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Impact of Surface Modification of Hemp Fibers Using a Coupling Agent in Solvent on the Properties of Polyethylene Composites

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Abstract
This study investigates the grafting of a coupling agent, maleic anhydride-grafted polyethylene (MAPE), onto hemp fibers in a 1,2,4-trichlorobenzene (TCB) solution, followed by an evaluation of the morphological, rheological, and mechanical properties of the resulting polyethylene composites containing 30% hemp. SEM analysis revealed the formation of a thin layer of MAPE on the surface of the modified fibers. This was further confirmed by the appearance of a MAPE degradation peak at 448 °C, observed in the modified fibers but absent in the unmodified counterparts. Composites made with unmodified hemp fibers (UT30) showed a significant increase in modulus but not in tensile strength. In contrast, the modification of hemp in solution significantly enhanced the tensile strength of the composites (UTE3S) without significantly affecting the modulus. Increasing the amount of coupling agent (in UTE6S and UTE9S) reinforced this trend, indicating that the thin polymer layer on the surface of the modified hemp fibers notably improved interfacial bonding, with minimal impact on the tensile modulus of the composites.

Keywords:
linear medium density polyethylene (LMDPE); maleic anhydride-grafted polyethylene (MAPE); hemp; rheological properties; mechanical properties

1. Introduction

Over the past years, the incorporation of natural fibers from annually renewable sources as reinforcement in composites has significantly increased. This trend is largely due to heightened environmental consciousness [1]. As a result, the development of more eco-friendly materials from renewable resources with optimized performance has become a key focus for researchers globally. This growing interest stems from the unique benefits these renewable resources offer over inorganic fibers. Unlike inorganic fillers, natural fibers from renewable sources are biodegradable, non-abrasive, cost-effective, and readily accessible, while also providing favorable specific properties [2,3]. Among these, hemp stands out as a bast fiber known for its exceptional strength and low lignin content [4–6].

In composite materials, the effectiveness of the interaction between the polymer and the reinforcement specifically in terms of wettability and adhesion ensures a robust interface, promoting optimal stress transfer and resulting in superior mechanical strength [7]. However, the hydroxyl groups in natural fibers make them hydrophilic, allowing them to attract water molecules. This hydrophilic nature renders them incompatible with thermoplastics, which are composed of tightly bonded carbon and hydrogen atoms, making them hydrophobic. Consequently, mixing natural fibers with thermoplastics like polyethylene results in an immiscible blend [1,8,9]. This incompatibility can be mitigated by modifying the surface characteristics of the fibers through surface modification tech-

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niques. A common method involves using a coupling agent to create covalent bonds with the hydroxyl groups of the cellulosic components of the fibers while simultaneously physically bonding to the polymer matrix through chain entanglement [10].

Generally, the coupling agent is incorporated with the polymer during the processing steps (extrusion and/or injection molding). Unfortunately, this approach does not always guarantee uniform distribution, which can result in segregation zones within the final material. These zones can cause poor fiber adhesion and, consequently, weaken the material's properties. This study aims to address this issue of incompatibility between hydrophilic natural fibers and hydrophobic thermoplastics in composite materials using a less-studied approach in current literature that can also help to prevent segregation.

This approach involves grafting a coupling agent onto the fibers in a solvent before introducing them into the matrix. The presence of the coupling agent layer on the fibers is expected to reduce fiber-fiber interactions, enhance dispersion, and improve compatibility. Each fiber is expected to develop local adhesion through the same mechanism described earlier, due to the coupling agent layer on its surface [11]. Ultimately, the goal is to produce materials with optimal properties and superior performance, particularly for applications in the automotive engineering field, where lightweight and high-strength materials are crucial.

Recent studies by Verdaguer and Rodrigue [12] and Raymond and Rodrigue [13] explored this approach by modifying mercerized wood fibers with a high molecular weight maleic anhydride-grafted polyethylene (MAPE) in a 1,2,4-trichlorobenzene (TCB) solution. This current research continues the effort by focusing on the surface modification of a different natural fiber and type of coupling agent (low molecular weight). It also investigates the amount and impact of the grafted material, aiming to deepen the understanding of this method and its effectiveness in enhancing the properties of hemp fiber composites.

To achieve this goal, the effects of grafting varying amounts of MAPE onto hemp fibers in a TCB solvent were investigated, examining how these modifications influenced the morphological, thermal, rheological and mechanical properties of the resulting linear medium density polyethylene (LMDPE) composites. Thermogravimetric analysis (TGA) and Scanning Electron Microscope (SEM) analyses were conducted on both modified and unmodified hemp fibers to confirm the grafting of MAPE. Micro structural changes were further explored through SEM imaging and rheological tests, including measurements of complex viscosity and storage modulus. Finally, tensile tests were performed to evaluate the impact of fiber modification on the mechanical properties of the composites.

2. Experimental Details

2.1. Materials

Hemp was obtained from Hemp Trade Alliance (Quebec, QC, Canada). The particle size used after sieving the material was between 250 and 1000 μm. The coupling agent used was Epolene (E-20P) by Westlake Chemical Co (Houston, TX, USA) with the following characteristics (Mw = 7500, MFI = 1.24 g/10 min (190 °C/2.16 kg), acid number = 16.9 mg-KOH, viscosity = 1305 CPS and a softening point of 113.8 °C). The solvent used was 1,2,4-trichlorobenzene (TCB), HPLC grade, from J.T. Baker (USA). White powder of linear medium density polyethylene (LMDPE, T_m = 125 °C, MFI = 3.5 g/10 min (190 °C/2.16 kg), density = 0.936 g/cm^3) obtained from Ashland Canada was used as the main matrix.

2.2. Methods of Chemical Modification of Hemp

Treatment of Hemp with MAPE in a TCB Solution

The TCB solution, containing the specified amount of MAPE (as shown in Table 1), was heated to 160 °C with stirring until the MAPE dissolved. The solution was then cooled to a temperature between 80 °C and 90 °C. Hemp fibers were added, and the mixture was stirred for 30 minutes. Subsequently, the modified hemp fibers were filtered and dried in an oven at 80 °C for 48 h [11]. The labels and compositions of the various samples examined in this study are presented in Table 1.

Table 1: Codes and compositions of composite samples.

Codes	Compositions
LMDPE	Linear medium density polyethylene
UT	LMDPE/30% hemp
UTE3S	LMDPE/ 30% hemp + 3% MAPE (E20P) in solution
UTE6S	LMDPE/ 30% hemp + 6% MAPE (E20P) in solution
UTE9S	LMDPE/ 30% hemp + 9% MAPE (E20P) in solution

2.3. Composites Fabrication

Dry hemp and LMDPE were mixed in a Haake twin-screw extruder Rheomex PTW 16 OS, (L/D = 25) having a 3.2 mm die diameter and a heating zones profile of as 150-150-150-150-155-155 °C from the feed hopper to the die. They were mixed at a speed of 80 rpm producing a

total mass flow rate of 0.5 kg/h. At the extruder exit, the compounds were cooled in a water bath and pelletized.

The 24 h dry pellets were thereafter, molded in a Nissei PS60E9ASE (Japan) injection machine with a temperature profile set as 180-170-170-160 °C (for the nozzle; front; middle and rear respectively) and a mold temperature of 30 °C.

2.4. Characterizations

2.4.1. Transform Infrared Spectroscopy (FTIR)

Infrared spectra were obtained with a Nicolet FTIR spectrometer (model 730, Nicolet Instruments, USA) equipped with a mercury-cadmium-telluride detector. The sample absorbance was measured in the region (4000–750 cm^{-1}) and each spectrum was obtained from 128 scans at a resolution of 4 cm^{-1}.

2.4.2. Thermogravimetric Analysis (TGA)

TGA analysis of fibers was investigated with a TGA Q5000 IR (TA Instruments) Between 6 to 10 mg of hemp samples were taken for analysis. The samples were heated up steadily at a rate of 10 °C/min from 50 to 600 °C in nitrogen medium.

2.4.3. SEM Investigation

Unmodified and modified hemp as well as the corresponding composites were examined using a Scanning Electron Microscope (SEM). The Model JEOL JSM-840A was used to take micrographs at various magnifications. The samples were subjected to cryogenic fracture (liquid nitrogen), coated with a thin layer of gold/palladium and then examined at 15 kV.

2.4.4. Rheological Analysis

An ARES Rheometer with a parallel-plate geometry (25 mm diameter) was used. The strain sweep tests were performed in a range of 0.09–100% to determine the deformation at which linear viscoelastic behaviour occurs. Then, a deformation of 3% was chosen to perform frequency sweeps in the range of 0.05–300 rad/s at 180 °C.

2.4.5. Tensile Test

The tensile properties were measured using an Instron model 5565 universal testing machine (Instron, Norwood, MA, USA) with a 500 N load cell. Dog-bone shaped samples were prepared according to type IV of ASTM D-638 and tested at 23 °C and a cross-head speed of 10 mm/min. A minimum of five samples were tested to get an average and standard deviation.

3. Results and Discussions

3.1. Surface Modification of Fibers

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1 displays the FTIR spectra of both untreated and modified hemp fibers treated with 6% MAPE in solution. The spectra indicate that the modified hemp fibers show increased intensity at the 1015 cm□¹ peak, as well as at 2920 cm□¹ and 2850 cm□¹. These peaks correspond to C-C stretching and symmetric and asymmetric aliphatic C-H vibrations, respectively [11]. These changes suggest an enhancement of C-C and C-H groups on the fiber surface after modification, likely due to the incorporation of polyethylene molecules of the coupling agent.

To further support these findings, TGA and DTG analyses of the untreated and modified hemp fibers are presented in Figures 2a and 2b, respectively.

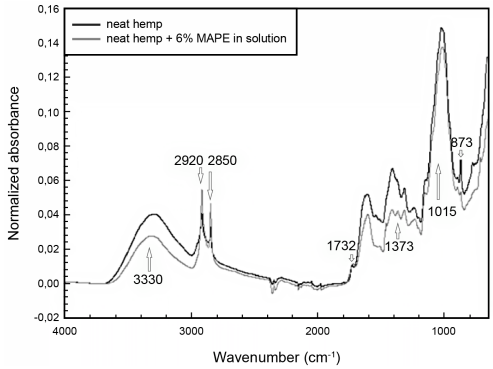


Figure 1: FTIR spectra of the neat and modified hemp with 6% of MAPE in solution.

3.1.2. Thermogravimetric Analysis

Figures 2a and 2b present the TGA and DTG curves for unmodified and MAPE-modified hemp, respectively. The TGA curves (Figure 2a) indicate that the MAPE modification enhances the thermal stability of the modified hemp compared to the unmodified sample, as the curves for the modified fibers are consistently above those of the unmodified fibers.

This improvement can be attributed to the presence of a thin MAPE layer on the surface of the hemp fibers, which provides greater thermal stability. This layer acts as a thermal barrier, enhancing the overall thermal stability of the system compared to the unmodified fibers, where the surfaces were directly exposed [11].

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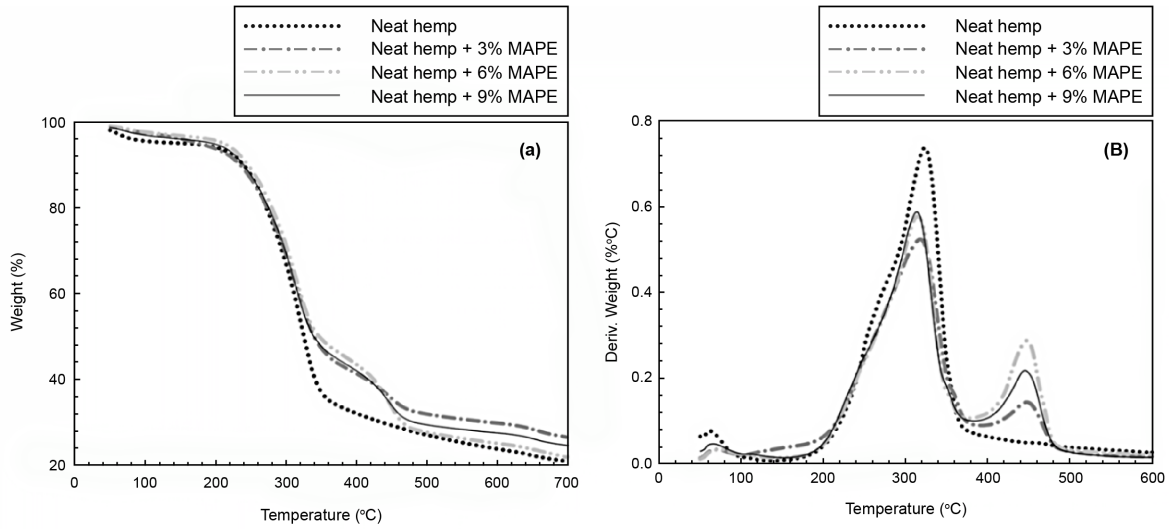


Figure 2: (**a**) TGA and (**b**) DTG curves of unmodified and MAPE solution modified unmodified hemp.

On the DTG curve of neat and modified hemp (Figure 2b), four main stages can be observed. The first stage corresponds to the peak observed at 67.4 °C due to the vaporisation of water from the fibers [14,15]. The reduction in this peak after modification suggests a decrease in the hydrophilicity nature of the modified hemp fibers. This is likely due to a reduction in available hydroxyl groups, which can bond to water molecules through hydrogen bonding, as these groups are now likely bound to the coupling agent. The second stage, marked by a shoulder peak around 200–280 °C, is associated with the thermal depolymerization of hemicelluloses and the cleavage of glycosidic linkages in cellulose [9,16,17]. This shoulder is less prominent in the fibers modified in solution, indicating a partial removal of these components, possibly because of the hot solvent. The third stage, occurring at approximately 350 °C, corresponds to cellulose degradation [16,18,19]. The fourth stage, observed around 448 °C and only in the curves of hemp modified in solution, represents the degradation peak of MAPE. This peak highlights the effectiveness of the modification and can be attributed to the presence of the coupling agent on the surface of the hemp fibers.

Figure 2b also shows that the height of the MAPE peak (between 400 and 500 °C) increases and reaches a maximum when the MAPE concentration in the solution increases from 3% to 6%. This suggests an increase in the amount of MAPE grafted onto the hemp fibers. However, a further increase in MAPE concentration from 6% to 9% results in a decrease in the peak height, indicating a reduction in the amount of MAPE grafted onto the fiber surface. This phenomenon may be attributed to the higher concentration of MAPE in the solution, which increases the likelihood of interaction and self-entanglement among the coupling agent (Epolene E20P) molecules. This self-entanglement reduces the availability of MAPE molecules to form bonds with the hemp fibers [11]. Consequently, less MAPE was grafted onto the hemp, as reflected by the reduction in peak height.

3.1.3. Scanning Electron Microscopy of the Fibers

Scanning Electron Microscopy (SEM) is used to evaluate either the effect of the modification on hemp fibers or the state of adhesion in the different composites.

The pictures of unmodified and modified hemp fibers are presented in Figures 3a and 3b. Figure 3a illustrates the surface of unmodified hemp, which is notably rough and covered with non-cellulosic materials and other impurities. In contrast, Figure 3b demonstrates that the solution modification results in the presence of fibers with modified surface texture that support the presence of the MAPE onto these fibers, indicating the successful reaction of hemp with MAPE in solution [11]. This finding aligns with the MAPE peak observed in the DTG analysis of the modified hemp fibers (Figure 2b).

3.2. Investigation on the Effect of Modification on the Composites

3.2.1. Morphology via SEM

The morphology of the nitrogen fractured surface of unmodified and modified hemp composites is illustrated in Figure 3c to Figure 3d. Figure 3c pertains to the composite

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containing unmodified hemp (UT). It reveals some voids (encircled) caused by fiber pull-out, indicating insufficient wettability and weak adhesion (poor interaction) between the fibers and the matrix [11]. The holes result from mechanical extraction under applied load during composite breakage. The fibers were easily pulled out, due to their weak wettability and adhesion [20]. This is expected, as the SEM image (Figure 3a) shows a high quantity of impurities and a rough surface on the hemp fibers. These factors have likely reduced the wettability and, consequently, the adhesion between hemp and LMDPE in UT. In contrast, the composites with hemp fibers modified in solution with 3% MAPE (UTE3S) in Figure 3d display a more homogeneous surface with fewer holes. However, the presence of some holes (circled) indicates a lack of compatibility, leading to fiber pull-out. This suggests that the amount of MAPE grafted onto the hemp was insufficient to achieve optimal interface enhancement, as supported by the MAPE peak height (Figure 2b). Conversely, the composites with hemp treated with 6% and 9% MAPE (Figures 3e and 3f, respectively) show a more homogeneous surface with significantly fewer holes, with the hemp fibers being well integrated into the matrix (as indicated by arrows). This indicates an improvement in the interface quality in these composites (UTE6S, UTE9S) [11].

However, the presence of a few remaining holes (circled) suggests that, although the interface quality has improved, it is still not optimal. This may be due to the presence of impurities on the hemp fibers, which could hinder the formation of an optimal number of bonds at the composite interface due to the steric hindrance of the active sites (hydroxyl groups on the surface) towards the incoming coupling agent by surface impurities. A pre-treatment, such as alkaline modification, may be beneficial in addressing this issue [21].

3.3. Rheological Analysis

Melt rheology of thermoplastic blends is vital to understand the composite's structural property relationship and their processability [8].

3.3.1. Storage Modulus

Figure 4a shows the storage modulus (G') plotted as a function of the frequency (ω) for LMDPE and the unmodified/modified hemp fibers composites. At low frequencies, LMDPE displays the characteristic terminal behavior of a linear polymer, i.e., $G' \approx \omega^2$ which is attributed to terminal relaxation of LMDPE molecules [22].

Due to the intrinsic rigidity of hemp, the G' of the composite (UT) is higher as compared to that of the matrix in all frequency ranges measured and this behaviour can be explained by the fact that filler particles restrict deformation [23]. A slight enhancement is observed at low ω for modified fibers composites with respect to UT and is to be attributed to the interfacial improvement due to MAPE [24].

It can also be seen that all the composites exhibit a no terminal relaxation as it is observed for the polymer. Such nonterminal behaviour was also reported for wood/MAPE/PP composite by Wang et al. [25] and was related to the particle–particle and particle–polymer interactions. Although the composite with solution-modified hemp shows a slight increase in (G') compared to UT, the (G') curves are nearly identical across all modified fiber composites. This behavior is attributed to two factors: firstly, all the modified composites contain the same fiber content (30%), and secondly, the amount of MAPE on the fiber surfaces is insufficient to significantly enhance the material's stiffness.

3.3.2. Complex Viscosity

Complex viscosity represents the viscoelastic resistance of the polymer melt during flow [26]. Figure 4c illustrates the complex viscosity (η*) as a function of ω for the composites at 180 °C. The addition of fibers to LMDPE significantly increases the complex viscosity of the composite, particularly at low frequencies. This type of behavior is well-documented in composite literature and can be explained using modified Cross models that incorporate a yield stress term as follows [27]:

$$\eta_{(\omega)} = \sigma_o/\omega + \eta_o/(1+(\lambda\omega)^{(1-n)}) \quad (1)$$

where σ_o is the yield stress, η_o is the zero-shear viscosity, λ is the melt relaxation time and n is controlling the slope of the pseudo-plastic region [27]. Equation (1) was fitted to the experimental data using Sigma Plot v.11, and the parameters are listed in Table 2. The regressions are also displayed in Figure 4c, demonstrating that Equation (1) accurately predicts the data for these samples, as all fittings achieved $R^2 > 0.99$ and p value < 0.001. The yield stress (σ_o) is attributed to the rigidity provided by the fibers and the enhanced quality of the composite inter-

Table 2: Modified Cross model parameters of the composites at 180 °C.

Labels	tan δ_{max}	σ_o (Pa)	η_o (Pa.s)	λ (s/rad)	n (-)	R (-)
LMDPE	-	-	2879	0.025	0.413	0.999
UT	4.80	115	3265	0.047	0.447	0.999
UTE3S	4.53	132	3420	0.052	0.458	0.999
UTE6S	4.06	203	3987	0.068	0.473	0.999
UTE9S	4.20	167	4223	0.085	0.494	0.999

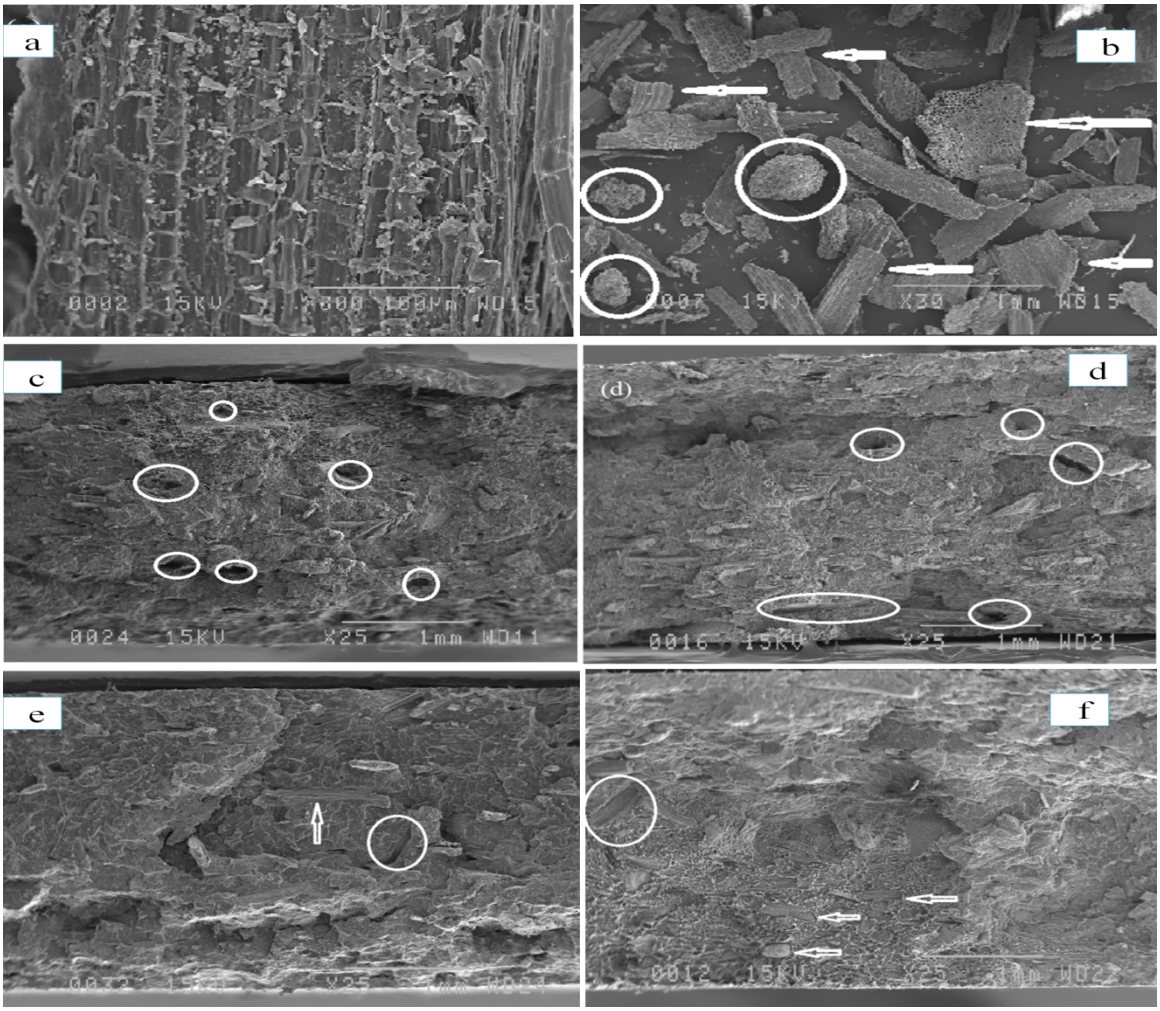


Figure 3: SEM images of hemp composites: (**a**) unmodified hemp fibers, (**b**) hemp modified by MAPE in TCB, (**c**) UT, (**d**) UTE3S, (**e**) UTE6S, (**f**) UTE9S.

face. Table 2 indicates that σ_o values increase by approximately 14.7%, 76.5%, and 45.2% for UTE3S, UTE6S, and UTE9S, respectively, compared to UT. This increase is linked to the presence of the PE phase on the fiber surface (Figure 3b), resulting in a more pronounced effect of the fibers in the respective composites. The observed reduction for UTE9S compared to UTE6S suggests a better interface in the latter.

Table 2 shows that, ηo and λ for UT increase by approximately 13.4% and 88%, respectively, compared to LMDPE. This behavior can be attributed to the presence of fibers, which disrupt the normal flow of the polymer and impede the mobility of the polymer chain segments [28]. For the composite with fibers modified with 3% MAPE in solution, ηo and λ increased by about 18.7% and 108%, respectively, compared to LMDPE. This improvement is attributed to the enhanced composite interface (as observed in SEM Figure 3d to Figure 3f), which increases constraint and further hinders the flow of polymer molecules. Table 2 and Figure 4c show that for the composite with fibers treated with 6% MAPE (UTE6S), ηo and λ increase by approximately 38.4% and 172%, respectively, while for the composite with fibers treated with 9% MAPE (UTE9S), the increases are about 46.6% and 240%, respectively, compared to LMDPE.

These results do not align with the DTG curves (Figure 2b). Indeed, Figure 2b shows that the height of the MAPE peak for hemp modified with 9% MAPE in solution was less significant than that for 6%, indicating a lower amount of MAPE. For both UTE6S and UTE9S, the increase is related to the MAPE grafted, while the unexpected increase for UTE9S can be attributed to the higher amount of MAPE used in the solution. This effect leads to a better composite interface in UTE6S and UTE9S, resulting in higher constraints in these composites, which

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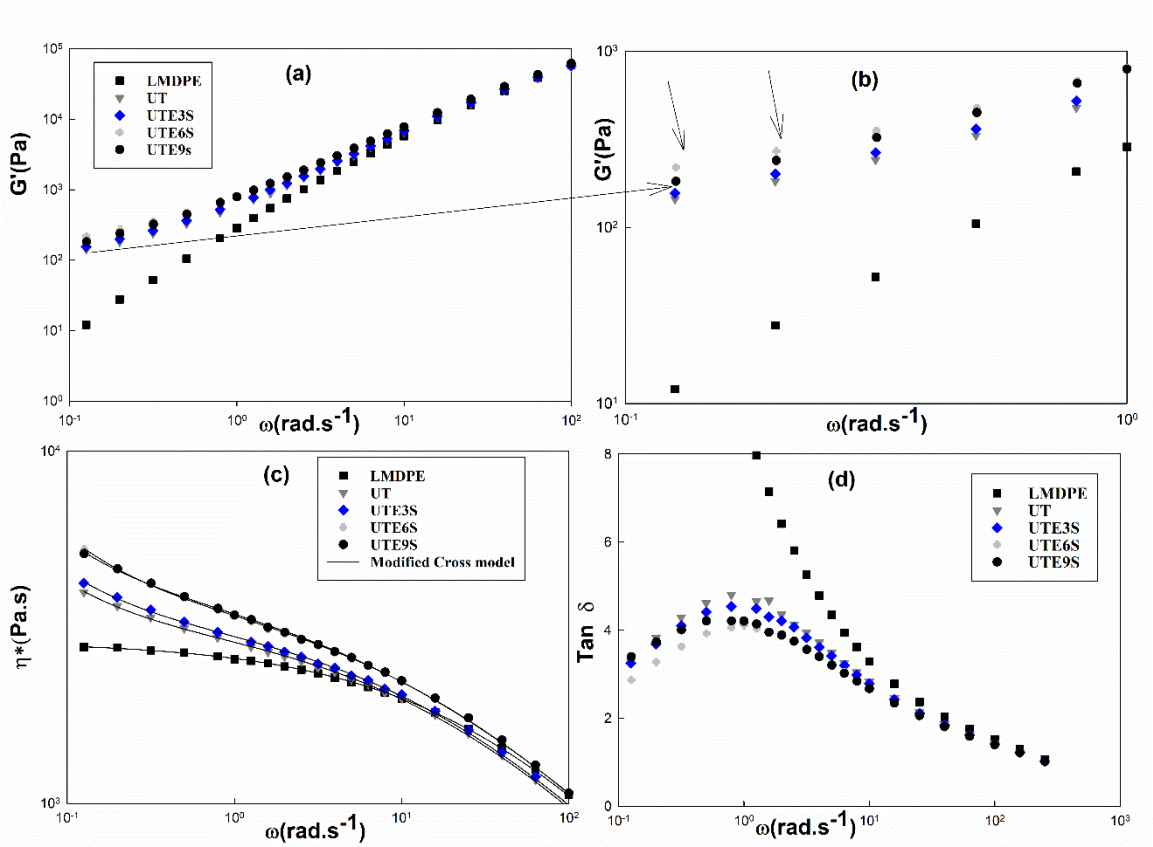


Figure 4: (a) Storage modulus (b) focus on the low frequency region of the storage modulus curve (c) Complex viscosities and (d) damping factor (Tan δ) of the samples.

ultimately explains the difference in viscosity observed compared to UTE3S and LMDPE.

As expected, all the composites show a shear-thinning behaviour (especially at high frequency) as shear thinning exponent *n* increases for these samples. This behavior is characteristic of filled polymer systems and can be explained by the increased degree of polymer-filler interaction, which necessitates higher shear stress and longer relaxation times for the composite to flow [23,29]. The shear thinning exponent *n* increases by 8.2%, 10.8%, 14.5% and 19.6% for UTE3S, UTE6S and UTE9S respectively and compared to LMDPE. According to Ares et al. [29], incorporating fillers into a molten polymer enhances shear thinning behaviour, which is traduced by the reduction of the value of the exponent (n) in the power law region of a dynamic viscosity versus frequency plot.

3.3.3. Damping Factor (Tan δ)

The damping factor (tan δ = G″/G′) provides insights into the energy dissipation efficiency of the composites [30–32]. As shown in Figure 4d, the LMDPE curve exhibits a linear behavior, typical for an unfilled system where the polymer chain segments are unconstrained. In contrast, the composite tan δ curves display a peak (tan δmax), indicating the point at which the internal links within the composite are completely broken, allowing the material to flow more easily. This peak is absent in the neat matrix tan δ curve, likely due to the lack of an interface. Therefore, a decrease of tan δ is to be associated to an improved interface in the composites [30–32]. The curves of tan δ versus ω for LMDPE and modified hemp fibers composites are shown in figure 4d. The decrease of tan δ is to be related to the interfacial tension between both phases suggesting an effective compatibilization. For the composites, this maximum was taken and presented in Table 2. The values of tan δmax decreases by 5.6%, 15.4% and 12.5% for UTE3S, UTE6S and UTE9S respectively and compared to UT. The trend suggests an increased interface for UTE3S, at better for UTE6S and a medium for UTE9S. This result agrees with the σ_o observed for UTE9S with respect to UTE6S confirming that the earlier exhibits a better interfacial bounding.

3.4. Mechanical Properties

To see the effect of the surface treatments on the mechanical properties of the composites, tensile test has been made and the obtained results are presented in Table 3.

Table 3: Effect of the MAPE solution modification on the mechanical properties of the composites.

Samples	E(MPa)	σ (MPa)	ε (%)
LMDPE	250 (07) [d]	13.1 (0.3) [c]	826 (19) [a]
UT30	569 (11) [a]	13.7 (0.6) [c]	14.8 (0.9) [b]
UTE3S	518 (25) [c]	15.8(0.4) [b]	14.4 (2.0) [b]
UTE6S	561 (26) [a]	17.3 (0.3) [a]	12.4 (1.0) [c]
UTE9S	545 (15) [a]	17.0 (0.3) [a]	12.1 (1.0) [c]

The values with the same letter for each property are not significantly different at the 5% significance level according to the student test. The values in the parentheses are standard deviations.

Incorporating 30% unmodified hemp into LMDPE (UT30) results in a substantial increase in the tensile modulus, approximately 138%. This enhancement in modulus is attributed to the stiffness provided by the reinforcing agent [29]. The modification of hemp with MAPE in solution leads to a significant decrease of Young modulus probably because of the reduction the fibers stiffness, due to the lignin and hemicelluloses extraction by the hot solvent as observed in Section 3.1.2.

The increase in the amount of MAPE in the solution from 3% to 6% results in an approximately 8% increase in the Young's modulus compared to UTE3S, with no significant difference observed relative to UT. In this case, the increase of Young modulus can be related to the reduction of the thermal degradation of hemp in solution because of the coating of the hemp by a thin layer of MAPE in solution which acted as a barrier to avoid the degradation as explained in Section 3.1.2.

When the amount of MAPE in the treatment solution is further increased from 6% to 9% no significant difference is also observed between both composite's Young moduli.

The fact that the Young modulus of UTE6S and UTE9S are not significantly different is explained on one hand by the fact that all the composites possess the same number of fibers (30%) and, on the other hand, because the thin layer of MAPE at the surface of modified hemp is too thin to have a significant contribution on the stiffness. These results of composites young moduli agree with the storage modulus trend.

Regarding tensile strength, it is important to remember that this property pertains to the composite's ability to withstand an applied load [33–36]. This is achieved by transferring the load from the continuous phase (matrix) to the discontinuous phase (fiber) through the composite's interface [34]. Consequently, the better the interface, the higher the tensile strength. Table 3 indicates that incorporating 30% unmodified hemp into LMDPE (UT30) results in no significant change in the tensile strength of the composite (UT) compared to the polymer. This outcome is attributed to the poor quality of the interface observed in this composite as indicated by SEM (Figure 3c). This inferior interface resulted in weak load transfer, leading to almost no change in tensile strength for UT compared to the neat polymer.

Modifying hemp with 3% MAPE in solution increases the tensile strength by approximately 15% compared to UT30. This improvement is linked to the enhanced composite interface due to the presence of MAPE on the hemp surface after modification, as revealed by DTG, FTIR, and SEM analyses. Increasing the MAPE concentration in the solution from 3% to 6% results in a 26% increase in tensile strength compared to UT30, representing an enhancement of about 10% compared to UTE3S. This is due to the improved interface quality of this composite, as discussed in previous sections.

However, further increasing the MAPE concentration from 6% to 9% does not significantly change the tensile strength of the composites (UTE9S) compared to UTE6S. This behavior can be explained by the reduced interface quality observed in this composite through SEM (Figures 2e and 2f).

The elongation at break for all the composites significantly decreases compared to the neat matrix (LMDPE), and the modification does not alter this outcome. Previous studies by Sojoudiasli et al. [33], Raj et al. [34]; Kakroodi et al. [35], Sinha et al. [37,38], have also noted this trend. This reduction can be attributed to the increased stiffness of the composite resulting from the incorporation of stiffer hemp. This can be explained by the conjunction of many factors. Firstly, incorporating fibers into the polymer matrix generally enhances the composite's stiffness and strength but often reduces ductility [33]. Moreover, the fibers serve as stress concentrators, which can lead to premature failure under tensile stress, thus lowering elongation at break [33–35]. Secondly, improved interfacial bonding, as indicated by enhanced interfacial properties, can restrict the mobility of polymer chains around the fibers. This restriction may further reduce elongation at break [34]. Strong interfacial adhesion promotes effective load transfer from the matrix to the fibers, which increases the composite's overall strength but limits its capacity for plastic deformation [35]. Lastly, the specific characteristics of hemp fibers and their interaction with the MAPE with low molecular weight as the one used in this study, may also contribute to this effect. Chemical bonding between MAPE and the fiber surface, as confirmed by our

FTIR and TGA analyses, indicates a strong interfacial interaction that likely produces a stiffer composite with reduced elongation at break.

4. Conclusions

The aim of this study was to investigate the effect of surface modification of hemp fibers with a coupling agent (MAPE) in TCB on the rheological, morphological, thermal, and mechanical properties of their LMDPE composites. From these investigations, several important conclusions can be drawn: the DTG curve of these fibers showed the appearance of the MAPE peak in the temperature range between 400 °C and 500 °C, and SEM micrographs revealed fibers coated with MAPE. An increase in Newtonian viscosity for UTE3S, UTE6S, and UTE9S, compared to LMDPE, indicated an enhanced composite interface. The introduction of fibers into LMDPE increased the Young's modulus of the composite by about 138%, with the treatment having no significant effect, which was in perfect agreement with the storage modulus values. While the introduction of fibers into LMDPE had no effect on UT tensile strength, the modification increased this property by approximately 21%, 32%, and 30% for UTE3S, UTE6S, and UTE9S, respectively. The next step is to see if a cleaning of the surface of the fibers with an alkaline solution before surface modification can lead to further improvement as well as the evaluation of the recycling possibility of the solvent to make the method more economical.

List of Abbreviations

TCB	1,2,4-Trichlorobenzene
MAPE	Maleic Anhydride-Grafted Polyethylene
LMDPE	Linear Medium Density Polyethylene
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
DTG	Derivative Thermogravimetry

Author Contributions

Conceptualization, methodology, investigation, data curation, formal analysis, writing—original draft preparation, and visualization: C.Y.D.; Validation, interpretation, and resources: S.J.B. and C.A.Y.; Writing—review and editing: S.J.B. and C.A.Y. All authors have read and agreed to the published version of the manuscript.

Availability of Data and Materials

All data available are presented in the study in the Result section of the manuscript.

Consent for Publication

Not applicable.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper. No financial or personal relationships with any individuals or organizations could have influenced the work reported in this manuscript.

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AI Declaration

AI-based tools were used solely for language editing and formatting. No AI tool was used to generate or paraphrase the content of the manuscript. The authors take full responsibility for the accuracy, originality, and integrity of the work.

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