Studies on Mechanical Properties of Polyethylene–Organic Fiber Composites. I. Nut Shell Flour

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SYNOPSIS

Composites were made from polyethylene and an organic fiber (pecan shell and peanut hull flour) using a compression-molding technique. Studies of variations in molding temperature (145–180°C), fiber concentration (0–40% by weight), and fiber mesh size (100, 200, and 325) were correlated to the mechanical properties of the composites (tensile strength, elongation, fracture energy, modulus, and impact strength). In untreated nut shell composites, tensile strength decreased steadily as the fiber concentration increased. This was due to poor bonding between the untreated fiber and polymer. Polyisocyanate was used as a coupling agent and its effect on mechanical properties of the composites was studied. Significant improvement in tensile strength was achieved with an isocyanate coupling agent, but it had no effect on modulus of the composites. Both untreated and isocyanate-treated composites had lower impact strength values; further composite matrix modifications would be necessary to maintain or improve impact strength.

INTRODUCTION

Organic fibers, residues, and wastes are used in quantity as an extender in thermosets and to a small extent as fillers in thermoplastic polymers.[1,2] The use of natural organic fibers in common thermoplastic resins such as polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), and polystyrene (PS) is attracting more attention because they offer significant weight advantages and provide the economic benefit of lower cost.[3–5] Cellulose fibers and ground nut shells contribute to a lower volume cost of filled resin, they are plentiful in supply, and, in addition, most of them are biodegradable. The market for biodegradable plastics is growing due to consumer awareness and the legislation drive. Some of the products are commercially available such as the commodity plastics employing different concentrations of starch (50%) in gelatinized or granular form.[6] The starch content is known to promote microbiological degradation and these materials are biodegradable within a reasonable time period. These products can be used in a variety of applications such as packaging, mulch films, shopping bags, films in hygenic products, medical implants, and marine applications.

Organic fillers, unlike those of inorganic fibers, are derived from renewable natural resources. Fillers such as nut shell flours are ground from walnut, peanut hull, and pecan shells. The most common limitation on the use of organic fillers is the poor compatibility between the hydrophilic filler and the hydrophobic thermoplastic polymer. A number of attempts have been made to improve the adhesion of cellulosic fibers to the polymer matrix by modifying the surface of the fiber or polymer matrix. Surface modification of the fibers is an important factor for the potential applications of fibers as reinforcements in thermoplastic polymers. Coupling/bonding agents, processing aids, and/or wetting agents are used according to the application of the material. The degree of adhesion can be widely different for each polymer–fiber combination, depending on the interface. The incorporation of various additives/coupling agents in polymer–fiber systems helps to promote the adhesion at the polymer–fiber interface, improves the degree of fiber dispersion,

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Table I Physical Characteristics of Fiber

	Mesh Size		
	100	200	325
Appearance	Gold-tan	Gold-tan	Light tan
Moisture content	6–7%	4–5%	4–6%
Specific gravity	1.21	1.23	1.25
Ash content	2.4%	2.4%	2.0%

increases the fiber loading in the polymer, and improves the processability (by controlling viscosity) and moldability.[7–11]

The purpose of this study was to examine the potential of low-cost nut shell flour as a reinforcing agent in high-density polyethylene. Reinforcing the polymer with nut shell flour can reduce the cost of the end product and increase its marketability for existing or any new applications. In the present work, the mechanical properties of high-density polyethylene (HDPE)–nut shell flour composites was investigated. A systematic study was made to determine the effect of variations in compression-molding temperature, the addition of a polyisocyanate coupling agent to improve fiber adhesion to the polyethylene matrix, fiber loading, and fiber mesh size on mechanical (tensile and impact) properties of HDPE–nut shell flour composites.

EXPERIMENTAL

Materials

High-density polyethylene (Novacor HDPE GRSN 8907, density: 0.954 g/cc, melt index: 7.5 g/10 min) was used as the polymer matrix. The nut shell flour was supplied by Southeastern Reduction Company, USA. Their physical characteristics are summarized in Table I. Figure 1(a) and (b) shows the fiber mesh sizes 100 and 325, respectively. The analysis of the three fiber mesh sizes (100, 200, and 325) is presented in Figure 2. The mesh 100 and 200 samples were blends consisting of 90% peanut hull and 10% pecan shell; the mesh 325 sample was 100% pecan shell flour. Peanut hull specifically refers to the light weight and light-colored outer shell and does not include a reddish brown thin cover next to the peanut (peanut skin). Also, pecan shell specifically refers to the hard tan-colored shell and does not include the reddish brown inner membrane. As produced, the moisture content of fiber was 4–7% and it tends to absorb ambient moisture rapidly. Therefore, the shells were predried at 60°C for 16 h before compounding them with the polymer. The coupling agent used was poly[methylene(polyphenyl isocyanate)] (PMPPIC; NCO content, 31.4%) obtained from BASF chemicals.

Preparation of Composites

Test samples were prepared by mixing PE and different concentrations of nut shell flour (0–40% by weight of fiber) in a C.W. Brabender roll mill equipped with corotating rollers. In a typical mixing process, a portion of the HDPE–nut shell flour mixture (in some cases with a coupling agent) was added to the heated rolls (170°C) and allowed to melt. The remaining mixture was gradually added and then the mixing was continued for 5 min. The resulting mixture was collected and ground to 20 mesh and compression-molded into dog-bone-shaped tensile specimens (ASTM D-638, Type V). In a typical compression-molding process, the mold was introduced at 85°C and the temperature on upper and lower platens was gradually increased to 155°C. After heating for 10 min under 3.4 MPa pressure, the molded samples were slowly cooled to room temperature while keeping the pressure constant during the process. Subsequently, test specimens were made at different molding temperatures (145, 165, and 180°C).

Mechanical Testing

Before testing, the samples were conditioned overnight at 23°C and 50% RH. Tensile properties were determined according to ASTM D-638 in an Instron Model 4201. A minimum of six samples was tested in each series and the test results were automatically calculated by an HP86B computer using the Instron 2412005 general tensile test program. The reported properties are (a) tensile strength, (b) elongation, (c) fracture energy (area under the stress–strain curve), and (d) tensile modulus (0.1% strain). Izod-impact strength (unnotched) of the samples was determined in a TMI 43-01 impact tester.

RESULTS AND DISCUSSION

Compression-Molding Temperature

Processing of a thermoplastic polymer–fiber system usually involves compounding and molding operations. A common limitation on the use of organic fibers in high-volume thermoplastics is temperature

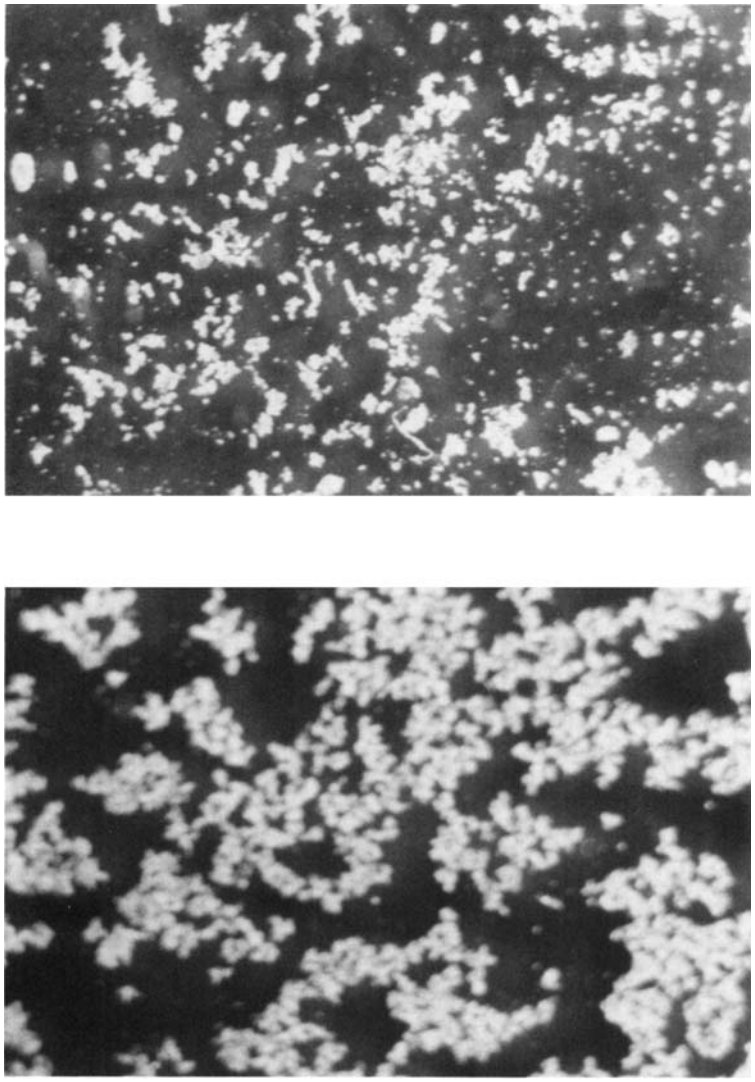

Figure 1 Optical micrograph of nut shell flour (a) mesh 100 and (b) mesh 325; magnification 250×.

stability. Therefore, the optimization of processing conditions to reduce the thermal degradation is a major concern for the fabrication of materials containing organic fiber. Figures 3 and 4 show the effect of variations in compression-molding temperature on tensile properties of HDPE–untreated nut shell flour (mesh 100) composites. Untreated nut shell flour was chosen specifically to study the maximum effect of processing conditions on the fiber. The results indicate a slight increase in tensile strength with the increase in molding temperature from 145 to 155°C. But, when the temperature was raised to 180°C, a decrease in tensile strength was observed (Fig. 3). Since the molding was done at higher temperature, it is possible that minor thermal degradation of the fiber occurred, which may be responsible in part for the decrease in tensile strength of the nut shell flour composites. It was revealed in an earlier study by Xanthos[12] that processing of PP–wood flour at high temperature led to degradation of the fiber and formation of voids in the composite.

Another interesting observation is that at 40% fiber content in the sample the tensile strength tends to decrease. The lower strength values at higher fiber loading, in untreated nut shell flour composites, is indicative of weak adhesion between the fiber and the PE matrix. Figure 3 also shows the plot of tensile modulus as a function of molding temperature. Tensile modulus was influenced less than was the tensile strength by the variation in molding temperature and it increased with the increase in nut shell flour loading in the composites.

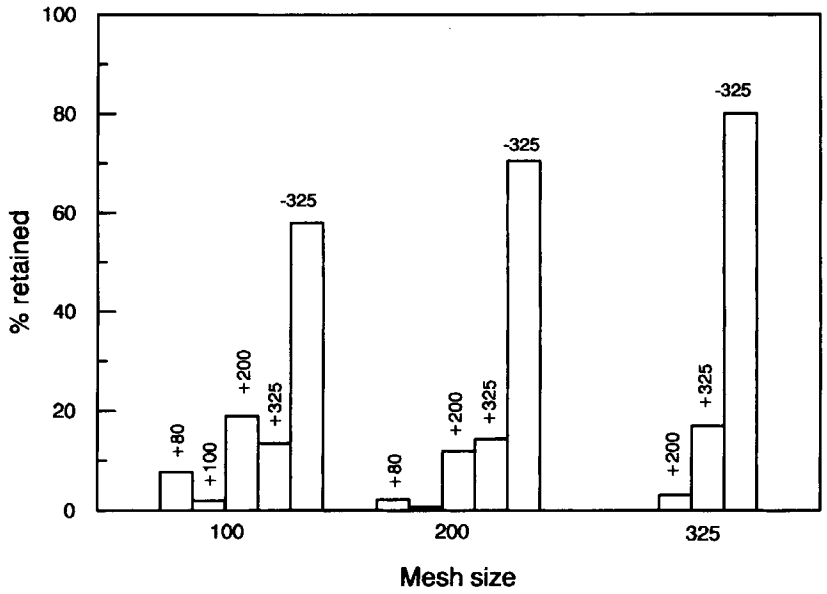

Figure 2 Particle-size distribution of different mesh sizes 100, 200, and 325.

Figure 4 shows the effects of molding temperature on elongation and fracture energy of the composites. With the increase in molding temperature, the values of elongation and fracture energy decreased. It can also be seen that both the elongation and fracture energy decrease with an increase in nut shell flour loading in the composite. Thus, the results indicate that the tensile properties of the composite depend on the nature of the matrix–fiber adhesion and fiber loading. It is well known[4,5] that as the tensile strength of the composite increases in value a given product increases in stiffness; this is usually at the expense of elongation.

PMPPIC Concentration

The application of coupling agents for fillers and reinforcements in polymer-filled systems has generally been directed toward improving the mechanical properties of composites. Coupling agents usu-

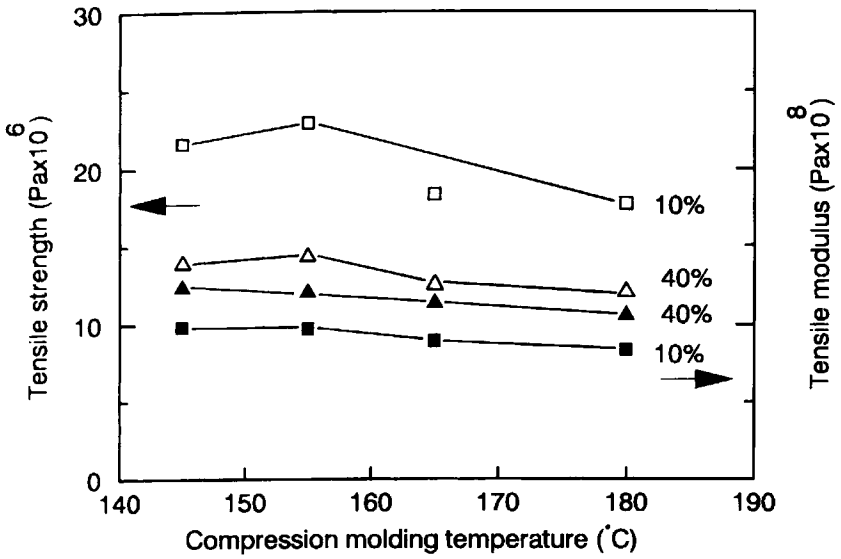

Figure 3 Tensile strength and modulus as a function of compression-molding temperature for HDPE–untreated nut shell flour (mesh 100) composites.

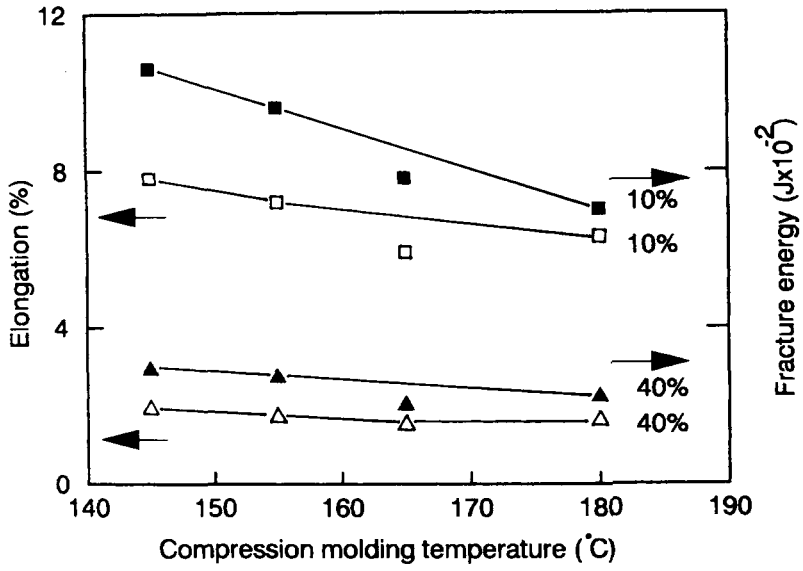

Figure 4 Elongation and fracture energy as a function of compression-molding temperature for HDPE–untreated nut shell flour (mesh 100) composites.

ally contain reactive groups capable of both reacting with the polymer and the fiber surface.[13,14] In the present study, a polyisocyanate was used as a coupling agent. Figure 5 shows the effect of isocyanate concentration on tensile strength and modulus of HDPE–nut shell flour (mesh 200) composites. Tensile strength increased significantly with the addition of PMPPIC. The PMPPIC-treated (5%) composites had a tensile strength of 30.1 Pa $\times$ 10^6 compared to 13.6 Pa $\times$ 10^6 of untreated shell flour composites at 40% fiber loading. The improvement in tensile strength with the addition of isocyanate is attributed to a higher degree of adhesion between the fiber and polymer as a result of the modification of fiber surface. The isocyanate reacts readily with hydroxyl groups of cellulose and lignin and forms a chemical linkage with the fiber surface. The modified fiber is linked to the polymer by secondary bonding to complete the bridgelike structure.

It can be seen that improvement in tensile

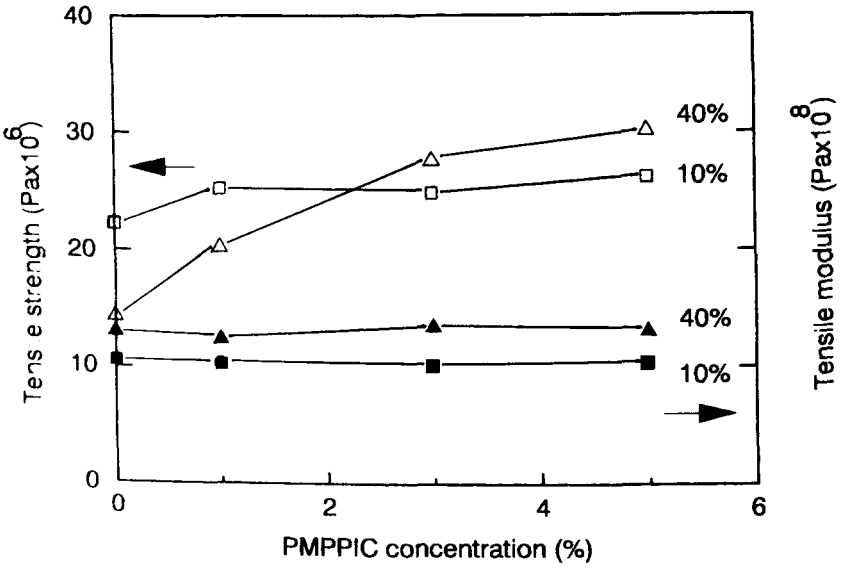

Figure 5 Effect of PMPPIC concentration on tensile strength and modulus of HDPE–nut shell flour (mesh 200) composites.

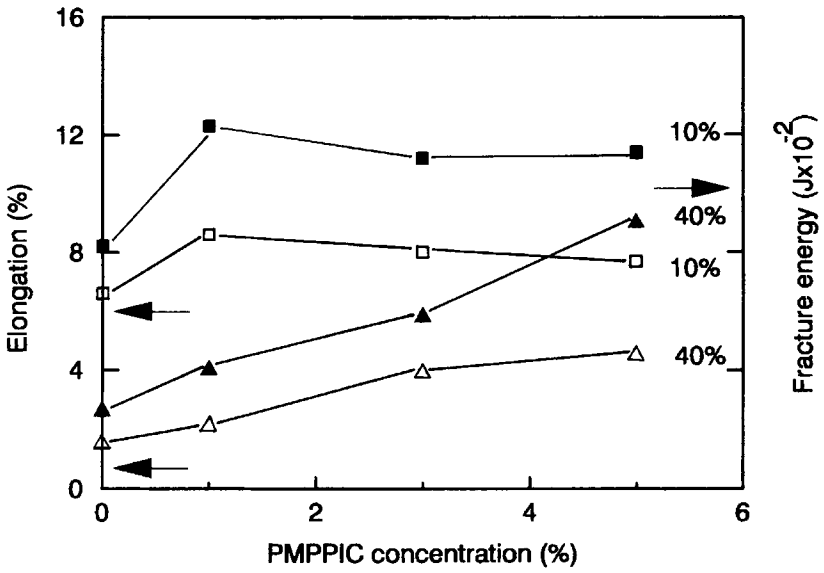

Figure 6 Effect of PMPPIC concentration on elongation and fracture energy of HDPE–nut shell flour (mesh 200) composites.

strength is greater at 40% nut shell flour loading than that of 10% nut shell flour in the composites. The results also show that the tensile strength increased steadily with PMPPIC concentration, at 40% nut shell flour, in the composites. The higher surface area of the fiber, with more hydroxyl groups capable of bonding, increases the bonding with the isocyanate. Thus, PMPPIC brings about improved surface coverage of the fiber, leading to an increase in tensile strength of the composite. In contrast, tensile modulus is not affected by the addition of PMPPIC and it increased with the increase in fiber loading (from 10 to 40%) in the composites.

The results from Figure 6 show that elongation and fracture energy are substantially higher for the samples containing 10% nut shell flour than for the samples with 40% nut shell flour. The elongation of the composite was also influenced by the PMPPIC concentration. At 5% PMPPIC concentration, the samples containing 40% nut shell flour showed an

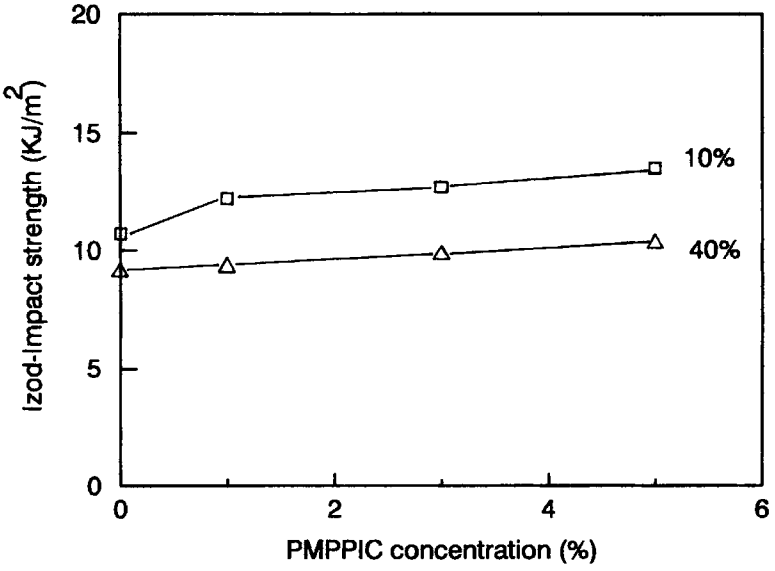

Figure 7 Effect of PMPPIC concentration on Izod-impact strength of HDPE–nut shell flour (mesh 200) composites.

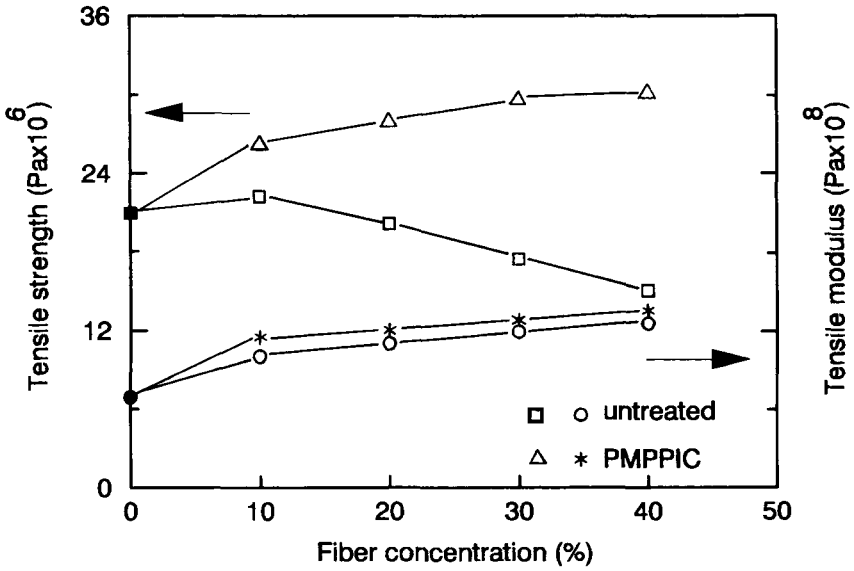

Figure 8 Tensile strength and modulus as a function of fiber concentration for HDPE–nut shell flour (mesh 200) composites.

elongation of 4.0% as compared to 1.7% of untreated fiber composite. The improved wetting of the fiber seems to have influenced the increase in elongation. The isocyanate coupling agent tends to increase the fracture energy of HDPE–nut shell flour composites. The best improvement in fracture energy was observed at 5% PMPPIC concentration, 6.7 J $\times$ 10^{-2}, as compared to 1.5 J $\times$ 10^{-2} of untreated fiber, which indicates a higher degree of interaction between fiber and matrix. The data from Figure 7 show that variation in isocyanate concentration has relatively a small effect on Izod-impact strength of the composites. However, lower impact strength values were observed, at 40% nut shell flour, with the increase in fiber loading in the composites.

Fiber Concentration

The strength of the composite depends on the efficiency with which the applied load is transferred through the matrix material to the reinforcing

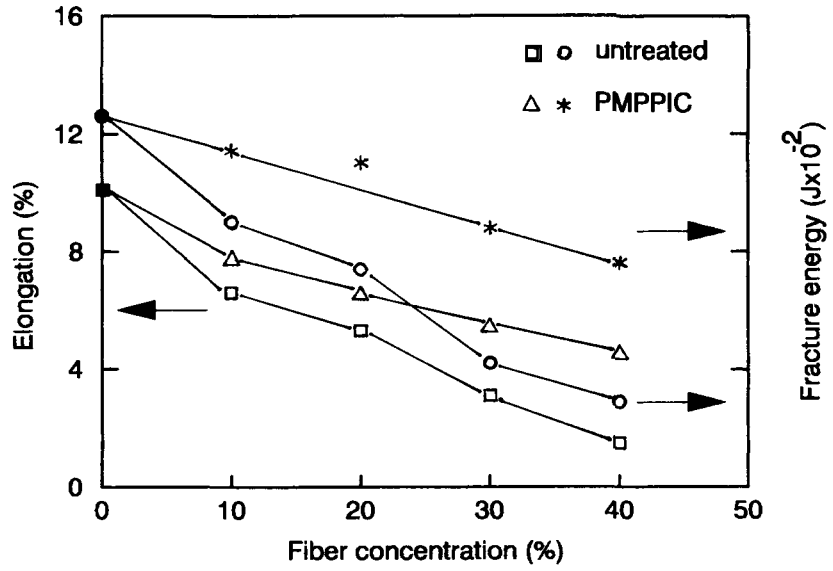

Figure 9 Elongation and fracture energy as a function of fiber concentration for HDPE–nut shell flour (mesh 200) composites.

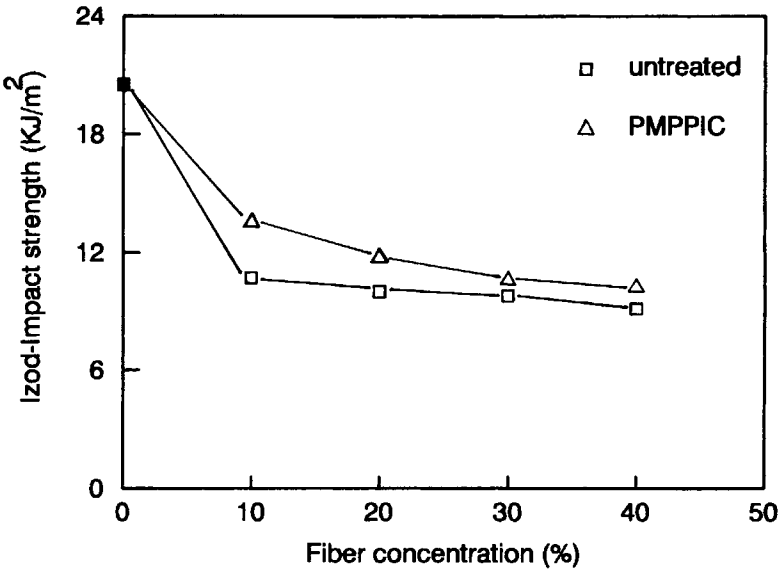

Figure 10 Izod-impact strength as a function of fiber concentration for HDPE–nut shell flour (mesh 200) composites.

agents, which is controlled by the adhesion at the fiber–matrix interface. Tensile properties of untreated and PMPPIC-treated (5%) nut shell flour (mesh 200) composites (molded at 155°C) as a function of fiber concentration is presented in Figures 8 and 9. Untreated nut shell flour composites showed a drastic drop in tensile strength with the increase in fiber concentration (Fig. 8). The opposite trend was found for HDPE filled with PMPPIC-treated nut shell flour, which showed a significant increase in tensile strength as the fiber concentration increased in the composite. At 40% fiber loading, the tensile strength reached 30.1×10^6 as compared to 26.2 Pa $\times$ 10^6 at 10% fiber loading. The results suggest that tensile strength of the composite is influenced by the fiber loading and the adhesion at the fiber–matrix interface. The isocyanate-treated samples also showed a more consistent increase in

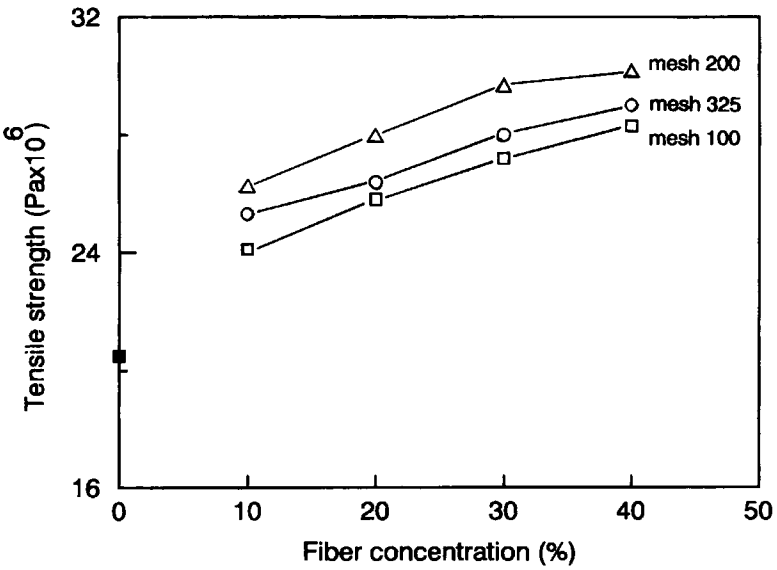

Figure 11 Effect of fiber mesh size on tensile strength of HDPE–nut shell flour composites.

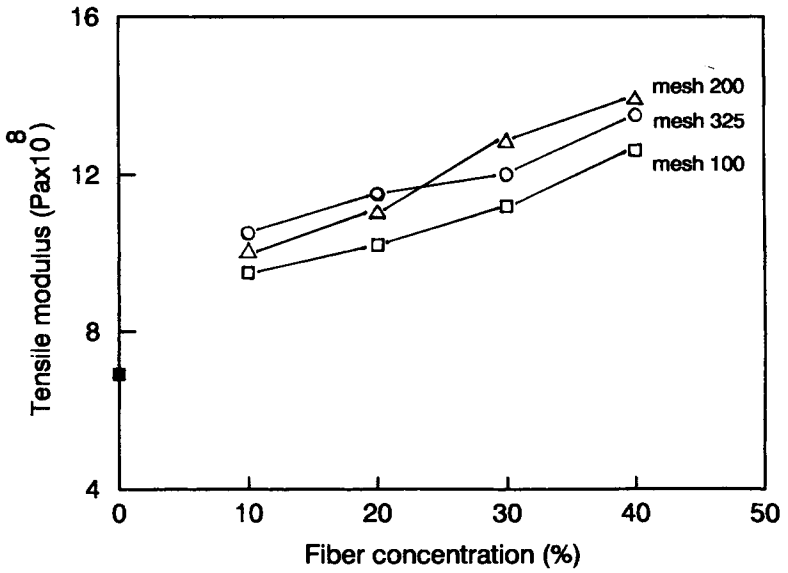

Figure 12 Effect of fiber mesh size on tensile modulus of HDPE–nut shell flour composites.

modulus than did the untreated nut shell flour composites.

Elongation of the composites containing untreated nut shell flour decreased more substantially with the increase in fiber loading as compared to samples containing PMPPIC-treated nut shell flour (Fig. 9). A similar trend was observed in the case of fracture energy of untreated and PMPPIC-treated nut shell flour composites with the increase in fiber loading. Izod-impact strength of the composites as a function of fiber concentration is shown in Figure 10. It can be seen that the impact strength decreased substantially with the addition of fiber and then it tends to level off at higher fiber loading in the composite. The addition of PMPPIC had only a moderate effect on impact strength. However, other matrix modifications are necessary to enhance the ability of the material to absorb energy under impact.

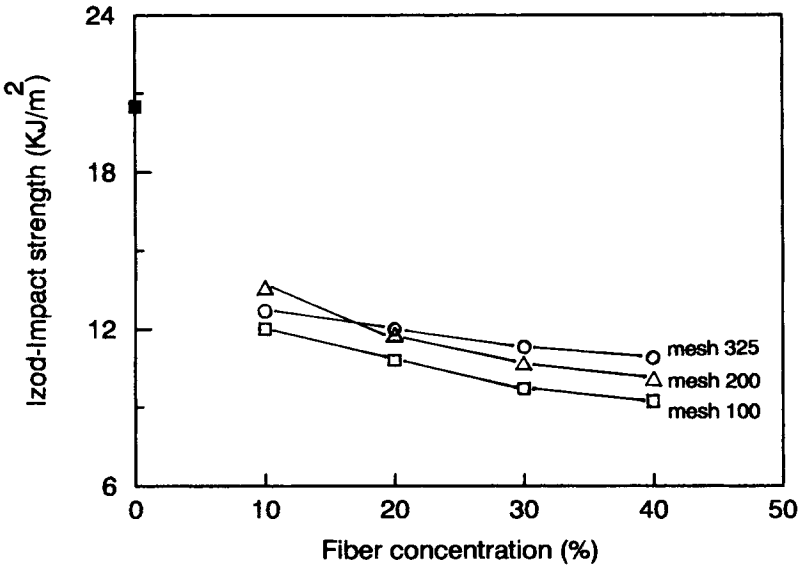

Figure 13 Effect of fiber mesh size on Izod-impact strength of HDPE–nut shell flour composites.

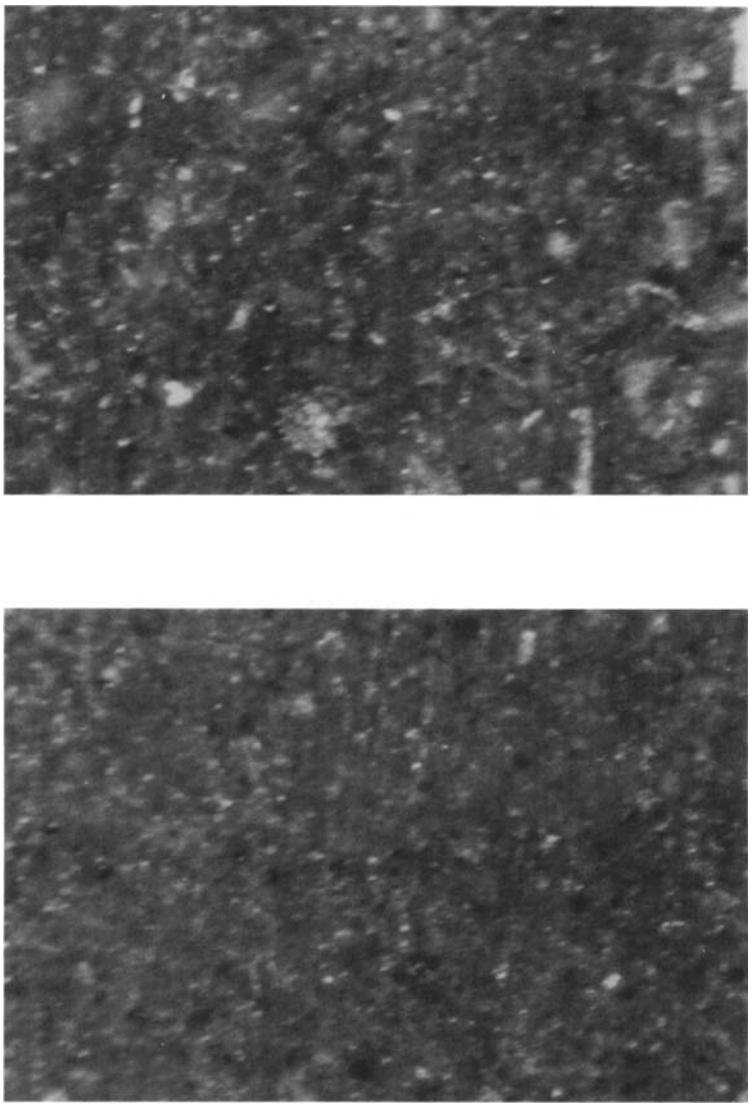

Figure 14 Fiber dispersion in HDPE–3% PMMPIC-treated nut shell flour composites (30% fiber loading); (a) mesh 100; (b) mesh 325. Magnification 500×.

Fiber Mesh Size

The effect of fiber mesh size on tensile strength and modulus of HDPE–nut shell flour (5% PMPPIC-treated) composites are presented in Figures 11 and 12, respectively. A moderate increase in tensile strength was observed with mesh 200 fibers (Fig. 11). Composites with mesh 100 pecan shell flour had slightly lower tensile strength as compared to mesh 200 and 325 nut shell flour composites. At lower fiber concentrations, tensile modulus was less affected by fiber mesh size (Fig. 12). However, at higher concentrations of fiber, a moderate increase in tensile modulus was observed for the samples containing mesh 200 and 325 nut shell flour. Composites with mesh 325 nut shell flour also showed higher impact strength values, at 30 and 40% fiber loading, as can be seen from Figure 13.

One of the possible explanations is that short fibers increase the amount of surface area contact between fiber and matrix. In an earlier study on PE–wood flour composites, Lightsey et al.[5] observed that decreasing particle sizes increased the interactions between filler and matrix. Also, in a discontinuous fiber composite, it is relatively easier to disperse short fibers in the polymer matrix than long fibers. The poor dispersion of mesh 100 nut shell flour was apparent in the optical micrograph of the composite [Fig. 14(a)]. On the other hand, composite containing mesh 325 nut shell flour showed a better

dispersion of fiber in the HDPE matrix [Fig. 14(b)] at the same concentration.

CONCLUSIONS

The addition of nut shell flour increases the stiffness of HDPE composites. Increase in fiber concentration reduced the elongation and impact strength of the composites. With the use of an isocyanate coupling agent, a significant improvement in tensile strength was achieved. Higher concentration of isocyanate had little effect on tensile modulus of the composites. Fiber mesh size had a small effect on mechanical properties. Izod-impact strength of HDPE–nut shell flour composite is low and was not influenced by the coupling agent or fiber mesh size. Additional composite matrix modification would be necessary for utilization requiring higher impact strength.

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