

Evaluation of the Durability of Lignin-reinforced Composites Based on Wheat Straw/Recycled Polypropylene Blends

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The influence of a lignin additive at different loading levels on the surface properties, mechanical, and thermal performance of recycled polypropylene composites reinforced with wheat straw, before and after accelerated weathering, was studied. Eight groups of samples were exposed to an ultraviolet (UV) accelerated weathering tester for a total of 1200 h. The weathered surface morphology, chemical change, and color change were characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR), and chroma meter analyses, respectively. Furthermore, the mechanical properties and oxidation induction time (OIT) were tested. It was shown that the use of lignin had a positive effect in improving mechanical properties and in reducing OIT values of filled composites due to the enhanced fiber/matrix interface bonding and its functions of anti-oxidation. Less fibers were falling off and shallower cracks occurred on the weathered surface of the lignin reinforced composites. The carbonyl index of wheat straw fibers reinforced recycled polypropylene composites (WSF/RPP) with 5 wt% lignin content showed a notable decrease of 4.9% when compared with the growth rate of the control groups. When the stabilizer was introduced to the blends, the mechanical properties and antioxidant capacity of the composites were improved during weathering.

Keywords: Lignin; Durability; Wheat straw; Recycled polypropylene; WPCs

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INTRODUCTION

In recent decades, wood-plastic composites (WPCs) have been widely used in buildings, transportation, packaging, and outdoor furniture because of their high strength and modulus to weight ratios and fatigue and corrosion resistance, especially when their low density and price are considered (Murayama *et al.* 2019). It is known that in order to achieve properties required for outdoor application of WPCs, using a variety of additives has been proven to be a cost-effective means to improve their photostability, such as adding UV absorbers (UVAs) and antioxidants (Liu *et al.* 2018). Many commercial UVAs are toxic and not very stable, so their safety should be taken into consideration when used at high concentrations (Ratanawilai and Taneerat 2018). On the other hand, the commercial additives exert the stabilizing effect of WPCs greatly even in landfills after expiry of the service life, which is not desired since it decelerates the decomposition of WPCs waste (Yu *et al.* 2016). It is evident that solving the problem of WPCs waste will continue to be an

essential goal. The lack of decomposition in landfills may be eliminated by using natural antioxidants, which could affect the degradation of the WPCs matrix, *e.g.*, lignin (Guilhen *et al.* 2017).

Lignin is an amorphous natural polymeric material that has potential for material applications. It is a complex phenolic polymer derived mainly biosynthesized from three hydroxycinnamyl alcohols or monolignols by free radical generation followed by chemical coupling process. The hydroxycinnamyl are namely p-coumaryl alcohol (MH), coniferyl alcohol (MG), and sinapyl alcohols (MS) (Nawawi *et al.* 2016). Due to its structure, a great deal of research work has been carried out to use lignin as a natural antioxidant and a compatibilizer (Kirschweng *et al.* 2017; Barana *et al.* 2018). Lignin's ability to be utilized as a natural antioxidant is due to the presence of phenols from guaiacyl and syringyl groups with methoxy substituents in the 2- and 6- positions. These phenolic groups have similar chemical structures to 2,6-di-*t*-butyl-*p*-hydroxytoluene, which is a commonly used hindered phenolic antioxidant, which hinders free radical formation and acts as a free radical scavenger during the thermal oxidation and photooxidation of the polymer (Gadioli *et al.* 2014; Yang *et al.* 2018). It was reported that in lignin/polypropylene blends, lignin not only acted as a rigid particle that was superior in mechanics to inorganic fillers, such as calcium carbonate and talc, but that it also had a positive effect on the thermal stability and flame retardancy of polypropylene (Maldhure *et al.* 2011; Peng *et al.* 2018). Moreover, the addition of lignin can increase the crystallization rate of polypropylene. Lignin is worth considering as a compatibilizer because it contains both aliphatic and polar groups, which can improve the compatibility between non-polar polymers and polar plant fibers. The role of lignin in composites can act as a coupling agent to improve the compatibility and mechanical properties (Khan *et al.* 2018; Yu *et al.* 2018).

In the context of this work, the focus was to investigate the influence of lignin additive at different loading levels on the surface properties, and mechanical and thermal performance of recycled polypropylene composites reinforced with wheat straw before and after accelerated weathering. For this purpose, lignin-reinforced composites based on wheat straw/recycled polypropylene blends were prepared and composite properties were characterized. But given that lignin is sensitive to UV light, which weakens the antioxidant effects of lignin in composites, a small amount of UV absorber (UV327) was added to the LU group. This also could help lignin exert a better antioxidant effect. This study also provides the theoretical foundation for the weathering of composites reinforced by natural antioxidants.

EXPERIMENTAL

Materials

Wheat straw fibers (WSF) with a size of 60-mesh were obtained from the Jiangsu Province, Zhenjiang, China. In order to enhance the interfacial compatibility and adhesion of WPCs, a silane coupling agent (KH550) from Yao Hua Co., Ltd. (Shanghai, China) was utilized to treat the WSF. Silane treatments of WSF were made *via* immersion methods. Before treatments, the WSF were first oven-dried at 105 °C for 6 h to reduce the moisture content level to less than 2%. They were immersed in an aqueous solution (ethanol: water = 9:1 by weight) including a silane coupling agent (2 wt% by the weight of WSF) at 25 °C for 30 min. After immersion, the silane-treated WSF were dried at 105 °C for 12 h. The Recycled PP (RPP) was obtained from Jiu Long Regenerated Resources Recycling Co.,

Ltd. (Jiangsu, China). The melting point was approximately 165 °C, and the density was approximately 0.9 g/cm³. Alkali lignin (L) powder was supplied by Ye Yuan Biological Technology Co., Ltd. (Shanghai, China). The stabilizer UV-327 (C₂₀H₂₄ClN₃O) was purchased from Mi Lan Chemical Co., Ltd. (Nanjing, China).

The experiment design included two factorial experiments. The first experiment was to investigate the effect of lignin loading levels consisting of three rates (*i.e.*, 5 wt%, 10 wt%, and 15 wt%), which were recorded as L1, L2, and L3. The second experiment was designed to study the effect of combined lignin and the stabilizer consisting of three blends and three rates for lignin (*i.e.*, 5 wt%, 10 wt%, and 15 wt%) and stabilizer (0.5 wt%) on WS/RPP composites, which were recorded as LU1, LU2, and LU3. The RPP/Fillers = 50/50 (wt%) was fixed for all composites. The WS/RPP composites without lignin (C) and WS/RPP composites with 0.5 wt% stabilizer (CU) were made as the control.

Composite manufacturing

The steps of composite manufacturing are shown in Fig. 1. A 500 g batch of each composite formulation (Table 1) was blended in a two-roll mill Mixer (X-160 Banbury; Chuangcheng Rubber, and Plastic Machinery Co., Ltd., Wuxi, China) at 175 °C for 5 to 7 min. The melting mixture was laid on a compression molding machine (XLB-0 Vulcanizing Machine; Shunli Rubber Machinery Co., Ltd., Huzhou, China) at 180 °C and 12.5 MPa for 12 min. The performed board dimension was 120 mm × 100 mm × 5 mm, and then cut to the required size. All specimens were conditioned for 72 h at a temperature of 23 ± 2 °C and a relative humidity of 50 ± 5% for later characterization.

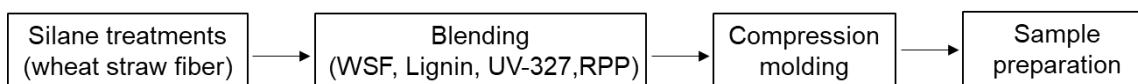


Fig. 1. Scheme for composite manufacturing

Table 1. Composite Formulation

ID	WSF (wt%)	Lignin (wt%)	UV-327 (wt%)	RPP (wt%)
C (Control)	50	0	0	50
CU	49.5	0	0.5	50
L1	45	5	0	50
L2	40	10	0	50
L3	35	15	0	50
LU1	44.5	5	0.5	50
LU2	39.5	10	0.5	50
LU3	34.5	15	0.5	50

Methods

Accelerated weathering process

The samples were subjected to an artificial weathering by exposure to 340 nm fluorescent UV lamps in a QUV accelerated weathering tester (ZN-P Aging Chamber; Nuoweier Electronic Technology Co., Ltd., Suzhou, China) for 1200 h. The weathering cycle involved a continuous UV light irradiation of 8 h (60 °C) followed by a water condensation for 4 h (50 °C). The specimens were exposed to the artificial weathering only on one side for the total time.

Characterization – Morphology observation

The morphologies of the selected composite samples were analyzed by a Hitachi S-3600N VP scanning electron microscope (SEM; Hitachi Ltd., Tokyo, Japan). The fractured surfaces of the selected test samples were coated with Pt to improve the surface conductivity before observation (Hitachi Ltd., Tokyo, Japan) and observed at an acceleration voltage of 15 kV.

Colorimetric analysis

The surface color of the composites was measured by a chroma meter (HP-200; Hanpu Ltd., Shenzhen, China) according to the CIE $L^*a^*b^*$ color system. Four specimens were taken for each formulation and were measured. For each of the specimens, five different points were measured, and the average value was calculated automatically by the chroma meter. The color difference (ΔE) was determined with the procedure outlined in ASTM D2244 (2014),

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{\frac{1}{2}} \quad (1)$$

where ΔL^* , Δa^* , and Δb^* are the total changes in the L^* , a^* , and b^* values during weathering, respectively. An increase in L^* means the sample is lightening (*i.e.*, a positive ΔL^* for lightening and a negative ΔL^* for darkening). A positive Δa^* signifies a color shift toward red, and a negative Δa^* signifies a color shift toward green. A positive Δb^* signifies a shift toward yellow, and a negative Δb^* signifies a shift toward blue.

Mechanical Properties

Flexural testing was performed on specimens of 100 mm × 10 mm × 5 mm in a three-point bending mode using a CMT6104 SANS Mechanical Testing Machine (Tesla Industrial systems Co., Guangdong, China) following the GB/T 9341 (2008) standard. A crosshead speed of 5 mm/min and a span length of 80 mm were used for all tests. The unnotched impact strength was determined from specimens of 80 mm × 10 mm × 5 mm in size using a XJJ-5 Impact Tester (Jinjian Testing Instrument Co., Chengde, China) according to the GB/T 1043 (2008) standard. Five specimens were taken for each test, and the average data along with the corresponding standard deviation were reported.

Fourier transform infrared (FTIR) spectra measurement

The surface chemical changes in the composites during accelerated weathering were monitored by a FTIR spectrometer (Nicolet iS10 FT-IR; Thermo Fisher Scientific, Massachusetts, USA). The FTIR spectra was obtained in the range of 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and a minimum of 60 scans.

Oxidation induction time analysis

The oxidation induction time (OIT) was determined using thermogravimetric analysis (TGA NETZSCH STA449F3 Instruments; NETZSCH Ltd., Frankfurt am Main, Germany) with the following procedure: heating to 180 °C at 20 °C min^{-1} under nitrogen atmosphere, isotherm for 5 min, change of atmosphere to pure oxygen, and isotherm for the time necessary to observe an exothermic process.

Data analysis

Duncan's multiple range tests for pairwise comparisons were used to test the effect of various treatments using statistical analysis software SPSS 20.0 (IBM Ltd., New York, USA). Statistical ranking at the 5% significance level was provided among the treatments for each property.

RESULTS AND DISCUSSION

Morphology

The surface morphology of composites after weathering is shown in Fig. 2. Before exposure, the WS/RPP composites showed a smooth surface, exhibiting that WSF could be completely wrapped by the RPP matrix (Fig. 2a). After 1200 h exposure, the degraded RPP was unable to bond to the WSF, which left many distinguishable uncovered fibers on the surface (Fig. 2b). These fibers were related to the swelling property of WSF when exposed to alternate wetting and drying cycles, which destroyed the interface between the fibers and matrix. Then, the degraded RPP particles were easily washed away by condensation water, which resulted in the debonding of WSF and facilitated UV radiation and water penetration into deeper composites.

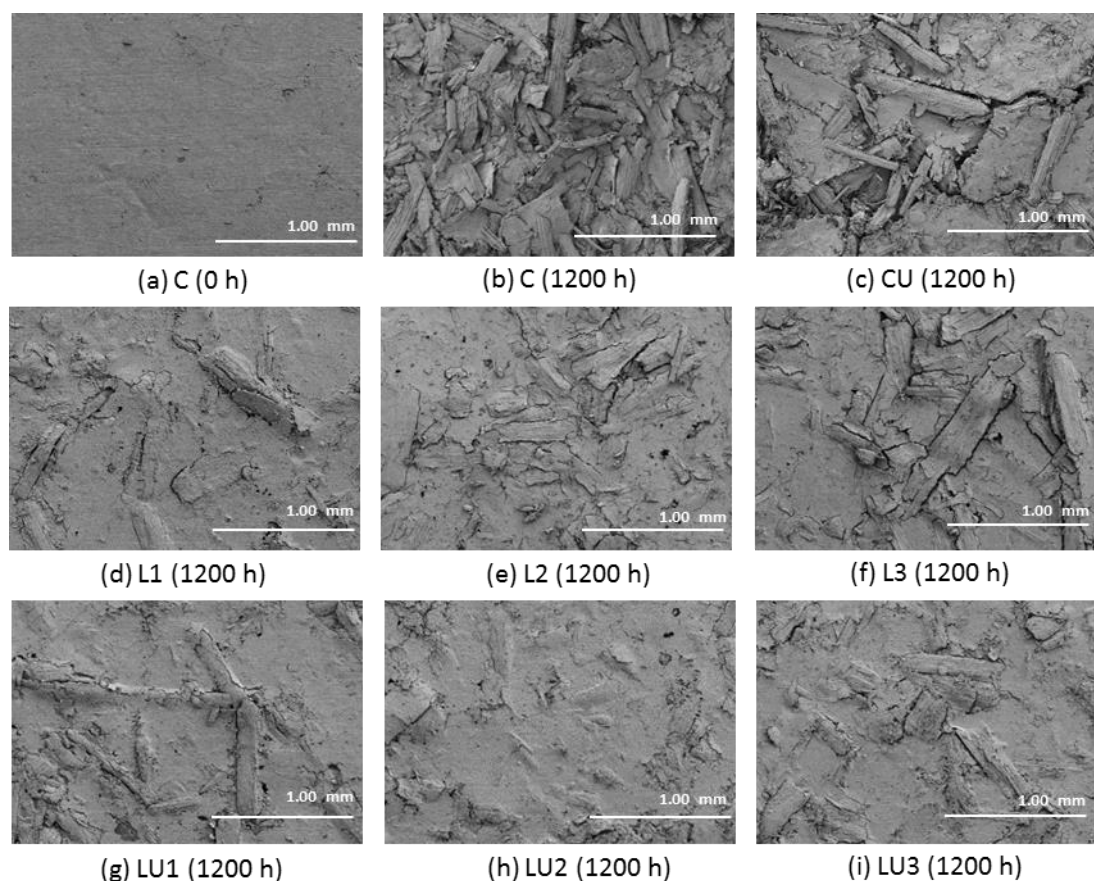


Fig. 2. SEM images of WS/RPP composites after accelerated aging

At the 5 wt% lignin loading level, the composites surface appeared relatively flat, with less fibers falling off and shallower cracks. These findings suggested that the addition of lignin reduced water absorption of composites and WSF swelling, which can improve the compatibility between the nonpolar polymer and wood fiber. Moreover, the hindered phenolic structure in lignin can inhibit the photochemical reaction of free radicals formed by UV excitation, which was suggested to be able to delay the photodegradation process (Peng *et al.* 2014). Therefore, adding the right amount of lignin had a positive effect on retarding the photodegradation of composites. With the lignin loading increased from 10 wt% to 15 wt%, more cracks and microparticles were observed on the surface of L3, which were due to lignin being the main component of the photodegradation reaction of wheat straw, and excessive lignin formed large numbers of free radicals after UV excitation, which resulted in the cracks worsening.

After adding the stabilizer in the control groups, less fibers were exposed on the CU groups and the RPP matrix was more complete, while the crack area was larger and the crevice was much deeper, indicating that compared to improving the compatibility between the fibers and the matrix, the stabilizer had a better anti-oxidation effect on the plastic matrix (Fig. 2c). When the stabilizer was added, the surface cracks of the LU groups were generally shallower. At the 10 wt% lignin and 0.5 wt% stabilizer loading levels, only some small cracks were observed on the surface of the LU2 groups. This was due to the combined effect of the stabilizer and lignin. As the stabilizer strongly absorbed the UV radiation and reduced the photodegradation, lignin played a better role in compatibilization and anti-oxidation, which created a good adhesion between the fibers and matrix and prevented UV light and water degradation of the interior materials.

Color Change

The total color change and lightness change for all the studied WPCs as a function of lignin loading levels are shown in Fig. 3.

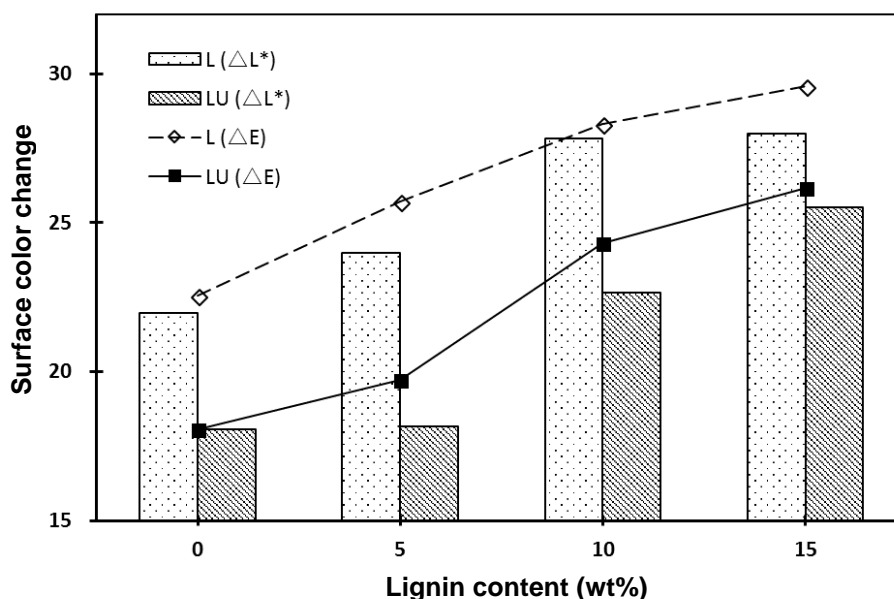


Fig. 3. Color change of WS/RPP composites after accelerated aging

The curves of ΔL^* substantially kept in step with ΔE , indicating that the parameters of the a^* and b^* values had little effect on the total color change. The ΔE values exhibited an increasing trend with increasing lignin content in the WSF/RPP composites. The L3 groups showed a remarkable increase of 31.1% when compared with the control group. This phenomenon can be attributed to two factors. On the one hand, lignin was poor in light stability due to its large amount of light absorbing groups. These groups easily produced peroxide, carboxyl, paraquinone, and other chromophore functional groups after the long-term UV radiation. It was reported that lignin accounted for 80 to 95% of the light absorption, which was suggested to have made a significant effect on the discoloration (Homkhiew *et al.* 2014). In contrast, the photo-degradation products of lignin contained many hydroperoxides, which played a part in the automatic catalysis of the polymer oxidation reaction, resulting in molecular weight reduction of the RPP matrix and accelerative degradation of the WSF/RPP composites. Though the discoloration process of the LU groups was weaker than that of the L groups, the ΔE value did not decrease significantly, especially at higher lignin loading levels. This was related to the fact that the stabilizer could achieve a better effect on protecting the RPP (Fig. 2c), which made the surface of the composites more complete, thus slowing the fading process. With the lignin content increased, many free radicals formed by lignin constantly exacerbated the photooxidation of the composites, which indicated the low content of stabilizer could not improve the light stability of the composites.

Surface Chemistry

Analyses of the FTIR spectra of the WSF/RPP composites (Fig. 4) show an increase in the intensity around 1650 cm^{-1} to 1600 cm^{-1} for the 1200 h weathered samples, which was due to the characteristic absorption of photodegradation products of lignin. The increase of this band may indicate phenolic hydroxyl groups were changed by light rapidly to form phenolic radicals, which in turn transformed into quinonoid structures (Peng *et al.* 2014).

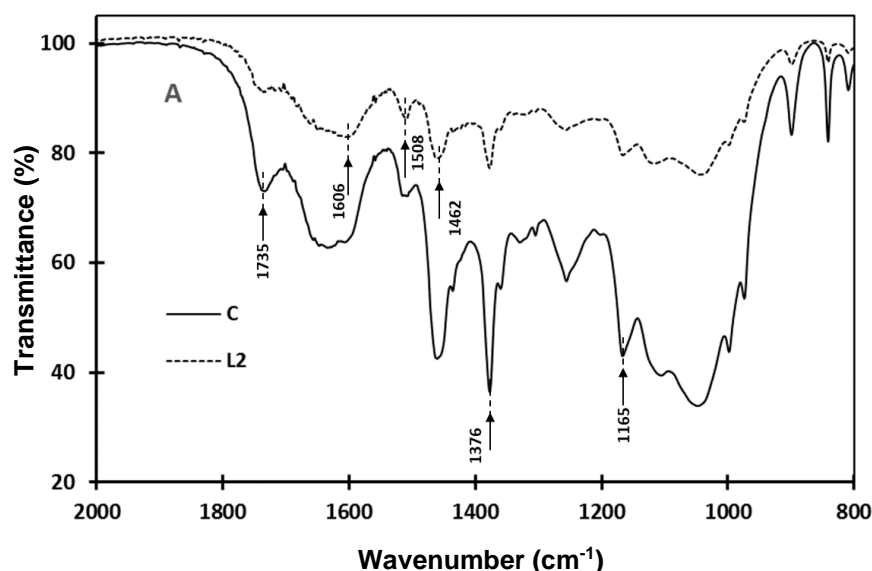


Fig. 4a. FTIR spectrum of WS/RPP composites before aging (A) and after aging (B)

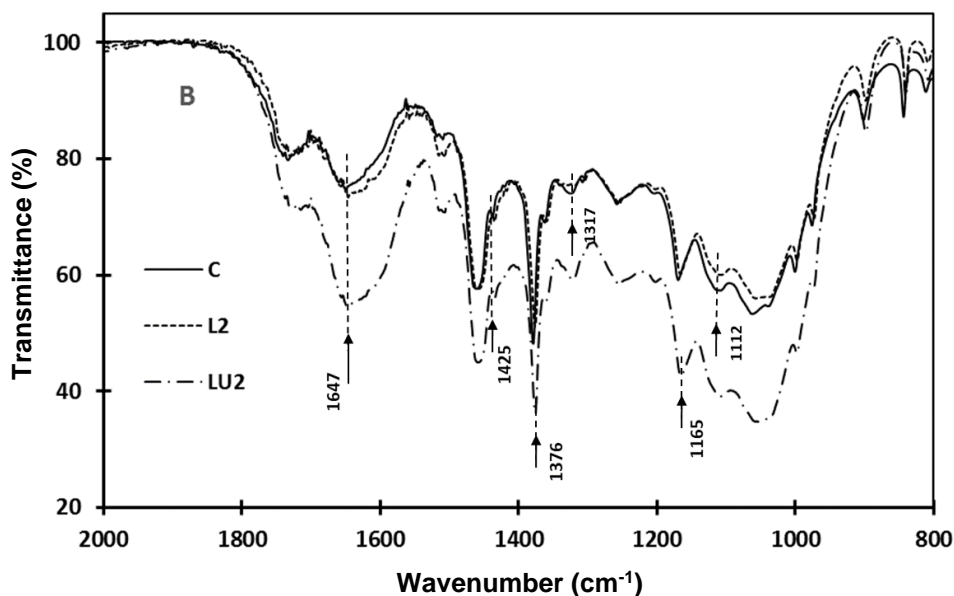


Fig. 4b. FTIR spectrum of WS/RPP composites before aging (A) and after aging (B)

The bands at 1425 cm^{-1} , 1317 cm^{-1} , and 1112 cm^{-1} to 1034 cm^{-1} were characteristic absorptions of the C-H asymmetric deformation vibration of cellulose crystalline I region and amorphous region, the CH_2 rocking vibration of cellulose crystalline I region, and the C-O and C-C stretching vibration of cellulose, and their concentration of C groups increases were much higher than that of the L2 and LU groups, indicating that there were more WSF exposed on the surface of the control sample (Lionetto *et al.* 2012). Strong bands were observed at 1376 cm^{-1} and 1165 cm^{-1} in the LU2 groups, which was assigned to the CH_3 symmetric deformation band of PP, indicating that the use of stabilizer and lignin could prevent the chemical degradation of PP.

A typical approach for spectral analysis of decomposition of organic matter consists of the monitoring of one or more bands of interest in relation to a band that does not change during the weathering process. Because the peak at 2920 cm^{-1} , which corresponds to asymmetric stretching vibrations of methylene ($-\text{CH}_2-$) groups of polypropylene, showed the least change during degradation, it was used as a reference (Mouaci *et al.* 2017). The carbonyl index was calculated using Eq. 2,

$$\text{Carbonyl Index} = I_{(1717)} / I_{(2920)} \quad (2)$$

where I denotes the intensity (cm^{-1}). The peak intensity in the carbonyl region normalized using the intensity of the peak at 2920 cm^{-1} , which corresponds to the asymmetric stretching vibrations of methylene groups.

The calculated values of the carbonyl index are shown in Fig. 5. Because lignin contains many conjugated carbonyl groups and non-conjugated carbonyl groups, such as aldehydes, ketones, and carboxyl groups, the carbonyl index increased with increasing lignin content (in the L and LU groups) before the aging test. After weathering, the carbonyl index of each group increased to different degrees. The WSF/RPP composites with 5 wt% lignin content showed a notable decrease of 4.9% when compared with the growth rate of the control groups. This was attributed to the phenolic groups in lignin having a chemical structure similar to the commonly used commercial hindered phenolic

antioxidants, which acted as radical scavengers during the degradation of the polymers (Kim *et al.* 2017). Under the combined action of stabilizer and lignin, the carbonyl index of the composites with lignin content of 10 wt% and 15 wt% decreased 9.3% and 7.8%, respectively, compared with the L2 and L3 groups.

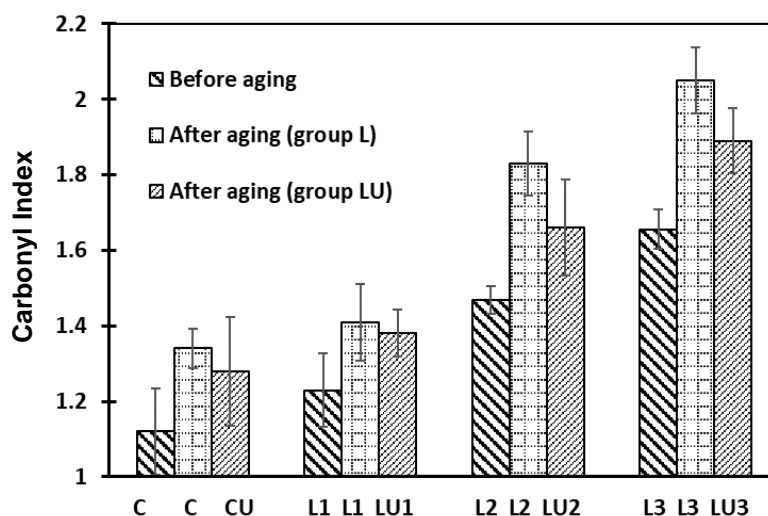
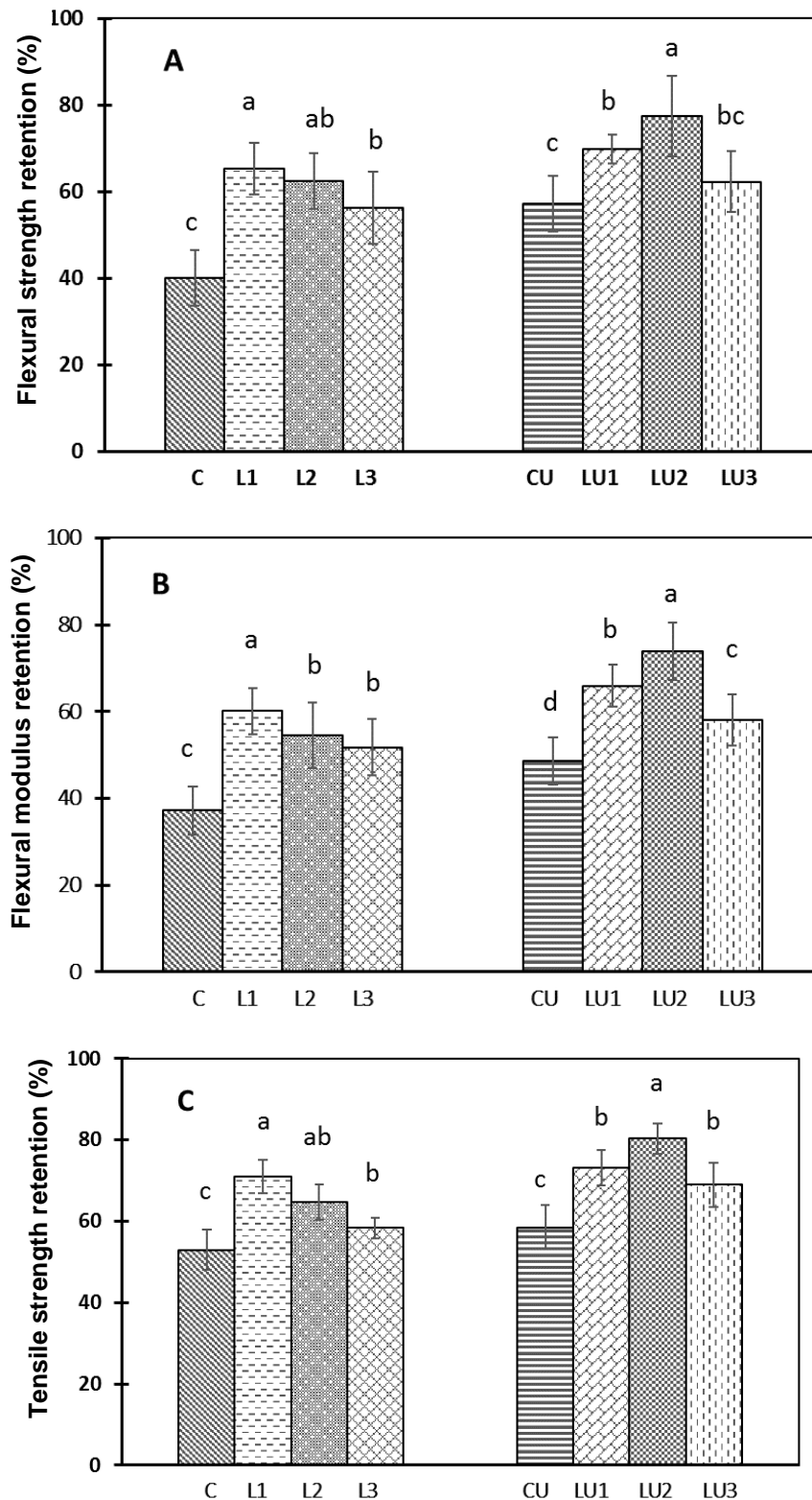


Fig. 5. Change in the carbonyl index of WS/RPP composites

Mechanical Properties

To study the effect of accelerated weathering on the mechanical properties of the WSF/RPP composites, the retention rates of the mechanical properties (calculated in relation to each sample before weathering) were calculated, and the results are shown in Fig. 6. An increase in the anti-aging effect on the composites was observed for the composites containing 5 wt% lignin, which made the bending strength and modulus retention rate increase 25.5% and 22.9%, respectively, compared to the control groups. Lignin could not only be used as a rigid particle filler to increase the rigidity of material, but also to help improve WSF/polymer interfacial adhesion (Fig. 2d), which played an important role in determining the efficiency of stress transferred from the matrix to the reinforcing fibers (Hu *et al.* 2015; Mounguengui *et al.* 2016). As the lignin content increased, the flexural properties of the composites did not show much further increase but slightly decreased, which indicated that to some extent the composites maintained their flexural strength and modulus well at high lignin levels. The incorporation of a stabilizer caused a noticeable increase in flexural properties. Noticeable increases, *i.e.*, almost 77.5% and 73.8%, in the retention rates of flexural strength and modulus were observed when the stabilizer content was 0.5 wt% and the lignin content reached 10 wt%. The reasons for this phenomenon include the fewer cracks and relatively sufficient interphase adhesion between the two phases, as shown in Figs. 2g, 2h, and 2i, which effectively transferred the stress from the plastic matrix to the reinforcing agent. Lignin also showed good performance in improving the tensile properties of the composites. It can be observed that the retention rate of the tensile strength increased noticeably (from approximately 18% to 10.3%) due to the introduction of lignin (from 5 wt% to 15 wt%) in them. The retention rate of impact strength increased 9.5% compared with the control groups. The use of lignin at the content levels exceeding 5 wt% had a negative effect on the impact properties of the

composites. It is believed that an appropriate content of lignin may help improve the mechanical retention behaviors of filled composites after weathering (Xu *et al.* 2017).



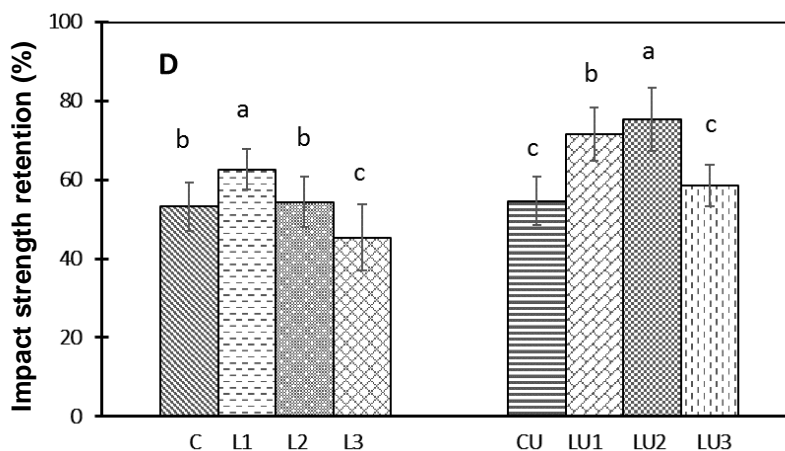


Fig. 6. Mechanical properties of WS/RPP composites after accelerated aging; mean values with the same letter for each property are not significantly different at the 5% significance level

Oxidative Induction Time

The OIT is maintained as a measure of the antioxidant degradation ability of a polymer at a certain temperature and in the presence of oxygen. The OIT of WSF/PP composites were determined to compare the exothermic event associated to the thermo-oxidation reactions of the composites at different lignin loading levels. The OIT values before and after weathering are depicted in Fig. 7. Before weathering, the OIT values increased with increased lignin content from 0% to 15%. The OIT values increased to 40.8 min from the control groups OIT of 20.8 min. At the 15% lignin level, the OIT was 1.96 times higher than that of the composites without lignin, which suggested the positive effect of WPC on the antioxidant of the composite. This is because lignin as a hindered phenolic polymer enhances antioxidant properties, which is similar to results reported previously (Gadioli *et al.* 2016).

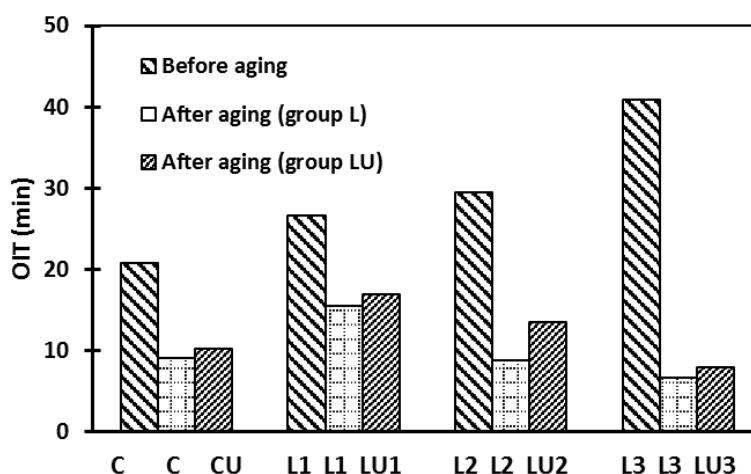


Fig. 7. Oxidative induction time of WS/RPP composites

After weathering, the OIT values of the composites containing 5% lignin decreased to 15.5 min, which was still higher than that of control groups, indicating that lignin played a role in the antioxidant during the accelerated aging process. With the lignin loading level

increased from 10% to 15%, the OIT values quickly declined from 8.7 min to 6.6 min, acting as defects locally initiating the degradation. When the stabilizer was introduced to the blends, the antioxidant capacity of all the LU groups were improved. This indicated that a light stabilizer could help lignin overcome the shortcoming of light stability so that lignin could better play the role of the antioxidant and enhance the antioxidant degradation of the composites.

CONCLUSIONS

The influence of lignin additive at different loading levels on the surface properties, as well as the mechanical and thermal performances of recycled polypropylene composites reinforced with wheat straw before and after accelerated weathering, was studied. The following conclusions can be drawn from the study.

1. Composites of recycled polypropylene with wheat straw fibers containing 5 wt% lignin presented flatter surfaces and improved mechanical properties compared to compared to composites without lignin, after 1200 h of accelerated degradation. Results obtained from FTIR analysis of the accelerated aged composites indicated the carbonyl index showed a notable decrease of 4.9% at the lignin loading level of 5 wt%, compared with the growth rate of the control groups. At the 15% lignin level, the OIT was 1.96 times higher than that of the composites without lignin, which suggested a positive effect of WPC on the antioxidant of the composite. After weathering, the OIT values of the composites containing 5% lignin decreased to 15.5 min, which was still higher than that of control groups, indicating that lignin could also play a role in the antioxidant during the accelerated aging process.
2. Two probable protection mechanisms have been proposed: addition of lignin to WS/RPP composites can improve the compatibility between the nonpolar polymer and wheat straw fiber, which reduced the water absorption and expansion of wood fiber during the alternate wetting and drying cycles of accelerated degradation, thus reducing the generation of surface cracks. The phenolic groups in lignin could act as radical scavengers and inhibit the photochemical reaction, which delayed the degradation of the polymers and made WS/RPP composites present higher stability.
3. With respect to color change results, the addition of lignin to the WS/RPP composites showed a negative effect on the anti-fading ability, due to its poor light stability. When 0.5 wt% of UV stabilizer was introduced to the blends, the results of each test were further improved, compared to composites with lignin. It was suggested that the light stabilizer could help lignin overcome the shortcoming of light stability.

Lignin has potential for anti-aging applications of WPCs due to its environmental suitability and economic feasibility. If a natural UV stabilizer could be found to work with lignin, it could make the WPCs more environmentally friendly.

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