Abiotic Degradation of Recycled Polymer/Wood Composites Exposed to Outdoor Applications

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Abstract: Wood-plastic composites (WPCs) have received increasing attention during the last decades, because of many advantages related to their use. Some of their main applications are represented by outdoor furnishing and decking; therefore, it is important to assess their behavior under Ultra Violet (UV) exposure. In this work, polypropylene/wood flour composites were prepared and their resistance to photo-oxidation investigated. The composites were prepared by extrusion and injection molding, and were subjected to mechanical and rheological tests, chemical analysis and colorimetric measurements. The results showed that the composites retained a higher fraction of the original mechanical properties after natural weathering. The study showed that for natural weathering, longer exposure time increased the degree of color change (and lightness). Weathering WPC exhibited decreased in mechanical properties when compared to no weathering WPCs respectively. From this study, relationships between chemical and color changes that occurred during exterior weathering of composites were too established. Climatic conditions directly affect the characteristics of all composites, thus indicating a significant photo-oxidation of the samples with a longer time of exposure to weathering.

Keywords: Wood plastic composite, color change, mechanical properties, surface properties, natural weathering.

Nomenclature

Eu: Eucalyptus grandis
Pi: Pinus elliottii
PP: Polypropylene
EVA: Ethylene vinyl acetate copolymer
CA: Coupling agent
MA: Maleic anhydride

Greek Letters

$\beta$: Type of chain scission
$\Delta$: Variable parameter (colorimetric test)

1. Introduction

Wood-polymer composites (WPCs) have attracted a significant interest in the last decades, thanks to the specific advantages they can grant in comparison with the classic mineral filler/plastic composites [1]. These materials can be used for many indoor and outdoor applications (panels for the automotive industry, decking, furnishing, packaging, etc.) [1-3]. Polyolefins, in particular polypropylene, one of the most widely used plastics, have been extensively studied in combination with wood derivatives (flour, flakes, fibers) [4-7]. Significant interest has also arisen about the outdoor performance of these composites, in particular their resistance to photo-oxidation.

The photo-degradation of polyolefins originates from excited polymer and oxygen complexes and is caused mainly by the introduction of catalyst residues, hydroperoxide groups, carbonyl groups and double bonds during polymer manufacturing. Even in the absence of a significant amount of UV absorption, small amounts of these impurities can be sufficient to induce polymer degradation [8].

Similarly, studies regarding photo-oxidation of
wood filled polymer composites reported a variety of results. Hon et al. [9] reported a light stabilizing effect of lignin (which is one of the major components of wood) to PP when added in low concentrations (up to 10 wt%), while it accelerated photo-degradation of PE at amounts higher than 10 wt%. Environmental degradation on HDPE/wood composites as investigated by Stark and Matuana [10] resulted in limited effects on the composites (confined to the surface layer) in dry environment conditions, while water had an important degradative action. Filson et al. [11] studied the photo-oxidation of polyvinyl chloride (PVC)/wood composites subject to accelerated weathering, finding that the composites retained a higher percentage of the original mechanical properties with the exposure time, in comparison to the neat polymer, explained by admitting that the photo-oxidation involves only the surface of the exposed composite; similar results were also found by Lundin [12]. However, the increase of the carbonyl index suggested an accelerating effect caused by the wood particles, attributed to the presence of chromophoric groups [13].

The effect of weathering on the physical and chemical structure of wood has been investigated extensively [14-16]. Chemical analysis of weathered wood surfaces has indicated degradation of lignin and hemicelluloses and depolymerization of cellulose upon exposure [14]. Lignin is the most sensitive to light, and photochemical reactions in wood are initiated by absorption of UV visible light by lignin, which leads to formation of lignin moieties having a-carbonyl, biphenyl and ring-conjugated double bond structures [14, 15]. These free radicals may then cause degradation of lignin and photo-oxidation of cellulose and hemicellulose. These compounds derived from photochemical reactions of lignin are responsible for most of the light-induced color change (e.g., yellowing). Thus, photo-degradation of WPC involves several factors including the wood flour content, coupling agents, manufacturing methods, and weathering conditions, among others [16].

The aim of this study was to investigate the degradation of polypropylene/ethylene vinyl acetate, wood flour composites caused by weathering using a combination of mechanical and rheological properties, chemical analysis by FTIR spectroscopy, colorimetric measures and their weight molecular, to determine the degree of abiotic degradation of WPC materials.

2. Experiments

The materials used were post-consumer waste from bottle caps of PP and ethylene vinyl acetate (EVA), latter present in the internal “liner” of covers, provided in the “flakes form”, and two types of wood flour: eucalyptus (Eu) and pine (Pi), from species *Eucalyptus grandis* and *Pinus elliottii*, respectively, from state of Rio Grande do Sul, Brazil.

Bottle caps for mineral water and soft drinks were chosen because they are materials with great consumption and large amounts generated for disposal after use. As the sample PP-EVA were already ground, a bottle cap was weighed with and without the internal “liner” to verify the EVA present proportion in the total mass, and it was found 9% w/w of EVA in bottle cap.

The coupling agent (CA) used was grafted copolymer of polypropylene with maleic anhydride (PP-g-MA), Fusabond MZ-109D from DuPont, with 0.57% maleic anhydride, melt flow index of 3.4 g/10 min and density of 0.91 g/cm³. The wood flour was submitted size separation in a sieves system with series of 32 and 60 Tyler mesh, and selected particle size of > 250 μm and < 500 μm.

The blends were processed on a single screw extruder (L/D: 22), the temperature profile of 170-190 °C and screw speed of 65 rpm, and perforated in the “pellets form”. Mixtures were processed in a single screw extruder (L/D: 22), with the temperature profile of 150-160-170 °C, residence time of 80 s and rotation of 65 rpm. Flakes of PP-EVA with the CA was first processed in the
extruder in order to functionalize the polyolefin, after added sieved wood flour (30% w/w). After mixing by extrusion, samples were cropped in the shredder.

The test specimens were prepared by injection molding (Mini Thermo Scientific Haake MiniJet II) at temperature of 180 °C and pressure of 600 bar for mechanical and rheological tests, chemical analysis and colorimetric measurements. The formulation of substrates was performed as shown in Table 1.

2.1 Exposure to Natural Weathering

The test was carried out according to ASTM 1435-13 [17] and ASTM G7/G7M-13 [18] standard. Tests conducted in accordance with this practice are used to evaluate the stability of plastic materials when they are exposed outdoors. The relative durability of plastics in outdoor use can be very different depending on the location of the exposure because of differences in ultraviolet (UV) radiation, time of wetness, temperature, pollutants, and other factors. The WPC samples (in the form of specimens for all tests) were exposed to natural sunlight outdoor in the north direction at 45º inclination with geographical location: latitude (30°05’ South); longitude (51°11’ West) and altitude (174 m), allowing normal incidence of solar radiation over the entire surface of the samples, for 270 days from the months of February to November of 2013, at Porto Alegre in the south of Brazil.

During the natural ageing test were monitored the average of UV radiation index, temperature and the rainfall were provided by the CPTED-INPE (Center for Weather and Climate Studies: National Institute for Space Research, from Brazil), and as listed in the Fig. 1.

2.2 Mechanical Tests

The tensile tests were measured according to the ASTM D638 [19], using an Instron machine (Model 4200). The tests were performed at crosshead speeds of 2 mm/min, using a 5,000 N load cell.

2.3 Colorimetric Analysis

Color measurements of weathered WPC specimen surfaces were recorded using a SpectroGuide spectrophotometer BYK, in accordance with ASTM D2467 [20] and ASTM D1003 [21], with light beam focusing angle of 60°. The experiment was performed at 23 °C and relative humidity of 55%. Spectrometer’s Spectro-Guide software transforms spectral data into CIELAB color coordinates (L*, a* and b*) based on a D65 light source [22]. Five replicates per WPC sample were measured at three locations on each specimen. An increase in L means the sample is lightening. A positive $\Delta a$ signifies a color shift toward red, and a negative $\Delta a$ signifies a color shift toward green. A positive $\Delta b$ signifies a shift toward yellow, and a negative $\Delta b$ signifies a shift toward blue.

2.4 Surface Chemistry

Changes in surface during weathering were monitored by infrared spectroscopy. The samples were cut into sheets for evaluation of surface. Spectra were collected using a Perkin-Elmer Frontier spectrometer operating in the attenuated total reflection (ATR) mode. Readings were made by transmittance in the range 400-4,000 cm$^{-1}$ at room temperature (25 ± 3 °C) using ASTM E-1252 standard [23].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Matrix (70% w/w)</th>
<th>Wood flour (30% w/w)</th>
<th>Coupling agent (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PP-EVA</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>PP-EVA</td>
<td>Eu</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>PP-EVA</td>
<td>Eu</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>PP-EVA</td>
<td>Pi</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>PP-EVA</td>
<td>Pi</td>
<td>3</td>
</tr>
</tbody>
</table>
3. Results and Discussion

3.1 Mechanical Properties

In Fig. 2a are the results of the tensile strength of the samples without and with exposure to weathering for 270 days (nine months). The composites after exposure showed a decrease in tensile strength with different answers depending on the composition, where it was observed that the presence of the coupling agent had better mechanical performance of composite before exposure but after three months of weathering these showed a decrease but lower than those no coupled.

These results are probably indicating that the samples suffered some kind of hydrolytic degradation, photo-oxidative, thermal among the most important, in which the division of some chains [25] could occur, thus directly affecting the mechanical properties and embrittlement of the material. Another important factor is that in the PP, the chain scission reactions through the photolysis of hydroperoxides also generates carbonyl groups [26].

Regarding to the Young’s modulus of the samples (Fig. 2b), it is observed that both the samples of polymer and composites, the weather conditions directly affect the results, with a gradual decrease in the elastic module with longer time of exposure, and this decrease was more pronounced with nine months of weathering.

3.2 Colorimetric Properties

The exposure of the composites to the natural environment changes its appearance as well as its mechanical properties. Therefore, special attention should be given to the color attribute for products made from wood, because this attribute adds value (perceived quality) for the product.

Various chemical reactions that result in change of color/appearance change are induced by solar [27] radiation. The presence of the chromophores in polymers and wood generally increases the absorption
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Fig. 2  Tensile strength (a) and elastic modulus (b) of the samples as a function of time of exposure to natural weathering.

of ultraviolet (UV) radiation, which later causes photodegradation of wood plastic composites [27]. Photo-yellowing of aged wood has been attributed to loss of lignin into water-soluble products, which eventually leads to the formation of chromophores functional groups such as carboxylic acids, quinones and hydroperoxide radicals [27]. Furthermore, metal-based additives may have chromophore groups for composites, and carbonyl and phenyl radicals are generated during the degradation of wood [27]. According to Stark and Matuana [28] the photoreactions that occur during the natural weathering of the polymer normally cause embrittlement and color change. Figs. 3 and 4 show results of color parameter “Δa”, “Δb” and “ΔL” respectively for the samples during natural weathering.

It is observed that there was a gradual decrease of the ΔL parameter (luminosity), indicating a color loss over the months. Evaluating “Δa” and “Δb” parameters in the PP-EVA matrix, the samples exposed to a longer natural aging time showed a decrease in these values, becoming more green (a-) and bluish with time (b-).

For composites, the appearance of color was more reddish (a+), but decreasing over the months, with a tendency to go more green (a-), as occurred with the coupled and no coupled PP-EVA-Eu composite after 9
months of weathering. In the “Δb” parameter, all the composites were yellowish (+b), but with decreasing values over time. This is probably because during the removal of dirt for the measurements, there was release of the degraded polymer powder from the surface of the specimen, indicating the intense degradation of the material on the surface, but that became protected the layer below the surface, thus presenting lower yellowing rates.

3.3 Surface Chemical Properties

FT-IR spectroscopy was used to determine structural changes in the surface chemistry of the wood-polypropylene/ethylene vinyl acetate composites after weathering. Table 2 shows the most significant bands in the infrared spectra of the wood and polypropylene/ethylene vinyl acetate samples, and distinctive functional groups assigned with these bands.

Some characteristic bands, such as 2,720 cm⁻¹ for polypropylene and 1,510 cm⁻¹ for the lignin component of wood were found in the FT-IR spectra of the surface layer of the composites. In the non-weathered composites, a carbonyl peak at 1,735 cm⁻¹ and a broad peak at 3,400 cm⁻¹, associated with hydroxyl and hydroperoxide groups, were originated from the wood [29]. The comparison of the FT-IR spectra for the surface layers of both the non-weathered

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,400</td>
<td>O-H stretch (hydrogen-bonded)</td>
<td>[30]</td>
</tr>
<tr>
<td>2,800-3,000</td>
<td>C-H stretch in methyl and methylene groups</td>
<td>[30]</td>
</tr>
<tr>
<td>1,728</td>
<td>C=O stretching of acetyl or carboxylic acid</td>
<td>[30]</td>
</tr>
<tr>
<td>1,650</td>
<td>for absorbed O-H and conjugated C-O</td>
<td>[30]</td>
</tr>
<tr>
<td>1,606</td>
<td>C=C stretching of the aromatic ring (lignin)</td>
<td>[30]</td>
</tr>
<tr>
<td>1,505-1,511</td>
<td>C=C stretching of the aromatic ring (lignin)</td>
<td>[30]</td>
</tr>
<tr>
<td>1,462</td>
<td>CH₂ deformation in lignin and carbohydrates</td>
<td>[30]</td>
</tr>
<tr>
<td>1,375</td>
<td>C-H deformation in cellulose and hemicellulose</td>
<td>[30]</td>
</tr>
<tr>
<td>1,268</td>
<td>guaiacyl ring breathing, C-O stretch in lignin and for C-O linkage in guaiacyl aromatic metoxyl group</td>
<td>[30]</td>
</tr>
<tr>
<td>1,163</td>
<td>C-O-C asymmetric vibration (in cellulose)</td>
<td>[30]</td>
</tr>
<tr>
<td>1,059</td>
<td>C-O stretch in cellulose and hemicellulose</td>
<td>[30]</td>
</tr>
<tr>
<td>897</td>
<td>Glucose ring stretch, C-H deformation in cellulose</td>
<td>[30]</td>
</tr>
<tr>
<td>Polypropylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,952, 2,918 and 2,838</td>
<td>C-H stretching</td>
<td>[30]</td>
</tr>
<tr>
<td>2,720</td>
<td>CH bending and CH₁ stretching</td>
<td>[30]</td>
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<td>1,456</td>
<td>CH₂ asymmetric deformation</td>
<td>[30]</td>
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<td>1,376</td>
<td>CH₁ symmetric deformation</td>
<td>[30]</td>
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<td>1,165</td>
<td>bending vibration of tertiary carbon</td>
<td>[30]</td>
</tr>
<tr>
<td>974, 841 and 808</td>
<td>C-H deformation out-of-plane</td>
<td>[30]</td>
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<tr>
<td>Ethylene vinyl acetate</td>
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<td></td>
</tr>
<tr>
<td>2,920</td>
<td>C-H (CH₂) asymmetric stretch</td>
<td>[31]</td>
</tr>
<tr>
<td>2,850</td>
<td>C-H (CH₂) symmetric stretch</td>
<td>[31]</td>
</tr>
<tr>
<td>1,737</td>
<td>C=O stretching of carbonyl groups</td>
<td>[31]</td>
</tr>
<tr>
<td>1,415-1,440</td>
<td>CH₂ deformation</td>
<td>[31]</td>
</tr>
<tr>
<td>1,369</td>
<td>CH₁ asymmetric deformation</td>
<td>[31]</td>
</tr>
<tr>
<td>1,242</td>
<td>C-O-C asymmetric vibration</td>
<td>[31]</td>
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<tr>
<td>1,020</td>
<td>C-O-C symmetric vibration</td>
<td>[31]</td>
</tr>
<tr>
<td>723</td>
<td>C-H deformation</td>
<td>[31]</td>
</tr>
</tbody>
</table>
and weathered composites indicated that all spectral features appear to be sensitive to long-term outdoor weathering.

The decrease in the intensities of different bands after outdoor weathering was attributed to degradation of the constituents of the wood-polypropylene composites. The carbonyl index $\text{COi}$ is a parameter often used to measure the extent of degradation of polypropylene [32]. The oxidation reactions occurring during the degradation lead to the formation of hydroperoxides and carbonyl groups, such as ketones. This oxidation was then monitored through the COi. Several absorption peaks at 840, 974, 1,455 and 2,720 cm$^{-1}$ are used as Refs. [33, 34] and in this work was chosen peak at 1,450 cm$^{-1}$, because it has no variation as a function of the aging time. The analysis of the oxidation products was taken accompanying the absorption band at 1,740 cm$^{-1}$ (C=O) and taking as reference band at 1,450 cm$^{-1}$. Thus, it was calculated the carbonyl index (COi) for the degraded samples by environmental exposure for three, six and nine months. This fact is due to presence of functional group C=O and C-O of the maleic anhydride from CA. All samples showed an increase in COi with exposure time in the face exposed to natural weathering, as shown in Fig. 5. The exposed face was not protected, showing that degradation of the composite was only superficial and fiber acted as a blocker. This effect was also reported by La Mantia and Morreale [35] in his study of polypropylene composites reinforced with wood.

3.4 Rheological Test

Fig. 6 shows the results of the melt flow index of PP-EVA samples and their composites with and without exposure to natural weathering. It can be seen that the PP-EVA post-consumer has a higher melt flow index (lower viscosity) when compared with other composites. With the presence of filler (wood), the viscosity increases, as expected, resulting in lower melt flow index (MFI), which may be related to the flow impediment by holding the vegetable fiber in the polymer matrix.

Regarding the incorporation of the CA it is observed that the coupled composites showed an increase compared to the MFI of composites without the presence of CA.

Already comparing the exposure time of the samples and their degradation, it is observed due to the high number of chain scission, the value of the MFI to exposed samples to weathering increased significantly. According to several authors [36-38], this type of behavior is a consequence of the mechanism of degradation of PP, involving chain-breaking reactions that occur through $\beta$-scission of alkoxy radicals generated by autoxidation of polypropylene or by hydroperoxide photo-cleavage [39].

As a product of these reactions there is the formation

![Fig. 5 COi variation of different samples exposed to natural weathering.](image)

![Fig. 6 Melt index of the samples after natural weathering of nine months.](image)
of carbonyl groups, which is the main characteristic chemical group of oxidative degradation of PP [39].

4. Conclusions

In this study, the resistance of thermoplastic composites with wood fiber for various outdoor applications was investigated under abiotic degradation. The prior exposure to natural aging and climatic conditions of the period to which the samples were exposed directly affected the degradation of materials and influenced the results. The different types of wood and the use of coupling agent also influenced some results, and the coupled composites despite having the function of increasing the adhesion between the polymer matrix and the vegetal fiber in the composite, were eventually more susceptible to degradation, indicating that the period of exposure to natural weathering could also have affected the structure of the coupling agent and increasing degradation of the material.

After 270 days of outdoor weathering, marks of surface degradation were detected in all composites. Previous natural weathering by UV radiation, rain water and high temperatures caused changes in chemical structure in the WPC surfaces and affected the mechanical properties. Thus, studies with longer times of previous exposure to natural weathering and use of stabilizers are needed to obtain more accurate and definitive evaluation of the application of the materials in outside conditions.

Acknowledgments

The authors are grateful to CAPES for the financial support, the Laboratory of Polymeric Materials (LAPOL) from UFRGS for the infrastructure available and also to the Research Center for Remote Sensing and Meteorology of UFRGS.

References

[16] M. Muasher, M. Sain, The efficacy of photostabilizers on


[34] B.T. Luppi, R. Gadioli, M.A. De Paoli, Lignin of Eucalyptus as an antioxidant for Polypropylene: Environmental and Accelerated Aging, 12° Brazilian Polymer Congress (12°CBPol), Florianópolis, SC, 2013. (in Portuguese)


