Effect of Treated and Untreated Filler Loading on the Mechanical, Morphological, and Water Absorption Properties of Water Hyacinth Fibers-Low Density Polyethylene Composites

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Abstract: *Cellulose obtained from water hyacinth* (Eichhornia crassiper) *fibers were blended with low-density polyethylene (LDPE), forming LDPE / water hyacinth fiber (WHF) composites. In this work, the effects of filler loading on the mechanical, morphological, and water absorbent properties of this composite were investigated. Two types of fibers were used, namely treated fibers (where some of the fibers were treated with coupling agent) and untreated fibers. It was found that the tensile strength of the composites increased with increasing of the filler concentration. The presence of coupling agent improved the interfacial bonding between the matrix and water hyacinth fibers, as evidenced by scanning electron microscopy (SEM). In addition, fiber loading increased the water absorption of the composites. The treated fibers showed a reduction in water uptake.*

Keywords: cellulose, water hyacinth fibers, low-density polyethylene

Abstrak: *Selulosa yang diperolehi dari serat keladi bunting* (Eichhornia crassiper) *yang diadunkan dalam polietilena berketumpatan rendah (LDPE) untuk menghasilkan komposit LDPE/serat keladi bunting (WHF). Dalam kajian ini, kesan pembebanan pengisi ke atas sifat-sifat mekanikal, sifat-sifat morfologi, dan penyerapan air telah dikaji. Dua jenis serat digunakan iaitu serat yang dirawat dan serat yang tidak dirawat, di mana sebahagian serat yang dirawat menggunakan agen pengserasi. Didapati bahawa kekuatan tensil komposit bertambah dengan pertambahan pembebanan pengisi. Kehadiran agen pengserasi telah meningkatkan ikatan antara muka di antara matrik dan serat keladi bunting seperti yang dilihat menggunakan mikroskop elektron imbasan (SEM). Penambahan pembebanan pengisi meningkatkan penyerapan air komposit. Serat yang telah dirawat menunjukkan pengurangan terhadap penyerapan air.*

Kata kunci: selulosa, serat keladi bunting, polietilena berketumpatan rendah

1. INTRODUCTION

Composites are comprised of a hard material with discontinuous reinforcement that is embedded in a weaker, continuous matrix. The reinforcement provides strength and rigidity, in order to help to support the structural load. The

matrix maintains the position and orientation of the reinforcement. Significantly, constituents of the composites retain their individual, physical and chemical properties. Yet together they produce a combination of qualities that the individual constituents would be incapable of producing alone.[1]

Recently, a number of results have been reported for thermoplastic composites. Many different types of organic fillers can be added into polyethylene, polypropylene and other thermoplastic polymers. Several different natural organic fillers such as wood fibers and flour, kenaf fibers, sago, rice starch, cornstarch, henequen fibers, and pineapple-leaf fibers, have been used as fillers in polymer matrices.[2–7] The addition of fillers into a polymer will affect the mechanical, thermal, and water absorbent properties of the composite. In addition, the properties of the composite will be unlike those of the pure polyethylene because of variations in the filler types, shape, dimension, percentage of filler loading, and presence of coupling agent.

According to Adhikary *et al.*,[2] the dimensional stability and strength of wood flour polyethylene composites can be improved by increasing the polymer content. Roshafima and Wan Aizan reported that the addition of starch into LDPE both decreased the mechanical properties and improved the biodegradebility of their composite.[5] In LDPE composites reinforced with pineapple-leaf fibers, George *et al*.[9] found that water uptake increased with the amount of fiber loading and that the mechanical properties of the composite decreased after exposure to water.

Although many researchers have experimented with organic filler polymer composites, there has been no study in which the cellulose obtained from water hyacinth *(E. crassiper)* has been used. Water hyacinth is an aquatic plant that can live and reproduce while freely floating on the surface of fresh water or while being anchored in mud. Water hyacinth can cause a variety of problems when its rapid mat-like proliferation covers large areas of fresh water. It can also cause practical problems for marine transportation, fishing, hydropower generation and irrigation. Water hyacinth has a high content of cellulose, which may be useful as a filler in polymeric composites.

Coupling agents play a critical role in composite materials. Zadorecki and Foldin[8] have found that some coupling agents, namely trichloro-striazine and di-methylol melamine, can produce covalent bonds between cellulosic materials and polymer matrices, leading to changes in performance and a reduced sensitivity to water. In the study by George *et al*.,[9] the addition of isocyanate (6% by weight of fibers) reduced the water uptake of LDPE composites reinforced with pineapple-leaf fibers. It was found that the presence of a silane

coupling agent had promoted the chemical interaction between henequen and high density polyethylene (HDPE) in the composite.[7]

In this study, the water hyacinth fibers were obtained from fresh water hyacinths in a local river. Some of the dried fibers underwent chemical treatments with the addition of coupling agents. The mechanical, morphological, and water absorbent properties of the treated and untreated fiber composites are studied.

2. EXPERIMENTAL

2.1 Materials

Water hyacinth fibers (WHF) were obtained from fresh water hyacinths in a local river. After a cleaning and drying process, the water hyacinth was ground into powder. Fibers that were smaller than 150 μm were selected by sieving analysis. The LDPE pallets (density = 0.91–0.94 g/cm^3, processing temperature = 134°C–210°C, melting temperature = 98°C–115°C, and melt flow index = 0.26) were supplied by Mega Makmur Sdn Bhd (Penang, Malaysia).

2.2 Preparation of Water Hyacinth Fibers

Stems of the fresh water hyacinth were cleaned and cut into small pieces. Then they were dried in an oven at 105°C for 1 h to evaporate the water content. The dried water hyacinth was then ground into powder, and labeled as water hyacinth fibers. After sieving, the fibers that were smaller than 150 μm were selected. The percentage of organic content was determined by heating the fibers for 3 h at 450°C.

The percentage of organic content was calculated by the following equation:

$$\mathrm{O_c}(\%) = \frac{W_I - W_F}{W_I} \times 100\% \quad (1)$$

where O_c is the percentage of organic content, W_I is the initial weight of the water hyacinth fibers and W_F is the weight of the fibers after heating. The level of organic content in the water hyacinth fibers was 80.15%.

2.3 Preparation of Treated Water Hyacinth Fibers

Water hyacinth fibers were treated with isocyanate, toluene, and polyethylene glycol (PEG). The fibers were dipped in a toluene solution containing isocyanate (5% by weight of ECP) for 30 min at 50°C. The fibers

were then decanted and dried in an air oven at 70°C for 2 h. Afterwards, the dried fibers were mixed with toluene, containing PEG (6% by weight of ECP), and dried at 120˚C for 30 min.

2.4 Composite Preparation

Composites were compounded using a Z-Blade mixer. Two types of composites were prepared by adding original water hyacinth fibers or treated WHF into LDPE matrix. Prior to the compounding process, the Z-Blade mixer was set at 180°C and the rotor speed was set to 50 rpm. Then, the LDPE pallets were loaded into the mixing chamber to preheat for 3 min. The WHF were then poured into the softened LDPE. The mixing process continued for 3 min in order to obtain homogeneous composites. Afterwards, the softened mixture was removed from the chamber and pressed into thick round pieces.

2.5 Compression Molding

In order to produce composites in the form of a plate, a hydraulic hot press was used. The machine was set at 180°C for both the top and bottom platens. Then, the empty mould was heated for 2 min. Later, the compounds were placed into the mould, preheated and compressed partially for 4 min. Once the compounds started to soften they were fully compressed for 2 min. After compression, the compounds were cooled for 2 min. The formulation of low-density polyethylene / water hyacinth composites, with and without treated WHF, is shown in Table 1.

Table 1: Formulations of LDPE / WHF composites, with and without treated fibers.

Blend composition	LDPE (phr)	WHF (phr)
LDPE	100	-
LDPE/WHF-5	100	5
LDPE/WHF-15	100	15
LDPE/WHF-25	100	25

2.6 Tensile Testing

An ASTM D638 was used in this study, with a crosshead speed of 50 mm/min. Dumbbell-shaped samples (50 mm in length and 4 mm wide at the neck) were used in all experiments. Five dumbbell-shaped samples were prepared for each different composition, in order to obtain the average value and standard deviation for each composite. The tensile strength, amount of elongation at the breaking point, and modulus of elasticity were obtained for each composite.

2.7 Scanning Electron Microscopy Study

Studies on the morphology of the tensile fracture surfaces of LDPE/WHF composites, with and without treated fibers, were carried out using a SEM, model JEOL JSM 6460LA. Sample surfaces were coated with a thin layer of palladium, approximately 12 μm thick, using an auto fine coater, model JEOL JFC 1600.

2.8 Water Absorption Test

The kinetics of water absorption was studied using a water absorption test. The sample dimensions were 20 x 10 x 1.5 mm. Prior to the test, the samples were dried in an oven at 50°C for 30 min in order to remove the water content. Then, the samples were totally immersed in distilled water for 14 days. After this period of immersion, samples were removed at fixed time intervals, wiped with filter paper to remove surface water and weighed using an analytical balance with a resolution of 0.1 mg.

The molar sorption, Q_t, of water by the composites at time t was calculated from

$$Q_t \text{ (mole \%)} = \frac{W_2 - W_1}{18 \; x \; W_1} \times 100\% \tag{2}$$

where W_1 is the weight of the dry sample and W_2 is the weight of the wet specimen. The molar sorption value for the last day (day 14) is represented by Q_∞.

According to Equation 3, the plot of log (Q_t/Q_∞) against log t shows how water absorption varies as a function of different compositions of LDPE/WHF composites.

$$\log \frac{Q_t}{Q_\infty} = \log k + n \log t \tag{3}$$

where k is a constant characteristic of the sample, which indicates the interaction between the sample and water.

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties

The effect of filler loading on the tensile strength of the LDPE/WHF composites is shown in Figure 1. The experimental results showed that the addition of untreated filler decreased the tensile strength of the LDPE/WHF composites. LDPE is hydrophobic by nature, while the cellulose fibers are

hydrophilic. Hence, these two incompatible constituents weaken the interfacial interactions between the molecules. The force needed to break these composites was lower than for pure LDPE.

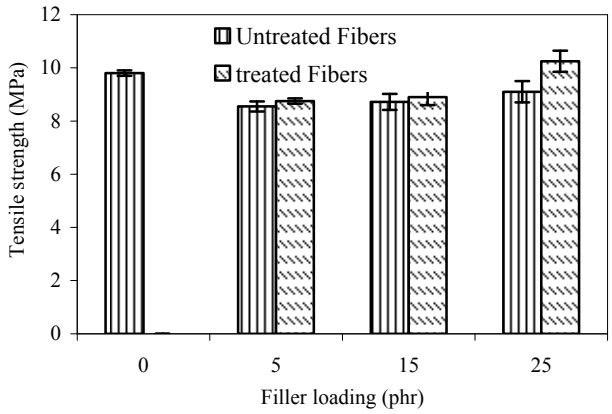


Figure 1: Effect of filler loading on the tensile strength of the LDPE/WHF composites with untreated and treated WHF.

However, as the filler loading continued to increase, from 5 phr to 25 phr, the tensile strength of the composites increased accordingly. As more fibers were added into the composites, the fibers were distributed homogeneously throughout the composites, thus increasing the tensile strength. The LDPE, acting as the matrix, will transfer the force to the fibers, which will carry most of the applied force. Hence, the fibers help to strengthen the composites. These results showed that as the filler loading reached 25 phr of the total weight of the LDPE, the tensile strength of the composite was comparable to that of pure LDPE.

The effect of having a coupling agent can also be seen in Figure 1. A similar trend of increasing tensile strength with filler loading was observed in treated fiber composites. At the same percentage of filler loading, the composites with treated fibers exhibited a slightly higher tensile strength compared to that of the untreated fiber composites. The presence of the coupling agent had improved the interfacial interaction between the two types of molecules, as shown in Figure 2. As a result, strong bonding was evident between the cellulose and the LDPE matrix. Therefore, the mechanical properties of the composites had improved.

Elongation at break of the pure LDPE was higher than the corresponding values for the treated or untreated fiber composites at any concentration of fiber. Even the presence of a coupling agent did not improve the miscibility of the components. In Figure 3, the pure LDPE exhibited high ductility before the break

and exceed 300% of the elongation at break. When 5 phr of the fillers were added to the composites, the elongation at break showed a sharp drop, to less than 70%. The elongation break is further reduced to less than 50% as the filler concentration increased to 15 phr and 25 phr. When the percentage of filler loading was increased, the ductility of the LDPE/WHF composites was greatly decreased. This demonstrates that the fillers had hardened the composites and reduced their ductility.

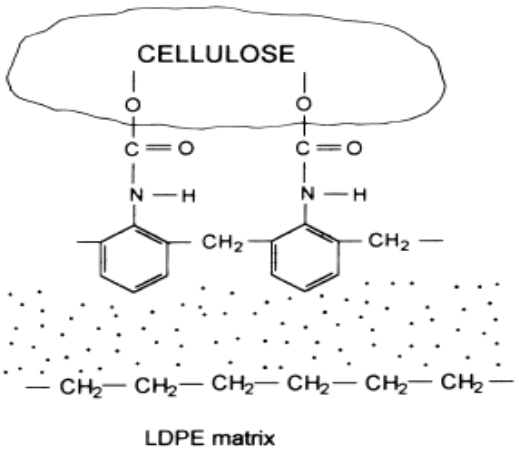


Figure 2: Reaction at the interface of fibers treated with isocyanate and LDPE.

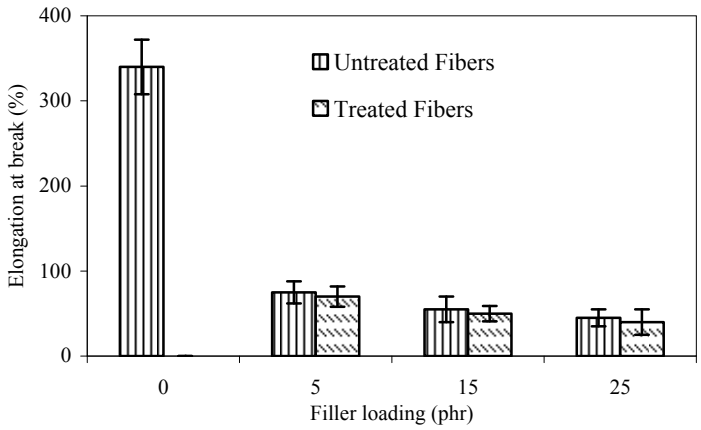


Figure 3: Effect of filler loading on the elongation at break of the LDPE/WHF composites with untreated and treated WHF.

Figure 4 shows Young's modulus for the pure LDPE and LDPE/WHF composites. Young's modulus of the composites increased as the filler loading increased from 5 phr to 15 phr and 25 phr. This result agrees with those from George et al.,[9] where the LDPE was reinforced with pineapple-leaf fibers. As the amount of filler loading with untreated fibers reaches 25 phr, Young's modulus increased nearly 150% compared to that of pure LDPE. The presence of the fillers had reduced the ductility of the composites and increased their stiffness.

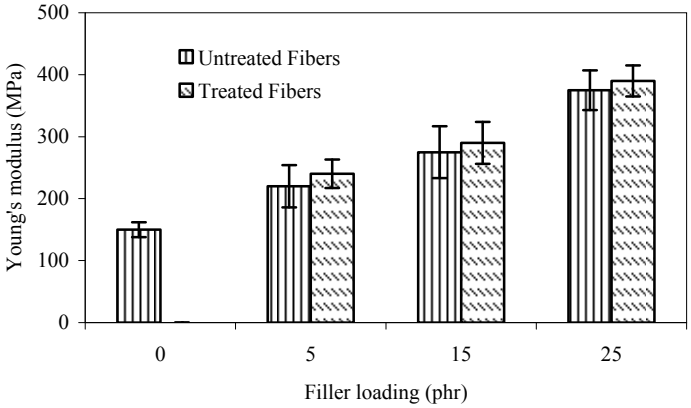


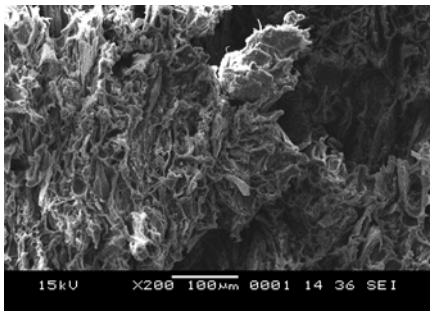
Figure 4: Effect of filler loading on Young's modulus of the LDPE/WHF composites with untreated and treated WHF.

3.2 Morphological Properties

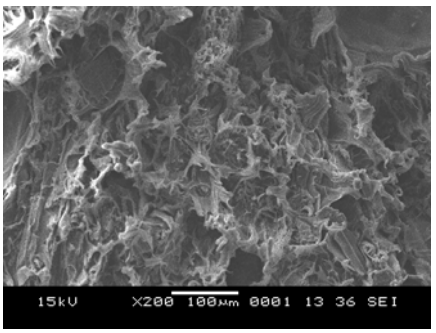
The same fracture surfaces, from the LDPE/WHF composites, used in the tensile tests were examined using the SEM. The fracture surface of the LDPE/WHF composites at a filler loading of 25 phr is shown in Figure 5 (a), in which numerous cavities and pulled-out fibers can be seen. The presence of these cavities and pulled-out fibers confirmed that the interfacial bonding between the filler and the polymer matrix was poor and weak. Also, the localised bunch of fibers and patches indicated the poor dispersion of fillers within the LDPE matrix. Thus, the fracture surface of the composite appeared to be dominated by pull-out damage rather than fiber breakage. A similar fracture surface was found by Adhikary et al. in wood plastic composites made of wood flour and HDPE.[2]

Figure 5 (b) shows the LDPE/WHF composites at a filler loading value of 25 phr, with the addition of isocyanate as a coupling agent. Because of the coupling agent, the composites showed better interfacial adhesion between the fibers and the matrix. There were more observable tear lines at the fracture surface of the composite. The tear lines indicated that the fracture occurred at the polymer matrix. Lesser cavities showed that the fibers are not pulled out directly

from the matrix, meaning that the permanent deformation occurs at the polymeric matrix.



(a)



(b)

Figure 5: SEM micrographs of the tensile fracture surface of LDPE/WHF composites with 25 phr of WHF: (a) without treated fibers, (b) with treated fibers.

3.2 Water Absorption Analysis

The absorption of water by non-polar polymers, which contain fillers, depends on the nature of the fibers. For cellulose fibers, which are hydrophilic fibers, an increase in water sorption can be expected. The equilibrium uptake values, Q_∞, of composites with different fiber loadings are given in Figure 7. It was clear that the Q_∞ value increased with increasing fiber content. Because LDPE is hydrophobic and the WHF is hydrophilic, the absorption of water depends solely on the fiber alone. As the fiber loading increased the cellulose content increased, which in turn resulted in the absorption of more water.

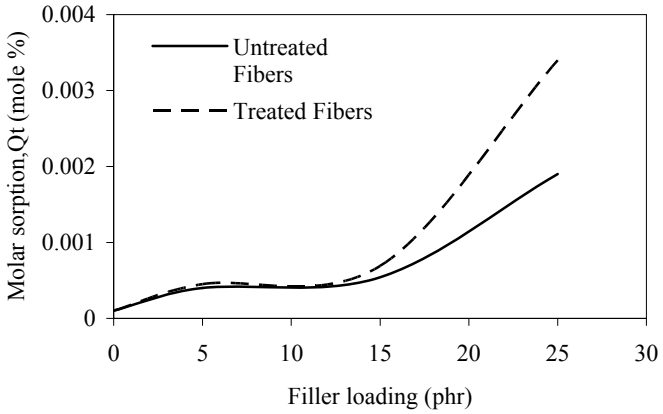


Figure 7: The effect of filler loading on the molar sorption of the composites.

George et al.[9] have reported that the hydrophilicity of the fibers can be reduced by a suitable chemical treatment. This finding agrees with the result shown in Figure 5. The treated fiber composites showed a lower degree of water absorption when compared to the untreated fiber composites. As a result of the chemical treatment, the hydroxyl group of the cellulose reacted with the functional group of the coupling agent, which in turn bonded to the polymer matrix and thus established a good fiber/matrix bonding interaction. Consequently, the chance of having hydroxyl groups come into contact with water molecules was reduced. Table 2 shows the effect of fiber loading on the water sorption constants *n* and *k*.

Table 2: The dependence of water sorption constants *n* and *k* on fiber loading for LDPE/WHF composites.

Type	Filler loading (wt%)	*n*	*k*
Pure LDPE	-	0.445	0.327
Untreated Fibers	5	0.272	0.432
	15	0.330	0.384
	25	0.325	0.414
	5	0.184	0.594
Treated Fibers	15	0.346	0.426
	25	0.325	0.404

4. CONCLUSION

The addition of WHF decreased the tensile strength of LDPE. However, as the fiber loading increased, the tensile strength was increased to the point of being comparable to that of pure LDPE. The presence of a coupling agent improved the mechanical properties of the composites. A comparison of the SEM micrographs for the fracture surfaces of the LDPE/WHF composites, with and without coupling agent, confirmed that the presence of the coupling agent, isocyanate, improved the interfacial bonding. The molar sorption of the composites increased with increasing fiber loading. The uptake of water was due to the increased cellulose content. In the presence of a coupling agent, the water uptake was reduced as better interfacial bonding was established.

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