicamp, Laboratório de Processamento de Polímeros, 13083-970 Campinas, SP, C. Postal 6154, Brazil

²Departamento de Física, Química e Matemática, UFSCar, Sorocaba, SP, 18052-780, Brazil

Correspondence to: M. Aurelio De Paoli (E-mail: mdepaoli@iqm.unicamp.br)

ABSTRACT: Lignin and Irganox 1010, a hindered phenol antioxidant, are compared as a primary stabilizer in formulations for polypropylene (PP) by exposition to accelerated aging. The concentration of lignin was adjusted to match the concentration of hindered phenolic groups of the commercial stabilizer. Upon aging, lignin formulation retains the initial mechanical properties longer than the formulation with Irganox 1010. The ratio of the areas of the carbonyl and the hydroxyl infrared absorption bands is proposed as a method to evaluate the photodegradation process. In this aspect, the formulation with lignin also presents better results than the formulation with Irganox 1010. There are two hypotheses for the best performance of lignin in the studied conditions: lower leaching of lignin, due to its crosslinked nature, and leaching of low molar mass products of Irganox 1010 hydrolysis. These results indicate lignin, from the Kraft process of Eucalyptus wood, as a promising green substituent to synthetic hindered phenol stabilizers. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43558.

KEYWORDS: ageing; cellulose and other wood products; degradation; polyolefins; thermoplastics

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INTRODUCTION

Lignin is the most abundant phenolic polymer and the second most abundant polymer in the world.¹ Lignin is present in plant structures and wood is its main industrial source, particularly those used in the paper industry.² Lignin was studied as an antioxidant for rubber and elastomers,^{3–5} composites,^{6,7} and as an antimicrobial.⁸ Lignin is biodegradable, carbon neutral, absorbs the UV radiation of sunlight,⁹ and, as a by-product of the paper industry, is available at low cost and in large amounts. For some uses, it requires chemical modifications, which increases the cost and logistical complexity of the product.

The International Union of Pure and Applied Chemistry (IUPAC) definition for lignin is “Macromolecular constituents of wood related to lignans,* composed of phenolic propyl benzene skeletal units, linked at various sites and apparently randomly”.¹⁰ Its chemical structure is complex and changes according to its source. In general, it is formed by crosslinking different phenolic structures (two examples are shown in Figure 1; center and right), bonded together by ether linkages and carbonic structures. The guaiacyl and syringyl phenolic units of lignin are responsible for its antioxidant activity.^{11,12} The pres-

ence of substituents in both ortho positions of the syringyl phenolic unit favors the free radical scavenging capacity of lignin, due to steric hindrance, similarly to what occurs with the hindered phenols used as primary antioxidants for polymers, e.g., Irganox 1010 (Figure 1, left), discussed later in the text.

Lignin is a by-product of the Kraft process, where aqueous solutions of NaOH and Na₂S are used at high temperatures to solubilize lignin and hemicellulose, producing cellulose for the paper industry. The solubilized product of the Kraft process contains partially depolymerized lignin, rich in phenolic hydroxyl groups.^{12–14} The lignin used in this work was obtained as a by-product of the industrial Kraft process of Eucalyptus wood (*Eucalyptus grandis* and *Eucalyptus urograndis*), and was previously characterized by Barbosa *et al.*¹⁵ as having a syringyl:guaiacyl ratio in the range of 2.1 to 2.5. This motivates the study of this particular lignin as an antioxidant for polymers. It is important to highlight that this and other characteristics may vary according to the type of industrial process as well as the vegetable species.

The degradation of polypropylene (PP) is well studied.¹⁶ It involves the formation of a free radical at the tertiary carbons of the polymer backbone as initial step. These free radicals react with oxygen generating hydroperoxides, carbonyl groups, and volatile compounds.¹⁷ Thus, free radical scavengers preclude the degradation of polypropylene.

*Defined by IUPAC as “Plant products of low molecular weight formed primarily from oxidative coupling of two p-propylphenol moieties at their β carbon atoms; products with units coupled in other ways are neolignans.”

Additional Supporting Information may be found in the online version of this article.

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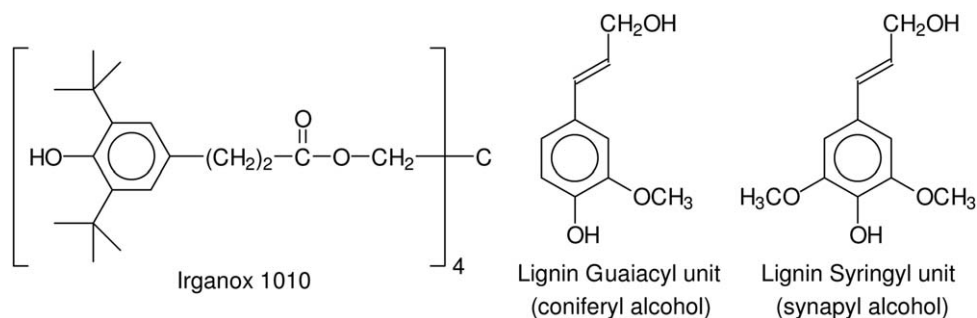


Figure 1. Chemical structures of Irganox 1010 (left), and two lignin phenolic units, Guaiacyl (center), and Syringyl (right).

Polymer stabilizers occur in two groups: primary antioxidants, which act as free radical scavengers and are, in general, sterically hindered phenols, and secondary antioxidants, which decompose hydroperoxides generating nonradical products. Phenolic antioxidants operate mainly by the combination of two characteristics: the high stability of the phenoxyl radical by resonance with the aromatic ring and the steric hindrance provided by the groups in ortho position in relation to the OH.¹⁸ Irganox 1010 is used as primary antioxidant for polypropylene, it deactivates the free radicals formed during its oxidative degradation generating the structure B in Figure 2. The phenoxyl radical, derived from the stabilizer, has low reactivity due to the steric hindrance provided by the two *tert*-butyl groups in the ortho position to the phenolic –OH (Figure 2, structure B). One of its resonance structures, the quinonoid (Figure 2, structure C), can react further with the polymer free radicals, precluding the formation of peroxy radicals by reaction with oxygen.

The main differences between Irganox 1010 and lignin are the lower steric hindrance of the groups ortho to the phenolic OH (Figure 1, right) and the higher mobility of Irganox 1010 in the polymer matrix. The highly crosslinked structure of lignin impedes its solubilization and reduces its diffusion in the polymer matrix. Consequently, Irganox 1010, and other hindered

phenol stabilizers, have a higher leaching rate than lignin. Higher electronegativity of alkoxy groups of lignin can also reduce the reactivity of the phenoxyl radical by inductive effect, reducing its electron density.

Secondary stabilizers complement the action of primary stabilizers. Secondary stabilizers decompose the hydroperoxides formed after reaction of the peroxy radicals with the polymer backbone. In association with the hindered phenol primary antioxidants, they help to impede the propagation of the degradation.¹⁹ The most common one for polypropylene is tris(2,4-di-*tert*-butylphenyl)phosphite, produced under the trade name of Irgafos 168.

The use of lignin in formulations with polypropylene is divided into two lines: in concentrations above 10 wt % forming composites,^{20–23} and in concentrations below 2 wt % as a stabilizer.²⁴ Acting as a composite, lignin has structural function, providing higher rigidity. As a stabilizer, it has had its free radical scavenging capacity demonstrated.¹² Lignin also has the advantage of having reactive groups, allowing its functionalization to obtain composites with different functionalities.²⁵

Irganox 1010 is the most common phenolic stabilizer for polypropylene, usually at 0.1 to 0.4 wt %. As the global demand for

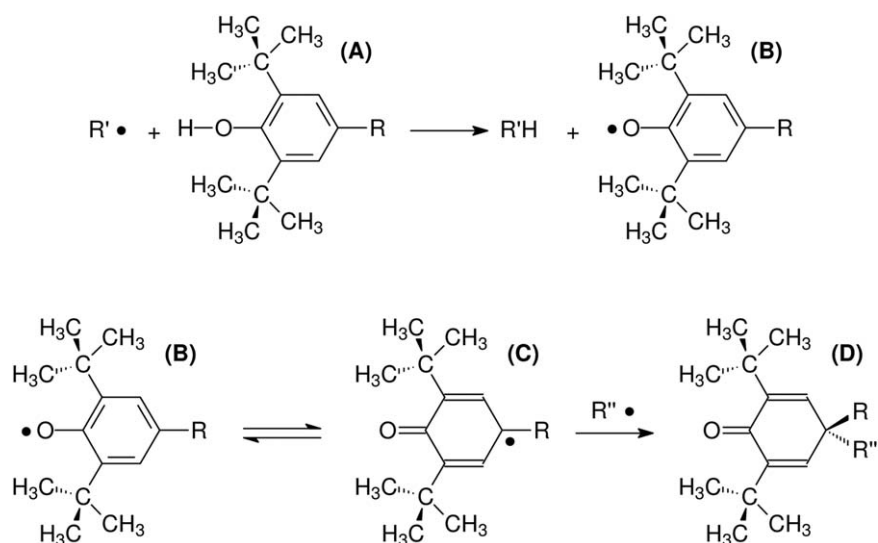


Figure 2. Proposed mechanism of stabilization of Irganox 1010: (A) structure of Irganox 1010; (B) Irganox 1010 radical after loss of hydrogen from hydroxyl; (C) quinonoid radical structure from B; and (D) "Inactivated" form of C, after reacting with a polymeric free radical. R is the long chain of Irganox 1010 (Figure 1); R' and R'' are the polymeric radicals generated in oxidative degradation.

Table I. Formulations in Wt % Prepared by Extrusion

Formulations	PP	Irganox 1010	Lignin	Irgafos 168
PP	100	—	—	—
PPLS	99.86	—	0.09 ^a	0.05
PPS	99.90	0.05	—	0.05

^aCalculated to match the concentration of syringyl groups (1.87 mmol g⁻¹) of lignin with the concentration of hindered phenols of Irganox 1010 (3.4 mmol g⁻¹).

polypropylene totaled 55.1 million tons in 2013, lignin could be a natural substituent for a stabilizer with a potential yearly demand of ca. 55.1 thousand tons. A drawback, and therefore a limit for lignin application as a stabilizer, is its dark color.

We aimed to study the stabilizing effect of lignin, obtained from the industrial Kraft Process of Eucalyptus wood, as a primary antioxidant for polypropylene. The concentration of lignin was adjusted to have a concentration of hindered phenolic groups equivalent to that of the commercial stabilizer. For this, lignin in the form of a powder was dispersed in the polymer by extrusion, and test samples were injection molded and aged. For comparison, we used the commercial stabilizer Irganox 1010. Lignin formulation presented stability towards photodegradation, as assessed by evaluation of mechanical properties and by reflectance infrared spectroscopy.

EXPERIMENTAL

Materials

Polypropylene H301 (melt flow index = 10 g/10 min) was supplied by Braskem (Triunfo), Irganox 1010 (tetrakis(methylene-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate)), and Irgafos168 (tris(2,4-di-*tert*-butylphenyl)phosphite) were both supplied by BASF. Lignin powder, used as supplied, was from the industrial Kraft Process of Eucalyptus wood in a paper mill and had a syringyl concentration of 1.87 mmol g⁻¹, according to a characterization made by the supplier. Other less sterically hindered phenol groups are present in lignin; however, they were not considered for comparison with the commercial stabilizer.

Processing

We prepared the different formulations by extrusion in a co-rotating interpenetrating twin-screw extruder (Coperion Werner Pfeleiderer ZSK26 L/D = 44). Brabender gravimetric feeders were used for dosing the formulations according to Table I. Extrusion conditions used were: temperature profile of 160, 160, 165, 165, 170, 170, 170, 170, 180, 175, and 170 °C from feeder to die, 300 rpm, and an appropriate screw profile. After extrusion, the pellets were dried in an oven (FANEM SE) at 100 °C for 1 h and injection molded (Arburg Allrounder 250-75 221 K) with the following temperature profile: 180, 185, 190, 200, and 205 °C, from feeder to die. Dimensions of the test samples according to ASTM-D638 standard.

Accelerated Aging

We used an aging chamber, built according to ASTM G154 standard, equipped with UVA lamps Phillips Cleo 80 W, with a

spectral range of 315 – 400 nm. Each cycle had 22 h of irradiation (chamber at ca. 50 °C) and 2 h of condensation (chamber at 35 °C). Test samples were positioned in supports for exposure in the chamber during 500 h. Sets of five specimen samples were removed every 100 h for characterization. In addition, one set of five specimen samples, as the control group t_0 , was kept for the same 500 h in a dark and controlled environment (23 ± 2 °C and 50 ± 5% relative humidity), and another set of five specimen samples, called time zero t_0 , was tested without aging.

Characterization Tests

Sets of samples were analyzed at different aging times by tensile mechanical tests (EMIC DL 2000-5000 N load cell) and reflectance Fourier transform infrared (FTIR) spectroscopy, Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) (IluminatIR II – Smiths coupled to Olympus BX51 microscope). Morphological characterizations were done at the National Laboratory of Nanotechnology (LNNano, Campinas) in a Quanta SEM-FEG equipment with 15 kV of accelerating voltage. Samples were cryofractured and the fracture surface metallized in a Bal-Tec SCD 005 Coater, for 60 sec and 40 mA.

RESULTS AND DISCUSSION

Morphological Characterization

Micrographs of the non-aged cryogenically fractured test samples, at low and high magnification, for the three formulations are shown in Figure 3. Images at other magnifications are available as Supporting Information. Fractures exhibited homogeneous surfaces without the presence of lignin particles (originally in the size range of 30–150 μm) or pull out holes, which originate when dispersed materials have poor adhesion to the matrix. The absence of both particulates and pull out holes is evidence of the good dispersion and adhesion of lignin to the polypropylene matrix. In addition, confirms that low molecular weight fractions of lignin are soluble in PP.²⁶

Mechanical Properties

All formulations were tensile tested and evaluated with respect to elongation, Young's modulus, and yield stress before and during the aging experiment. The results shown in Table II are compared to the control samples. It was not possible to calculate the loss of elongation, because elongations higher than 24% were not measured by this method and the initial values in all samples have fallen on this condition. The used concentration of lignin did not affect the mechanical properties, as observed previously by other authors using a concentration of 0.1 wt %.²⁷

For better comparison, the results in Table II are represented as curves for the variation of elongation and yield stress (Figure 4) and Young's Modulus (Figure 5) as a function of time. Elongation and yield stress presented almost the same behavior, polypropylene (PP) < PP stabilized exclusively with commercial stabilizers (PPS) < PP stabilized with lignin and secondary stabilizer (PPLS), regarding the maintenance of the mechanical properties until the highest property loss. In these curves, we also observe the same initial values and approximately the same amount of property loss for all samples, showing that, within the experimental error, lignin has the same stabilizing effect as Irganox 1010 in retarding the loss of these properties.

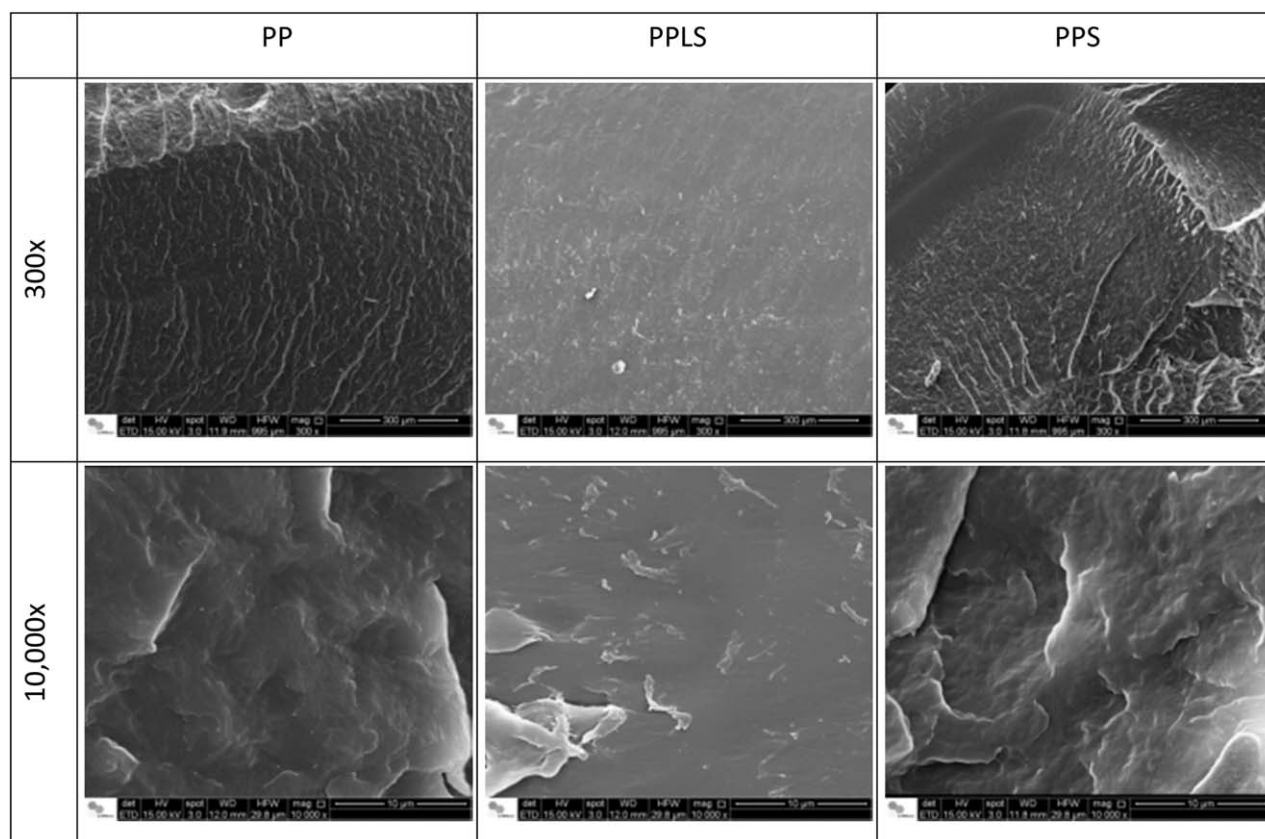


Figure 3. Micrographs at 300 and 10,000 times magnification for pure polypropylene (PP), polypropylene stabilized with lignin and Irgafos 168 (PPLS), and polypropylene stabilized with Irganox 1010 and Irgafos 168 (PPS).

Regarding elongation (Figure 4, left), it is important to highlight the high standard deviation for 200 h of accelerated aging of PPLS, which was higher than the other results. For pure PP, the highest loss of elongation occurred between 0 and 100 h of aging, while for PPS, the highest loss happened between 100

and 200 h of aging. For PPLS, the higher dispersion of values at ca. 200 h of aging indicates the loss of mechanical properties at the moment of measurement. It is known that there is dispersion of values also in time, which is not measured in this kind of experiment because of the practical limitations to collect the

Table II. Mechanical Properties for Pure Polypropylene (PP) and PP Stabilized with Commercial Stabilizers (PPS) or with Lignin as a Primary Stabilizer (PPLS) at all Aging Times and Ratio of the Property in Relation to the Control Samples (t_5/t_c). All Values Correspond to the Average of Five Specimens, Calculated Using Error Propagation to Determine the Standard Deviation

Properties	t_0 (0 h)	t_1 (100 h)	t_2 (200 h)	t_3 (300 h)	t_4 (400 h)	t_5 (500 h)	t_c	t_5/t_c (%)
PP								
Yield stress (MPa)	31.4 ± 0.2	13.1 ± 0.5	22.0 ± 0.2	20.8 ± 0.4	20.9 ± 0.3	18.0 ± 0.2	31.0 ± 0.6	58 ± 2
Young's modulus (MPa)	728 ± 156	936 ± 111	694 ± 126	770 ± 94	799 ± 116	587 ± 42	710 ± 80	83 ± 15
Elongation (%)	>24	1.4 ± 0.1	5.9 ± 0.2	6.6 ± 0.5	6.8 ± 0.5	7.0 ± 1.0	>24	— ^b
PPLS								
Yield stress (MPa)	31.0 ± 0.1	31.1 ± 0.1	31 ± 4	18 ± 3	17 ± 5	21 ± 1	30.8 ± 0.5	68 ± 4
Young's modulus (MPa)	840 ± 117	984 ± 151	1168 ± 132	974 ± 140	1126 ± 163	712 ± 70	854 ± 109	83 ± 19
Elongation (%)	>24	>24	12.0 ± 8.0^a	2.1 ± 0.5	2.0 ± 1.0	8.0 ± 1.0	>24	— ^b
PPS								
Yield stress (MPa)	31.4 ± 0.2	31.4 ± 0.1	17.0 ± 4	20.3 ± 0.7	21 ± 1	17.2 ± 0.3	31.1 ± 0.6	55 ± 2
Young's modulus (MPa)	906 ± 117	883 ± 83	1023 ± 177	925 ± 140	1004 ± 82	583 ± 30	817 ± 73	71 ± 10
Elongation (%)	>24	>24	2.1 ± 0.7	6.0 ± 1.0	5.0 ± 1.0	6.3 ± 0.5	>24	— ^b

^aTwo specimens did not break.

^bNot calculated due to equipment limitation.

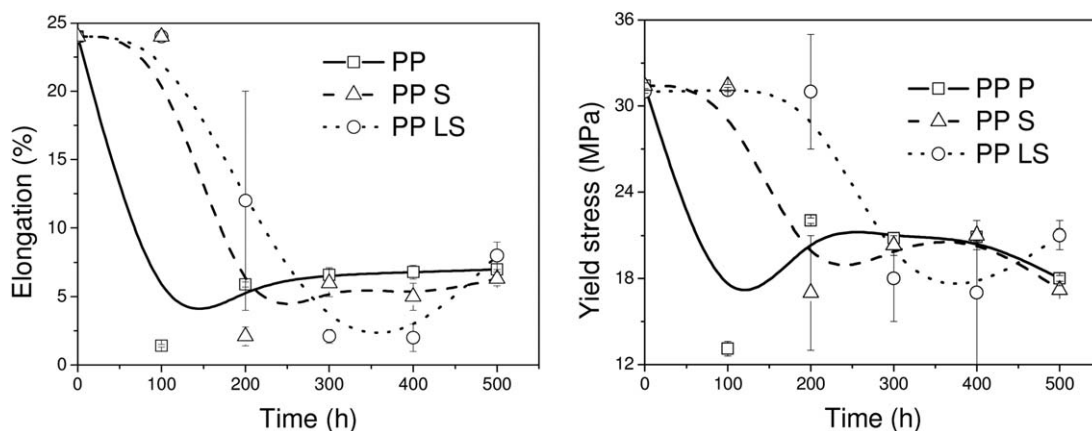


Figure 4. Variation of elongation and yield stress as a function of aging time for pure polypropylene (PP), PP stabilized exclusively with commercial stabilizers (PPS), and PP stabilized with lignin and secondary stabilizer (PPLS).

samples quickly. The higher dispersion of values indicates the loss of mechanical properties happening right at 200 h of aging. For the other times, this large dispersion of values was not observed, because the loss of mechanical properties happened after or before the instant of sample collection. A similar behavior was observed in the results for yield stress (Figure 4, right), but with lower intensity.

After the highest property loss point, the samples presented a partial recovery in elongation and yield stress. This is explained by the evolution of the photodegradation process, which can be best described in the following steps^{28,29}:

1. Chain scission takes place initially, with a consequent increase in free volume and mobility of the chains, producing higher crystallinity and the formation of cracks on the surface. The formation of a brittle surface layer starts at this step.
2. The photodegradation evolves with propagation of cracks to deeper undegraded layers, which can cause the brittle behavior under mechanical loading.

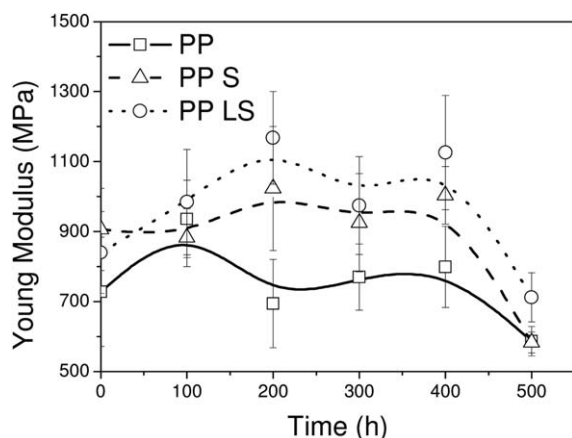


Figure 5. Young's Modulus variation as a function of aging time for pure polypropylene (PP), PP stabilized exclusively with commercial stabilizers (PPS), and PP stabilized with lignin (PPLS).

3. With the increase in thickness of the degraded surface layer, cracks reach deeper layers, increasing the loss of mechanical properties. This only occurs if the degraded layer has enough mechanical integrity to transmit mechanical loading.
4. With the evolution of photodegradation, the degraded layer becomes brittle enough to detach mechanically the deeper layers, preventing the full transmission of the mechanical loading and allowing partial recovery of the mechanical properties.

Regarding Young's modulus, the results overlapped (Figure 5); therefore, there was no statistically significant difference between different formulations. However, we can also observe a trend where the average values of the PPLS formulation are always above the results for PPS and pure PP, showing a higher stability for PPLS.

In general, lignin blended with Irgafos 168 showed higher efficiency for the stabilization of polypropylene in relation to the loss of mechanical properties. We interpret this as the sum of two factors: the lowest leaching rate of lignin and the lower efficiency of Irganox 1010 under the aging test conditions. Irganox 1010 has ester bonds which, under the 50% humidity atmosphere of the aging chamber, react by hydrolysis at the polymer surface, leaching out the low molar mass products.³⁰ This result suggests the use of lignin as a natural primary stabilizer, or even in consortium with commercial primary and secondary stabilizers, for applications under high humidity and temperature conditions, like in tropical countries.

FTIR-ATR

We used these spectra, measured at the same time intervals as the mechanical properties, to follow the chemical effects of aging on the surface of the samples. Figure 6 shows the spectral evolution for pure PP. Different oxidation products are formed, like hydroperoxides, alcohols, ketones, aldehydes, carboxylic acids, and esters.³¹ From the spectra of all samples, we obtained the carbonyl index variation (Figure 7), calculated as the ratio of the area of the C=O stretching band ($\nu_{\max}/1720 \text{ cm}^{-1}$) and a reference band ($\nu_{\max}/1167 \text{ cm}^{-1}$).³² The curves of carbonyl index versus aging time (Figure 7) showed a lower carbonyl

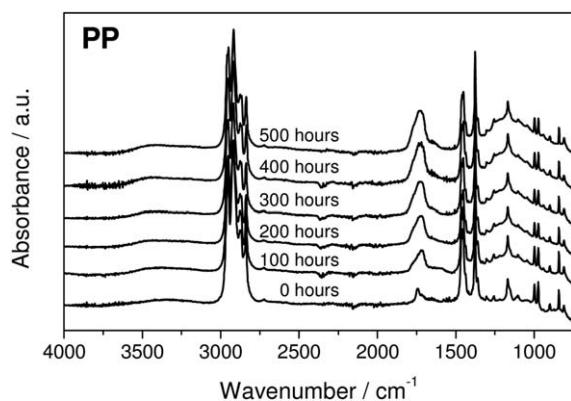


Figure 6. FTIR-ATR spectra of pure polypropylene at different aging times.

evolution for PPLS, and practically no difference between PPS and PP. A previous work using semi-bleached cellulose fibers reports this stabilization effect.³³ In that case, presence of residual lignin in the fibers causes the photo protective effect.

The autocatalytic process of polypropylene photodegradation involves the initial formation of a free radical at the tertiary carbons. The inductive effect of the methyl substituent causes β -scission, generating another alkyl radical and a terminal double C=C bond. Both free radicals react with oxygen-producing peroxy radicals, which will further react and generate hydroperoxides, carbonyls, and more free radicals. Hydroperoxides and carbonyls are evidenced by the FTIR absorptions at 3500 and 1750 cm^{-1} , O—H and C=O stretching bands, respectively. The study of the variation of the area of the carbonyl-stretching band alone, in the case of FTIR-ATR, has a limitation due to the surface roughness of the sample, which increases with aging time. The use of a reference band also has a limitation caused by the strong variation of baseline in reflectance infrared spectra, which increases with the photodegradation time (Figure 6). The combination of these effects reduces the accuracy of the carbonyl index calculation, precluding an accurate interpretation of the results.

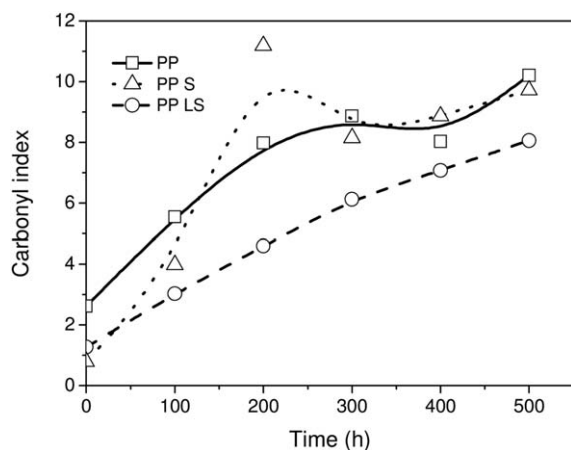


Figure 7. Carbonyl index variation for all formulations as a function of aging time.

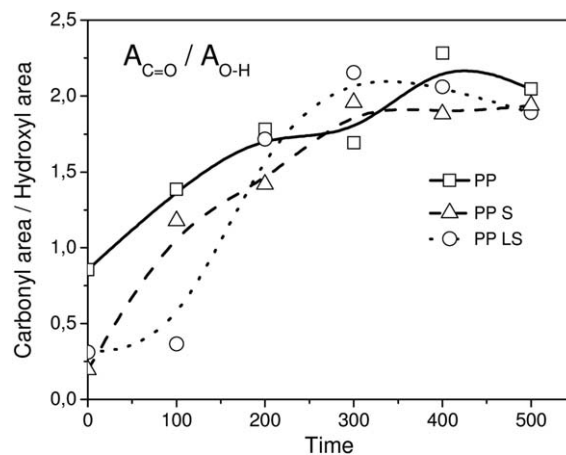


Figure 8. Variation of the ratio of carbonyl and hydroxyl stretching bands area for all formulations as a function of aging time.

The photodegradation step of formation of hydroperoxides always precedes the formation of carbonyls, along with chain scission, after a Norrish type reaction. With the evolution of the photodegradation process, the polymer surface becomes brittle and crystalline, with practically no more reactions. The rate between the concentrations of carbonyl in relation to the concentration of hydroxyl allows the assessment of the maturity of this process. Thus, for a more accurate interpretation of the dynamics of chemical surface changes during aging, we propose, to our knowledge for the first time, assessment of the evolution of the photodegradation process by the ratio between the carbonyl and hydroxyl stretching band areas. Calculating the carbonyl/hydroxyl ratio in the same reflectance spectrum will minimize the interference of the sample surface heterogeneities or some differences in measuring conditions. At the same time, we assess the evolution of the photodegradation process. We made this calculation for the spectra of all samples measured during the aging experiment, Figure 8. At the beginning of polypropylene photodegradation, we expect a higher concentration of hydroxyl in relation to carbonyl groups, with low values of the carbonyl/hydroxyl ratio, as seen in Figure 8. With the progression of the photodegradation process, the concentration of carbonyl groups increases for all formulations, until there is an almost constant carbonyl/hydroxyl ratio. In Figure 8, we observe that the increase in carbonyl/hydroxyl ratio starts after 100 h of exposure for PPLS, while for pure PP and PPS, it is possible to observe an increase of the carbonyl/hydroxyl ratio from the initial exposure time. Pure PP has a higher initial value of carbonyl/hydroxyl ratio at time 0, probably due to degradation during processing. With the calculation of carbonyl/hydroxyl ratio, it was possible to obtain complementary information with respect to carbonyl formation, allowing assessment of the photodegradation process stage.

CONCLUSIONS

Lignin showed an appropriate dispersion in the polypropylene matrix, without displaying heterogeneities at low or high magnification of the cryogenic fracture surface of the test samples. This dispersion is possible when using a twin-screw extruder

with a proper screw design. Regarding the stabilizing function, the formulation with lignin preserved for longer time the initial values of yield stress and elongation and, at the same time, having the lowest kinetic evolution of carbonyl, with respect to the amount of hydroxyl groups. Thus, it is possible to use lignin as a primary stabilizer for polypropylene exposed to humid and warm conditions, like in tropical regions.

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