

## Comparative Study of Maleated and Glycidyl Methacrylate Functionalized Terpolymers as Compatibilizers for Low-Density Polyethylene–Wood Flour Composites

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**ABSTRACT:** Two types of terpolymers, maleic anhydride (MA) and glycidyl methacrylate (GMA) functionalized, are used as compatibilizer in low-density polyethylene–wood flour composites. The type and amount of compatibilizer on the tensile, impact, morphological, and water absorption properties of composites are investigated. The effect of preimpregnation with a compatibilizer solution is also studied. The MA functionalized compatibilizer increases the mechanical properties of composites, when it is used either directly or with preimpregnation. GMA functionalized compatibilizer is not as effective as MA functionalized compatibilizer giving rise to small improvements in properties. An important point is doubling of the modulus with MA preimpregnated compatibilizer. With both compatibilizers the water absorption value of composites are reduced and the preimpregnation with both compatibilizers do not change the total amount of absorbed water with respect to the non-preimpregnated ones. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** low-density polyethylene; wood flour; compatibilization; adhesion; water uptake

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### INTRODUCTION

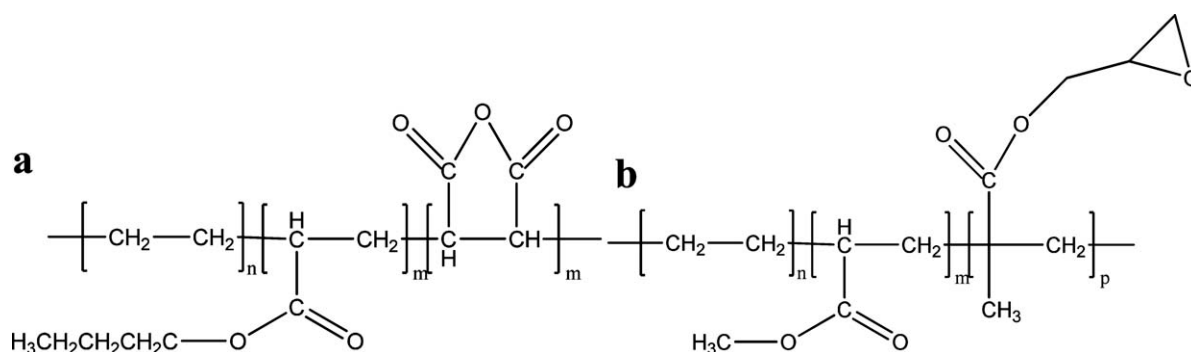
Wood plastic composites (WPC) gain considerable importance in different industries, especially in automotive and construction industry due to their low-cost, low-density, and certain specific properties.<sup>1</sup> Despite these advantages, some problems exist for wider application of WPC such as low thermal stability of lignocellulosics, poor interfacial adhesion between polar lignocellulosics and nonpolar matrix material and moisture uptake.<sup>1–3</sup> Accordingly, the studies are focused on finding solutions to these problems.

The major factor affecting the final mechanical properties of WPC is the effective stress transfer at the interface between lignocellulosics and matrix material. This can be achieved via strong adhesion between matrix and lignocellulosics. Different physical and chemical methods can be used to increase the interfacial adhesion between lignocellulosics and matrix material.<sup>1–3</sup>

Polyethylene (PE) is widely preferred thermoplastic for household, packaging, and building applications due to good combination of price and properties, such as high tensile and impact strength. For

composite applications, numerous studies have been carried out for the improvement of interfacial adhesion between lignocellulosics and PE using different types of coupling agents. Lai et al. studied the effect of four kinds of maleated polyolefins on mechanical properties of high-density PE (HDPE)–wood flour (WF) composites.<sup>4</sup> They found out that the maleated linear low-density PE (LLDPE) and HDPE gave high tensile and impact strengths. Li and Matuana<sup>5</sup> investigated maleic anhydride (MA) and acrylic acid functionalized polyolefin based coupling agents on the mechanical properties of HDPE–WF composites. The results showed that maleated polyolefins performed better than acrylic acid functionalized ones. Wang et al.<sup>6</sup> also investigated MA and acrylic acid functionalized polyolefins in HDPE–WF composites, and they found that MA grafted LLDPE showed maximum tensile and impact strength. Raj et al.<sup>7</sup> worked with different kinds of silane coupling agents to increase the adhesion between fiber and LLDPE, and the results showed that the inclusion of silane coupling agents increased the mechanical properties of composites. Oksman et al.<sup>8</sup> used MA grafted styrene ethylene butylene styrene (SEBS-MA) as compatibilizer in LDPE–WF composites. The results indicated that the MA part of SEBS-MA reacts with wood

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**Figure 1.** The chemical structures of compatibilizers. (a) LOTADER® 2210 (MA-comp) and (b) LOTADER® AX 8900 (GMA-comp).

and increases the interfacial adhesion between PE and WF. Geng et al. investigated the use of a commercial paper wet strength agent (Kymene) with and without stearic acid and stearic anhydride as compatibilizer. The result showed that the stearic anhydride–Kymene combination gives the best modulus values of the composite.<sup>9</sup> Pracella et al.<sup>10</sup> investigated the effect of glycidyl methacrylate (GMA) functionalized compatibilizers (PP-GMA and SEBS-GMA) and fibrous structure on mechanical and thermal properties of polypropylene–hemp fiber composites. All modified composites showed improved fiber dispersion and higher interfacial adhesion with respect to the unmodified composites.

In this study, we investigate the effect of two compatibilizing agents, MA and GMA functionalized terpolymers, at different concentrations on the mechanical, morphological, and water uptake properties of LDPE–WF composites. The amount of WF is kept constant at 30% of total weight of the composite that is produced by melt compounding. Another parameter that is investigated in this study is the effect of solution preimpregnation of WF with the compatibilizers. The previous studies investigated the effect of preimpregnation with dilute solution of matrix material to increase the adhesion between lignocellulosics and matrix material by mechanical interlocking.<sup>11,12</sup> The preimpregnation of WF may increase the interfacial attractions through the formation of covalent bonds between hydroxyl groups on WF and the functional groups of the compatibilizers.

## EXPERIMENTAL PROCEDURE

### Materials

The main materials used in this study are LDPE, WF, and two kinds of functionalized terpolymers. LDPE is obtained from PETKIM A.S. (Izmir, Turkey) under the trade name LDPE F2-12. The density is 0.92 g/cm<sup>3</sup>, and the melt flow index is 2–3.5 g/10 min (2.16 kg, 190°C) as provided by the supplier. WF

from pine (20-mesh size) is obtained from local sources. LOTADER® 2210, a random terpolymer of ethylene, acrylic ester, and MA, and LOTADER® AX 8900, a random terpolymer of ethylene, acrylic ester, and GMA, are purchased from ARKEMA (Colombes, France). The chemical structures and the properties of compatibilizers are given in Figure 1 and Table I, respectively. Sodium hydroxide (NaOH), chloroform, and toluene, all reagent grade are supplied by Sigma–Aldrich.

### WF Treatments

**Alkaline Treatment.** The purpose of alkaline treatment is to dissolve alkali-soluble components from the WF structure partially like resins, hemicellulose, lignin, and pectin.<sup>11</sup> It is thought that surface cleaning and activation is achieved via NaOH(aq) treatment. The WF is treated with 18 wt % solution of NaOH for 45 min under continuous mixing. The volume of the solution is equivalent to five times the volume of WF. WF is then washed with water, until all NaOH is eliminated. A few drops of acetic acid added to neutralize the last rinsing solution. The WF is air-dried at 60°C for 52 h. After the drying process, WF is stored in a desiccator until the extrusion process. All composites are prepared with NaOH-treated WF. Scanning electron microscopy (SEM) images of pristine WF and NaOH-treated WF are shown in Figure 2. According to SEM images, the surface of WF becomes rough after NaOH treatment due to the removal of alkali-soluble components.

**Preimpregnation with Compatibilizer Solution.** The WF is preimpregnated with both compatibilizer solutions. The predetermined amount of GMA-comp is dissolved in chloroform at 50°C. After the complete dissolution of the compatibilizer, the predetermined amount of WF is added and mixed vigorously for 30 min. After mixing, chloroform is evaporated at 50°C for 48 h. The amount of GMA-comp in solution is adjusted to the

**Table 1.** Properties of Coupling Agents Used

Coupling agent	Density (g/cm <sup>3</sup> )	Melt index <sup>a</sup> (g/10 min)	$T_m^b$ (°C)	Composition (%)
LOTADER® 2210	0.94	3	107	Butyl acrylate (6) MA (2.8)
LOTADER® AX 8900	0.94	6	65	Methyl acrylate (24) GMA (8)

<sup>a</sup>Measured at 190°C under 2.16 kg load, <sup>b</sup>Melting temperature.

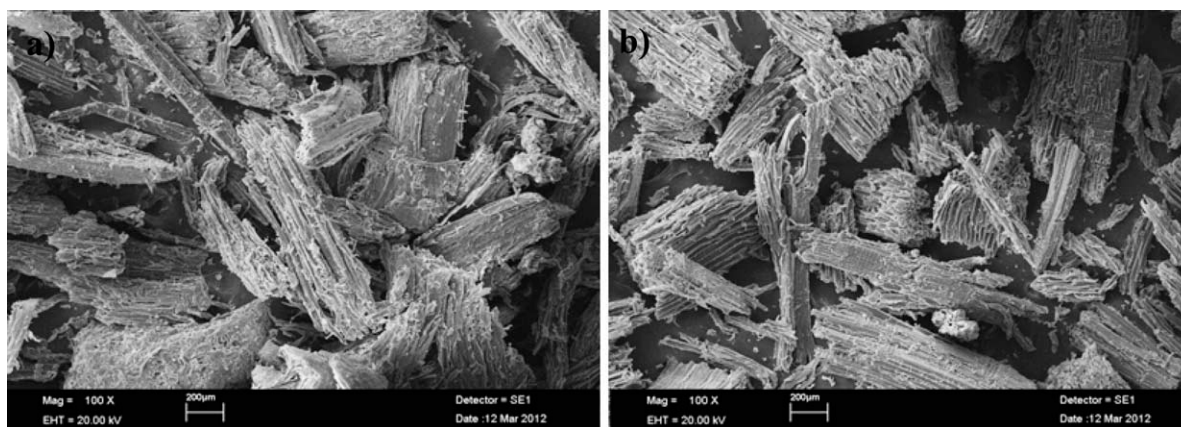


Figure 2. The SEM images of (a) pristine WF and (b) NaOH-treated WF.

1, 3, and 5 wt % of WF. The predetermined amount of MA-comp that corresponds to 10 wt % of WF is refluxed in toluene at 110°C. After the complete dissolution, WF is added and mixed vigorously for 30 min. After mixing, toluene is evaporated at 80°C for 48 h.

#### Preparation of WF–PE Composites

The mixing of LDPE, WF, and compatibilizers at various composition ratios is carried out with a counter rotating twin screw microextruder (15 mL microcompounder<sup>®</sup>, DSM Xplore, Geleen, The Netherlands) at 100 rpm at 190°C for 3 min. The extrudate is pelletized and then oven-dried for 48 h at 60°C and is stored in desiccator for injection molding. The specimens for mechanical tests are molded by a laboratory scale injection-molding machine (Microinjector, Daca Instruments, Santa Barbara, USA) at a barrel temperature of 190°C and mold temperature of 30°C and are stored in a desiccator. The following procedure is applied for the preparation of composites: all compositions contain the same amount of WF (30 wt %), and the added amount of compatibilizer is removed from the LDPE content. WF and LDPE are also mixed without using compatibilizer as for reference sample. The WF, LDPE, and compatibilizers are directly extruded with compatibilizer ratios, which correspond to 3, 5, 10, and 15 wt % of WF content to determine the optimum compatibilizer to WF

ratio. After the mechanical tests of these nine trials, preimpregnation ratios are determined. For MA-comp, preimpregnation is performed at 10 wt % loading of WF. For GMA-comp, preimpregnation is carried out at loading levels of 1, 3, and 5 wt % of WF.

#### Fourier Transform Infrared Spectroscopy Analysis

Attenuated total reflectance-Fourier transform infrared spectroscopy (FTIR) is used to assign peaks to the compatibilizers involved at the surfaces of the fillers before and after surface treatment. IR spectra of compatibilizers, preimpregnated WFs are obtained with FTIR (Bruker Optics IFS 66/S series (Ettlingen, Germany) FTIR spectrometer) at an optical resolution of 4  $\text{cm}^{-1}$  with 32 scans.

#### SEM

The morphology of freeze-fractured surfaces of composites in liquid nitrogen is examined with SEM (LEO 440 computer controlled digital, 20 kV, Beaverton, USA). All specimens are sputter-coated with gold before examination.

#### Mechanical Properties

The specimens are stored in a desiccator for some days before testing. Tension test measurements are performed using Lloyd LR 5K (West Sussex, UK) tensile testing machine equipped with 5-kN load cell at room temperature according to ASTM D 638

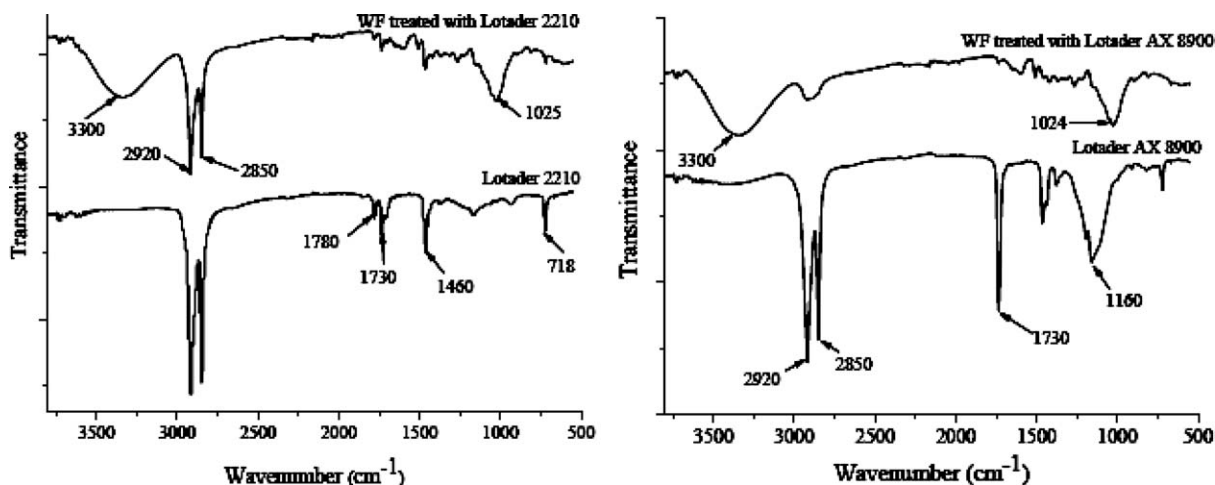
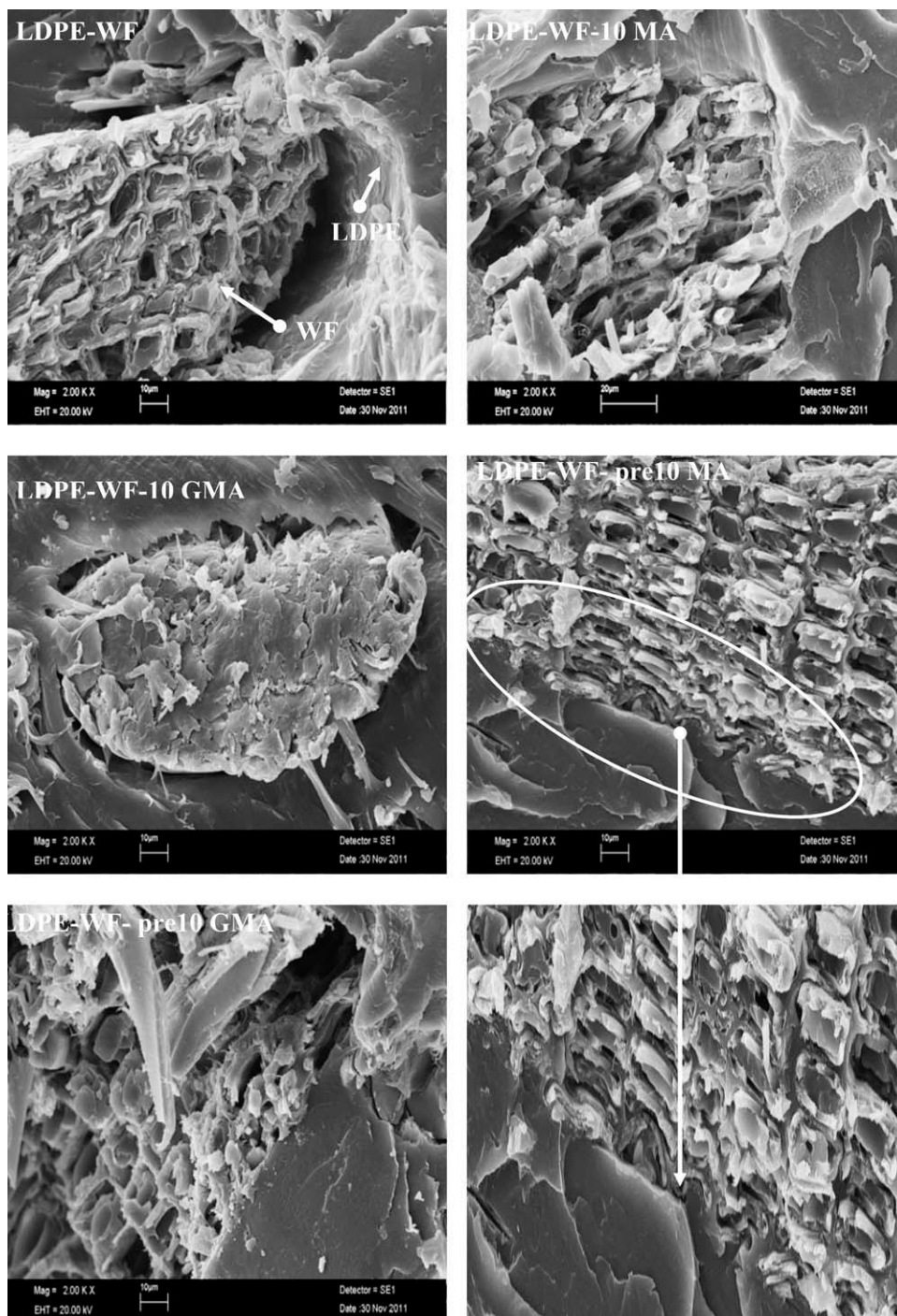


Figure 3. The FTIR spectra of compatibilizers and preimpregnated WFs.



**Figure 4.** SEM images of freeze-fractured surfaces of selected composites 2000 $\times$  magnification.

standard. Tension tests are conducted on  $7.4 \times 2.1 \times 80 \text{ mm}^3$  samples at a cross-head speed of 5 mm/min. Tensile strength, percentage elongation at break, and modulus values were recorded. Notched Izot impact strength is measured with Coesfeld-Material (Dortmund, Germany) impact tester according to ASTM D256 with notched samples at room temperature. All the results represent an average value of five samples with standard deviations.

#### Water Absorption

The samples with dimensions ( $7.4 \times 2.1 \times 80 \text{ mm}^3$ ) were used for the measurement of water absorption. The specimens are periodically taken out of the water, wiped with tissue paper to remove surface water, reweighed, and immediately put back into water. The predried ( $W_0$ ) is used to calculate the degree of water absorption by the following formula:

**Table II.** The Mechanical Properties of Composites

Sample code	Tensile strength (MPa)	Percentage strain at break (%)	Modulus (GPa)	Impact strength (J/m)
LDPE-WF	11.3 ± 0.2	9.7 ± 1.0	0.38 ± 0.03	40.6 ± 1.6
LDPE-WF-3 MA	12.1 ± 0.6	10.6 ± 0.9	0.46 ± 0.06	43.0 ± 4.6
LDPE-WF-5 MA	12.8 ± 0.2	9.5 ± 0.8	0.48 ± 0.05	43.4 ± 3.6
LDPE-WF-10 MA	13.0 ± 0.3	10.8 ± 0.3	0.68 ± 0.08	47.3 ± 5.3
LDPE-WF-15 MA	12.6 ± 0.4	12.2 ± 1.5	0.57 ± 0.02	51.3 ± 3.9
LDPE-WF-pre 10 MA	14.4 ± 0.4	10.8 ± 0.3	0.76 ± 0.07	56.3 ± 3.6
LDPE-WF-3 GMA	10.1 ± 0.5	11.4 ± 1.8	0.32 ± 0.05	38.5 ± 4.5
LDPE-WF-5 GMA	10.2 ± 0.6	10.7 ± 0.5	0.34 ± 0.07	41.4 ± 2.1
LDPE-WF-10 GMA	9.6 ± 0.3	10.8 ± 1.0	0.30 ± 0.08	41.7 ± 3.8
LDPE-WF-15 GMA	9.9 ± 0.4	11.6 ± 0.9	0.32 ± 0.04	43.4 ± 2.3
LDPE-WF-pre 1 GMA	11.5 ± 0.2	10.1 ± 0.4	0.38 ± 0.03	41.4 ± 3.2
LDPE-WF-pre 3 GMA	12.2 ± 0.4	10.9 ± 0.9	0.48 ± 0.05	45.4 ± 3.5
LDPE-WF-pre 5 GMA	11.3 ± 0.0	10.8 ± 0.4	0.38 ± 0.04	45.5 ± 3.3

pre represents preimpregnated WF were used, and number shows the compatibilizer WF ratio (wt %).

Water absorption (%) =  $(W_f - W_0)/W_0 \times 100$ ,

where  $W_f$  is the mass of the sample after immersion.

## RESULTS AND DISCUSSION

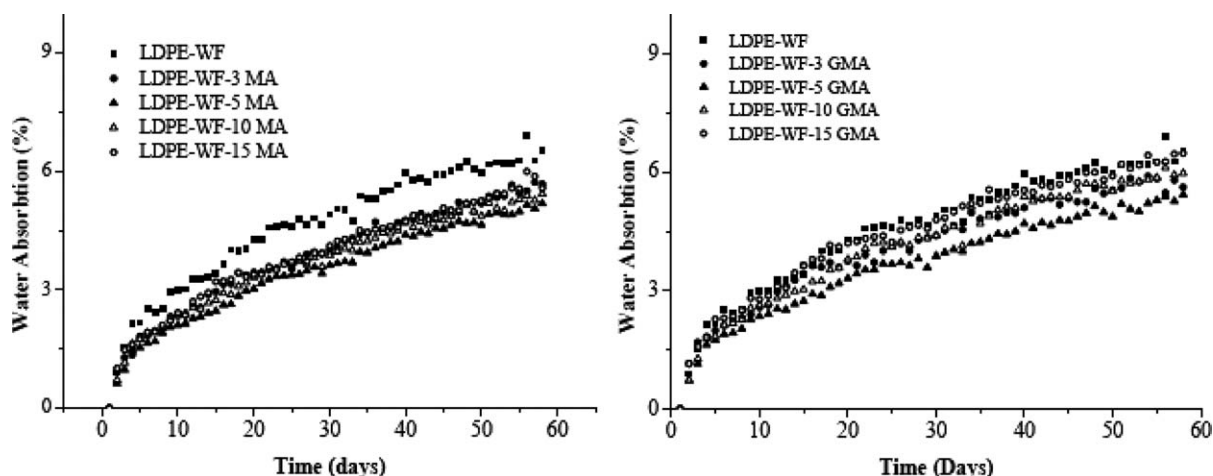
### FTIR Analysis

The FTIR spectra of compatibilizers and preimpregnated WFs are shown in Figure 3. The spectra of both compatibilizers show a pair of very strong absorption bands at 2850 and 2920  $\text{cm}^{-1}$  due to symmetrical and asymmetrical  $\text{CH}_2$  stretching vibrations of ethylene part of compatibilizers.<sup>13,14</sup> The absorption bands at 1450 and 718  $\text{cm}^{-1}$  arise from deformation and skeletal vibrations of  $\text{CH}_2$  group in ethylene part of compatibilizers.<sup>13</sup> MA-comp (LOTADER<sup>®</sup> 2210) shows two distinct peaks at 1730 and 1780  $\text{cm}^{-1}$  that can be attributed to carbonyl groups in the anhydride structure.<sup>4,13</sup> GMA-comp (LOTADER<sup>®</sup> AX 8900) shows a single absorption band at 1730  $\text{cm}^{-1}$  arising from carbonyl group in the ester bond and a broad peak at 1160  $\text{cm}^{-1}$  arising

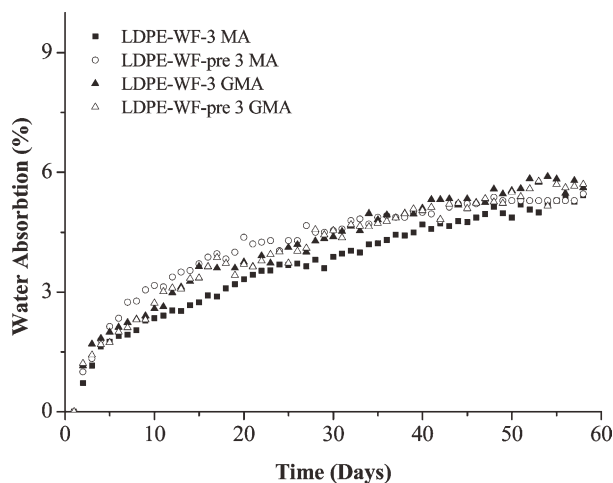
from C—O group in the ester bond and epoxy group that masks each other.<sup>15</sup> The FTIR spectra of WF treated with compatibilizers show two characteristic broad peaks at 3300 and 1025  $\text{cm}^{-1}$  associated with hydroxyl group vibrations and C—O vibrations of cellulose in WF structure, respectively.<sup>15</sup> The presence of compatibilizers absorbed on WF is confirmed by the peaks at 2850 and 2920  $\text{cm}^{-1}$  arising from the ethylene unit of them in FTIR spectra of WF treated with compatibilizers.

### Morphology

The effect of compatibilizer inclusion and preimpregnation on the morphology of the composites is studied by SEM. Representative SEM micrographs of freeze-fractured surfaces of selected composites are shown in Figure 4. From SEM image of LDPE-WF, a wide gap is observed between WF and LDPE at the interface after fracture indicating poor adhesion. However, the addition of MA-comp greatly improves the interfacial adhesion between WF and LDPE, because the LPDE still covers the WF



**Figure 5.** The effect of compatibilizers type and ratio on water absorption values of composites.



**Figure 6.** The effect of preimpregnation on water absorption property of the composites.

surface after fracture. This provides qualitative evidence for the existence of adhesive bonds between surfaces in the presence of MA-comp. With the addition of GMA-comp, LDPE partially adheres on to the WF surface, and small gaps are observed at the interface in accordance with the poor performance of GMA as a compatibilizer. The preimpregnation increases the adhesion between WF and LDPE for both compatibilizers, because the matrix material still covers the surface of WF after fracture. It is noticed at the magnified SEM image of LDPE–WF-pre 10 MA, LDPE penetrates into the cavities on WF surface that promotes mechanical interlocking. Mechanical properties of corresponding composites also support this conclusion.

### Mechanical Properties

In this study, the effect of compatibilizers to WF ratio in extrusion and also the effect of preimpregnation on the mechanical properties of the composites are investigated. The results are given in Table II.

When compatibilizers are directly used, the MA-comp generally has a positive effect on the maximum tensile strength, impact strength, and modulus values of LDPE–WF composites. No improvement is observed for GMA-comp containing composite samples. The tensile strength and modulus values of composites increase with the increasing amount of MA-comp ratio and reach their maximum level at 10 wt %. It is well known that the usage of maleated coupling agents in WPCs improves the interfacial adhesion between WF and matrix.<sup>16–19</sup> In the case of MA-comp, the interaction between MA part of coupling agent and the WF, and the diffusion of the ethylene part of the coupling agent into LDPE promotes establishment of strong interactions. Further addition of MA-comp (15 wt %) does not improve tensile strength and modulus values. Excessive use of compatibilizer results in the formation of a weak elastomeric phase that starts to deteriorate the composite's mechanical properties. The preimpregnation ratio is therefore chosen as the optimum value of 10 wt % for the MA compatibilizer. The preimpregnation further increased the tensile strength and modulus values by 27 and 100%, respectively, compared to LDPE–WF

due to the better mechanical interlocking that increases the dispersion of WF particles.<sup>11,12</sup> The preimpregnation of GMA-comp is also used to WF at amounts of 1, 3, and 5 wt % of WF. When GMA-comp is used directly without preimpregnation, no improvement in mechanical properties was observed. With GMA-comp at 3 wt % preimpregnated sample some amount of improvement is obtained. As in MA-comp, increased interaction between the matrix and WF is responsible for the observed increase in tensile strength and modulus values. One possible explanation for poor performance of the epoxy functionalized compatibilizer can be polymer bridging.

It is well known in the surface science that the bridging of the particles by multifunctional compatibilizer polymer molecules is possible.<sup>20</sup> Polymer bridging eventually can give rise to flocculation of WF. The poor performance of GMA as a compatibilizer is probably due to the poor dispersion of WF due to bridging and formation of WF flocs.

The impact strength for notched samples is governed by crack propagation of fracture initiated at the predominant stress concentration at the notch tip.<sup>21</sup> The degree of WF dispersion and the interfacial bonding between the WF and matrix are the main parameters determining the amount of absorbed energy during fracture propagation.<sup>21–23</sup> Almost the same trend is observed between impact and tensile test results due to the same factors governing mechanical properties of the composites. The WF agglomeration increases the regions of stress concentration that require less energy to break.<sup>24</sup> Poor adhesion between WF and matrix results the formation of microvoids that reduce efficient stress transfer from continuous polymer matrix to the dispersed WF and cause the material to absorb less energy.<sup>21–24</sup>

All notched samples are completely broken during the test, and the results are listed in Table II. The impact strength increases as the amount of MA-comp increases, and the highest value is obtained at 15 wt % when directly extruded. Although the tensile strength is reduced at 15 wt % loading, the impact strength increases, as the excess amount of MA-comp may increase the toughness of the matrix. The preimpregnation with MA-comp further increased the impact strength of the composite due to better WF dispersion and good adhesion between matrix and WF by mechanical interlocking. The impact strength of the GMA-comp, which is widely used as impact modifier, containing composites with direct extrusion are slightly higher than LDPE–WF. The preimpregnation further increased the impact strength of the composites due to the better WF dispersion and good adhesion between matrix and WF and the maximum impact strengths obtained at concentrations of 3 and 5 wt %.

### Water Absorption

Water absorption in WPCs is mainly related to hydrogen bonding of water molecules to the hydroxyl groups present on wood surface.<sup>25–27</sup> One other effect is the lack of adhesion between the PE and WF that gives rise to capillaries (pores) in the WPC structure. Good adhesion between PE and WF in the presence of compatibilizer reduces number of capillaries and water uptake (suction). Figure 5 shows the effect of compatibilizer type and ratio on water absorption values of composites. The highest water absorption is obtained in the case where no

compatibilizers is used. The addition of compatibilizer regardless of its kind and ratio reduces the water uptake of composites, and the lowest water uptake value for both compatibilizers is obtained at a concentration of 5 wt % of WF, which seems to be the best composition that optimizes both effects (hydrogen bond and capillary formation). It turns out that due to multitude of effects MA-comp absorbs slightly less amount of water compared to GMA-comp. It may be due to dispersion effect, sizes of capillaries and amount of polymer bridging to count a few. Figure 6 shows the effect of preimpregnation on water absorption property of the composites. It becomes clear that preimpregnation has no effect on water absorption values of composites, and they absorb approximately the same amount of water at the end of 60 days.

## CONCLUSIONS

In this study, we assessed the possibility of using two terpolymers, MA and GMA functionalized, as compatibilizers for LDPE–WF composites. The effect of preimpregnation is also studied. FTIR results show that both compatibilizers adhere on WF surface after preimpregnation.

It is observed that MA-comp increases tensile and impact strengths when it is directly used, and it shows highest values at a concentration 10 wt % of WF. The preimpregnation with MA-comp further increases tensile and impact strengths. The addition MA-comp increases the adhesion between LDPE and WF as suggested by SEM results. Compared to MA-comp, the GMA-comp does not increase the tensile strength as much and slightly increases the impact strength. Compared to pristine WF composite, the preimpregnation with GMA-comp increases both tensile strength and impact strength.

The use of both type of compatibilizer reduces the water absorption value of the LDPE–WF composite, and lowest value is obtained at a compatibilizer concentration of 5 wt % of WF. MA-comp containing composites show lower water absorption values than the GMA-comp ones. It is also observed that preimpregnation has no effect on final water uptake value of composites at the end of 60 days. Finally, it can be concluded that MA-comp is more effective than GMA-comp as a compatibilizer in LDPE–WF composites.

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