LIGNOCELLULOSE-POLYETHYLENE COMPOSITE: INFLUENCE OF DELIGNIFICATION, FILLER CONTENT AND FILLER TYPE

SEYED MOHAMMAD MIRMEHDI, GUSTAVO HENRIQUE DENZIN TONOLI and FATEMEH DABBAGH

Department of Forest Science, University of Lavras (UFLA), CP 3037, Lavras, MG, Brasil
✉ *Corresponding author: S. M. Mirmehdi, mohamadmirmehdi@yahoo.com*

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The present study developed a lignocellulose-polyethylene composite, using date palm annual pruning residue, such as rachis or leaflet, as filler and investigated the effects of filler content and type on the physical and mechanical properties of the obtained composite. The effect of lignin in the lignocellulosic residue on the properties of the composite was also evaluated. 2% Maleic anhydride modified polyethylene (MAPE) was used as a compatibilizer. It was observed that the increase of filler content caused the decrease of the flexural strength (MOR), tensile strength and impact strength, while increasing flexural modulus (MOE), water absorption and thickness swelling. In general, leaflet flour led to better properties of the composites than rachis flour. Delignified fibers increased the tensile strength, tensile modulus, impact strength, water absorption and thickness swelling of the composite.

Keywords: polymer-matrix composite, cellulose, lignin, mechanical properties, physical properties

INTRODUCTION

Wood plastic composites are primarily composed of wood (or other lignocellulosic materials) and virgin or waste thermoplastic polymers. Lignocellulosic materials include wood, agricultural crops, such as kenaf, agricultural residues, such as bagasse or corn stalks, agricultural pruning residue, such as date palm fronds, resulting from the annual pruning of date palm trees and other plant substances. In general, the characteristics of wood and other lignocellulosic biomass are similar, even though they may differ in chemical composition and fiber morphology (length and diameter). In fact, natural fibers are available in many different forms and produce different properties when added to thermoplastics.[1-4]

In general, wood flour is used as filler for plastic, which tends to increase the stiffness of the composite, but does not improve its strength. Natural fibers, however, can be used as reinforcement (increasing strength and stiffness) to the plastics, rather than just as filler. Individualized wood fibers (*e.g.* Kraft pulp) and other lignocellulosic fibers typically have higher aspect ratio than that of wood flour. At a critical fiber length, the stress is transferred from the matrix to the fiber, resulting in a stronger composite.[5] Stress can be transferred from the matrix to the fiber in the composites, if the fiber length exceeds critical length, resulting in a stronger composite. Most of the lignocellulose-plastics products are less stiff than solid wood and adding wood flour to plastic can stiffen it, while, on the other hand, it can also make it more brittle.[6]

The present work contributes to the widespread use of date palm residual fibers as a raw material for developing flour-polyethylene composites.

The objective of this study was to evaluate the influence of the date palm filler amount and type (lignocellulosic flour (DPLF) or holocellulose fiber (delignified fibers)) on the mechanical and physical properties of the reinforced linear low density polyethylene (LLDPE) composites.

The type of lignocellulosic fiber and its chemical composition (lignin, cellulose and hemicelluloses content) have a strong influence on mechanical properties.[7] Lignin is a phenolic substance that binds the vegetable fibers and vessels, which constitute wood and other lignocellulosic materials.

Middle East is the major producer of palm dates in the world and Iran is the second producer (after Egypt) of dates in this area.[8] Indeed, date palm leaves are one of the important natural sources of fibers and their applications have been extended to almost all fields.[9] Moreover, we need to consider date palm as a raw material source for industrial purposes.[10]

Lignin generally makes the product weaker, because it easily burns in the course of processing and releases CO_2, making the product density lower, and greatly accelerating fading of the lignocellulose-plastic after outdoor exposure. In this study, date palm lignocellulosic flour with and without lignin was used to make boards for investigating the role of lignin on the performance of the composites.

EXPERIMENTAL

Matrix polymer

Linear low density polyethylene (LLDPE), LL0220CA (off-grade), with a melt flow index of 2-2.5 g/10 min (at 190 °C), a density of 0.917-0.920 g/cm^3 and a melting temperature of 150 °C, was used as powder polymer matrix and was obtained from Arak Petrochemical Corporation (Iran). The melting point was determined employing the differential scanning calorimetry method (DSC), according to ASTM D3418.

Filler

The lignocellulosic flour used as filler was obtained from the rachis and leaflet of the date palm tree, resulting from its annual pruning, Sayer cultivar from Khuzestan, in Iran. The contents of flour used in the present research were of 35, 50 and 65% by weight, which were used as the discontinuous phase in the composites.

Before grinding, the date palm tree pruning residues were air-dried until they reached moisture equilibrium and then a part was ground with a small laboratory grinder. The content retained on the 40-mesh screen was oven-dried at 100±5 °C for 24 h to remove moisture and then it was stored in sealed plastic bags prior to compounding. The rest was delignified with the use of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) as a main liquid of the Kraft process. The Kraft process is the most common pulping method for conversion of wood into wood pulp consisting of individualized cellulose fibers.[11]

Compatibilizing agent

Polyethylene maleic anhydride (MAPE) was used as a compatibilizing agent. A fixed amount of 2% (by mass) of MAPE was used in the sample preparation, as selected in previous research. MAPE was used to obtain better bonding between the hydrophilic fibers and particles, and the hydrophobic LLDPE matrix. Maleated polyolefins are usually used at 1-5% by weight in a WPC formulation. An improvement in the properties of WPC materials can be achieved by a number of methods, like optimizing the manufacturing conditions and using additives in the formulation. Adding a coupling agent can amend the properties as well, but it should be considered that adding the right amount of it will not necessarily improve the properties. Also, a comparison among different sets of data regarding WPC boards reported by different researchers is difficult, considering the different production equipment, manufacturing speeds, coupling agents, their different levels *etc.* used to produce the composites.[12]

Compounding

The mix-design used for the composites is presented in Table 1. The materials for each treatment, DPLF/LLDPE composites were prepared in a twin-screw extruder, model 4815, L/D ratio 21, at 7 rpm with the temperature profile of 150, 150, 145, 145, 150 and 145 °C at the zones 1, 2, 3, 4, 5, 6 and 7 (die zone), respectively. LDPE typically has long side-chain branching off the main molecular chain and therefore is a more amorphous polymer. It has a relatively low-melting temperature (typically between 106 and 130 °C, depending on the density/branching of PE).[12] The composites were granulated and dried at 103±2 °C for 24 h to eliminate residual humidity from the fiber and stored in sealed packs containing a desiccant to avoid unexpected moisture infiltration before hot-press forming.[11]

Three panels were produced for each treatment (three replicates). To prepare the composites, each mixture was separately spread as randomly as possible inside a metal frame and a wooden box with dimensions of 20×15 ×0.5 cm in order to form a mat (Fig. 1a). This mat was cold pressed by using a wooden sheet (Fig. 1b) and wrapped in aluminum foil (Fig. 1c). The final composites were made by pressing the prepared mats between the hot steel plates by employing the combinations of temperature and pressure in three stages. The final composites were made by pressing the wrapped mat at 160 °C for 1 min at 30-35 bar pressure, followed by removal of the pressure for 4 min to allow steam to be ejected. Then, a second time the 30-35 bar pressure was applied for 5 min. The composite was cooled at 30-35 bar pressure by placing it between two cold plates for another 5 min. All the obtained materials were kept at 25 °C with 25% humidity during 48 h before mechanical testing according to ASTM D618-99.

Table 1
DPLF-plastic composite formulations (percent by weight)

Denotation	Filler type	Filler (%)	LLDPE (%)	MAPE (%)
L/35	Leaflet	35	63	2
L/50	Leaflet	50	48	2
L/65	Leaflet	65	33	2
R/35	Rachis	35	63	2
R/50	Rachis	50	48	2
R/65	Rachis	65	33	2
L/35/D	Leaflet (delignified)	35	63	2
L/50/D	Leaflet (delignified)	50	48	2
L/65/D	Leaflet (delignified)	65	33	2
R/35/D	Rachis (delignified)	35	63	2
R/50/D	Rachis (delignified)	50	48	2
R/65/D	Rachis (delignified)	60	33	2

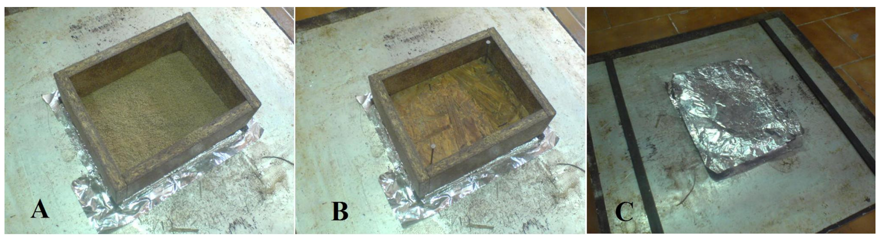

Figure 1: Randomly dispersed mat (A), cold pressing (B) and wrapping in aluminum foil (C)

The chemical constituents of different parts of date pam tree fronds and the fiber properties of date leaflet and rachis, as well as a comparison of particle dimensions, are reported in our previous study.[11]

Mechanical and physical tests

The tensile and flexural strengths (modulus of rupture-MOR and modulus of elasticity-MOE) were evaluated following ASTM D-638 and ASTM D-7031 standards, respectively. Tensile and flexural testing was performed using a universal testing machine (Schenck Trebel, USA). Impact strength (J/m) was evaluated following ASTM D-256 standard by a Santam testing machine (England). ASTM D-570 standard was used for water absorption and thickness swelling tests. These tests were carried out at 25 °C. The obtained results presented here are the average of three measurements obtained for each treatment.

RESULTS AND DISCUSSION

It was observed that the increase of filler content caused a decrease of the flexural strength (MOR), tensile strength and impact strength, while increasing the flexural modulus (MOE), water absorption and thickness swelling. In general, leaflet flour led to better properties of the composites than rachis flour. Delignified fibers increased the tensile strength, tensile modulus, impact strength, water absorption and thickness swelling of the composites.

The composites presented lower properties when the filler content increased, and an increase in mechanical properties was observed when pulped particles were used. It indicates that this behavior is associated to the low resistance of the filler-matrix interface and the incorporation of a bonding agent or fiber treatment is necessary when preparing any material that demands higher mechanical resistance.

Flexural strength (MOR)

The MOR values of the specimens under different conditions are shown in Figure 2. In general, the flexural strength decreased as the DPLF content increased. This implies that the decrease in flexural strength resulting from the addition of the DPLF is inversely related to the increase in brittleness.

The strength of the composite is dictated in part by the quality of the bond at the particle-matrix interface, which allows stress transfer from the matrix to the filler. It seems that there was no sufficient quality bond between the matrix and DPLF.

No significant difference was observed between the composites made with leaflet flour and those with rachis flour, while both had significantly lower flexural strength than the composites made with delignified fibers. It seems that the higher aspect ratio and higher cellulose content in the delignified fibers provide higher flexural properties for the ensuing composites. Higher cellulose content means higher OH available groups at the fiber surface for bonding with the matrix.

This result is consistent with previous findings. Zabihzade *et al.*[4] found that an increase of filler content reduced the flexural strength of rapeseed/PP composites significantly. Halimatuddahliana *et al.*[13] also reported that decreased flexural strength was caused by an increase in the filler content. This has been attributed to the poor filler dispersion and increasing tendency of particle agglomeration as filler loading increases.

Flexural modulus (MOE)

Increasing the filler content increased flexural modulus (Fig. 3). Figure 3 shows the MOE values of the composites under different conditions. No clear differences can be observed between composites made with leaf and rachis flour, for both treatments before and after pulping. The MOE of the constituents has a major effect on the MOE of the final composite, so regarding the higher modulus of lignocellulosic flour than that of polyethylene, it can be expected that with increasing filler content, the flexural modulus will increase. With the exception of the composites with 65% of leaflet pulped fibers, the composites made with pulped fibers presented lower MOE values compared to the composites reinforced with particles before pulping.

Tensile strength

The factor that crucially affects the mechanical properties of fiber-reinforced materials is the fiber-matrix interfacial adhesion. The quality of interfacial bonding is determined by several factors, such as the nature of fiber and polymer components, the fiber aspect ratio, the processing method and the treatment of the fiber.[14] The results for the tensile strength of DPLF/LLDPE composites are shown in Figure 4.

The highest tensile strength was observed for the 35% delignified leaflet fiber specimens and the lowest tensile strength for those with 65% stem flour. There is a statistical significance in tensile strength between composites with different filler contents and between those with DPLF with and without lignin. The highest tensile strength among specimens with particles before pulping was obtained with leaflet flour. The loss in tensile strength with an increased filler content may be due to agglomeration of the particles, which decreases the wettability of the particles by the LLDE matrix, and thus weakens the filler–matrix interface. Tensile strength is dependent on interfacial adhesion between the phases. If adhesion is not perfect, it is expected that voids will appear in the interfacial region and will favor the failure of the composite in this region. Lack of adhesion between particles and the matrix makes this region weaker.[15-18] Also, lack of lignin in the pulped fibers improved the interfacial adhesion between the phases.

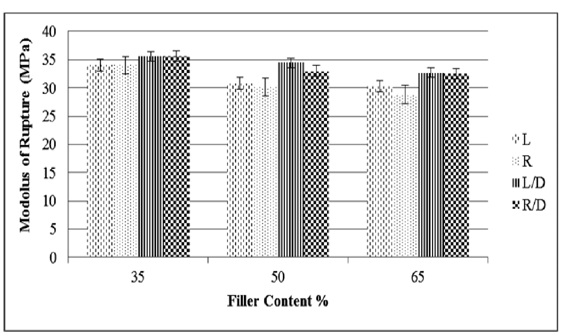

Figure 2: Modulus of rupture of composites with different DPLF content and different filler type

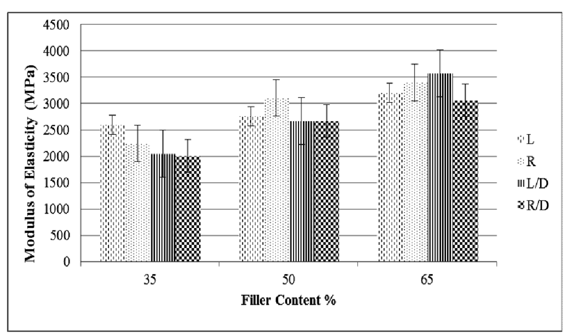

Figure 3: Modulus of elasticity of composites with different DPLF content and different filler type

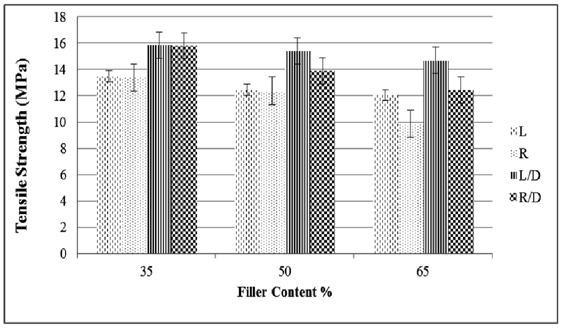

Figure 4: Tensile strength of composites with different DPLF content and different filler type

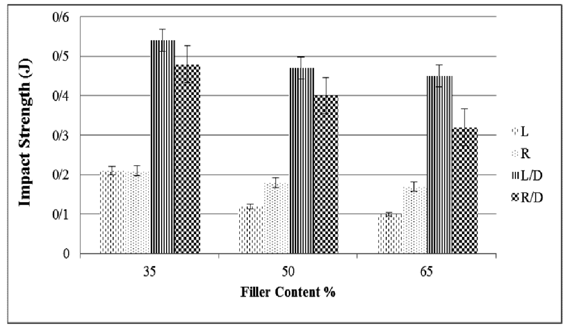

Figure 5: Impact strength of composites with different DPLF content and different filler type

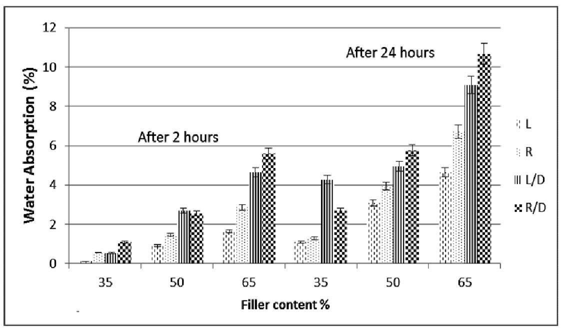

Figure 6: Water absorption of composites with different DPLF content and different filler type

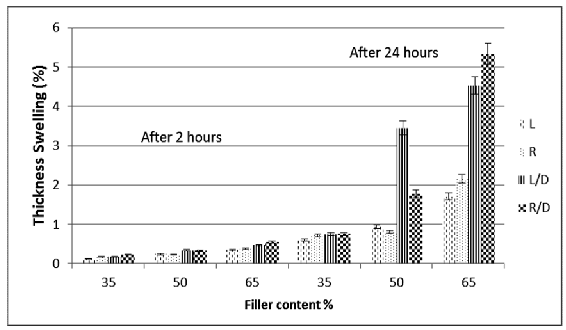

Figure 7: Thickness swelling of composites with different DPLF content and different filler type

Impact strength

The impact strength of the composites is shown in Figure 5. As may be noted, the higher the filler content the lower the impact strength values. The main factor influencing impact strength was the aspect ratio of the lignocellulosic filler. It is observed that the composites with pulped fibers presented higher impact strength than those reinforced with particles before pulping (delignified fibers). For delignified fibers, it was observed that leaflet flour composites showed better performance than rachis flour composites. The contrary was observed for the composites with particles before pulping, thus the composites with unmodified rachis presented improved performance in impact strength compared to the composites with unmodified leaflet particles. When impact load is applied to a composite specimen, stress concentration occurs, consequently, specimen fracture appears at the interface area between the reinforcement and the matrix. Therefore, a longer reinforcing filler can stand greater impact forces than a shorter aspect ratio reinforcing component. On the other hand, the lignin content of leaflet flour is higher than that of rachis flour and the lignin content of delignified rachis is higher than that of leaflet flour. Consequently, a smaller amount of lignin caused better strength. Higher content of cellulose is expected to contribute to higher impact strength in the composite due to an improved interfacial adhesion between the two different phases. MAPE seems to improve the particle-matrix interface and helps absorbing impact energy, as a result, its presence leads to higher impact strength.

Water absorption and thickness swelling

A number of studies have clearly shown that lignocellulose-plastics gradually absorb moisture and eventually decay, whereas there is a belief that the plastic encapsulates lignocellulose particles and thereby protects them from fungal attack.[19]

The water sorption and thickness swelling (2 and 24 h) of the composites were found to increase with an increase in the filler content (Figs. 6 and 7). Pulping of the particles increased the water absorption and the thickness swelling of the composites. In general, lignocellulosic-plastic composites absorb a small amount of moisture if they are made in such a way that the wood component is fully encapsulated by the plastic, consequently, it seems that the pulped fibers were not encapsulated well enough. Also, lignin is a hydrophobic substance and its partial removal from the particles during pulping causes higher water absorption by the cellulose and hemicellulose.[20]

CONCLUSION

This paper reports the results of an experimental investigation on the effect of fiber pulping on the mechanical properties of date palm lignocellulosic flour-polyethylene composites. The results of the composites made with various parts of date palm tree pruning showed that the aspect ratio and DPLF chemical components lead to important effects on the composite strength. It was observed that the increase of filler content causes a decrease of the flexural strength (MOR), tensile strength and impact strength, while increasing the flexural modulus (MOE), water absorption and thickness swelling of the composites. In general, leaflet flour led to better properties of the composites than rachis flour particles. Also, it could be concluded that the presence of delignified fibers increased the tensile strength, tensile modulus, impact strength, water absorption and thickness swelling of the composites.

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