

Effect of Epolene E-43 as a Compatibilizer on the Mechanical Properties of Palm Fiber–Poly(propylene) Composites

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ABSTRACT: Composites of palm fibers and poly(propylene) (PP) were compounded in an extruder at 200°C. The composites were subsequently injection molded into standard tensile specimens for mechanical characterization. The fracture morphology of the specimens was analyzed by scanning electron microscopy. It was observed that the composite modulus increased with the increase of fiber content, indicating the existence of adhesion between PP and the much stiffer palm fibers. However, the adhesion was not satisfactory and resulted in a decrease in the composite tensile strength with fiber addition. The compatibilizer

Epolene E-43 was used to minimize this incompatibility between the wood fibers and the PP matrix. The maleated PP additive enhanced the fiber–matrix adhesion, resulting in an improvement in composite performance. Also, small fibers showed better mechanical properties than those of long fibers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2581–2592, 2004

Key words: fibers; poly(propylene) (PP); composites; compatibilization; maleated PP

INTRODUCTION

Composite materials based on fibers of natural polymers, such as wood cellulose fibers, and thermoplastics continue to attract much attention because of their remarkable environmental and economical advantages. The primary advantages of using cellulosic fibers as reinforcements in thermoplastics can be listed as low densities, low cost, nonabrasive nature, possibility of high filling levels, low energy consumption, high specific properties, biodegradability, availability of a wide variety of fibers throughout the world, and generation of a rural/agricultural-based economy.^{1–10}

Poly(propylene) (PP)/wood fiber composites have attracted special attention because of their wide applicability in automobile and panel manufacturing applications. These composites take advantage of the superior properties of PP compared to those of other thermoplastics, including easy processibility by all processing methods (molding, extrusion, film, and fiber manufacturing). In addition, PP is far superior to polyethylene in terms of heat resistance and mechanical properties. Its low density makes it especially attractive in lightweight applications that require strength. Furthermore, PP composites can be used in

electrical applications because of their excellent electrical properties.

The processing temperature of the cellulosic fibers in thermoplastics is limited, given the potential fiber degradation at higher temperatures. This limits their application to just the plastics with low melting temperatures. However, it has been reported that no deterioration of properties are observed when processing temperatures are maintained below about 200°C.¹¹ It has also been noted that, if the composite compositions are treated with sodium borate, boric acid, or phenolic resin, the chance of burning of the compositions during processing can be decreased.^{12,13}

The inherent polar and hydrophilic nature of the cellulosic fibers and the nonpolar characteristics of polyolefins create difficulties in compounding and result in inefficient composites. However, it has been shown that the use of compatibilizing and coupling agents for treating fibers before, or as an addition in, the compounding step enhances the compatibility and adhesion between the fibers and the matrix and the fiber dispersion in the matrix, thus improving the mechanical properties.^{14–24} The most common method for compatibilization is grafting matrix-compatible components to cellulose or grafting cellulose-compatible species to the thermoplastic molecules. Grafting can be achieved using plasma treatment, ionizing radiation, or reactive chemical additives. Another compatibilizing method is the use of coupling agents, which are materials that are compatible with cellulose and matrix polymer, such as silanes and

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stearic acid.²⁵ Electron-beam treatment of cellulose-thermoplastic composites significantly improved the properties of the composites in the presence of reactive agents.^{26,27}

Various chemical reagents have been used to enhance the compatibility between the constituent materials. These include Epolene G-3002,²⁸ Epolene E-43 (maleic anhydride-modified PP),¹⁷ poly[methylene-(polyphenyl isocyanate)]³⁰ (PMPPIC), γ -methacryloxypropyltrimethoxysilane, poly(propylene acrylic acid), poly(propylene-ethylene acrylic acid),²⁹ and 3-aminopropyltriethoxysilane.³¹

Maleated (maleic anhydride-modified) PP has been particularly successful as a coupling agent in cellulose-PP composites, improving the mechanical properties as a consequence of enhanced interfacial adhesion.^{4,11,17,30-34} It has been reported that cellulose fibers treated with the copolymer turned totally hydrophobic as a result of the concentration of a considerable amount of copolymer on the fiber surfaces.⁴

It has also been reported that cellulose fibers can be surface modified using propylene-maleic anhydride copolymers and that the modifying agent was covalently bonded to the fibers through esterification.³⁵ Another study also showed that the maleic anhydride grafter styrene-ethylene/butylene-styrene block copolymer rubber (MAH-SEBS) forms strong chemical bonds with the surface of the cellulose fibers.³⁵

The objective of this study was to investigate the feasibility, in terms of mechanical properties, for using wood fibers obtained from waste palm tree branches in reinforcing PP with Epolene E-43 (maleated PP) as the compatibilizer. Palm trees are abundant in the Kingdom of Saudi Arabia and PP is locally produced by Saudi Basic Industries (SABIC). If shown to be feasible, the use of waste palm tree branches in reinforcing thermoplastics would be an economical and useful service to the environment and society.

EXPERIMENTAL

Materials

Poly(propylene) used in the study was supplied by SABIC (Ladene-PP570P). The melt index of PP is 8 (2.16 kg and 230°C, ASTM 1238). It is a homopolymer commonly used for producing rigid injection-molded articles, with particular use in houseware items. The compatibilizer used in the study was Epolene E-43 (maleic anhydride-modified PP), supplied by Eastman Chemicals (Rochester, NY). Ethanol (97%) and toluene (98%) were supplied by BDH (Poole, UK).

Fiber preparation

Branches obtained from local palm trees were cut into pieces about 6 in. long. Thereafter the samples were

dried in the sun for a few days for moisture removal. The pieces of branches were then granulated to a small size using a granulator. The fibers were then size separated by use of a sieving machine. Two different size distributions of fibers (designated large and small fibers) were used for the study. The fiber size distributions were characterized using a digital vernier caliper. The lengths of the fibers were determined to be 4.77 ± 1.75 and 2.96 ± 1.19 mm for large and small fibers, respectively, both with an aspect ratio of about 11.

The obtained fibers were then cleaned to remove the organic compounds. Ethanol and toluene were used for cleaning in the ratio of 1 : 2 (v/v). The mixture of these two chemicals was prepared in a large container. The fibers were then soaked in the mixture and kept for about 2 days. The fibers were then washed with water and placed in an oven at 80°C to remove the moisture.

Composite processing

Mixing of the composite components was performed in a Model S-650/G126 single-screw extruder (Brabender Instruments, South Hackensack, NJ). The fibers and the resins were first physically mixed in a bowl and then transferred to the extruder. Optimum processing conditions that will produce samples with maximum dispersion of fibers, good mechanical properties, and good color and smell were determined through a detailed investigation. The study of the effect of compounding techniques will be reported in a separate communication. The mixed composite thus obtained from the extruder had a lumpy shape. It was granulated and transferred into a molding machine (Model ES 80/25 ST Pressure 160 bar, $T = 200^\circ\text{C}$; Engel Electronics, Ontario, Canada) to obtain tensile specimens of ASTM test standard D-648-94B.

Material characterization

The samples were mechanically characterized using an Instron 5560 mechanical testing machine (Instron, Poole, UK) according to ASTM test standard D-638. The tests were conducted at a constant strain rate of 2 mm/min.

The thermal characterization was carried out in a Mettler Toledo DSC 822C Star thermal analysis system (Columbus, OH). Weight of the samples was about 5 mg. All samples were subjected to the same sample thermal history by first heating to 220°C, and cooling from 220 to 20°C at a rate of 10°C/min. Thereafter the samples were heated at 10°C/min to 220°C.

A JSM-T-300 scanning electron microscope (JEOL, Tokyo, Japan) was used to analyze the fracture surface of the composites from the tensile tests. The objective was to obtain information regarding the effect of the

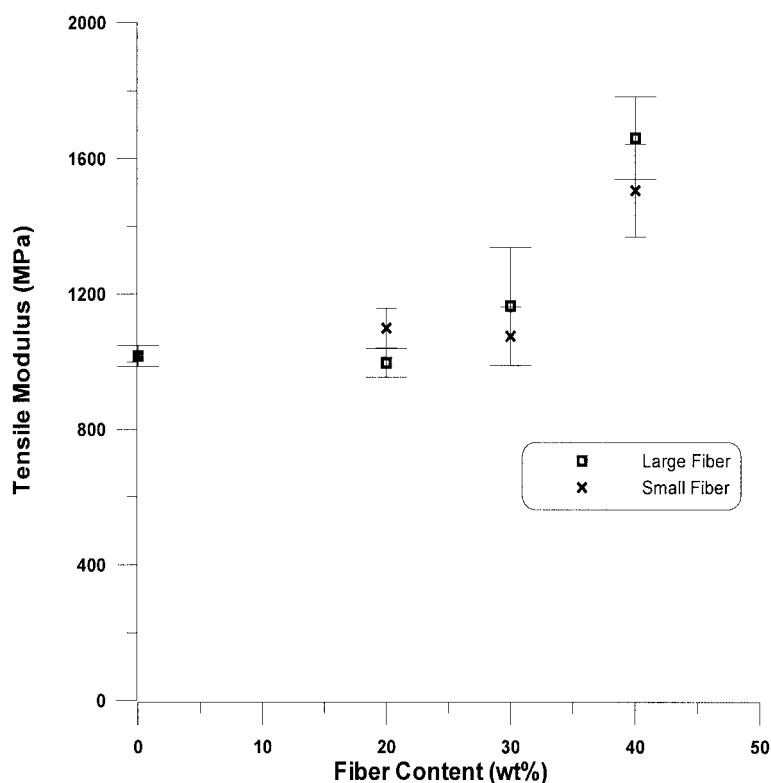


Figure 1 Tensile modulus versus fiber content for PP reinforced with small and large palm fibers.

compatibilizer on fiber dispersion and adhesion quality between fibers and the matrix. A JEOL fine-coat ion sputter was used to coat a thin layer of gold on the specimen to avoid electrostatic charging during examination. The fracture ends of the specimens were thereafter mounted on an aluminum stub for analysis.

RESULTS AND DISCUSSION

Figure 1 shows the effect of fiber size and content on the tensile modulus of the palm fiber–PP composite. As seen in the figure, the increase in fiber content increases the composite modulus for both small and large fibers, which is an indication of the existence of adhesion, to some extent, between PP and much stiffer palm fibers. For both small and large fibers, the increase in fiber content up to 30% showed only a slight increase in modulus. However, increasing the fiber content above 30% resulted in an appreciable increase in modulus.

Figure 2 shows the effect of fiber size and content on the tensile strength of palm fiber–PP composites. As the fiber content is increased, the tensile strength decreased. This might be attributed to the poor adhesion between the fiber and PP. Thus, does this result contradict the improvement in composite stiffness with fiber addition as just discussed above? The answer is no. The modulus is related to the stiffness of the

material before fracture and it is obtained from the slope of the straight portion of the stress–strain curve. Existence of adhesion (even weak) between fibers and the matrix would then improve the composite modulus. However, composite tensile strength is a result of material fracture at the weakest point of the material, which might occur below the matrix (PP) strength if the adhesion between the fibers and the matrix fails at a lower stress.

As also shown in Figures 1 and 2, the difference in the results obtained with small or large fibers was not significant, considering also the scatter in data. However, the composite strength with small fibers was still observed to be consistently higher than that with large fibers, whereas the same effect was not observed in the case of composite modulus. This was probably because of better mixing and more uniform distribution of small fibers in the PP matrix than that of large fibers. It is known that the composite properties greatly depend on the fiber aspect ratio.³⁶ Given that both small and large fibers have the same aspect ratio, the lower strength observed in the long fiber composites may be attributed to fiber–fiber interaction. Accumulation or nonuniform orientation of fibers at some parts of the composite can result in fracture at these weak points, thus giving lower strength in the case of larger fibers. Nonuniformities in fiber distribution here and there (if not so extensive) would not affect

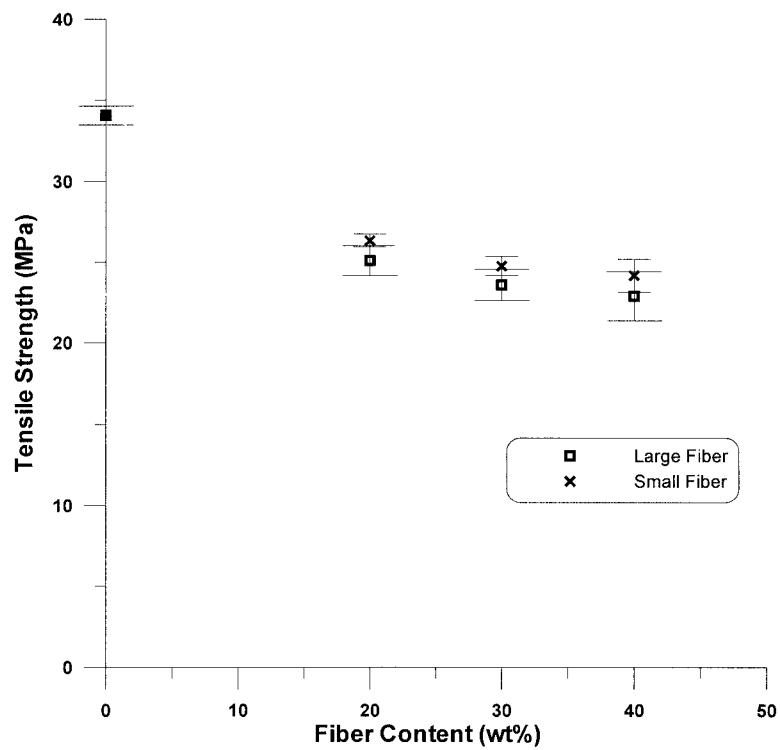


Figure 2 Tensile strength versus fiber content for PP reinforced with small and large palm fibers.

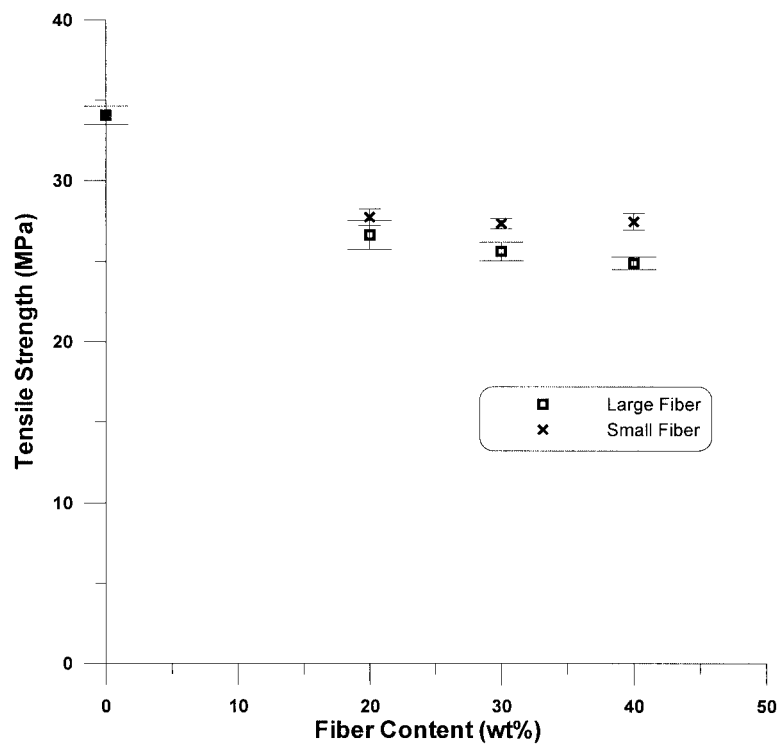


Figure 3 Tensile strength versus fiber content for palm fiber-PP matrix composites compatibilized by 2 wt % Epolene E-43.

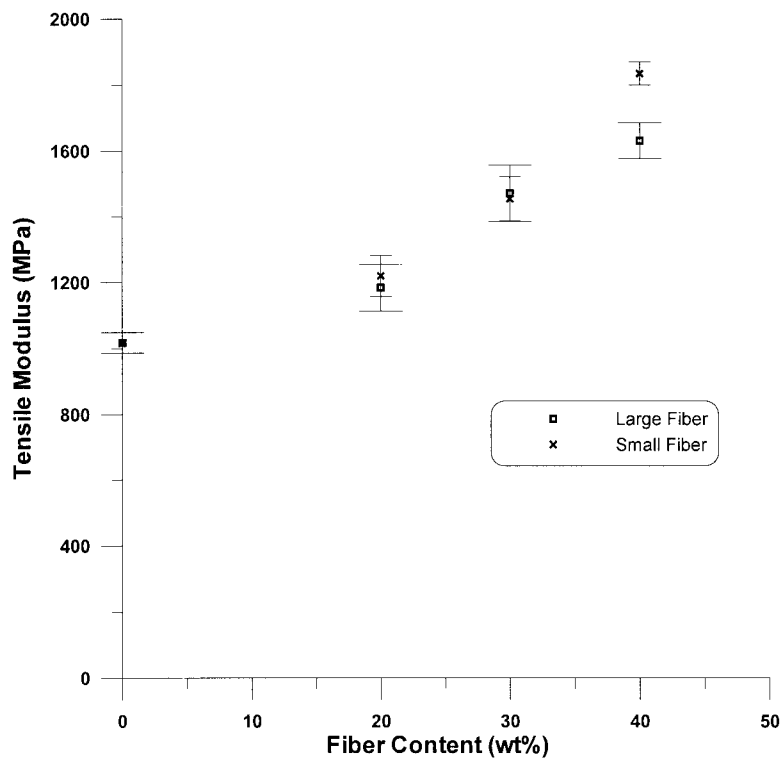


Figure 4 Tensile modulus versus fiber content for palm fiber-PP matrix composites compatibilized by 2 wt % Epolene E-43.

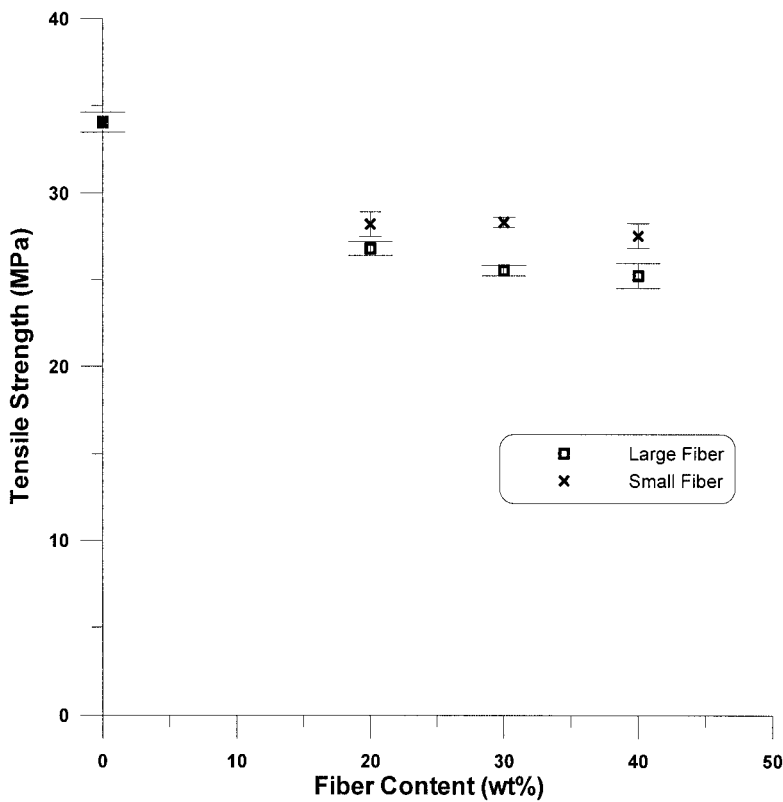


Figure 5 Tensile strength versus fiber content for palm fiber-PP matrix composites compatibilized by 4 wt % Epolene E-43.

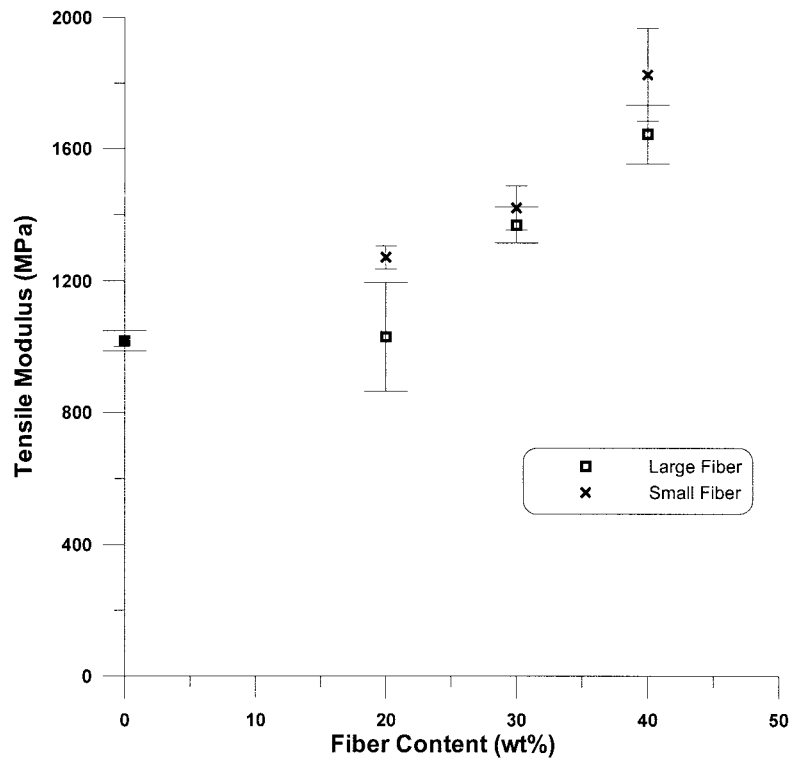


Figure 6 Tensile modulus versus fiber content for palm fiber-PP matrix composites compatibilized by 4 wt % Epolene E-43.

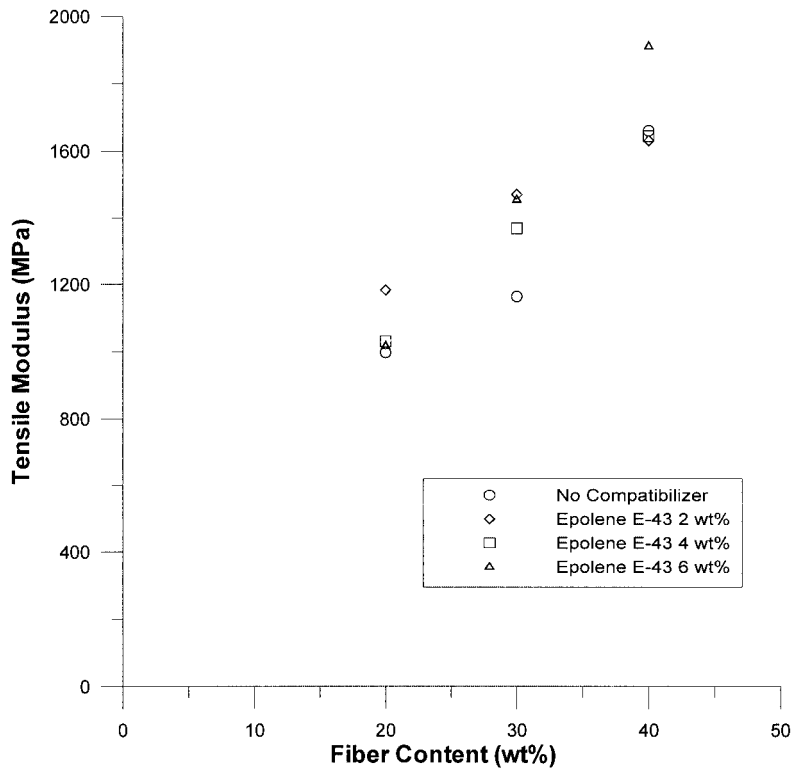


Figure 7 Tensile modulus versus fiber content for PP reinforced with large palm fibers without any treatment and with use of compatibilizer Epolene E-43 at various amounts.

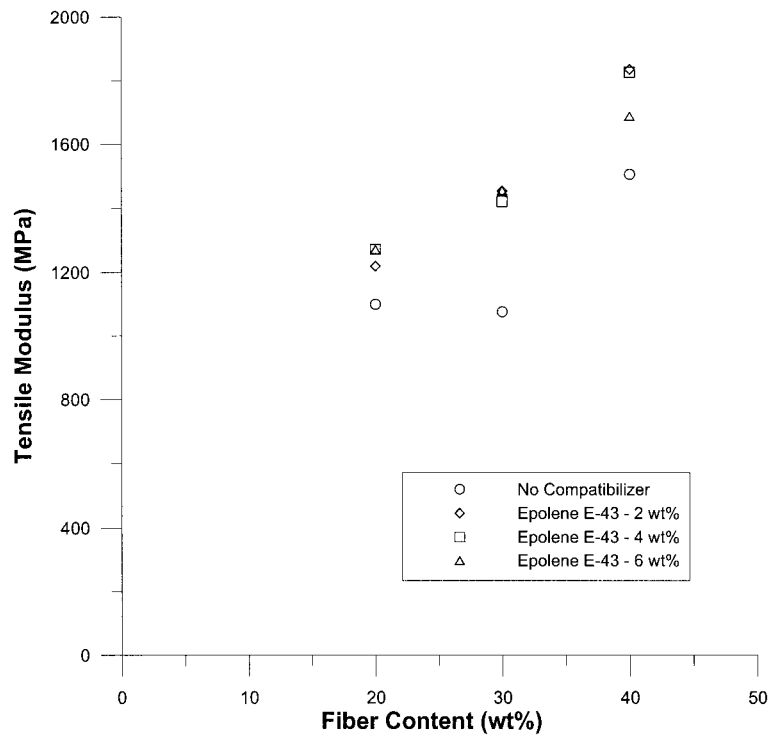


Figure 8 Tensile modulus versus fiber content for PP reinforced with small palm fibers without any treatment and with use of compatibilizer Epolene E-43 at various amounts.

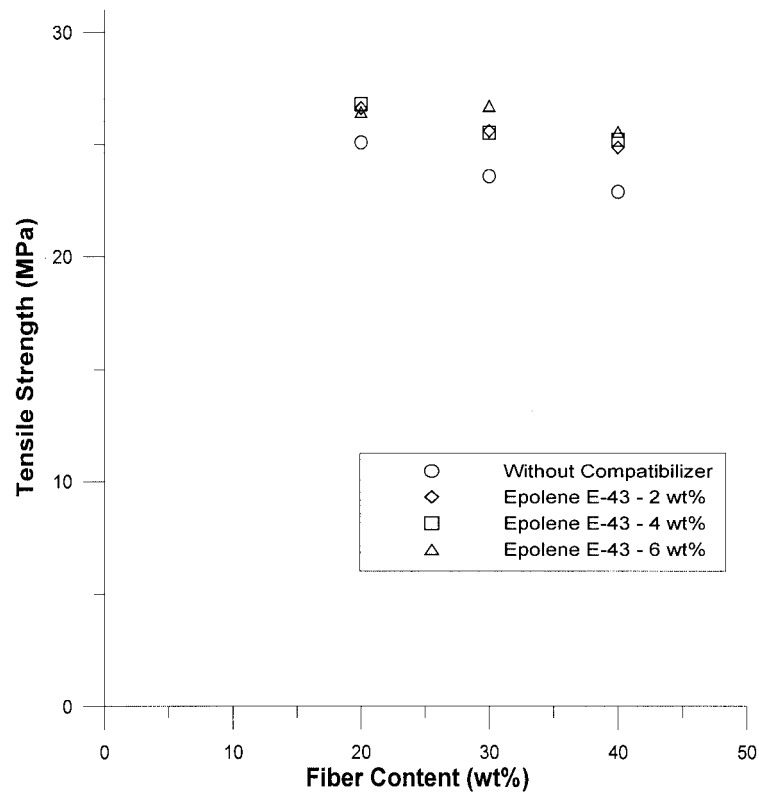


Figure 9 Tensile strength versus fiber content for PP reinforced with large palm fibers without any treatment and with use of compatibilizer Epolene E-43 at various amounts.

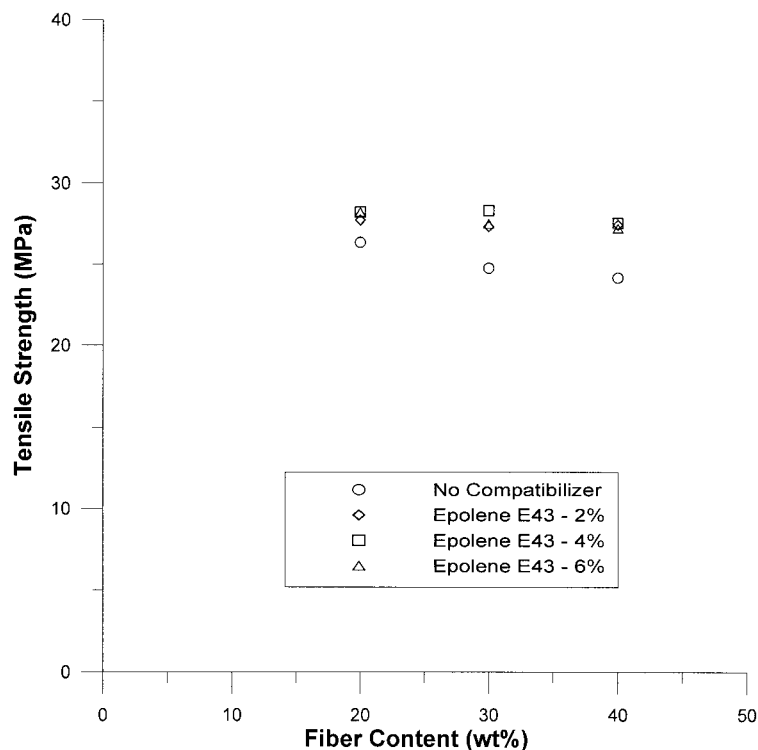


Figure 10 Tensile strength versus fiber content for PP reinforced with small palm fibers without any treatment and with use of compatibilizer Epolene E-43 at various amounts.

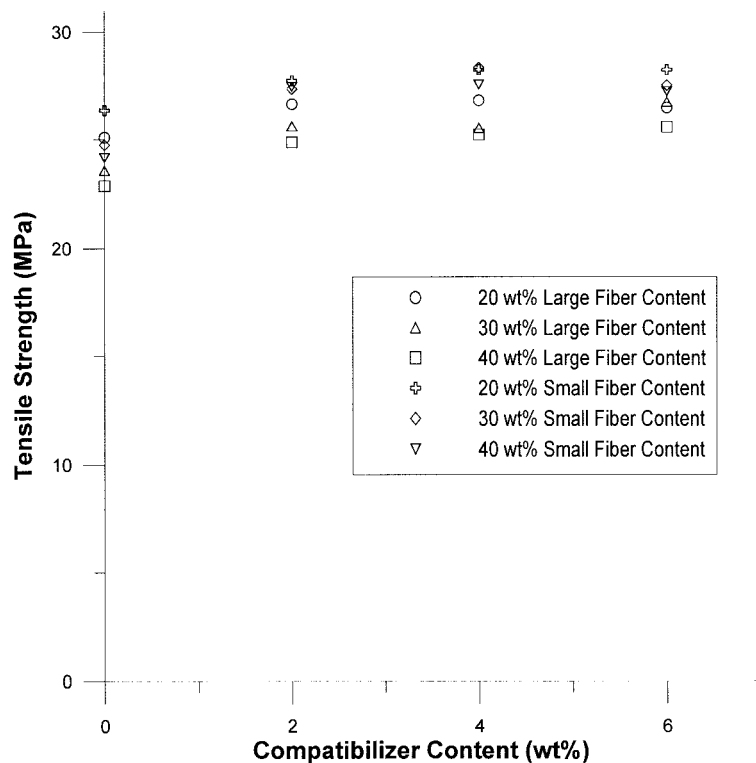


Figure 11 Tensile strength versus compatibilizer content for PP reinforced with palm fibers without any treatment and with use of compatibilizer Epolene E-43 at various amounts.

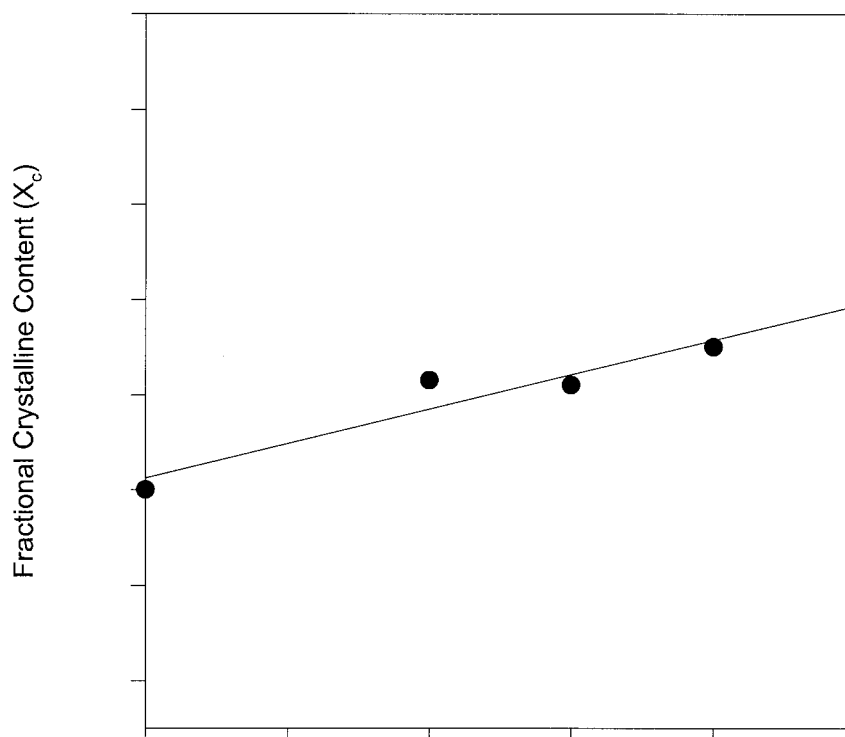


Figure 12 DSC results of percentage crystallinity versus fiber content for PP/fiber composite.

the composite modulus to the same extent because the modulus is a bulk material property before fracture.

The next step was to use the compatibilizer to investigate its effect on composite performance. Figures 3 and 4 show the effect of adding 2 wt % Epolene E-43 with varying fiber loading and fiber length distribution on the tensile strength and modulus of the composite, respectively. The composite behavior is similar to that of the uncompatibilized one. Again, the tensile

strength decreases as fiber loading is increased. Small fibers result in somewhat better composite strength than large fibers, and the modulus increases with increasing fiber loading. However, higher composite strength values, relative to those of uncompatibilized ones, is an indication of improvement in fiber-matrix adhesion with 2 wt % Epolene E-43.

Figures 5 and 6 show the effect of adding 4 wt % Epolene E-43 on composite strength and modulus with varying fiber loading and fiber length distribution. The composite behavior is similar to that of the composite compatibilized with 2 wt % Epolene E-43, just discussed above. The performance of the composite with 6 wt % compatibilizer Epolene E-43 was not different either (results are not shown here).

The results discussed above are combined together in Figures 7–10, to show the effect of compatibilizer amount on the composite properties in a more convenient way for PP reinforced with small and large palm fibers. As seen in Figures 7 and 8 the composite modulus increases with fiber content for composites with the compatibilizer added at various amounts (2, 4, and 6 wt %), as well as for those with no compatibilizer. As also discussed above, this is an indication of the existence of adhesion between palm fibers and the PP matrix even in the composites without any compatibilizer.

However, the use of compatibilizer might have increased the adhesion strength, which is not that clear



Figure 13 SEM micrograph of a fractured surface of a 30 wt % palm fiber-PP composite with small fibers and no compatibilizer.

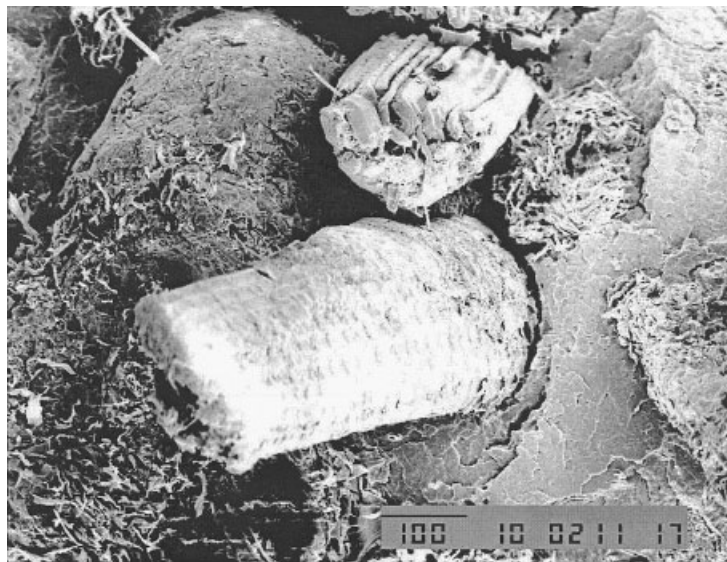


Figure 14 SEM micrograph of a fractured surface of a 30 wt % palm fiber-PP composite with small fibers and no compatibilizer (a close-up of Fig. 13).

in the plots of modulus versus fiber content (considering also the scatter in data), although this phenomenon is quite clear in Figures 9 and 10, which present plots of tensile strength versus fiber content for uncompatibilized and compatibilized palm fiber-PP composites with small and large fibers. As seen and also as discussed previously, there is an obvious improvement in tensile strength with addition of the compatibilizer.

The data presented above can be rearranged to be able to discuss the effect of varying compatibilizer content on the mechanical properties of the PP composite. Figure 11 shows the tensile strength versus

compatibilizer content for Epolene E-43 with varying fiber loading. It is seen as a general trend for the two fiber length distributions that increasing the amount of compatibilizer content increases the tensile strength (even though not so significantly), which is an indication of a probable increase in fiber-matrix adhesion strength. Because Epolene E-43 is a derivative of PP, it is compatible with PP. Epolene E-43 serves as a bridge that couples the incompatible phases. The maleic anhydride groups form bonds with the fiber, whereas the nonpolar part of Epolene E-43 becomes entangled with the PP matrix. This bridging action results in the observed increase in strength.^{4,35}



Figure 15 SEM micrograph of a fractured surface of a 30 wt % palm fiber-PP composite (with small fibers) compatibilized with 6 wt % Epolene E-43.

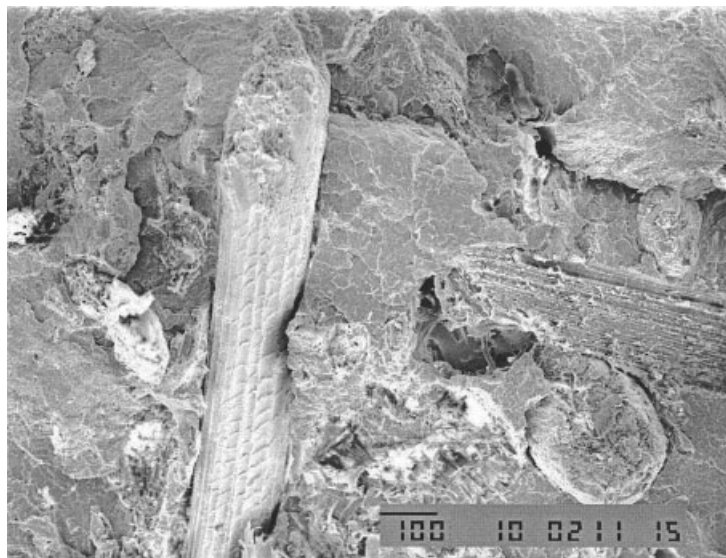


Figure 16 SEM micrograph of a fractured surface of a 30 wt % palm fiber-PP composite (with small fibers) compatibilized with 6 wt % Epolene E-43 (a close-up of Fig. 15).

To investigate the influence of fiber content on crystallinity, DSC was used to measure the percentage crystallinity (X_c) of PP in the compatibilized PP/fiber composites as a function of fiber content. As shown in Figure 12, increasing fiber content was found to slightly increase the X_c of the polymer matrix. This suggests that the crystalline cellulose fibers enhanced the chain folding of PP, possibly by providing a template for its crystallization. However, the increase in crystallinity was not significant enough to explain the increase in modulus of the compatibilized composite with fiber content. To determine the influence of fiber/matrix bonding on properties, SEM was used to characterize the fracture surfaces.

Fracture surfaces of the mechanically tested composite specimens were analyzed by SEM. It was seen that PP composites containing no compatibilizer resulted in rough fracture surfaces with extensive fiber pullout (Figs. 13 and 14). This is an indication of poor bonding between the fibers and the PP matrix (compared to that of the composites with compatibilizer-treated fibers, discussion of which will follow). This explains why composites with untreated fibers perform worse than those with compatibilizer-treated fibers. In addition, the SEM micrographs reveal that the palm fiber forms an irregular shape with the matrix, indicating poor mixing. Proper mixing plays an important role in enhancing the adhesion between fibers and matrix material.³⁷ The effect of using different compounding techniques on strength of the composites will be discussed in a future publication.

Once the compatibilizer Epolene E-43 was incorporated, it was observed that instead of fiber pullout, a smoother fracture surface is observed (Figs. 15 and 16) compared to that of the composite without the com-

patibilizer (Figs. 13 and 14). The reason for this phenomenon is probably that the incorporation of the compatibilizer E-43 enhanced the interfacial adhesion between the fibers and matrix and that is why a higher load was transferred onto the fibers; thus a higher composite strength was observed.

CONCLUSIONS

1. An increase in PP modulus with fiber addition was observed, indicating the presence of adhesion between palm fibers and PP.
2. However, the fiber-matrix bond strength in the palm fiber-PP system was not satisfactory, resulting in a decrease in PP strength with fiber addition.
3. Small fibers resulted in better composite performance than that of large fibers because of better mixing and more uniform distribution of small fibers in the PP matrix.
4. Use of the compatibilizer Epolene E-43 improved the fiber-matrix adhesion, resulting in an improvement in composite performance.

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