

## Effect of surface modification on the interface quality between hemp and linear medium-density polyethylene

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**ABSTRACT:** In this work, hemp fibers (mercerized or not) were modified by a coupling agent (maleated polyethylene) to evaluate the level of interfacial improvement related to wettability or adhesion in LMDPE composites. To do so, different analyses in the solid (thermogravimetric analysis, dynamic mechanical analysis, and scanning electron microscopy) and melt (rheology) states were combined. From the results obtained, it can be shown that mercerization mostly controls the level of wettability (physical contact) of the fibers, while the addition of a coupling agent mostly controls interfacial adhesion (chemical interactions). These conclusions were obtained based on shifts in transition temperatures ( $T_g$  and  $T_\alpha$ ), as well as maxima in van Gurp–Palmen plots. Overall, the best properties were obtained when mercerization was combined with coupling agent addition under optimized processing conditions. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43802.

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### INTRODUCTION

Because of environmental awareness, natural fibers are emerging as reinforcement alternatives to glass and other synthetic fibers in polymer composites by forming natural fiber composites (NFC). In addition to being renewable and biodegradable, natural fibers exhibit lower density and costs. Moreover, they are locally available and less abrasive.<sup>1–6</sup> Among all the natural fibers used, hemp is a bast fiber that has recently gained more attention because of its durability, resistance to rot, and low lignin content. In addition, it is stronger than common wood fibers, and its Young's modulus is one of the highest among natural fibers<sup>1,4,7</sup>: between 30 and 60 GPa.<sup>8</sup>

The mechanical properties of composite materials depend on three main factors: the strength and elasticity of the reinforcing agent, the strength and stability of the matrix, and the quality of the interface between both elements to ensure optimum stress transfer.<sup>9</sup> But highly polar and hydrophilic natural fibers are incompatible with most thermoplastic matrices (nonpolar and hydrophobic).<sup>9–12</sup> Nevertheless, this incompatibility can be improved by modifying the topology of the fibers via surface modification.<sup>2</sup> In this context, several treatments have been developed: physical methods (such as intensive mixing or plasma treatment), chemical methods (coupling agents, acrylation, acetylation), and thermal methods or rectification.<sup>1,13</sup>

These methods are expected to increase the interface quality and improve the mechanical properties.

Some work has been done to characterize interfacial improvement by surface modification. For example, Kubat *et al.*<sup>14</sup> observed that interfacial interaction can have a significant effect on the stress relaxation of glass fiber–HDPE composites in the solid state and proposed an adhesion criterion to characterize the composite interface. Several works, such as Correa *et al.*<sup>15</sup> and Ghasemi *et al.*,<sup>16</sup> used this parameter to evaluate the interfacial properties of different NFCs (polypropylene/pine wood waste fibers and polypropylene/wood flour/kenaf fiber hybrid composites) and observed that the adhesion factor obtained for neat fiber-filled composites was the highest (suggesting a weak interface), while the modified fiber composites presented the lowest value, a result that was in agreement with the theoretical predictions and experimental observations of Kubat *et al.*<sup>14</sup> Based on dynamic mechanical analysis (DMA) observations, they concluded that chemically improved filler–matrix interactions can be quantified by the adhesion factor as reported. In addition, the interface of composite materials was also shown to be indirectly quantified through other DMA parameters. Since this method can be used to determine the glass-transition temperature ( $T_g$ ), activation energy ( $E_a$ ), and viscoelastic properties (damping factor) of the composites, they can be used to evaluate the mobility of polymer molecules, which is an indirect

evaluation of the quality of the composite interface. Mohanty *et al.*<sup>17</sup> studied the dynamic mechanical and thermal properties of jute–HDPE composites treated by MAPE. They found that 1% MAPE was the best concentration to obtain good mechanical properties, due to an optimum composite interface revealed by a  $T_g$  shift to higher temperature. Pothan *et al.*<sup>18</sup> studied the behavior of polyester and unmodified banana fiber composites. They observed that the height of the damping-factor peak was a function of fiber content. In this case, the best properties were obtained for highly filled (40%) composites because, for this concentration,  $T_g$  and  $E_a$  were at a maximum. They also observed a broadening of the  $\tan \delta$  peak with respect to the neat matrix and reported that this behavior implies some molecular relaxations in the composite that were not present in the neat matrix.

Based on the literature, it is obvious that interface improvement plays an important role in optimizing the composite's mechanical properties. Unfortunately, several methods used to improve the composite's interface present some limitations, like fiber attrition after intensive mixing,<sup>19</sup> degradation after thermal treatment,<sup>13</sup> and the high costs of using functionalized polymers.<sup>20</sup> All these limitations lower the cost–performance properties of the final composites. It is now important to develop and understand new and easy processes to produce better NFCs. One possibility is to increase the number of active sites on the fiber surface (pretreatment) followed by other modifications before being introduced into the matrix. Recently, this possibility was investigated by Verdaguer and Rodrigue<sup>21</sup> and Raymond and Rodrigue<sup>22</sup> by treating mercerized wood fibers with a compatibilizer (maleic anhydride grafted high-density polyethylene, MAPE) in solution (1,2,4-trichlorobenzene), as well as hemp fibers by Chimeni *et al.*<sup>23</sup> These works showed that the tensile properties of the modified fiber composites were significantly improved by MAPE in solution, and the results were attributed to increased wettability and adhesion, but without any distinction between both effects and their respective level of improvement.

Using the same materials and conditions as in our previous work,<sup>23</sup> we present here a second step in our continuing effort to quantify the amount of MAPE grafted onto the mercerized hemp, as well as to evaluate the level of interfacial improvement related to better wettability and better adhesion. To achieve these goals, thermogravimetric analysis (TGA) is used to quantify the amount of MAPE grafted onto the hemp surface. Then, scanning electron microscopy (SEM) and DMA (damping factor, adhesion factor, transition temperature, and viscosity at  $T_g$ ) are used to characterize the properties of the composite in the solid state. Finally, rheology (van Gorp–Palmen plots) is used to evaluate the efficiency of the different fiber modifications on the interfacial properties of hemp–LMDPE composites using data gathered in the melt state.

## EXPERIMENTAL

### Materials

Hemp fibers were obtained from the Hemp Trade Alliance (Quebec, Canada) and sieved to keep only the fraction between 60 and 18 mesh Tyler (250 and 1000  $\mu\text{m}$ ). Sodium hydroxide

**Table I.** Codes and Compositions of the Samples Produced

Code	Composition
LMDPE	Linear medium-density polyethylene
UT	LMDPE/neat hemp
UTE3S	LMDPE/neat hemp + 3% MAPE in solution
UTE3D	LMDPE/neat hemp + 3% MAPE direct mixing
TN	LMDPE/mercerized hemp
TNE3S	LMDPE/mercerized hemp + 3% MAPE in solution
TNE6S	LMDPE/mercerized hemp + 6% MAPE in solution
TNE9S	LMDPE/mercerized hemp + 9% MAPE in solution
TNE3D	LMDPE/mercerized hemp + 3% MAPE direct mixing
TNE3S&D	LMDPE/mercerized hemp + 3% MAPE (1.5% in solution + 1.5% direct mixing)

(ACS grade) was purchased from the Aldrich Chemical Company (Ontario, Canada) and used as received. The coupling agent used was a maleic anhydride grafted high-density polyethylene (HDPE-g-MAH or MAPE) from Westlake Chemical Co. (Houston, USA) under the trade name Epolene E-20 ( $M_w = 7500$  g/mol, melt flow index = 1.24 g/10 min (190 °C/2.16 kg), acid number = 16.9 mg KOH, and softening point 113.8 °C). The solvent used was 1,2,4-trichlorobenzene (TCB) HPLC grade, from J. T. Baker (Center Valley, USA) and used as received. The matrix was linear medium-density polyethylene (LMDPE) Hival 103538 in a powder form ( $T_m = 125$  °C, melt flow rate = 3.5 g/10 min (190 °C/2.16 kg), and density = 0.936 g/cm<sup>3</sup>) from Ashland (ontario, Canada). More details on the materials and methods can be found elsewhere.<sup>23</sup>

### Chemical Modifications of Hemp

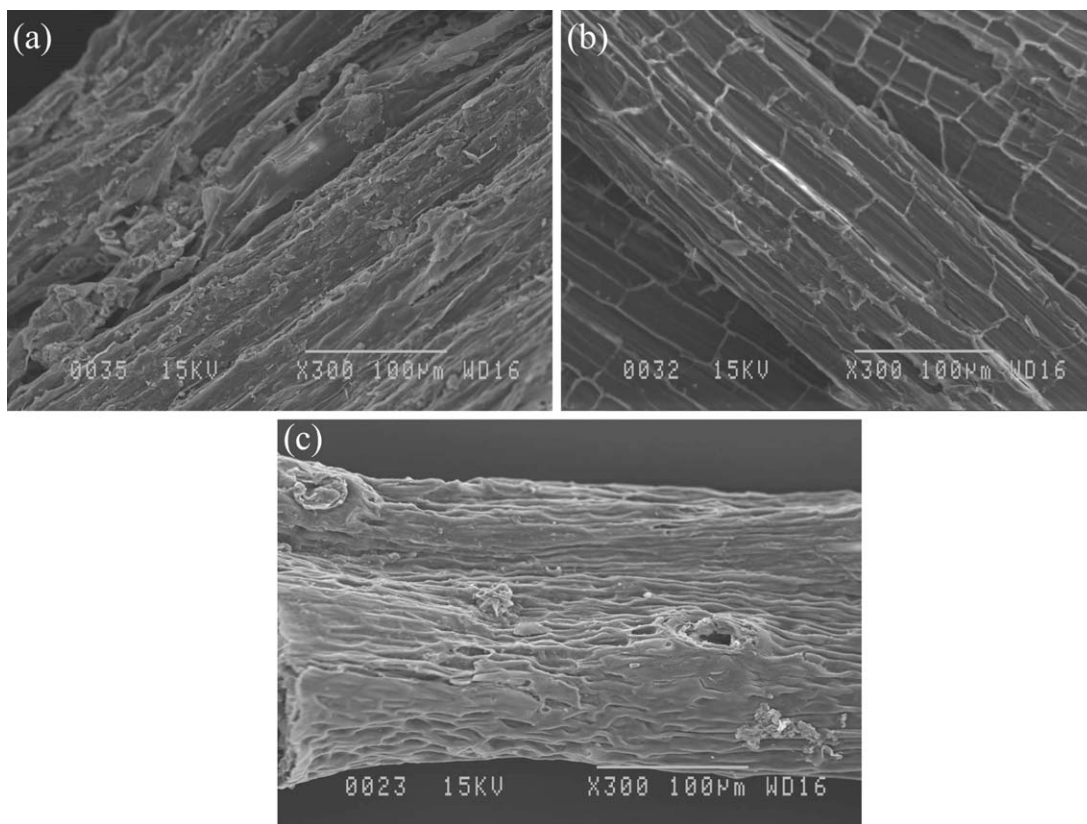
**Alkaline Pretreatment (Mercerization).** Hemp fibers were pretreated with a 8% w/v NaOH solution at room temperature ( $23 \pm 1$  °C) for 3 h (mercerization). The solid:solution ratio was 1:10 w/v. The mercerized fibers were then washed with distilled water to neutral pH and dried in an oven (80 °C for 24 h).

**Hemp Treatment with MAPE in Solution.** The TCB solution containing the chosen amount of MAPE (Table I) was raised to 160 °C with stirring until complete MAPE dissolution. The solution was then cooled to a temperature between 80 °C and 90 °C before hemp (mercerized or not) was added and left under stirring for 30 min. Finally, the solution-modified hemp was filtered and dried in an oven (80 °C for 48 h).

**Treatment of Hemp with MAPE (Direct Mixing).** MAPE direct treatment was performed by dry-blending the LMDPE powder with MAPE powder prior to mixing (extrusion). The hemp content was fixed at 30 wt %, and the amount of MAPE is based on the total amount of the material in the composite.

### Composite Fabrication

To start, the fibers were dried overnight at 70 °C in an oven. To prepare the composites (hemp + LMDPE), a Haake twin-screw extruder (Karlsruhe, Germany) Rheomex PTW 16 OS, ( $L/D = 25$ ) was used at a screw speed of 80 rpm producing a mass flow rate of 0.5 kg/h. The temperatures for the different heating zones of the extruder were 150, 150, 150, 150, 155, and 155 °C from the feed



**Figure 1.** Typical SEM micrographs of (a) untreated hemp, (b) mercerized hemp, and (c) mercerized hemp + 6% MAPE in solution.

hopper to the die (3.2 mm in diameter). The compounds at the extruder exit were cooled in a water bath and pelletized. Thereafter, the pellets were dried at 80 °C in a heated vacuum oven for 24 h to be molded in an injection machine Nissei PS60E9ASE (Nagano, Japan). The injection temperature profile was set as 180, 170, 170, and 160 °C (nozzle, front, middle, rear) with a mold temperature of 30 °C. The mold has four cavities: two dumbbell shapes (according to type IV of ASTM D638) and two rectangular bars (width and thickness of 12.45 and 3.14 mm with two lengths of 80 and 125 mm).

#### Characterization

**Thermogravimetric Analysis.** Thermogravimetric analysis (TGA) was performed on a model Q5000IR from TA Instruments (New Castle DE 19720, USA). Between 6 and 10 mg of material was analyzed by heating up steadily at a rate of 10 °C/min from 50 to 600 °C in nitrogen.

**Morphological Investigation.** Unmodified and modified hemp, as well as the composites, were examined using an SEM. A JEOL model JSM-840A (Tokyo, Japan) was used to take micrographs at different magnifications. The composites were subjected to cryogenic fracture (liquid nitrogen), and all samples were coated with a thin layer of gold/palladium before being examined at 15 kV.

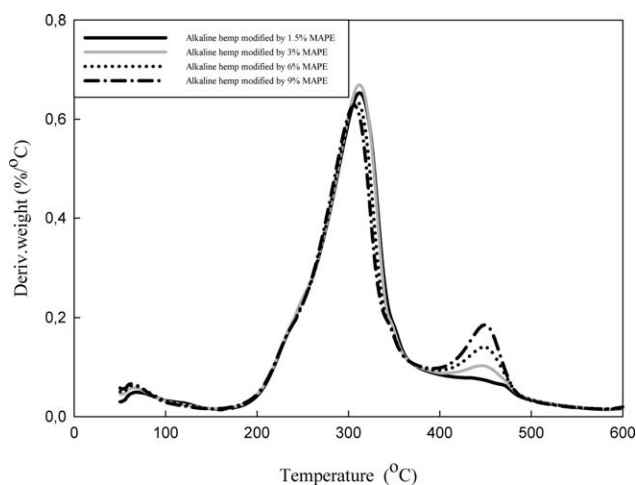
**Dynamic Mechanical Analysis.** The composites were characterized on a dynamic mechanical analyzer RSA3 (TA Instrument, USA). Rectangular samples (40 × 12.4 × 3.14 mm<sup>3</sup>) were analyzed in the linear viscoelastic range (deformation of 3% in a

three-point bending mode) of the materials through temperature ramps (5 °C/min) at a frequency of 1 Hz for temperatures between −120 and 120 °C under a nitrogen atmosphere.

**Rheological Analysis.** The rheological properties were measured on an ARES rheometer (TA Instruments) with a parallel-plate geometry (25 mm diameter) and 5-mm gap under a nitrogen atmosphere. Strain sweep tests were performed in the range 0.09–100% to determine the deformation at which the linear viscoelastic range ends. Then, frequency sweeps (0.05–315 rad/s) at 180 °C and 2% deformation were performed to determine the behavior of the composites in the melt state. The results obtained were used to draw the van Gurp–Palmen plots.<sup>24,25</sup>

## RESULTS AND DISCUSSION

Figure 1 presents typical SEM images for the neat, mercerized, and MAPE solution-modified hemp fibers. Figure 1(a) shows the micrograph of a neat hemp covered by noncellulosic materials (impurities), leading to a very rough surface, while mercerized hems in Figure 1(b) present a smoother surface because of the removal of all the noncellulosic materials. Such effects of an alkaline solution on hemp fibers has been reported elsewhere.<sup>26,27</sup> The modification of mercerized hemp with MAPE in solution leads to a thin MAPE layer [Figure 1(c)] related to the formation of chemical bonds between the carbonyl groups of MAPE and the hydroxyl groups of hemp.<sup>17</sup> The presence of the coupling-agent layer after solution modification of wood and hemp fibers was also reported in previous studies.<sup>21–23</sup>



**Figure 2.** DTG curves of the different hems studied: neat, mercerized, and solution-modified by MAPE.

### Quantification of the Level of MAPE Grafted onto Hemp Fibers

Figure 2 shows the differential thermogravimetry (DTG) curve of the mercerized and solution-modified hemp fibers. The DTG curves can be divided into four stages. Stage 1 is an initial peak around 70 °C belonging to water evaporation.<sup>28</sup> Stage 2 corresponds to the shoulder peak around 200–280 °C and is related to the thermal depolymerization of hemicelluloses and the cleavage of glycosidic links of cellulose.<sup>12,29,30</sup> Stage 3 corresponds to the peak around 320 °C and is attributed to cellulose degradation.<sup>12,31</sup> Stage 4 corresponds to the peak at 450 °C, which is only seen in mercerized hemp modified in solution and is related to the degradation peak of MAPE.<sup>23</sup> To complete our understanding of these results and to explain them, the amount of MAPE grafted onto the fiber's surface must be determined. To do this, a statistical analysis using the DTG data is carried out. As the MAPE degradation (loss weight) peak is between 400 °C and 500 °C, the mass loss ( $\Delta m$ ) in this interval is determined according to

$$\Delta m = m_1 - m_2 \quad (1)$$

where  $m_1$  and  $m_2$  are the masses of hemp (mercerized or solution modified) at 400 °C and 500 °C, respectively (Figure 2). But the mercerized hemp alone (without solution treatment) still shows a small weight loss in this temperature range, for which the amount ( $P$ ) can be approximated as

$$P = \Delta m(\text{mercerized fibers}) \times 100/m_1 \quad (2)$$

Therefore, a correction on the weight loss of the MAPE-modified fibers [eq. (3)] in that temperature range is necessary to obtain the real mass of grafted MAPE ( $m_{\text{MAPE}}$ ):

$$m_{\text{MAPE}} = \Delta m - [(m_1 \times P)/100] \quad (3)$$

Then, the amount of MAPE grafted ( $T_{\text{GR}}$ ) is determined as

$$T_{\text{GR}} = m_{\text{MAPE}} \times 100/m_1 \quad (4)$$

A set of four runs was used to determine an average and standard deviation for  $T_{\text{GR}}$  where the value obtained for  $P$  is  $14.5 \pm 0.5\%$ . Based on this result, the amounts of grafted MAPE for the conditions tested are presented in Table II.

Table II shows that increasing MAPE from 1.5% up to 6% in the solution increases  $T_{\text{GR}}$ , while no statistically significant difference is observed between 6 and 9%. This behavior can be explained by the existence of a saturation point (between 6 and 9%) where most of the fiber surface is covered and additional MAPE molecules in the solution cannot produce more covalent bonding with the fibers. This behavior is in agreement with a maximum observed in the tensile strength of the composites, as reported elsewhere.<sup>23</sup>

### Interfacial Investigations by SEM

The state of dispersion, wetting, and adhesion of the different hems inside the polymer matrix is analyzed using SEM. The microphotographs of the composite's fractured surfaces are presented in Figure 3. Figure 3(a) belongs to the composite with neat hemp (UT). It shows large holes (circles) resulting from fiber pullout and debonding areas. This behavior is generally seen in composites with poor wettability or adhesion between the reinforcement and the matrix. In this case, the fibers are not able to support a significant part of the load applied and are easily extracted.<sup>32</sup> This can be associated with the presence of a high amount of impurities (roughness) on the neat fiber surface [Figure 1(a)], which reduced their wettability.

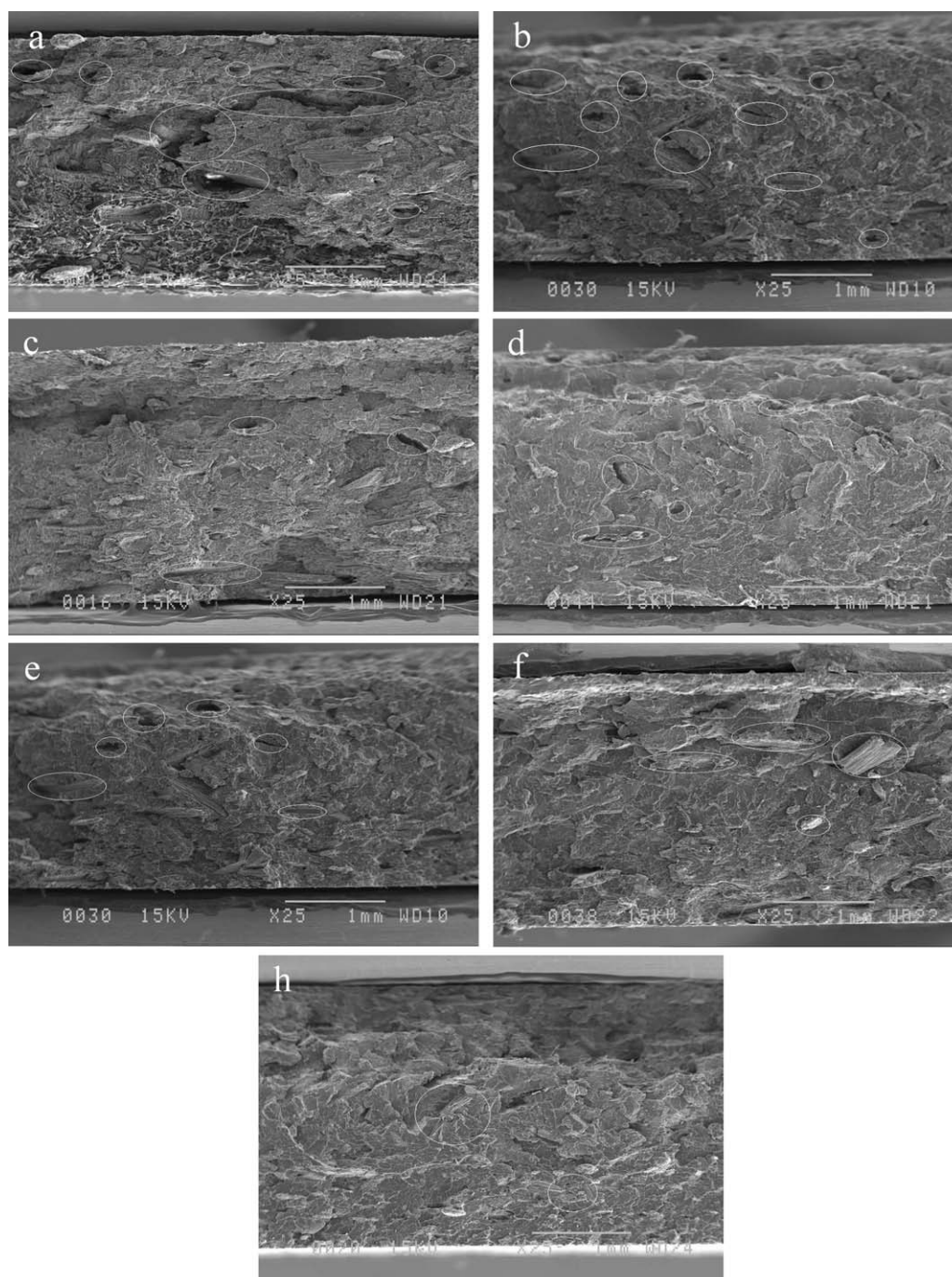
The composite with mercerized hemp (TN) [Figure 3(b)] shows a more homogeneous surface. This can be associated with increased wettability because Figure 1(b) showed that mercerization led to a smoother surface: as the contact area (accessible fiber surface) increased, so did the wettability. But the presence of some gaps in Figure 3(b) (circle) suggests that fiber pullout is still present, reflecting a lack of compatibility (adhesion). In contrast, all the composites with MAPE (solution modification [Figure 3(c,e)], direct use [Figure 3(d,f)], or both direct and solution [Figure 3(h)]) revealed a more homogeneous surface with fewer holes combined with hemp fibers perfectly inserted into the matrix. Moreover, the micrographs show that good fiber dispersion was achieved. This indicates that, in addition to enhanced wettability after mercerization, there is an increase of both dispersion and compatibility for MAPE-modified hemp composites. These observations can be explained by the carbonyl groups of MAPE being covalently linked with the hydroxyl groups of hemp, while the nonpolar part of MAPE (HDPE chains) is compatible with the polymer matrix through physical entanglement, as reported by Mohanty *et al.*<sup>17</sup> Unfortunately, it is not possible to evaluate the level of adhesion in the different modified hemp composites by morphological observation. Therefore, further investigations must be carried out to access complementary interfacial information about the level of improvement. Here, a combination of characterizations in the solid and melt state is presented.

**Table II.** Amount of MAPE Grafted on Mercerized Hemp After Solution Modification

MAPE in solution (%)	1.5	3	6	9
$T_{\text{GR}}$ (%)	15.4 (0.7)	17.2 (0.8)	21.1 (1.5)	23.9 (1.6)

The values in parentheses are standard deviations.





**Figure 3.** Typical SEM micrographs of the composites based on (a) UT, (b) TN, (c) UTE3S, (d) UTE3D, (e) TNE3S, (f) TNE3D, and (h) TNE3S&D.

### DMA Analysis

Stress transfer from the matrix to the fibers through their interface is highly dependent on the degree of adhesion between the phases. According to Rosa *et al.*,<sup>3</sup> increasing adhesion in natural fiber–polymer composites significantly affects their dynamic mechanical properties. Therefore, the level of interfacial adhesion can be indirectly quantified by using the damping factor ( $\tan \delta$ ) as an indicator of the molecular motion in a material. For a weak interface, more energy is dissipated, leading to higher  $\tan \delta$  values during testing.<sup>15,18,33</sup>

**Effect of Modifications on the Damping Factor ( $\tan \delta$ ).** Polyethylene usually shows three relaxation peaks via DMA, namely  $\alpha$ ,  $\beta$ , and  $\gamma$ . The  $\alpha$  relaxation is associated with chain segment mobility in the crystalline phase, which is related to reorientation of defect areas in the crystals.<sup>34,35</sup> The  $\gamma$  relaxation corresponds to the glass-transition temperature ( $T_g$ ) of the polymer and is related to the amorphous phase.<sup>17,34,35</sup> The  $\beta$  transition corresponds to the movement of side branches like in LDPE, but absent in HDPE.<sup>17,35</sup> In the present investigation, the damping factor ( $\tan \delta$ ) behavior of the neat polymer (LMDPE)

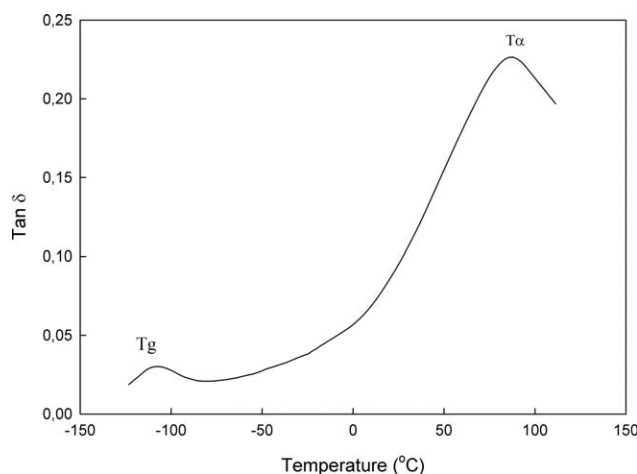


Figure 4. Loss factor ( $\tan \delta$ ) of neat LMDPE.

is shown in Figure 4, and the results for the composites around  $T_\alpha$  are shown in Figure 5. For neat LMDPE, two relaxation peaks at  $-108.8^\circ\text{C}$  ( $\gamma$ ) and  $85.5^\circ\text{C}$  ( $\alpha$ ) are observed, while the  $\beta$  transition seems to be a minor transition in this polymer because of its linear structure.

Figure 5 shows that the introduction of neat hemp in LMDPE (UT) leads to a reduction of  $\tan \delta$ . This is related to the presence of rigid fibers and to the formation of an interface, which are responsible for molecular motion restriction in the polymer matrix.<sup>35,36</sup> According to Figure 5, there is a tendency to decreased  $\tan \delta$  for mercerized hemp composites (TN), and even more for the composites based on mercerized hemp modified by MAPE (direct or in solution), indicating an increased level of wettability or interfacial adhesion compared to UT.

Although a reduction of  $\tan \delta$  for UT is observed with respect to the neat polymer, this reduction is less pronounced in UT than in other composites, showing that polymer molecules are under less constraint. It can be concluded that a poor interface has been formed in UT. Indeed, Mohanty *et al.*<sup>34</sup> observed that composites with poor interfacial bonding tend to dissipate more energy, showing a higher magnitude of the damping factor peak in comparison with a material with a strong interface. Moreover, this observation is in agreement with the SEM micrograph [Figure 3(a)], where a high number of holes (fiber pullout) and debonding (voids associated with a lack of wettability) are observed. The composite made by direct mixing of 3% MAPE and neat hemp (UTE3D) exhibits an additional reduction in  $\tan \delta$  compared to UT, suggesting a better interfacial quality that is due to the links imparted by the coupling agent. The composite with only mercerized hemp (TN) and the one with neat hemp modified in solution by 3% MAPE (UTE3S) exhibit almost the same damping magnitude. In the case of TN, the reduction of  $\tan \delta$  reveals an increase of the interface quality, but their SEM images [Figure 3(b)] showed some holes, suggesting a lack of adhesion. Therefore, the increased quality of the interface in this case can only be attributed to a better wettability that is due to greater contact surface area [revealed by SEM in Figure 1(b) after mercerization]. For UTE3S, the better interfacial quality can be attributed to a

larger number of bonds between hemp and LMDPE that are due to MAPE. This explanation is more likely, that the combination of both hemp mercerization and their modification in solution leads to a composite (TNE3S) with additional lowering of  $\tan \delta$  compared to all the previous composites. This additional lowering observed for TNE3S can be explained by the fact that mercerization increased both the contact area (wettability) and the number of active sites (adhesion) where the coupling agent can link. Therefore, more bonds have been formed than in the previous composites and hence a better interface.

Among all the composites studied, the lowest  $\tan \delta$  is observed for the composite made from mercerized hemp, where the mixture of the solution and direct use of the 3% MAPE (TNE3S&D) was performed, followed by the composite with mercerized hemp and the direct use of 3% MAPE (TNE3D). The further lowering of the  $\tan \delta$  magnitude observed for TNE3D compared to TNE3S suggests that a high-quality interface was formed in this composite. The explanation of this result can be found in the processing conditions of both composites. In the case of TNE3D, the whole amount of MAPE was directly used, while for TNE3S only a small quantity of the available MAPE present in the solution coated the surface of the hemp fibers (see Table II), hence explaining the difference in interface quality. The lowest  $\tan \delta$  obtained was for TNE3S&D, suggesting that this composite has the best interface among all the composites studied. This result is in agreement with the SEM and the mechanical properties of this composite and is probably due to the combined action of mercerization and both types of modification by MAPE (solution and direct): mercerization increased the hemp wettability by LMDPE, while fiber modification in solution facilitated the entanglement between the MAPE-coated fibers and the matrix containing the other half of the MAPE, increasing both the amount and the quality of bonds and hence the quality of the interface in TNE3S&D compared to the other composites.

**Effect of the Modifications on the Adhesion Factor and the Viscosity at  $T_g$ .** To verify the trend of the interface quality observed through  $\tan \delta$ , the adhesion factor ( $A$ ) of the fiber-

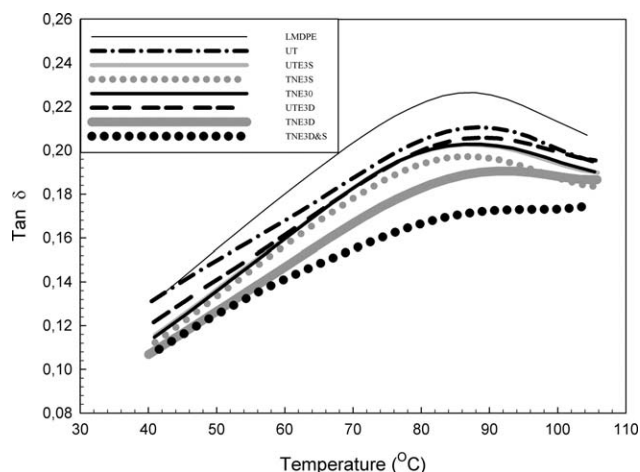


Figure 5. Loss factor ( $\tan \delta$ ) for the different composites around  $T_\alpha$ .

**Table III.** Transition Temperatures ( $T_g$ ,  $T_\alpha$ ), Viscosity at  $T_g$ , and Adhesion Factor of the Composites

Sample code	Transition temperature ( $T_g$ , °C)	Transition temperature ( $T_\alpha$ , °C)	Viscosity at $T_g$ ( $10^8$ Pa s)	Adhesion factor at $T_g$	Adhesion factor at 23 °C
LMDPE	-108.5	87.8	1.52	—	—
UT	-109.6	88.5	1.77	1.20	0.74
UTE3S	-107.0	86.6	2.48	0.50	0.32
UTE3D	-108.8	88.6	2.44	0.58	0.49
TN	-102.6	86.5	2.75	0.06	0.18
TNE3S	-105.3	88.7	2.39	0.22	0.28
TNE3D	-104.9	91.1	2.98	0.01	0.03
TNE3S&D	-102.6	92.8	2.53	0.01	0.09

matrix interface is evaluated at  $T_g$  and at  $T = 23$  °C (room temperature used for mechanical tests) by using the formula<sup>15,16</sup>

$$A = [(\tan \delta_c / \tan \delta_m) - 1] / (1 - v_f) \quad (5)$$

where  $v_f$  is the volume fraction of the fibers in the composite, and  $\tan \delta_c$  and  $\tan \delta_m$  are the values of  $\tan \delta$  for the composite and neat matrix, respectively. Based on eq. (5), the adhesion factor is inversely related to the fiber–matrix adhesion quality; that is, a lower adhesion factor indicates more interaction between the fibers and the matrix.<sup>15</sup> Kubat *et al.*<sup>14</sup> and Correa *et al.*<sup>15</sup> observed that, during dynamic loading, polymer molecular mobility surrounding the filler was reduced. Thus, low values of the damping and of the adhesion factor were observed. On the other hand, Lozano *et al.*<sup>37</sup> observed that in filled polymer systems the presence of fibers perturbs the normal flow of polymer and hinders the mobility of chain segments, leading to increased viscosity. This effect should be important as the interfacial quality or the level of adhesion in the composite increases. Therefore, it is believed that these parameters can help to indirectly access the quality of the interface in a composite.

The results for the adhesion factor and the viscosity at  $T_g$  are presented in Table III. At the glass-transition temperature, the composite based on neat hemp (UT) presents the highest value of the adhesion factors with a limited increase of the complex viscosity at  $T_g$  (17%) compared to LMDPE. This means that a weak interface was formed in this composite. The composites with mercerized hemp (TN) and hemp modified by MAPE directly (UTE3D and TNE3D) or in solution (UTE3S and TNE3S) exhibit an additional reduction of the adhesion factor with higher complex viscosity at  $T_g$ : 80% (TN), 60% (UTE3D), 96% (TNE3D), 63% (UTE3S), and 57% (TNE3S) compared to LMDPE. These observations suggest that mercerization and MAPE treatment improved the interaction between hemp and the polymer, promoting bonding (more restriction), which consequently increased the complex viscosity. All these effects led to lower adhesion factors around  $T_g$ , as observed for all the modified hemp composites. TNE3D and TNE3S&D exhibit the lowest values (0.01) and highest values of the complex viscosity at  $T_g$  (about 96% and 67% higher than LMDPE, respectively), showing better interfacial quality in these composites. This again confirms that improved wettability and adhesion occurred, as reported above.

At room temperature (23 °C), at which all the mechanical tests were performed, the adhesion factor presents almost the same trend as for the glass-transition temperature ( $T_g$ ), so the same explanations hold.

**Effect of Modifications on the Composite Transition Temperatures.** The shift of transition temperatures to higher values with respect to the neat polymer can be associated with decreased mobility of the polymer chains in the composite. Therefore, increased  $T_g$  and  $T_\alpha$  temperatures are taken as a measure of interfacial interactions.<sup>18</sup> From Table III, it can be observed that the  $T_g$  and  $T_\alpha$  transition temperatures are slightly affected when compared to the neat matrix (LMDPE) and the composite based on neat hemp (UT):  $T_g$  is almost unchanged, while  $T_\alpha$  increased by less than 1 °C (87.8 °C to 88.5 °C). These observations indicate less constraint or poor bonding between neat hemp and LMDPE in UT. This is in agreement with the high number of holes and the debonding zone observed in SEM [Figure 3(a)] and the DMA results, as previously discussed. The direct modification of neat hemp (UTE3D) led to a negligible effect on  $T_g$  and a limited shift of  $T_\alpha$  (about 1 °C), while the solution modification of neat hemp (UTE3S) led to a  $T_g$  value of -107.0 °C (an increase of 1.5 °C) with no effect on  $T_\alpha$ . These observations show that the use of MAPE (direct and in solution) with neat hemp slightly increased the molecular constraint in the corresponding composite, probably because of the presence of a high amount of impurities at the surface of neat hemp [see Figure 1(a)]. This high amount of impurities leads to the formation of a lower number of bonds with the matrix and hence limited interface quality improvement. In the case of mercerized hemp (TN), a large shift of  $T_g$  at -102.6 °C (an increase of 5.9 °C compared to LMDPE) and no effect on  $T_\alpha$  are observed. This can be explained by the fact that at the  $T_g$  mercerized hemp is only strongly wetted by LMDPE. Thus, as temperature increases, the links (wetting of mercerized hemp by LMDPE) are not strong enough to sustain the stresses and are easily broken, hence leading to a shift of  $T_g$  and none for  $T_\alpha$ . This explanation shows that mercerization increases wettability but not adhesion. In the case of mercerized hemp with MAPE added directly or in solution (TNE3S, TNE3D, and TNE3S&D), a shift of both  $T_g$  and  $T_\alpha$  is observed. Compared to neat LMDPE, TNE3S&D exhibits the highest shift of the transition



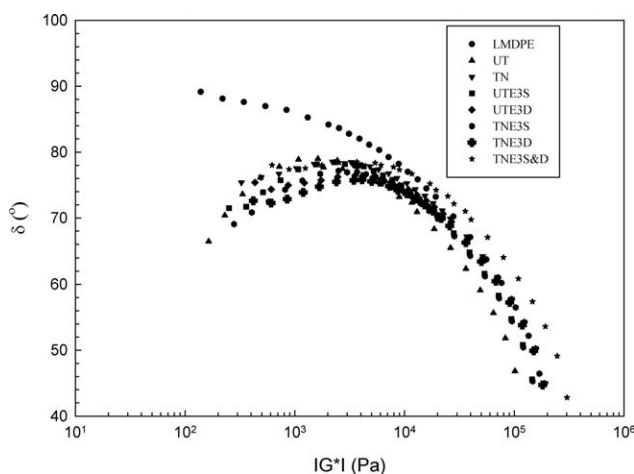


Figure 6. Results of the van Gorp–Palmen plots at 180 °C.

temperatures:  $T_g = -103.0^\circ\text{C}$  and  $T_z = 92.8^\circ\text{C}$ , which are  $5.5^\circ\text{C}$  and  $5.0^\circ\text{C}$  higher than LMDPE, respectively. In addition, TNE3D shows transition temperatures of  $T_g = -104.9^\circ\text{C}$  and  $T_z = 91.1^\circ\text{C}$ , which are only  $3.6^\circ\text{C}$  and  $3.3^\circ\text{C}$  higher than LMDPE, respectively, but are still higher than TNE3S ( $T_g = -105.3^\circ\text{C}$  and  $T_z = 88.7^\circ\text{C}$ ). These results vary with the same trends as for the  $\tan \delta$  and adhesion factor, confirming the different interface qualities observed as reported above.

#### Rheological Analysis

Melt rheology is an important tool to understand the structure–property relationships of materials and their processability.<sup>11</sup> Several methods have been developed to characterize these relationships, but van Gorp–Palmen plots, presenting the relationships between the phase angle ( $\delta$ ) [eq. (6)] and complex modulus ( $G^*$ ) [eq. (7)], can be used to investigate the compatibility between two phases<sup>24,25</sup>:

$$\delta = \arctan(G''/G') \quad (6)$$

$$|G^*| = (G'^2 + G''^2)^{1/2} \quad (7)$$

According to Li *et al.*,<sup>25</sup> the introduction of fibers into a matrix produces a maximum in the van Gorp–Palmen plots, while Lin *et al.*<sup>24</sup> reported that a shift of this maximum to higher modulus can be associated with a decrease in interfacial tension between the composite's phases, suggesting an effective compatibilization. This principle is applied here, and Figure 6 presents the van Gorp–Palmen plots of neat LMDPE and the composites studied.

As observed by Lin *et al.*,<sup>24</sup> the van Gorp–Palmen curve of the matrix (LMDPE) reaches a plateau close to  $90^\circ$  when going from high to low modulus values, while the composites exhibit lower  $\delta$  values ( $\delta_{\max}$  in Table III) and a maximum at intermediate modulus values. From this analysis, the modulus corresponding to this maximum ( $|G^*|_{\delta_{\max}}$ ) is also reported in Table IV.

Table IV. Complex Modulus at the Maximum Phase Angle of the van Gorp–Palmen Plots

Samples	LMDPE	UT	TN	UTE3S	UTE3D	TNE3S	TNE3D	TNE3S&D
$\delta_{\max}$ (°)	—	79	79	78	76	77	76	78
$ G^* _{\delta_{\max}}$ (kPa)	—	1.62	2.20	2.35	3.56	2.50	4.10	3.68

Table IV shows that the composite with mercerized hemp (TN) has a  $|G^*|_{\delta_{\max}}$  about 36% higher than the composite based on neat hemp (UT). Nevertheless, this increase is the lowest among all the composites and confirms again that the improvement obtained, as observed from DMA for this composite, can be associated with mercerization. For composites with neat and mercerized hemp modified with MAPE in solution (UTE3S and TNE3S),  $|G^*|_{\delta_{\max}}$  is further increased by about 45% and 54%, while for those with MAPE directly used (UTE3D and TNE3D) the increase is about 119% and 126%, respectively, when compared to UT. These results are in agreement with all the previous observations, showing that the use of the coupling agent enhanced the compatibility between hemp and LMDPE due to MAPE. On the other hand, the direct use of MAPE is responsible for a significant increase of  $|G^*|_{\delta_{\max}}$  compared to solution modification (UTE3S vs. UTE3D and TNE3S vs. TNE3D). This is in agreement with the amount of grafted coupling agent on the fiber surfaces, as reported in Table II. The increase of the  $|G^*|_{\delta_{\max}}$  value between untreated and pretreated hemp composites containing MAPE (9% between UTE3S and TNE3S and 7% between UTE3D and TNE3D) confirms that mercerization improved the fiber's wettability (observed in TN) and increased the number of active sites, which increased the number of bonding possibilities between the modified fibers and LMDPE, favoring the improvement of the interface quality, as observed for TNE3S&D and TNE3D. Indeed, TNE3S&D and TNE3D exhibit the highest  $|G^*|_{\delta_{\max}}$  increases (about 126% and 152%, respectively) compared to UT, which is in agreement with the DMA results and confirms the improvement of both wettability and adhesion (compatibility) in these composites, as previously discussed.

#### CONCLUSIONS

The main objective of this study was to investigate the effect of different surface modifications (mercerization followed by maleated polyethylene in solution) on hemp fibers and their interfacial properties in LMDPE composites. From the results obtained, the main conclusions are the following:

- SEM images of the fibers showed that the alkaline pretreatment (mercerization) was effective in making the hemp surface smoother, while the modification in solution was responsible for the deposition of a thin MAPE layer on the fiber surfaces, the amount of which was determined via statistical analysis of DTG data. Moreover, SEM images of the composites showed that mercerization increased the hemp wettability by LMDPE. This increase slightly improved the interfacial contact, while the combination of mercerization and MAPE modification in solution increased both wettability and adhesion.
- DMA analysis of the composite showed that the presence of MAPE on neat hemp was responsible for the observed shift



in  $T_g$  and  $T_\infty$ , a reduction of the damping factor ( $\tan \delta$ ) peak and the adhesion factor, a shift of the transition temperatures to higher values, and an increase of the complex viscosity of the composite, confirming an improvement of the quality of the interface of the corresponding composite. In addition, the combination of mercerization and MAPE (directly or in solution) was responsible for further significant improvement associated with an improvement in both wettability and adhesion. It was shown that mercerization and MAPE were both responsible for increased interfacial compatibility between hemp and LMDPE. Nevertheless, the combined results showed that wettability is mainly controlled by mercerization (physical adhesion), while MAPE was controlling adhesion (chemical adhesion). This is why the combination of both methods under optimized conditions leads to optimum composite properties.

- Rheological data were used to get van Gurp–Palmen plots showing that a shift of the phase angle ( $\delta$ ) and peak modulus  $|G^*|$  to higher values after surface treatment was observed that showed the level of interfacial improvement in the composites, which was in agreement with the DMA results.

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