

Interfacial Shear Strength Evaluation of Pinewood Residue/High-Density Polyethylene Composites Exposed to UV Radiation and Moisture Absorption-Desorption Cycles

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In outdoor applications, the mechanical performance of wood-plastic composites (WPCs) is affected by UV radiation, facilitating moisture intake and damaging the wood-polymer interfacial region. The purpose of this study was to evaluate the effect of moisture absorption-desorption cycles (MADCs), and the exposure to UV radiation on the interfacial shear strength (IFSS) of WPCs with 40% pinewood residue and 60% high-density polyethylene. One of the WPCs incorporated 5% coupling agent (CA) with respect to wood content. The IFSS was evaluated following the losipescu test method. The specimens were exposed to UV radiation using an accelerated weathering test device and subsequently subjected to four MADCs. Characterization was also performed by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The absorption and desorption of moisture was slower in non-UV-irradiated WPCs, particularly in those with the CA. The UV radiation did not significantly contribute to the loss of the IFSS. Statistically, the CA had a favorable effect on the IFSS. Exposure of the samples to MADCs contributed to reduce the IFSS. The FTIR showed lignin degradation and the occurrence of hydrolysis reactions after exposure to MADCs. SEM confirmed that UV radiation did not significantly affect the IFSS.

Keywords: Pinewood residue; Recycling; Plastic composites; UV degradation; Moisture absorption

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INTRODUCTION

In recent years, researchers have turned their attention to the exploitation of lignocellulosic materials (*e.g.*, pinewood residue) as reinforcement or fillers in thermoplastic polymer matrices to replace glass fibers and other synthetic materials. This use of lignocellulosic materials contributes to protecting the environment and also produces a unique combination of high functionality, versatile, and processing advantages at a favorable cost, using raw materials that could end up being wasted in landfills.

Composite materials mostly based on wood and thermoplastic polymers have been introduced in industries such as construction, transportation, furniture, automotive, and consumer goods; the building products industry currently constitutes the largest portion of the market for these so-called wood-plastic composites (WPCs) in the USA and Europe. Commercial WPC-based products are supposed to be highly durable, requiring minimal maintenance. However, research involving exposure to ultraviolet (UV) radiation and

moisture, either using an accelerated weathering test device or by immersing the materials in water, has shown that the material undergoes changes in its physical appearance and loss of its mechanical properties (García-Hernández *et al.* 2004; Yang *et al.* 2006, 2007). Wood-plastic composites generally contain a polyolefin such as high-density polyethylene with a hydrophobic character so they do not absorb a substantial amount of water in humid environments. However, wood is highly hygroscopic and is not dimensionally stable. Thus, when the resulting composite is exposed to the environment, it is susceptible to moisture absorption because of the hydrophilic nature of the filler (*i.e.*, wood). This amount of absorbed water is detrimental, as the mechanical performance of the material decreases (Huang *et al.* 2006; Flores-Cerón *et al.* 2011). Moisture absorption in a WPC also depends on the chemical nature of the polymer, the dimensions, the filler morphology, and the interfacial adhesion between the polymer matrix and the wood (Stark 2006; Jahadi *et al.* 2011).

During exposure to weathering, the polymer matrix is degraded by the action of UV rays, thereby enabling the water of the environment to reach the wood particles (Stark 2006). When this happens, a "mechano-sorptive" phenomenon occurs in the material, consisting of changes in moisture content and simultaneous stress generation that induces acceleration in the reduction of mechanical strength over time (Hanhijärvi 2000). This phenomenon can cause three situations in WPCs: (1) the interfacial region is damaged by repeated swelling and shrinkage of wood particles; (2) microcracks are produced in the plastic matrix; and (3) the wood particles are internally fractured by swelling. To avoid these situations, it is essential to improve the bonding between the wood particles and thermoplastic matrix, which can improve the composites' overall properties. This can be accomplished by treatments such as using cold plasma to modify the surface properties of wood particles and thereby improve the acid-base interactions in the final composite.

Another option is to add a coupling agent to the blend. In this regard, Yan *et al.* (2007) studied the effect of using a maleic anhydride-grafted polyethylene as a coupling agent (CA) on the tensile and impact mechanical properties of low- and high-density polyethylene-based WPCs. They reported an improvement in these properties, which can be attributed to a stronger polymer matrix-reinforcement interfacial region. In another study, Yan *et al.* (2006) worked with composites made with wood, polypropylene, and a coupling agent. They related the diminishment of water absorption with the use of the CA. It is convenient, then, to analyze the effect of a coupling agent on the resistance to moisture absorption of a WPC and relate it to the strength of the wood-polymer interfacial region and to the composite's final physicochemical and mechanical properties.

The mechanical performance of WPCs has been correlated with the interfacial shear strength (IFSS), which can be evaluated following the Iosipescu test method. This technique has been used together with micromechanical techniques such as the extraction of a single fiber to observe the qualitative correspondence of a composite micromechanical performance with its performance in macroscopic terms. It is important, however, to consider that the response to mechanical stresses depends on the size, volume, or weight fraction of wood particles, the type of arrangement, and the distribution of them within the polymer matrix (García-Hernández *et al.* 2004). Accordingly, this paper analyzes whether or not the exposure to moisture absorption-desorption cycles (MADCs) caused the diminishment of the mechanical performance of pinewood residue/high-density polyethylene (HDPE) composites due to the diminishment of the IFSS. To do this, the composites were subjected to MADCs after exposure to UV radiation. Then, the Iosipescu shear test method was utilized to evaluate the composites' IFSS.

EXPERIMENTAL

Raw Materials

Pinewood residue (PR) provided by Maderas Bajce (Merida, Mexico) was used as reinforcement. The content of lignin is 28.2%, according to the analyses conducted in the Department of Wood, Cellulose and Paper of the University of Guadalajara (Mexico). HDPE (grade 56035) with a melt flow index of 0.3133 g/10 min supplied by Petroquímica Morelos (Coatzacoalcos, Mexico) was used as a thermoplastic matrix. Two processing additives were used in the formulation of the tested composite: HDPE grafted with maleic anhydride (Polybond 3009 from Brenntag México S.A. de C.V.) as the coupling agent (CA) and Struktol TPW113 (Struktol Company of America) as the processing aid (PA).

Composite Preparation

Pinewood residue was dried for 24 h at 80 °C using a convection oven (Fisher Scientific, Pittsburgh, PA) to eliminate moisture. Afterward, they were milled using a Pagani mill machine (model 1520, Molino Pagani SpA, Borghetto, Italy) fitted with a screen plate drilled with holes of 1 mm in diameter and then screened in a Tyler nest of sieves (meshes #30, 40, and 50) for 5 min, using a sieve shaker (model RX-29, W.S. Tyler® Industrial Group, Ohio, USA). The particles that passed through mesh #30 but were retained on mesh #40 were used (sizes ranging from approximately 0.43 to 0.60 mm). The HDPE, CA, and PA were milled with a granulating machine (model TI 880804, C.W. Brabender® Instruments, Inc., NJ, USA) fitted with a screen plate drilled with holes of 1 mm in diameter. Pinewood, HDPE, and additives were premixed in a horizontal mixer with a helical agitator (model ML-5; Intertécnica Co., Mexico City, Mexico) and dried in the convection oven at 85 °C for 24 h before compounding. Two different formulations were prepared. Details are shown in Table 1.

Table 1. Formulations of WPCs Based on Pinewood Residue and HDPE

Composite	Wood (wt.%)	HDPE (wt.%)	CA (wt.%)	PA (wt.%)
A	39.5	59.3	00.0	01.2
B	38.8	58.1	01.9	01.2

Notes: The wood/HDPE ratio is 40/60 in both composites
The wt.% of CA with respect to wood is 5 for composite B

Compounding was carried out in a laboratory-scale conical twin-screw extruder (EP1-V5501, C.W. Brabender® Instruments, Inc., NJ, USA) using a 4-cm long extrusion cylindrical die with a 5-mm internal diameter fitted to the extruder. During extrusion, the screw speed was 50 rpm and the barrel and die temperatures were set at 180 °C. The obtained extrudates were pelletized using a laboratory pelletizer machine (type 12-72-000, C.W. Brabender® Instruments, Inc., NJ, USA).

Iosipescu Sample Preparation

Test specimens were prepared using the pellets obtained by means of the twin-screw-extrusion procedure detailed above. Pellets were hot-pressed using an automatic hydraulic press (model 3819, Carver, Inc., IN, USA) at 160 °C for 5 min using a compression force of approximately 26,689 N (6,000 lbf) to obtain 15 cm x 15 cm x 3 mm flat plaques. The resultant plaques were machined to obtain specimens with the dimensions and geometry specified in the ASTM D5379/D5379M (2012) standard test method.

Accelerated Weathering Tests

An Uvcon tester (ATLAS MTT, Moussy Le Neuf, France) was used to expose the test samples to 24-h cycles of continuous UV light irradiation for 384 h (16 days) at 60 °C with UVB-313 type fluorescent lamps (Atlas Electric Devices, Chicago, IL). The ASTM G151 (2010), ASTM G154 (2012), and ASTM D4329 (2013) standard test methods were considered as references. Prior to their exposure, samples (10 replicates per material) were conditioned according to the ASTM D618 (2013) standard method (105 °C for 24 h).

Exposure to Moisture Absorption-Desorption Cycles

To observe the effects of the mechano-sorptive phenomenon, the samples were exposed to four cycles of absorption and desorption of moisture. Each cycle (*i.e.*, a moisture absorption-desorption cycle, MADC) consisted of maintaining the samples immersed in distilled water for a total period of 10 days (240 h) and then drying them for a total period of five days (120 h). The temperature of the immersion water and the drying was 60 °C. The conditions for the MADC experiments were established according to the procedure described by Flores-Cerón *et al.* (2011). The variation of the percentage of absorbed moisture ($M_A\%$) was monitored by weighing the samples every 24 h; the first sample weighing was after 4 h of immersion. The weighing procedure was the one described in the ASTM D5229/D5229M (2014) standard test method. A similar procedure was followed to record the variation of the percentage of moisture loss ($M_D\%$) (*i.e.*, desorption). The experiments were performed according to the ASTM D5229/D5229M (2014) standard test method. Before that, the test specimens were conditioned according to the ASTM D570 (2010) standard. The UV-irradiated and non-UV-irradiated samples were subjected to MADCs. A recirculating bath and a programmable temperature controller (model 1156D, PolyScience, Illinois, USA) were used for the water-absorption process. The drying was carried out in the Fisher Scientific oven. An analytical balance (Voyager Pro, model VP214CN, OHAUS, Parsippany, NJ, USA) was used to register the change in the weight of the samples during the MADC experiments. The weight percent of absorbed moisture ($M_A\%$) was calculated using Eq. 1,

$$M_A\% = [(m_H - m_0)/m_0] \times 100 \quad (1)$$

where m_H is the weight of the sample after being subjected to a humid environment and m_0 is its initial weight. The weight percent of desorbed moisture ($M_D\%$) was calculated using Eq. 2,

$$M_D\% = [(m_S - m_0)/m_0] \times 100 \quad (2)$$

where m_S is the sample's weight after the drying period and m_0 is its initial weight.

Characterization Experiments

Iosipescu shear tests

The tests were performed using a universal testing machine (model AGS-X, Shimadzu Scientific Instruments, Columbia, Maryland, USA) following the ASTM D5379/D5379M (2012) standard test method, using a 1000-N load cell and a crosshead speed of 1 mm/min. At least 10 specimens corresponding to each type of material were tested to obtain IFSS values. All samples were conditioned at 23 ± 2 °C and $50 \pm 5\%$ relative humidity for at least 40 h before testing in accordance with the ASTM D618 (2013) standard. The characterization was performed for UV-irradiated and non-UV-irradiated

materials, as well as for materials with and without the coupling agent; all were subjected to each of the four MADCs. The experiments were conducted using a “Wyoming” test fixture attached to the universal testing machine according to the ASTM D5379/D5379M (2012) standard.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was conducted with a Nicolet Protégé 460 spectrophotometer (Cole-Parmer, Vernon Hills, IL, USA) in transmittance mode to quantify the amount of lignin and the possibility of hydrolysis in the samples. The specimens for each type of material were prepared by grinding/mixing/homogenizing 2 mg of powdered particles of the material with 135 mg of potassium bromide (KBr) powder (grade FTIR, Sigma-Aldrich Química, S.L., Toluca, Mexico) in an agate mortar. Then, the mixture was pressed into a tablet. Scans were run at a resolution of 4 cm⁻¹. For each sample, 100 scans were recorded from 4000 to 500 cm⁻¹. The peak intensities were normalized using the peak at 2917 cm⁻¹, corresponding to the alkane C-H stretching vibrations of methylene groups. This peak was chosen as a reference because it changed the least with weathering (Stark and Matuana 2004; López-Naranjo *et al.* 2013). The amount of lignin and the possibility of hydrolysis in the samples were respectively quantified by means of the lignin and carboxylate anion indexes (the carboxylate anion is a hydrolysis product). They were respectively calculated using Eqs. 3 and 4,

$$\text{Lignin index} = (I_{1504}/I_{2917}) \times 100 \quad (3)$$

$$\text{Carboxylate anion index} = (I_{1600}/I_{2917}) \times 100 \quad (4)$$

where I_{1504} represents the intensity of the peak corresponding to the aromatic skeletal vibration of lignin, I_{1600} represents the intensity of the peak corresponding to carboxylate anion stretching, and I_{2917} represents the intensity of the peak corresponding to methyl group vibrations, used for normalizing the peak intensities.

Scanning electron microscopy

Morphological analysis was performed on fracture surfaces of Iosipescu samples by scanning electron microscopy (SEM) with the purpose of observing the type of failure that occurred in the interfacial region, to qualitatively estimate the degree of adhesion between wood particles and the thermoplastic matrix. This would allow an assessment of the effect of the mechano-sorptive phenomenon in the interfacial region. Samples were cut into small sections (6 mm X 6 mm) using a razor blade and then mounted onto stubs and gold-coated employing a sputter coater (Denton Vacuum Desk II, Moorestown, NJ, USA). The samples were examined with an electron microscope (JSM-6360 LV, JEOL USA, Inc., Peabody, MA) at a working distance of approximately 10 mm and a voltage of 10 kV.

Statistics

To identify what factors significantly affected the interfacial shear strength, an analysis of variance (ANOVA) was performed using a statistical software (Minitab Inc., State College, PA, <https://www.minitab.com>). The results obtained from Iosipescu shear tests were considered as variables. The factors evaluated were the presence of the coupling agent (A), the exposure to UV radiation (B), and the exposure to moisture absorption-desorption cycles (C). Similarly, the combined effect of each of the factors were evaluated; that is, AB, AC, BC, and ABC. Statistical significance was defined as $P < 0.05$.

RESULTS AND DISCUSSION

Moisture Absorption-Desorption Cycles

The $M_A\%$ and $M_D\%$ of non-UV-irradiated (NUVI) and UV-irradiated (UVI) Iosipescu test specimens subjected to MADCs are respectively shown in Figs. 1 and 2. The maximum values of $M_A\%$ and $M_D\%$ for each MADC are presented in parentheses. The variation of $M_D\%$ and $M_A\%$ was similar for all materials, whether or not they were UV-irradiated. However, it appears that the UVI samples shown in Fig. 2 absorbed and desorbed a greater amount of moisture than the non-UV-irradiated ones shown in Fig. 1. This suggests that the UV radiation favors the entry of water to the WPC because its surface is damaged, leaving the wood particles more exposed to absorb more moisture (Stark 2006; Stark and Gardner 2008). When analyzing the effect of the use of a coupling agent, it can be observed that specimens with the CA shown in Figs. 1(c) and (d) and Figs. 2(c) and (d) absorbed and desorbed less moisture than those without it, as expressed in Figs. 1(a) and (b), and Figs. 2(a) and (b); this was more evident in UV-irradiated samples. This may be because a better interphase was achieved using the coupling agent, which limits water absorption in the WPCs because the hydrophilic groups of the wood are blocked by the creation of ester bonds between the coupling agent and the lignocellulosic particles (Lin *et al.* 2002; Yan *et al.* 2006). Gauthier *et al.* (1998) and Lin *et al.* (2002) mention that the use of a coupling agent reduces the amount of defects and voids at the wood-thermoplastic matrix interphase, which reduces the chances that water is introduced into the WPCs.

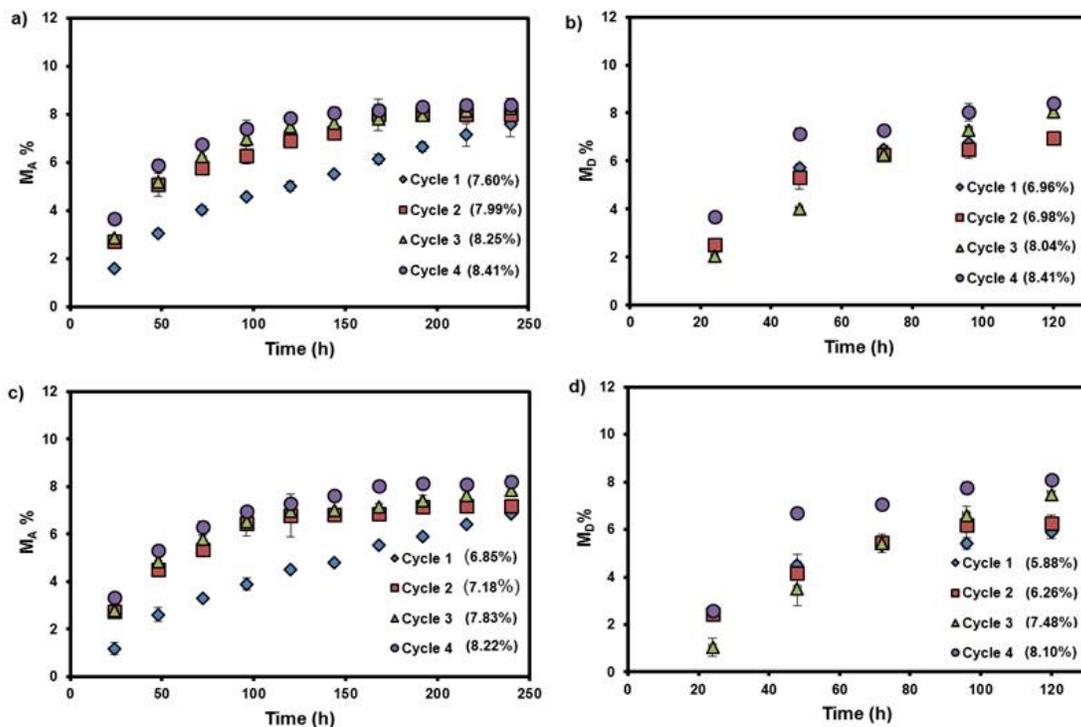


Fig. 1. $M_A\%$ and $M_D\%$ of non-UV-irradiated (NUVI) Iosipescu test specimens subjected to MADCs: (a), (b) specimens with 0 wt.% CA, and (c), (d) specimens with 5 wt.% CA

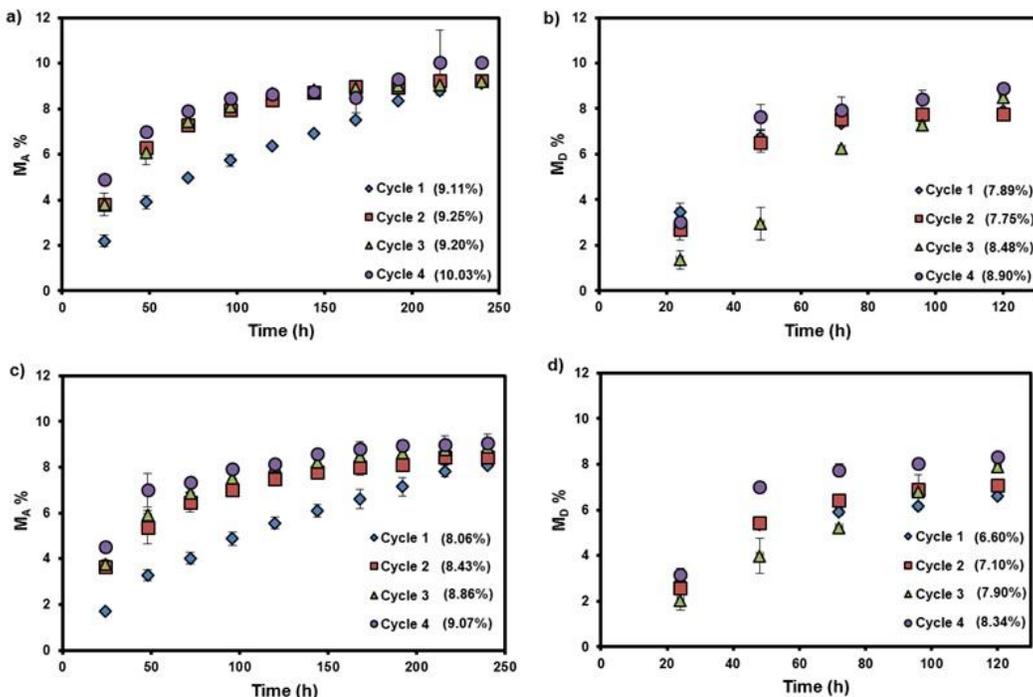


Fig. 2. $M_A\%$ and $M_D\%$ of UV-irradiated (UVI) losipesco test specimens subjected to MADCs: (a), (b) specimens with 0 wt.% CA, and (c), (d) specimens with 5 wt.% CA

From Fig. 1, it can be seen that the maximum values of $M_A\%$ and $M_D\%$ for non-UV-irradiated samples subjected to the fourth MADC were similar, regardless of whether or not they contained a CA. It then follows that the coupling agent itself effectively slowed the moisture absorption-desorption process, but there was a limit beyond which it could not thereafter continue to perform this function. This was not observed for the UV-irradiated specimens shown in Fig. 2. That is to say, the specimens with 5% CA desorbed and absorbed less water than those without it (observe the maximum values for the fourth MADC).

Caufield *et al.* (1999) mention that the rate of water absorption in lignocellulosic composites may be delayed by the action of the coupling agent, but a point is reached at which the CA no longer fulfills its function. There may be two possible reasons that cause this situation. First, the use of lubricants and processing aids can interfere with the proper functioning of the coupling agent. Panthapulakkal *et al.* (2006) suggest that the presence of a processing aid in WPCs plasticizes the matrix and decreases the interaction between the lignocellulosic particles and the thermoplastic, which may reduce the possibility that the CA functions properly to bond the continuous and disperse phases. This can accelerate the absorption of water in the WPCs and cause dimensional changes. The second possibility is that the maleic anhydride of a CA is susceptible to hydrolysis and is degraded. From a chemical point of view, there is no conclusive information about the changes from water absorption in WPCs, especially about the hydrolysis of unreacted ester or anhydride functional groups. As for hydrolysis of the ester functional groups that bind the cellulose and maleic anhydride, it is important to consider that the water absorbed by the lignocellulosic material is located at the hydroxyl group. This binding takes place by hydrogen bonds, and it is not likely that they will hydrolyze. However, whether or not

hydrolysis of the coupling agent occurs will be verified through discussion of the results of the FTIR analysis in the corresponding section of this paper.

Although a clear trend was not observed with respect to reaching the equilibrium in the desorption process for each material, there was a trend to decrease the difference between the maximum values of $M_A\%$ and $M_D\%$ for each MADC (shown in Fig. 3). This is important because it may indicate that the wood particles were degrading because the amount of cellulose and hemicellulose, which are able to retain water, were decreasing. This would result in mechanical strength diminishment. For example, Fig. 3 shows that for NUVI materials, the difference between the maximum values of $M_A\%$ and $M_D\%$ for the fourth MADC was almost zero (*i.e.*, apparently all absorbed moisture was desorbed). For UVI materials, there was also a trend to reduce that difference, but the values were greater than for the non-irradiated ones; that is to say, not all absorbed moisture was desorbed. This can be explained because all components of wood are susceptible to photodegradation. In this regard, it is known that photodegradation causes lignin to degrade via multiple mechanisms, creating free phenoxy radicals, including a long lasting guaiacoxy radical. The free radicals formed undergo further reactions creating quinoid structures, which cause discoloration of wood.

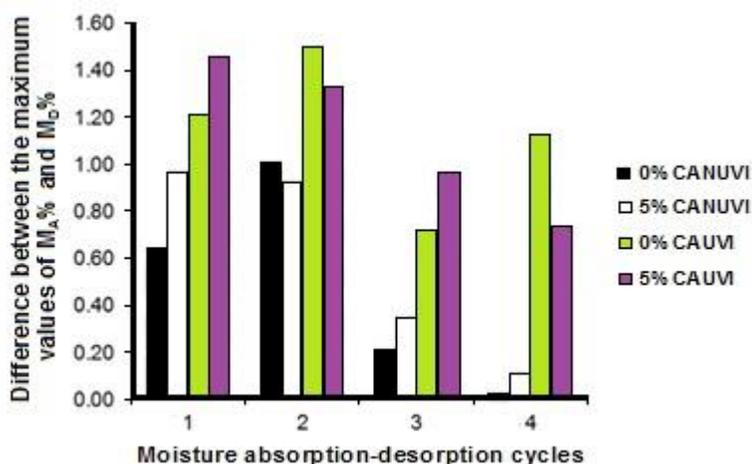


Fig. 3. Difference between the maximum values of $M_A\%$ and $M_D\%$ for each MADC and type of WPC; 0% CANUVI: non-UV-irradiated specimens with 0% CA, 5% CANUVI: non-UV-irradiated specimens with 5% CA, 0% CAUVI: UV-irradiated specimens with 0% CA, and 5% CAUVI: UV-irradiated specimens with 5% CA

Fischer (1987) studied the changes in lignin and cellulose of beech wood subjected to UV irradiation, and noted that oxidative processes occurred more easily in the lignin than in the cellulose. On the other hand, Stachowiak-Wencek *et al.* (2015) exposed Scots pine wood surface to UV-VIS light with a wavelength of 320 to 800 nm and they found changes in color and chemical composition, as a result of lignin degradation that was accompanied by the formation of new carbonyl groups. Also, Lanzalunga and Bietti (2000) studied the photo- and radiation chemical induced degradation of lignin model compounds, and found that lignin absorbs at longer wavelengths than cellulose and is a much better absorber in the 280 to 300 nm region. Actually, lignin is the component of the wood that absorbs more UV light (*i.e.*, 80% to 95% of UV radiation is absorbed by lignin). In this regard, UV light degrades lignin into water-soluble components, leaving a cellulose-rich surface with a fibrous appearance (Stark and Gardner 2008). Now, because the cellulose is

more hydrophilic than lignin, it may not allow desorption of all the absorbed moisture. On this point, Najafi *et al.* (2006) found a strong correlation between the total cellulose and hemicellulose fraction of wood particles with the amount of water absorbed. It has been reported that if the trend to diminish the difference between $M_A\%$ and $M_D\%$ is continued, a point will be reached where it will be null for both irradiated and non-irradiated materials (Flores-Cerón *et al.* 2011). Therefore, from this section, it may be concluded that UV radiation accelerates the moisture absorption-desorption process, regardless of whether or not the WPC has a CA.

Iosipescu Shear Tests

The IFSS values for composites A and B, both non- and UV-irradiated, and subjected and not subjected to the MADCs are presented in Table 2. On the other hand, the results of the ANOVA are presented in Table 3.

Table 2. IFSS Values for Composites A and B, both Non- and UV-Irradiated, and Subjected and Not Subjected to MADCs

MADC	Interfacial shear strength (MPa)			
	NUVI specimens		UVI specimens	
	Composite A	Composite B	Composite A	Composite B
0	9.33 (± 0.32)	10.23 (± 0.38)	9.49 (± 0.51)	10.02 (± 0.45)
1	9.21 (± 0.49)	9.37 (± 0.59)	8.63 (± 0.43)	9.17 (± 0.37)
2	9.04 (± 0.59)	9.56 (± 0.50)	9.49 (± 0.62)	9.66 (± 0.19)
3	9.02 (± 0.33)	9.53 (± 0.48)	9.30 (± 0.45)	9.96 (± 0.64)
4	8.86 (± 0.28)	8.78 (± 0.38)	8.99 (± 0.11)	9.35 (± 0.37)

Standard deviation is indicated in parenthesis, Composite A has 0 wt.% CA, Composite B has 5 wt.% CA

Table 3. Results of the ANOVA

Factor	P
A	0.001*
B	0.183
C	0.000*
AB	0.861
AC	0.022*
BC	0.125
ABC	0.099

*Significant values ($P < 0.05$)

As shown, the significant factors were the presence of coupling agent, the exposure to moisture absorption-desorption cycles, and the combination of both (Table 3), whereas the exposure to UV radiation was not statistically significant. Regarding the effect of the exposure to MADCs, overall there was a slight downward trend in the IFSS when the number of them is increased (Table 2). As for the effect of the coupling agent, all specimens with it had higher IFSS values than those without. This makes it possible to infer that the CA has a favorable effect on the wood-HDPE interfacial region. The exposure to UV radiation was not a significant factor and therefore did not affect the IFSS.

Regarding the significance of UV radiation on the IFSS, various studies have been conducted in which wood-HDPE composites were subjected to accelerated weathering, exposing them to either continuous UV light irradiation only or cycles combining UV

radiation and condensation (Stark and Matuana 2004, 2006; Stark 2006). These studies report that the loss of mechanical properties is due to moisture, which damages the interfacial region, and that the UV radiation is a surface phenomenon (*i.e.*, it damages the WPC surface) that favors the entry of water to the composite. This is because the combination of UV radiation and condensation changes the mechanism of moisture absorption. That is, the degradation of lignin by photo-oxidation leaves cellulose exposed, which increases the surface wettability of the material. This is detrimental for two reasons: the first is that the presence of water in the wood accelerates oxidation reactions that are a direct result of photodegradation. The second reason is that the cell walls of the wood swell when water penetrates them, compromising the interfacial region. This can lead to the formation of interfacial cracks that contribute to a lower efficiency of stress transfer between the wood particles and the matrix, causing a decrease in the mechanical strength. This was observed in the present study, *i.e.*, the UV radiation factor was not statistically significant in contributing to the loss of IFSS, but it did accelerate the absorption of moisture. Therefore, because the MADC factor was statistically significant, it suggests that the interfacial region is what is actually being affected by moisture.

Regarding the effect of the coupling agent, it appears that the materials subjected to the fourth MADC had similar values of IFSS, regardless of whether or not they had a CA, as shown in Table 2. Caulfield *et al.* (1999) report that a point is reached at which the CA no longer fulfills its function. They attribute this to the degradation of the lignocellulosic filler in the presence of water.

About the relationship between moisture adsorption and shear strength, Cauch-Cupul *et al.* (2011) have studied the role of moisture uptake on the deterioration of the IFSS of an epoxy/carbon fiber composite. The authors pointed out that the contribution of the radial stresses and the mechanical component of fiber–matrix adhesion decrease rapidly for higher moisture contents in the fiber-matrix-interface. In the same way, Chen *et al.* (2009) reported a detailed study on the moisture sorption characteristics of bamboo strips and their influence on the interfacial shear strength of a bamboo/vinyl ester composite. The IFSS, determined by pull-out tests, decreased dramatically as the humidity during the composite production was increased. The interface of the bamboo/vinyl ester composite can also be damaged due to moisture exposure after fabrication. The IFSS of the composite decreased by nearly 40% in the first 9 days of water immersion. Bradley and Grant (1995) pointed out that the degradation in transverse tensile strength and interfacial shear strength, due to moisture absorption, has been found to vary from 0% to 22% for thermoset/graphite and vinylester/glass systems. The observed correlation in the decrease of the interfacial shear strength, due to moisture absorption, with the decrease of the transverse tensile strength, supports the hypothesis that the moisture-induced degradation is associated with a decrease in the interfacial strength rather than the degradation of matrix mechanical properties.

Fourier Transform Infrared Spectroscopy

The effects of exposure to UV radiation are shown in Fig. 4, which presents the FTIR spectra of WPCs specimens with 0 and 5% of the coupling agent (UV and non-UV-irradiated), and not subjected to MADCs. It is possible to observe the characteristic absorption peaks corresponding to the components of wood (peaks at 898, 1061, 1269, 1504, 2924, and 3383 cm^{-1}), and HDPE (peaks at 2917, 1462, 719, and 2846 cm^{-1}) (Fabiyyi and McDonald 2010; Wade 2010). The characteristic peaks of the CA may be confused with the carbonyl groups (1800 to 1680 cm^{-1}) formed during oxidation reactions by thermal

degradation of the HDPE during the WPCs production process and specimens preparation (Stark and Matuana 2004). The carbonyl groups that are formed due to thermal or photo-oxidative degradation of HDPE are conjugated ketones (1700 to 1685 cm^{-1}), carboxylic acids with hydrogen bonds (1725 to 1715 cm^{-1}), esters (1745 to 1730 cm^{-1}), and γ -lactone (1800 to 1765 cm^{-1}). Carbonyl concentration may vary with the time of thermal exposure or UV radiation (Fabiya *et al.* 2008). The effects of the MADCs are shown in Figs. 5 and 6. For simplicity, only the spectra of the WPCs subjected to 0 and 4 MADCs are presented.

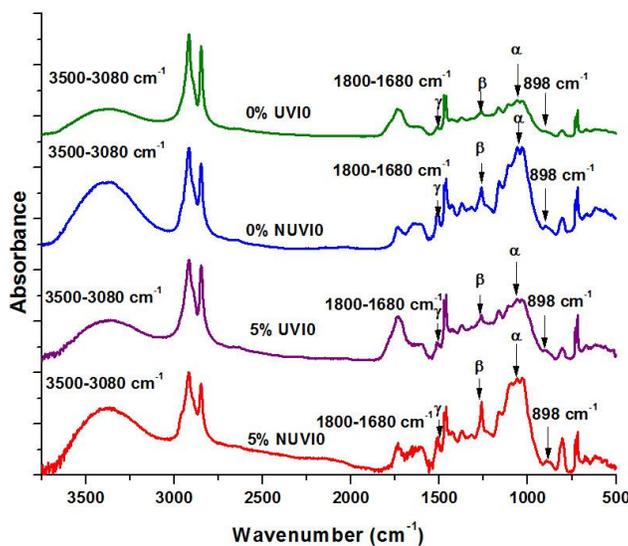


Fig. 4. Comparison of the FTIR spectra of WPCs not subjected to MADCs. 0%UVIO: UV-irradiated specimens with 0% CA, 0%NUVIO: non-UV-irradiated specimens with 0% CA, 5%UVIO: UV-irradiated specimens with 5% CA, and 5%NUVIO: non-UV-irradiated specimens with 5% CA ($\alpha = 1061$ cm^{-1} , $\beta = 1269$ cm^{-1} , $\gamma = 1504$ cm^{-1})

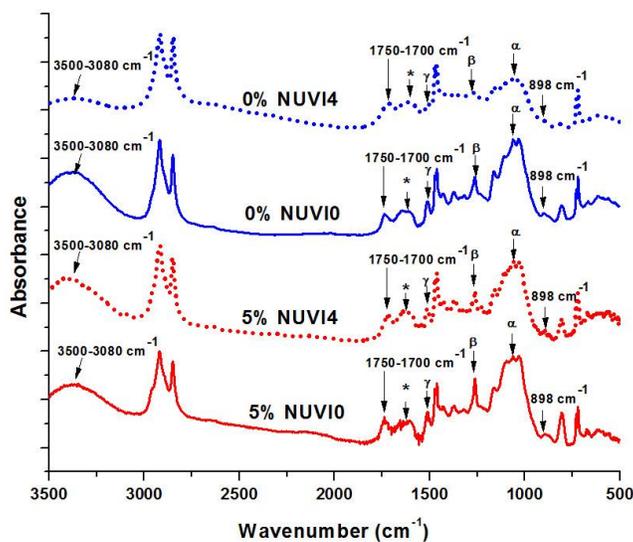


Fig. 5. Comparison of the FTIR spectra of non-UV-irradiated WPCs subjected to 0 and 4 MADCs. 0%NUVI4: specimens with 0% CA subjected to 4 MADCs, 0%NUVIO: specimens with 0% CA subjected to 0 MADCs, 5%NUVI4: specimens with 5% CA subjected to 4 MADCs, and 5%NUVIO: specimens with 5% CA subjected to 0 MADCs (*band in the interval 1650 to 1580 cm^{-1} , $\alpha = 1061$ cm^{-1} , $\beta = 1269$ cm^{-1} , $\gamma = 1504$ cm^{-1})

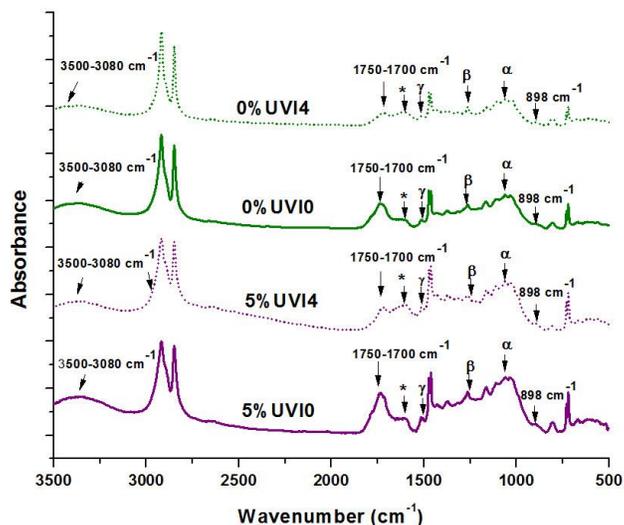


Fig. 6. Comparison of the FTIR spectra of UV-irradiated WPCs subjected to 0 and 4 MADCs. 0%UVI4: specimens with 0% CA subjected to 4 MADCs, 0%UVI0: specimens with 0% subjected to 0 MADCs, 5%UVI4: specimens with 5% CA subjected to 4 MADCs, and 5%UVI0: specimens with 5% CA subjected to 0 MADCs (*band in the interval 1650 to 1580 cm^{-1} , $\alpha = 1061 \text{ cm}^{-1}$, $\beta = 1269 \text{ cm}^{-1}$, $\gamma = 1504 \text{ cm}^{-1}$)

Figures 5 and 6 show that, in general, the intensity of some peaks corresponding to wood (898, 1061, 1269, and 1504 cm^{-1}) was decreased by increasing the number of MADCs. We believe that this reduction was enhanced on the WPCs that were UV-irradiated (Fig. 6), especially because of the photo-oxidation of wood. Another observed effect is the reduction of the peak found between 1750 and 1700 cm^{-1} for the WPC's that were UV-irradiated, as this is one of the characteristic peaks of the carbonyl group, which is formed by photo-oxidation reactions. Also, a slight increase in the peaks found in the interval 1650 to 1580 cm^{-1} was observed. An explanation for this may be that the functional groups corresponding to the interval 1750 to 1700 cm^{-1} (esters and carboxylic acids) can react or solubilize with water (Wade 2010). On the other hand, the presence of the band in the interval 1650 to 1580 cm^{-1} is attributable to the stretching vibration in the carboxylate anion (Wade 2010).

As for the changes associated with UV radiation, the FTIR analysis revealed that some bands appeared or disappeared, while the intensity of others was increased slightly. Assignment of the absorption peaks corresponding to carbonyl groups was discussed before (Fig. 4). Their increasing intensity suggests that oxidation reactions increased because of UV radiation. The degradation of wood on the surface of irradiated WPCs may be associated with decreasing the intensity of the characteristic band of the hydroxyl group (3500 to 3080 cm^{-1}), and that of the other characteristic peaks already mentioned above (898, 1061, and 1269 cm^{-1}), especially that of the peak corresponding to an aromatic skeletal vibration of lignin (1504 cm^{-1}) that decreased to a greater extent. The lignin index, calculated using Eq. 3, is presented in Table 4. As can be seen, the apparent lignin content on the WPCs decreased as the number of MADCs increased, regardless of the UV treatment and the CA content. However, it is evident in Table 4 that the CA affected the lignin lixiviation, *e.g.*, the lignin index was diminished around 55% for the WPCs that had

CA, and around 95% for the ones without it, regardless of whether the samples were UV-irradiated or not. This behavior suggests that the CA allows for a better impregnation of the polyolefin matrix into the PR, which causes the diminishment of the amount of lignin exposed to the UV light. On the other hand, the compounds formed by the photo-oxidation of lignin were solubilized by water and lixiviated. These results are in good agreement with what is reported in the literature (Stark and Matuana 2004; Stark 2006; Fabiyi *et al.* 2008; Fabiyi and McDonald 2010; López-Naranjo *et al.* 2013).

Table 4. Lignin and Carboxylate Anion Indexes

Specimen *	Lignin index	Carboxylate anion index
0%NUVIO	41.76	1.50
0%NUVI4	2.02	1.02
5%NUVIO	64.01	1.61
5%NUVI4	27.41	5.05
0%UVIO	4.5	0.98
0%UVI4	0.33	0.95
5%UVIO	4.3	1.02
5%UVI4	2.8	9.22

* Specimen nomenclature is as defined in Figs. 4, 5, and 6

Regarding the carboxylate anion index shown in Table 4, it is generally observed that it was similar for the materials with 0% coupling agent (UV-irradiated or not), subjected to 0 and 4 MADCs. We assume that it remained almost constant because there were no components with ester bonds that could be hydrolyzed, as these materials did not have the CA. In general, an increase in the index for WPCs with 5% CA (UV-irradiated or not) can be observed, suggesting that compounds with carboxylic groups were formed. The presence of ester bonds between the CA and the wood particles makes the composite susceptible to hydrolysis.

Scanning Electron Microscopy

The appearance of WPC specimens (UV and non-UV-irradiated) was practically the same. This agrees with what was discussed above, in which UV radiation was not a significant factor because it is a surface phenomenon. Therefore, for simplicity, only the SEM micrographs of the fracture surfaces corresponding to WPC Iosipescu irradiated specimens are shown in Fig. 7. Similarly, only micrographs of the composites subjected to 0 (Figs. 7(a) and 7(e)) and 4 MADCs (Figs. 7(c) and 7(g)) are presented.

Comparing the micrographs of the samples with and without the CA, the samples with the CA contained fewer exposed wood particles (some of them marked with blue circles with dotted lines) than those without. On completion of the fourth MADC, exposed particles were observable for both cases, meaning that the CA was degraded and therefore no longer had the same effect on the wood-polymer interfacial region (*i.e.*, the CA no longer fulfilled its function), which has been discussed previously in the corresponding section of this work. A closer look at the wood particles is presented in Figs. 7(b), (d), (f), and (h). It is generally observed that they protruded from the polymer matrix. It is also observed that in the composites without the CA, the surface of the wood particles was smoother, in contrast to what is observed in composites with the CA. In the latter, the wood particles were embedded in the polymer matrix, and those protruding from it had scabs or fibrils (encircled in red), evidence of improved adhesion to the matrix. Lu *et al.* (2005) reported similar results when a coupling agent was used in the preparation of WPCs.

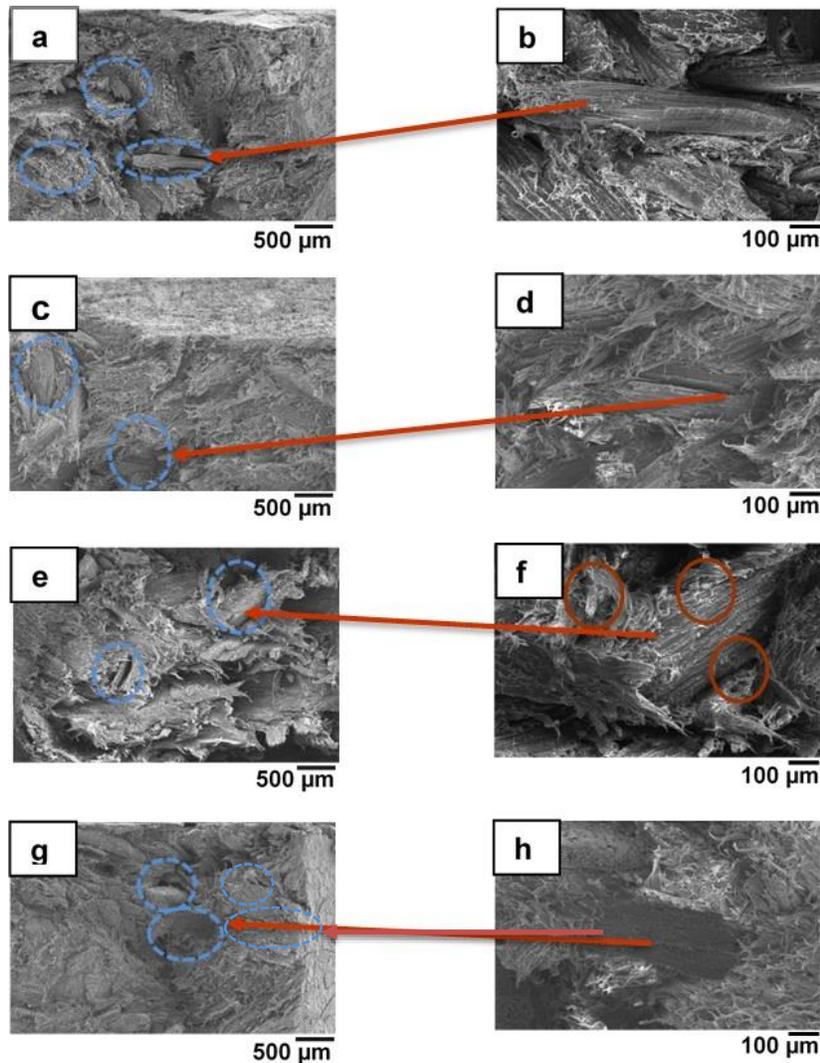


Fig. 7. SEM micrographs of fracture surfaces of UVI Iosipescu test specimens: (a) with 0 wt.% CA subjected to 0 MADCs; (b) magnification of (a); (c) with 0 wt.% CA subjected to 4 MADCs; (d) magnification of (c); (e) with 5 wt.% CA subjected to 0 MADCs; (f) magnification of (e); (g) with 5 wt.% CA subjected to 4 MADCs; and (h) magnification of (g)

CONCLUSIONS

1. The results of this research suggest that the decrease in the mechanical performance of the studied WPCs can be associated with the damage that occurred in the interfacial region, primarily because of moisture absorption-desorption cycles.
2. The absorption and desorption of moisture was slower in non-UV-irradiated WPCs, particularly in those with a coupling agent. The coupling agent itself effectively delayed the moisture absorption-desorption process, but there was a limit after which it could no longer continue to perform this function.

3. The UV radiation did not significantly contribute to the loss of IFSS. Statistically, the coupling agent had a favorable effect on the IFSS. The opposite was found for the exposure to moisture absorption-desorption cycles.
4. Regarding the effect of the MADCs, FTIR analysis showed that they caused the reduction of the absorption peaks corresponding to carbonyl groups as well as those corresponding to some characteristic groups of wood, in particular those of lignin.
5. The SEM analysis confirmed that UV radiation, acting alone, was not a significant factor.

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