

# Comparative Study of Maleated Polypropylene as a Coupling Agent for Recycled Low-Density Polyethylene/Wood Flour Composites

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**ABSTRACT:** The effects of the type of coupling agent and virgin polypropylene (PP) content on the mechanical properties and water absorption behavior of recycled low-density polyethylene/wood flour (WF) composites were investigated. The fractured surfaces of these recycled wood/plastic composites (rWPCs) were examined to gain insight into the distribution and dispersion of WF within the polymer matrix. The results indicate that the use of 100% recycled polymer led to inferior mechanical properties and to a greater degree of moisture absorption and swelling when compared to recycled polymer–virgin PP wood/plastic composites. This could have been related to the poor melt strength and inferior processability of the recycled

polymer. The extent of improvement of the mechanical properties depended not only on the virgin PP content in the matrix but also on the presence of maleic anhydride (MA) modified PP as the coupling agent. Higher concentrations of MA group were beneficial; this improvement was attributed to increased chemical bonding (ester linkages) between hydroxyl moieties in WF and anhydride moieties in the coupling agent. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1731–1741, 2011

**Key words:** composites; recycling; polymer extrusion; polyolefins

## INTRODUCTION

The Chilean aquaculture industry generates annually about 4200 tons of nonbiodegradable plastic waste, which is mostly disposed in landfills and constitutes both an environmental problem and an economic opportunity. The possibility of its use in the development of composite materials, especially wood/plastic composites (WPCs), is indeed very attractive because Chile possesses huge forest resources: 4.4 million m<sup>3</sup>/year of wood waste was generated in 2008, primarily from the processing of *Pinus radiata* and *Eucalyptus globulus* sp.<sup>1</sup>

WPCs are being promoted as premium construction materials because of their superior stability and

mechanical properties. Traditionally, WPCs have been based on the use of a virgin polymer, such as high-density polyethylene (HDPE), polypropylene (PP), or poly(vinyl chloride). Recycled plastics for WPCs are gaining popularity because of their low cost and savings in waste disposal. Previous studies<sup>2–5</sup> have shown that the mechanical properties of recycled-HDPE-based WPCs were not very different from those prepared with virgin resin, and therefore, recycled HDPE could be used in the manufacture of WPCs.

The performance of WPCs containing a recycled or virgin resin matrix is affected by the size and orientation of the fibers and by the interfacial adhesion between the hydrophilic fibers and the hydrophobic polymer. The latter is well known to be a major issue in obtaining composites with superior mechanical properties. A number of published studies have reported the use of polyolefins functionalized with maleic anhydride (MA) as a coupling agent.<sup>6–10</sup> Thus, for example, Adhikary et al.<sup>8</sup> studied the influence of the coupling agent (MA-g-PP) content on the dimensional stability and mechanical properties of WPCs made with recycled HDPE and *P. radiata* wood flour (WF). The composites containing 50 wt% recycled HDPE with 3 and 5 wt% coupling agent had equivalent mechanical properties that were superior to those

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**TABLE I**  
**Melt Flow Index (MFI) and the Thermal and Mechanical Properties of Recycled LDPE (indicated by an rPE in sample names)**

MFI (g/10 min)	Degradation temperature (°C)	Tensile strength at yield (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)
0.85 ± 0.02	442	13.1 ± 0.6	138 ± 4	176 ± 18	3,3 ± 0.1	128 ± 23

prepared without a coupling agent. On the other hand, La Mantia and coworkers<sup>9,10</sup> compared the effectiveness of several coupling agents in improving mechanical properties of WPCs prepared with recycled polyolefin blends. The composition of the recycled polyolefin blend<sup>9</sup> was about 80% polyethylenes (PEs) and 20% PP, with small amounts of other polymers heavier than water [e.g., poly(vinyl chloride), poly(ethylene terephthalate), and polystyrene]. They used two different functionalized PPs grafted with MA or acrylic acid, and the mechanical properties were improved with a small amount of these compatibilizers. They also reported the beneficial effects<sup>10</sup> of several coupling agents, including polar copolymers and MA-grafted PE; the tensile and impact strength and morphology of WPCs prepared with recycled polyethylene and WF were both improved. MA-grafted PE improved the tensile properties at higher WF contents; this was attributed to a better filler dispersion and wetting within the polymer matrix. However, the impact strength was not influenced by the addition of this coupling agent. Other authors<sup>11–14</sup> reported the use of a coupling agent, together with surface treatments of WF (in the preparation of rWPCs), to further improve interfacial adhesion. For example,<sup>14</sup> when WF was modified by surface treatment before it was mixed with recycled HDPE and MA-g-PP, the mechanical properties improved in the following order: alkaline followed by silane treatment > silane treatment > alkaline treatment. The greatest degree of reduction of free OH groups was achieved for esterification of the hydroxyl groups during the silane treatment of WF; this reduced the hydrophilic nature of WF and thus improved the compatibility between the hydrophobic polymer matrix and WF.

Most rWPCs studied to date use a single type of plastic waste, generally HDPE or PP, or their combination. Even though there is a large percentage of low-density polyethylene (LDPE) in typical solid waste streams, only a few studies of WPCs with recycled LDPE have been reported. For example, Oksman and Lindberg<sup>15</sup> studied the influence of the content of the maleated triblock copolymer styrene-ethylene/butylene-styrene (SEBS), used as coupling agent in the preparation of rWPC made with recycled LDPE, and found that the tensile strength reached its maximum level with 4 wt % SEBS-MA, but there was a reduction in the composite stiffness. Redighieri and Costa<sup>16</sup> reported that the use of MA-

grafted PE as a coupling agent enhanced the adhesion between the recycled LDPE matrix and WF; this led to an improvement in the mechanical properties. In this case, the coupling agent was incorporated through pretreatment with xylene as a solvent.

We investigated here the influence of PP functionalization (grafting) with MA as a coupling agent on both the mechanical properties and the morphology of rWPCs. The key compatibility issues in the design of WPCs were the molecular weight and degree of grafting. Therefore, we evaluated the effect of the extent of grafting in MA-g-PP on their mechanical properties and water absorption behavior. The addition of virgin PP (indicated by vPP in sample names) was of interest for improving both the processability and the mechanical properties of the composites.

## EXPERIMENTAL

### Materials

*P. radiata* WF was collected from a sawmill and dried to less than 2% humidity in a rotary dryer before use; the mesh size distributions were less than 0.05, 0.83, 6.4, 8.4, 32, and 52 wt % on sieve numbers +10, 10–20, 20–40, 40–50, 50–100, and –100, respectively. The plastic waste, derived mainly from post-consumer packaging, was obtained from the salmon farming industry; the bags were washed with a detergent, cut into tiny pieces, and dried simultaneously. The dried waste was processed in a corotating twin-screw extruder (TSA Industriale, Cernobbio, Italy) to make pellets, which were then used as the main matrix. Its relevant properties are summarized in Table I. Two different commercial PP samples functionalized with MA (MA-g-PP), Fusabond P MD353D, Delaware, United States (indicated by an F in sample names, DuPont) and Licocene PP MA 6452 (indicated by an L in sample names, Clariant, Muttenz, Switzerland), were used to enhance the WF/matrix adhesion. Lubricant A-C Optipak111 (Honeywell), a polyester-based wax, was used to increase the extrusion rate and reduce the water absorbancy. As antioxidants, we used Irgafos 168 and Irganox 1010 from Ciba (BASF); they were added, in a 2 : 1 ratio, to the mixture as a master batch of virgin LDPE and 20 wt% antioxidant. In the preparation of rWPCs, we also used PP from Petroquim Chile (PH-0241) for

TABLE II  
Specification of the PP, Coupling Agents, and Additives Used

Material	Trade name	Description	Supplier
PP homopolymer	PH-0241	MFI (2.16 kg/230°C) = 2 g/10 min Izod impact test (23°C) = 90 J/m Tensile strength (at yield point) = 37 MPa Flexural modulus = 1750 MPa	Petroquim S. A.
Coupling agent	Licocene PP MA 6452	Acid value $\approx$ 43 mg of KOH/g Softening point $\approx$ 140°C Viscosity at 170°C $\approx$ 1100 mPa s $M_n$ = 3800 g/mol and $M_w$ = 10,000 g/mol	Clariant
	Fusabond P MD353D	Acid value $\approx$ 12 mg of KOH/g MFI (160°C/325 g) = 22.4 g/10 min mp = 136°C $M_n$ = 11,063 g/mol and $M_w$ = 88,500 g/mol	DuPont
Lubricant	A-C Optipak111	Polyester based wax Acid number = 1–4 mg of KOH/g Viscosity at 270°F = 9–14 cS	Honeywell
Antioxidant	Irgafos168	Chemical name: tris(2,4-di- <i>tert</i> -butylphenyl)phosphite Molecular weight = 646.9 g/mol	Ciba
	Irganox1010	Chemical name: tetrakis[3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate Molecular weight = 1178 g/mol	Ciba

$M_n$  = number-average molecular weight;  $M_w$  = weight-average molecular weight.

comparison with the recycled LDPE/WF composites and for blending with recycled polymer. The relevant specifications of these materials are listed in Table II.<sup>17,18</sup>

### Composite preparation

A corotating twin-screw extruder (TSA Industriale, Cernobbio, Italy screw diameter = 45 mm, length/diameter = 40) was used to compound the WPCs. The seven-zone temperature profile was controlled from the feeder to the heating zones at 180, 190, 180, 175, 175, 180, and 172°C, and the die temperature was above 180°C. The designed screw configuration, with a sequential arrangement of conveying elements (SE) and kneading blocks (KB), is shown in Table III.

The compositions of the WPCs tested are indicated in Table IV. The resin, antioxidant master batch, and pellets were tumble-mixed and introduced simultaneously into the hopper. The WF, together with the lubricant, was introduced through a gravimetric side feeder located in the third zone of the extruder in such a way that it was fed downstream into the molten polymeric mixture. The feed rate and screw speed were 30 kg/h and 80 rpm, respectively. Wood/plastic pellets were produced

with a conventional pelletizer and then dried overnight at 100°C. The extruded and dried WPCs were injection-molded into test samples with an Arburg 420C machine (Lossburg, Germany); the processing temperature was kept constant at 180°C in the cylinder.

### Mechanical properties

Standardized tensile and flexural testing was carried out on a Karg Industrie Etechnik machine (Krailling, Germany) according to ASTM D638/97 and D790/97, respectively. Before the measurements, all specimens were conditioned for 40 h at 23°C and 50% relative humidity. The flexural measurements were done with a three-point bending configuration and up to 2% deformation. The crosshead speed was set at 1.27 and 50 mm/min for the flexural and tensile tests, respectively. The Young's modulus, strength, and percentage elongation at break were derived from the stress-strain curves. The reported values are averages from 15 individual measurements. The collected data were analyzed with a one-way analysis of variance at the 95% confidence level. Differences among the mean values of variables were determined with Duncan's multiple-range test. Table V summarizes the factors and levels used in the

TABLE III  
Screw Profile Used in the Experiments from the Die to the Hopper

Length (mm)	540	45	180	540	45	45	90	315
Pitch (mm)	SE 45/45	KB 9/90	KB 9/45	SE 45/45	KB 9/–45	KB 9/90	KB 9/45	SE 45/45

TABLE IV  
Compositions of the Tested WPCs

Identified sample	Polymer matrix (wt %)		WF (wt %)	PP-g-MA content (wt %)		Lubricant (wt %)	Antioxidant (wt %)
	recycled LDPE	Virgin PP		Fusabond	Licocene		
rPE-F	47.2	—	47.2	0.9	—	3.8	0.9
vPP-F	—	47.6	47.6	1.0	—	3.8	—
rPE-L	47.2	—	47.2	—	0.9	3.8	0.9
vPP-L	—	47.6	47.6	—	1.0	3.8	—
rPE-F-5%	44.8	5.0	44.8	1.0	—	3.6	0.9
rPE-F-10%	42.4	10.0	42.4	1.0	—	3.4	0.8
rPE-F-15%	40.0	15.0	40.0	1.1	—	3.2	0.8
rPE-L-5%	44.8	5.0	44.8	—	1.0	3.6	0.9
rPE-L-10%	42.4	10.0	42.4	—	1.0	3.4	0.8
rPE-L-15%	40.0	15.0	40.0	—	1.1	3.2	0.8

experiments. The normality, homoscedasticity, and independence in each case were determined with the Kolmogorov–Smirnov test, Levene's test, and residual versus observation plots, respectively. All of the statistical calculations were made with Statgraphics Plus (version 5.1) software, Statistical Graphics, Washington, United States.

#### Fracture morphology analysis

The fracture surfaces of the mechanical test specimens (sputtered with a gold coating of ca. 50 nm) were examined (at different magnifications, ranging from 100 to 5000 $\times$ ) with a field emission scanning electron microscope (JEOL JSM 6380 LV, Tokyo, Japan) operated at 20 kV.

#### Fourier transform infrared (FTIR) spectroscopy

The composition of plastic waste and the surface chemistry of the untreated wood particles and wood particles in WPCs were evaluated with a Nicolet FTIR spectrometer (model Nexu, Waltham, United States). The composition of plastic waste was analyzed in film form, and it was compared to neat LDPE (PE-656S) supplied by Petroquímica-DOW, Chile. The WF and rWPC were analyzed in KBr disk form. The film and disk measurements were performed in transmission mode. For each sample, 64 scans were recorded from 4000 to 400  $\text{cm}^{-1}$ .

#### Moisture uptake and thickness swelling (TS)

All of the injection-molded samples ( $0.34 \times 1.25 \times 12.67 \text{ cm}^3$ ) were tested for moisture content, density, TS, and moisture absorption by water immersion. The moisture content was determined according to ASTM D570-98 by measurement of the weight of WPCs before and after drying for 24 h at 105°C. The apparent density was calculated from sample weight and volume. The density and moisture content values reported are the averages of 10 measurements.

Water absorption and TS tests were also conducted in accordance with ASTM D570-98. Ten samples of each formulation were selected and dried for 24 h at 105°C. The specimens were placed in distilled water and kept at  $23 \pm 1^\circ\text{C}$  for 16 days until a quasi steady state was reached. For each measurement, a specimen was removed from the water, and surface moisture was removed with absorbing paper. The sample weight and thickness were measured to precision of 0.001 g and 0.001 mm, respectively, at different times during prolonged immersion. The water absorption test was finished after the increase in weight over a week was less than 1% in three consecutive measurements. The amount absorbed was calculated with the following expression:

$$\text{MA}(\%) = (m_t - m_0)/m_0 \times 100$$

where MA is the percentage moisture absorbed and  $m_0$  and  $m_t$  are the oven-dry weight and weight after time  $t$ , respectively.

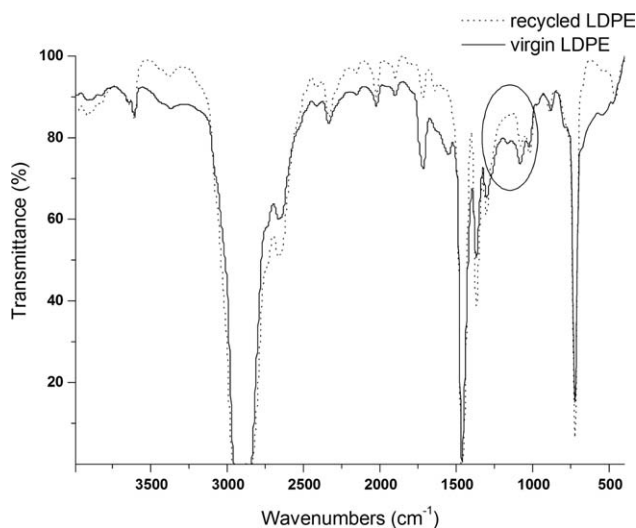
TS was calculated as the average thickness gain of each specimen during the immersion tests ( $h_t$ ) over the oven-dry thickness ( $h_0$ ) of the specimen:

$$\text{TS}(\%) = (h_t - h_0)/h_0 \times 100$$

TABLE V  
Levels of Virgin PP Content Factor and Type of Coupling Agent Factor Used in the Experiments

	Level	Virgin PP content (wt %)			
		0	5	10	15
Type of coupling agent	Fusabond	E1			
	Licocene	E3	E4	E5	E6
		E2			

E1, E2, E3, E4, E5, and E6 are experiments carried out for each dependent variable. For example, E1 represents the experiments with formulations made with Fusabond and different virgin PP contents.



**Figure 1** Transmission FTIR spectra of rPE and virgin PE films.

## RESULTS AND DISCUSSION

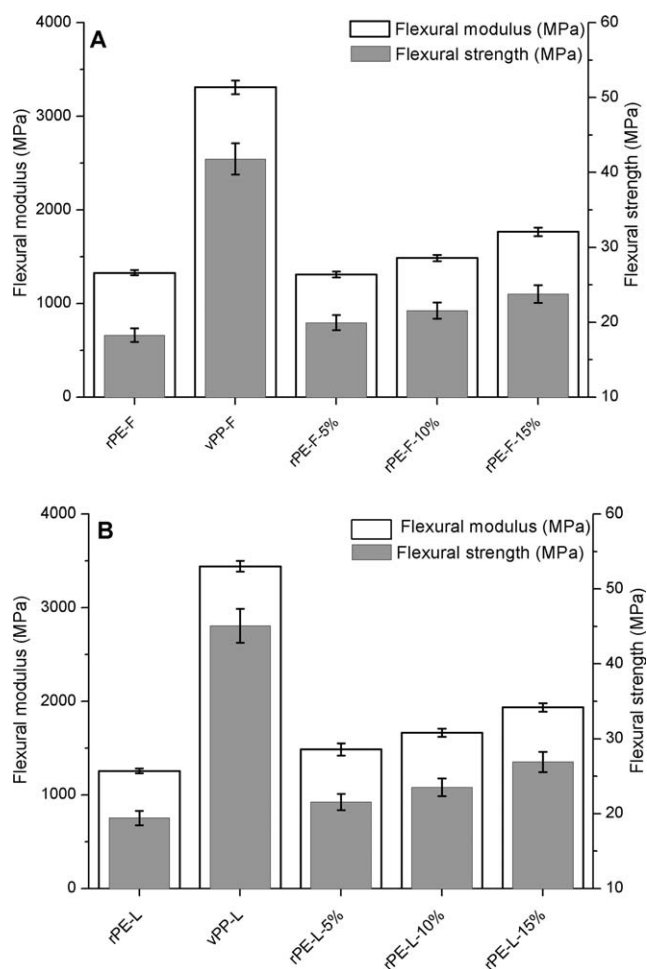
The plastic waste material was composed mainly of a matrix of LDPE and a part of PP, a combination frequently found in waste streams.<sup>19</sup> The FTIR spectra (Fig. 1) showed that all of the dominant bands in the range 400–4000  $\text{cm}^{-1}$  for the recycled LDPE were the characteristic bands of the control LDPE sample. On the other hand, the presence of PP was evident from a weak band at 1166  $\text{cm}^{-1}$ , characteristic of axial stretching of C–C in the PP backbone.<sup>20</sup> The other characteristic peak, located at 997  $\text{cm}^{-1}$ , corresponding to the C–C stretching from the  $-(\text{CHR}-\text{CH}_2)-$  group of PP, where R is  $\text{CH}_3$ , was not observed because of the broad background peak at about 1000–1200  $\text{cm}^{-1}$ . We discuss below how these chemical characteristics influenced the mechanical properties and moisture resistance of the LDPE/WF composites.

### Mechanical properties

Our recycled plastic material exhibited mediocre mechanical properties, which could be improved by the addition of other plastic materials and fillers. We used WF as a filler and small amount of PP as a material to make WPCs from recycled LDPE. The elastic modulus, tensile and flexural strengths, and elongation at break of the reprocessed plastic waste are reported in Table I. This material showed inferior mechanical properties with respect to other recycled LDPE/WF composites, except for the elongation at break. Elongation is usually inversely proportional to the tensile strength, so the addition of WF resulted in a stiffer composite material. Thus, there was also the opposite trend: composite ductility was reduced as a

consequence of the reinforcing effect of WF; and the modulus and strength were considerably increased.

The use of recycled instead of virgin plastic reduced the mechanical performance of the WPCs. This is documented in Figure 2. As expected, the flexural strength and modulus of the virgin PP/WF composites were superior to those of the composites made with recycled LDPE. Choudury and Adhikari<sup>21</sup> reported that rWPC made with a blend of (50 : 50) virgin and recycled LDPE and jute fiber exhibited significantly better mechanical properties than a recycled LDPE/jute fiber composite. This was ascribed to structural disorder caused by thermomechanical or thermooxidative degradation during recycling, which resulted in poor melt strength and inferior processability of the recycled polymer compared to its virgin counterpart. In our case, when virgin PP was added to rWPCs, even in small proportions (5–15 wt%), the melt viscosity of recycled plastic decreased and allowed better mixing of the composite components. Furthermore, the virgin PP in our WPC sample allowed the following process: once the maleic group in the functionalized polyolefin coupling agent



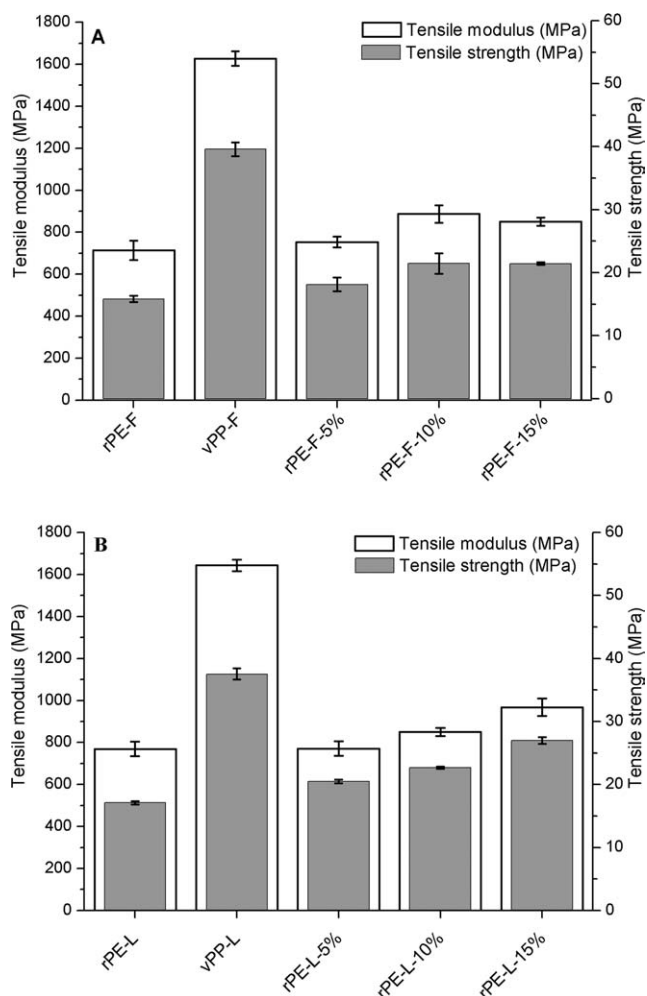
**Figure 2** Flexural properties of WPCs prepared with different coupling agents: (A) Fusabond and (B) Licocene.

reacted with the surface hydroxyl groups of WF, the exposed PP chain of the coupling agent diffused better into the polyolefin matrix phase and entangled mainly with recycled and virgin PP chains, which, in turn, resulted in better mechanical properties (e.g., strength and modulus).

Both the flexural strength and modulus of the recycled polymer–virgin PP/WF composites improved with increasing virgin PP content, even though the WF content in the mixture was as low as 7 wt% [see Fig. 2(A,B)]. The Duncan test revealed that there was a statistically significant difference at the 95% confidence level between the means of the flexural modulus and strength from one level of virgin PP content to another. It should be noted that the underlying statistical assumptions were not satisfied only in the case of flexural strength of rWPCs formulated with Fusabond and various virgin PP contents; so it was not possible to arrive at a reliable conclusion from a statistical point of view. On the other hand, a comparison between WPCs made with the same proportion of virgin PP but with a different coupling agent showed that the flexural strength and modulus were statistically higher for composites formulated with Licocene than for those formulated with Fusabond. The former is a coupling agent with more polar groups in its backbone (see Table II), and this was expected to favor the formation of chemical bonds (ester linkages) between the hydroxyl groups in WF and anhydride groups in the coupling agent, which, in turn, is known to improve interfacial adhesion.<sup>22</sup>

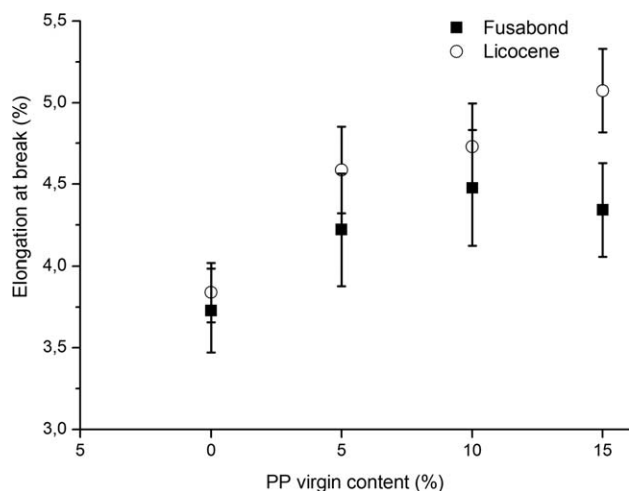
The morphological findings from scanning electron microscopy (SEM) images seemed to corroborate this (as discussed later); thus, for example, there was a higher concentration of holes in the composites prepared with Fusabond than in those prepared with Licocene.

Regarding the type of coupling agent, a positive effect on the tensile properties of the WPCs prepared with Licocene can be seen in Figure 3: with an increase in virgin PP content above 5 wt%, there was an enhancement of the composite tensile properties. Thus, for example, at the same virgin PP content, the tensile modulus was statistically higher for WPCs prepared with Licocene. Only the comparison of the tensile strength of WPCs made with 15 wt % virgin PP and different coupling agents could be validated statistically; it was higher for the WPCs made with Licocene. As in the case of the flexural properties, such behavior was attributed to better WF/polymer interfacial interaction. In contrast, the tensile modulus of rWPCs prepared with Fusabond initially increased; however, a higher content of virgin PP (>10 wt%) had no significant additional effect. In the case of the tensile strength of WPCs made with Fusabond with various virgin PP contents, the underlying statistical assumptions were again not satisfied (see Supporting Information).



**Figure 3** Tensile modulus and strength of WPCs prepared with different coupling agents: (A) Fusabond and (B) Licocene.

The elongation at break of the composites was compared to that of the recycled LDPE matrix. As expected, it was lower; this was due to lower values of the elongation at break and tensile strength of the wood fibers. Furthermore, incorporation of WF produced discontinuity in the matrix, which, in turn, reduced its ductility and caused a decrease in the elongation at break. In Figure 4, we compare the elongation at break of rWPCs made with Licocene versus Fusabond. The elongation at break for the rWPCs made with Licocene increased with increasing virgin PP matrix content. On the other hand, at constant virgin PP content but with different coupling agents, the elongation at break was statistically higher only for the Licocene-based composites formulated with 0 and 15 wt% virgin PP. For Fusabond-based rWPCs and with various virgin PP contents, it was again not possible to reach a statistically confident conclusion with the data of the percentage elongation at break (see Supporting Information). It is important to note that the elongation properties of the rWPCs

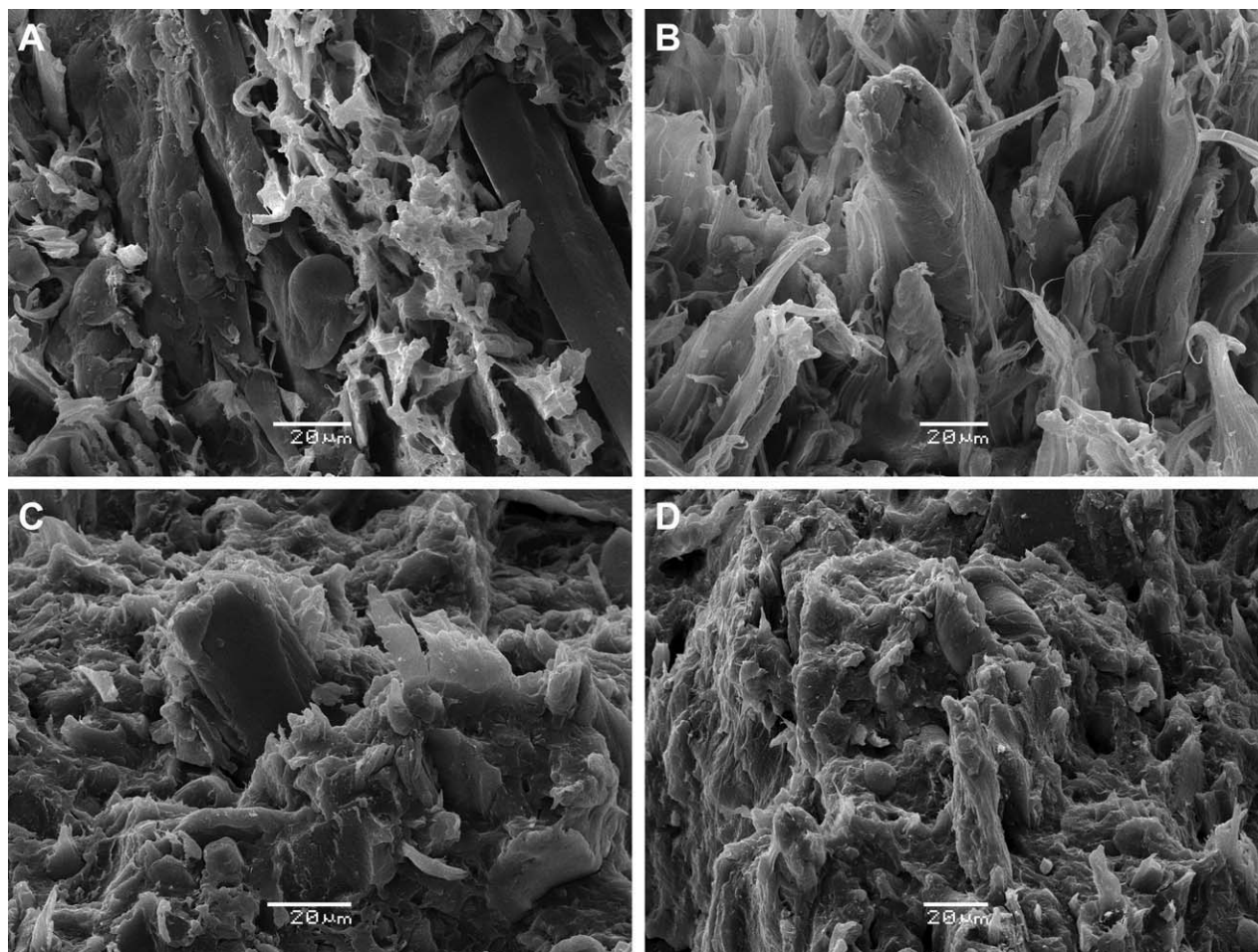


**Figure 4** Elongation at break of rWPCs made with Fusabond and Licocene as a function of the virgin PP content.

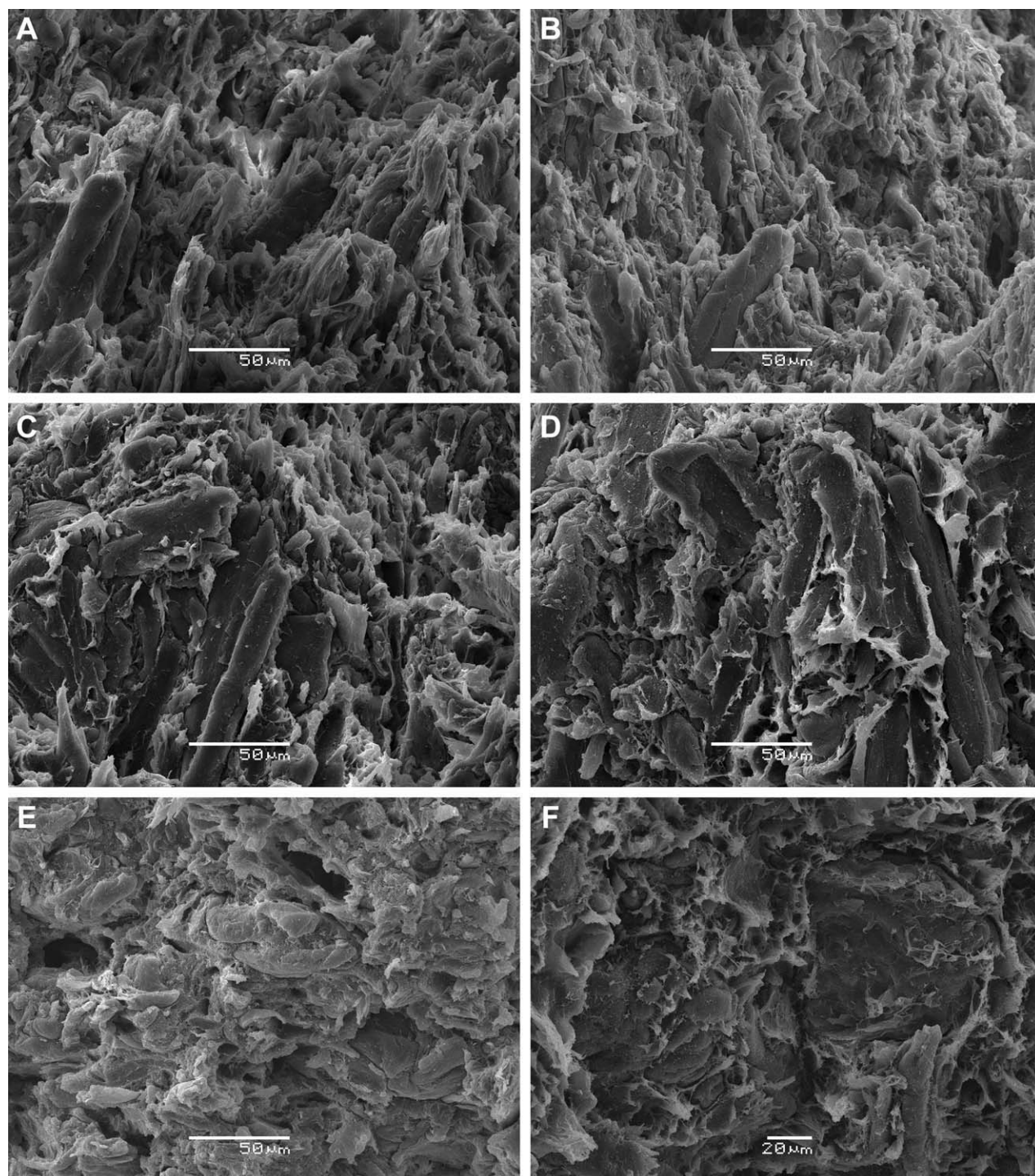
could have been affected by the presence of WF and PP in the LDPE matrix; WF has lower values of elongation at break and tensile strength,<sup>23</sup> and PP is not

compatible in the melt with LDPE.<sup>19</sup> However, elongation at break increased as the virgin PP content increased for the Licocene-based composites; this was related to better stress transfer at the fiber–polymer matrix interphase. On the other hand, reduction of elongation at break was not dramatic from a technological point of view because WPC materials are typically used for nonstructural outdoor applications.

The lack of data homogeneity in the tensile and flexural tests of rWPCs made with Fusabond was interpreted as a consequence of two factors: (1) use of a coupling agent with lower grafting affinity, which did not favor interfacial adhesion between the WF and the polymer matrix and (2) irregular structure of the recycled polymer (predominantly the polymer matrix) due to its thermomechanical degradation during recycling, which led to less than optimal WF distribution and orientation and the fracture of WF during the mixing process.<sup>24</sup> A combination of these factors could have been the cause of the greater variability in the mechanical properties of rWPCs made with Fusabond.



**Figure 5** SEM photographs of the fracture surfaces of tensile specimens of (A,B) recycled polymer/WF and (C,D) virgin PP/WF composites where A and C are composites made with Fusabond and B and D are composites made with Licocene.



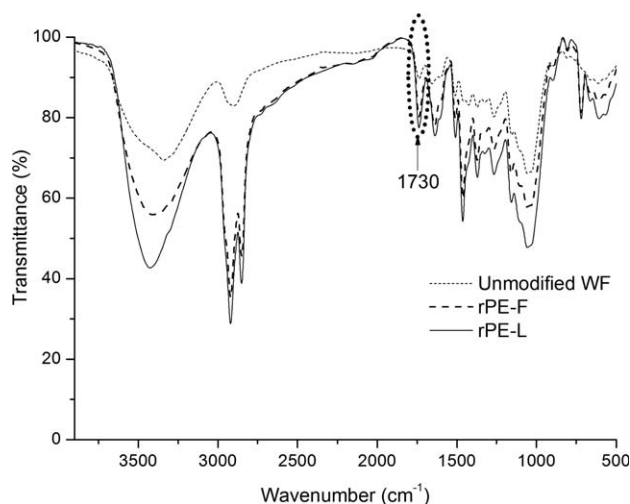
**Figure 6** SEM photographs of the fracture surfaces of tensile specimens of virgin PP-recycled polymer/WF made with Fusabond [(A) rPE-F-5%, (C) rPE-F-10%, and (E) rPE-F-15%] and Licocene [(B) rPE-L-5%, (D) rPE-L-10%, and (F) rPE-L-15%].

#### Fracture morphology analysis

The SEM micrographs in Figures 5 and 6 reveal the morphology of typical fracture surfaces of the tensile composite specimens. Significant differences in the interfacial adhesion (Fig. 5) were clearly observed. The recycled polymer/WF composite contained many areas where WF was apparently free from

polymer matrix and had large holes due to pullout of WF from the matrix [Fig. 5(A,B)]. Additionally, there were finite gap regions between the recycled matrix and WF; this confirmed poor adhesion in these composites. There were no WF agglomerates within the recycled matrix, which we attribute to the presence of coupling agent and its beneficial effect on the mechanical properties. The weak WF-matrix





**Figure 7** FTIR spectra (transmission mode, KBr disks) of the unmodified wood particles and wood particles in the WPCs.

bonding was due to different surface energies between the WF and the recycled polymer, as was reported previously.<sup>25</sup> On the other hand, less WF pullout and fewer holes were observed within the matrix in the virgin polymer/WF composites [Fig. 5(C,D)], and there were also no obvious gaps at the irregular interfaces between the virgin polymer and the WF.

Figure 6 suggests that there was no significant morphological difference at the interface of composites made with the same virgin PP and different coupling agents. However, as the loading of virgin PP increased, an improvement in interfacial adhesion was seen: there was less WF pullout, and holes within the plastic matrix were also evident. For the recycled polymer–virgin PP/WF composites with 15 wt% virgin PP, the interfacial region appeared to resemble that of the virgin PP/WF composite; this suggested the formation of a strong interface [Fig. 6(E,F)]. On the other hand, composites made with Fusabond [Fig. 6(E)] had a higher density of holes within the polymer matrix, which indicated that the matrix/WF bonding was weaker than in the composites made with Licocene [Fig. 6(F)].

The FTIR measurements (see Fig. 7) were made in pursuit of evidence of chemical bonding between the maleated PP and wood fibers. Our focus was on the 1750–1720-cm<sup>-1</sup> region because ester functional groups absorb in this region. Both the virgin WF and WPCs did show a band near 1730 cm<sup>-1</sup>; in the former case, these groups arose from the carbonyl (C=O) of acetyl groups in hemicellulose, carbonyl aldehyde in lignin and extractives and/or carbonyl (C=O) of carboxyl groups in hemicellulose, lignin, and extractives; and also esters in lignin and extractives. However, the band near 1730 cm<sup>-1</sup> was more intense in WPC than in untreated WF (see Fig. 7); this suggested the formation of ether bridges between the OH groups of WF and MA-g-PP.<sup>26,27</sup> Unfortunately, it was not possible by this technique to determine which of the two MA-g-PPs, Licocene or Fusabond, favored the formation of ester groups to a greater extent in the WPC products.

### Swelling and moisture uptake

The densities and moisture contents of the different composites are listed in Table VI. The density values were in the range 1.10–1.13 g/cm<sup>3</sup>. In agreement with previous findings,<sup>25</sup> these values were similar to those obtained for WPCs containing pine WF (average diameter < 300 μm), polyolefin as matrix, and MA-functionalized polyolefin as the coupling agent. However, the moisture content values were lower than other reported values for polyolefin-based WPCs;<sup>5,28</sup> this could be interpreted as a reduction of lumens, fine pores, and hydrogen-bonding sites in the superficial part of our injection WPC specimens.<sup>29</sup>

The moisture content of the composites ranged between 0.2 and 0.4 wt%, and it was slightly higher for composites made only with recycled polymer. This could be related to the irregular structure of the recycled polymer, which prevented better compounding between the WF and the matrix.<sup>24</sup>

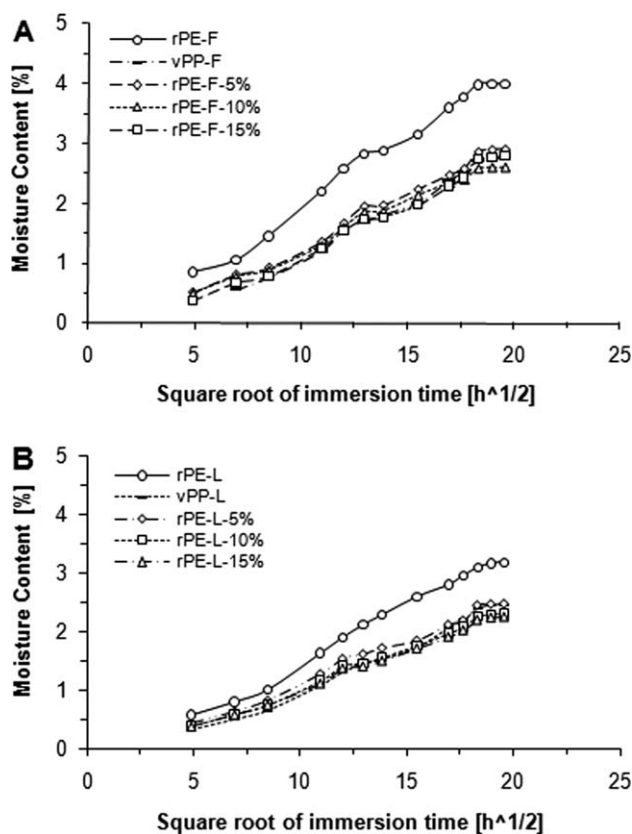
Long-term water uptake of the injection-molded samples was monitored over a period of 384 h until there was less than a 1% mass change over a week. There was a linear increase in the moisture content

**TABLE VI**  
Density and Moisture Content (MC) of Different WPCs

Code	Fusabond		Code	Licocene	
	Density (g/cm <sup>3</sup> ) <sup>a</sup>	MC (%) <sup>b</sup>		Density (g/cm <sup>3</sup> ) <sup>a</sup>	MC (%) <sup>b</sup>
rPE-F	1.129 (0.003)	0.38	rPE-L	1.122 (0.003)	0.44
vPP-F	1.106 (0.002)	0.21	vPP-L	1.102 (0.002)	0.22
rPE-F-5%	1.121 (0.002)	0.35	rPE-L-5%	1.104 (0.003)	0.33
rPE-F-10%	1.121 (0.003)	0.32	rPE-L-10%	1.105 (0.003)	0.33
rPE-F-15%	1.101 (0.003)	0.28	rPE-L-15%	1.110 (0.003)	0.33

<sup>a</sup> Values given between parentheses correspond to standard deviations.

<sup>b</sup> Standard deviations of 0.01.



**Figure 8** Water uptake against the square root of the immersion time ( $h^{1/2}$ ) for WPCs made with (A) Fusabond and (B) Licocene.

as a function of the square root of immersion time, as shown in Figure 8. (In all cases, the correlation coefficient was ca. 0.99.) Such a trend suggests that there were no changes (e.g., cracking, damage, and/or capillary uptake) during this diffusion-controlled process.<sup>30</sup>

Water absorption was highest for the recycled polymer/WF composites (see Fig. 8). This was attributed to the poorest interfacial adhesion in the recycled polymer/WF composite, as confirmed by comparing the SEM micrographs of composites made with recycled versus virgin PP (see Fig. 5). The uptakes of virgin PP/WF composites were similar to those of recycled polymer–virgin PP/WF com-

posites made with the same coupling agent, even though the latter had a lower WF content. In general, addition of virgin PP improved composite processability because the higher wood surface area was covered by the polymer during compounding; furthermore, as the virgin PP content increased, there was a decrease in the gap (between the WF and the plastic matrix) and the flaws; this reduced the availability of water absorption sites (see Fig. 6). It is interesting to note that the Licocene-based rWPC samples had a 15% lower water uptake than their Fusabond-based counterparts; this was attributed to the presence of fine pores, gaps, and flaws at the WF/polymer interface in the latter [see Figs. 6(A–C)].

The TS of the WPCs increased at longer immersion times, and it exhibited a similar trend to that observed for water uptake. Thus, composites made with Licocene had lower TS values than those made with Fusabond; this was in agreement with the notion that the compatibility between WF and the polymer matrix was improved with the addition of Licocene. After 384 h, the TS values were inferior (by ca. 10%) for the composites made with Licocene (Table VII). Also, samples with a lower WF content had lower TS values in both composites. With possible interactions between free OH groups and other components of the composites taken into account, additional studies are needed (e.g., using materials with a wider range of WF contents) to confirm the intuitively obvious cause–effect relationship between the abundance of hygroscopic sites in WF and the TS extent in the composites.<sup>30</sup>

## CONCLUSIONS

We have shown that Licocene, a coupling agent with a higher grafting capacity (acid number = 43 mg/gKOH), provided significant enhancement in the tensile and flexural moduli and flexural strength of recycled LDPE/WF composite. This improvement was attributed to strong interfacial adhesion between MA in the coupling agent and the hydroxyl groups of WF. When a virgin PP–recycled LDPE blend was used as the polymer matrix instead of pure recycled

**TABLE VII**  
Water Absorption and TS of WPCs

Code	Fusabond		Licocene		
	Water absorption (%)	TS (%)	Code	Water absorption (%)	TS (%)
rPE-F	3.99 (0.04)	6.01	rPE-L	3.17 (0.05)	5.43
vPP-F	2.75 (0.05)	5.54	vPP-L	2.45 (0.03)	5.15
rPE-F-5%	2.90 (0.06)	5.23	rPE-L-5%	2.47 (0.01)	4.98
rPE-F-10%	2.61 (0.09)	5.31	rPE-L-10%	2.29 (0.05)	4.89
rPE-F-15%	2.80 (0.03)	5.20	rPE-L-15%	2.24 (0.03)	4.92

The water absorption and TS values correspond to 384 h of immersion. The values are averages of 10 replicates, and the values in parentheses correspond to their standard deviations.

LDPE, significantly improved mechanical properties of the rWPCs made with Licocene were also obtained. The water absorption was shown to obey a Fickian diffusion mechanism. Both the uptake and TS of rWPCs were reduced with the incorporation of virgin PP in the composite formulation. Furthermore, for rWPC made with Licocene, they were lower than for those for rWPCs made with Fusabond; this was attributed to better filler wetting within the polymer matrix in the former case as a consequence of better WF/polymer matrix interaction when Licocene was used as the coupling agent.

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