

Modification of Oil Palm Empty Fruit Bunches with Maleic Anhydride: The Effect on the Tensile and Dimensional Stability Properties of Empty Fruit Bunch/Polypropylene Composites

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ABSTRACT: Oil palm empty fruit bunch (EFB)-filled polypropylene (PP) composites were produced. The EFB filler was chemically modified with maleic anhydride (MAH). The effects of the filler size and chemical modification of EFBs on the tensile and dimensional stability properties of EFB-PP composites were studied. The composites with MAH-treated EFBs showed higher tensile strengths than those with untreated EFBs. This was attributed to the enhanced compatibility between the MAH-treated EFBs and PP matrix, as shown in a scanning electron microscopy

study. Fourier transform infrared analysis showed evidence of C=C and C=O bonds from MAH at 1630 and 1730 cm^{-1} , respectively. The MAH-treated PP composites showed lower water absorption and thickness swelling than those with untreated EFBs. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 827–835, 2003

Key words: compatibility; composites; poly(propylene) (PP); renewable resources

INTRODUCTION

Various studies have been performed to improve the mechanical and physical properties of lignocellulose-filled thermoplastic composites.^{1–3} One of the areas of interest is the compatibility between lignocellulose fillers and thermoplastic matrices. The compatibility and interfacial bond strength between these two components are expected to be poor in this kind of composite. This is due to the difference in the natures of the lignocelluloses and polymer matrices. Lignocelluloses are hydrophilic (a contribution from hydroxyl groups in cellulose, lignin, and hemicellulose), whereas thermoplastics such as polypropylene (PP) and polyethylene (PE) are hydrophobic. Despite the advantages contributed by lignocellulose materials, the lack of good interfacial adhesion and poor resistance to moisture absorption render the use of lignocellulose-filled composites less attractive.⁴ These problems can be overcome to a certain extent by treatment of lignocellulose fibers with various chemicals. Various chemicals have been employed to enhance the compatibility between the constituent materials, including maleic anhydride (MAH)-modified PP,¹ poly[methylene (polyphenyl isocyanate)],² poly(propylene acrylic acid), and si-

lane.³ In this study, MAH was used to chemically modify the lignocellulose fiber before its incorporation into PP. The anhydride group was expected to be sufficiently reactive with the hydroxyl groups of the lignocellulose fiber. MAH, chemically attached to the lignocellulose surface, might serve as a bridge between the former and the PP matrix. Through this chemical modification, the compatibility between these two components was expected to be improved and to subsequently enhance the mechanical and physical properties of the composite.

EXPERIMENTAL

Materials

Empty fruit bunches (EFBs) in fiber form were obtained from Sabutek (M) Sdn. Bhd. (Teluk Intan, Perak, Malaysia). PP used was purchased from Polypropylene (M) Sdn. Bhd. (Pahang, Malaysia) with a melt flow index and density of 12.0 g/10 min and 0.903 g/cm^3 , respectively. MAH used in a solid form was purchased from Komita (M) Sdn. Bhd. (Penang, Malaysia).

Methods

Preparation of the fibers

The EFB filler was obtained in the form of long strands of fibers. The fibers were ground into small particles.

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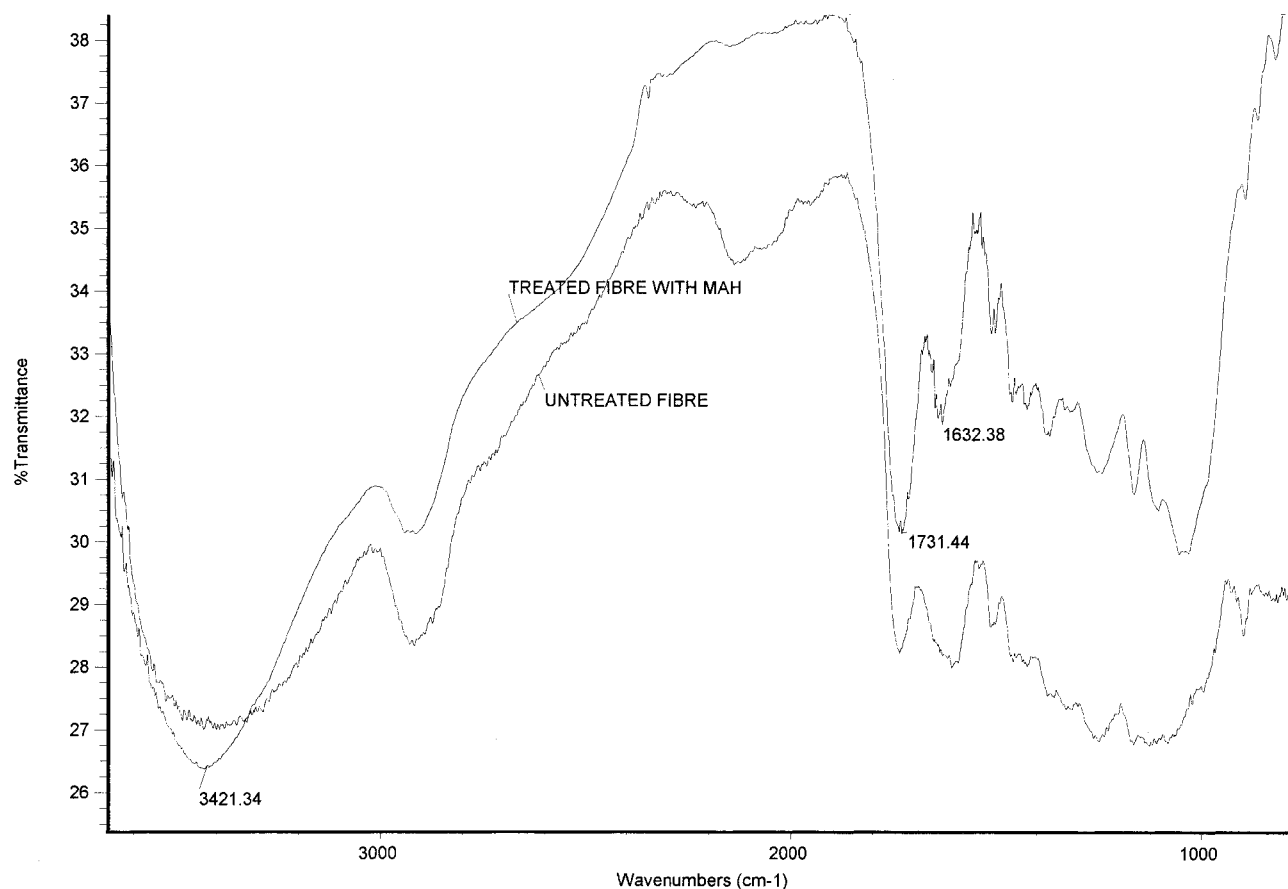


Figure 1 FTIR spectra for the untreated and MAH-treated filler.

An endecott sieve was used to sieve the filler into two sizes, 60-mesh and 80-mesh.

Extraction of the filler

The filler was extracted for about 3 h with a solution mixture consisting of toluene, ethanol, and acetone (4:1:1 v/v/v). The extracted filler was dried in an oven for approximately 16 h at 105°C.

Filler treatment

MAH was dissolved in dimethylformamide (DMF; 3:7 v/v), and this was followed by the addition of 5% hydroquinone (based on the weight of MAH). Approximately 90 g of the extracted filler was placed in a round-bottom flask. The solution of MAH was added to the flask with constant stirring and heated at 90°C for 1 h. The treated filler was then filtered and rinsed with acetone for the removal of unreacted MAH. The filler was then washed through refluxing with fresh acetone for 3 h. The treated filler was dried at 105°C for 16 h. The weight percentage gain (WPG) of the treated filler was calculated with the following formula:

$$\text{WPG (\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 represent the weights of the filler before and after treatment, respectively.

Compounding and processing

The compounding of MAH-treated and untreated fillers were carried out in a Haake twin-screw extruder (Germany). Two percent dicumyl peroxide (based on the WPG of the treated filler) was added during the compounding process. The mixing was carried out from 165 to 180°C from the feeding zone to the die zone, respectively, at a rotor speed at 35 rpm. The mixture was then extruded and pelletized. The pellets were placed into a mold (17.0 cm × 17.0 cm × 0.3 cm). The pellets were preheated for 10 min at 180°C, and this was followed by hot pressing at the same temperature for another 10 min. Cooling was carried out for 5 min under pressure.

Testing

Tensile testing

Tensile tests were conducted according to ASTM Standard D 618. The sheet produced was cut into test

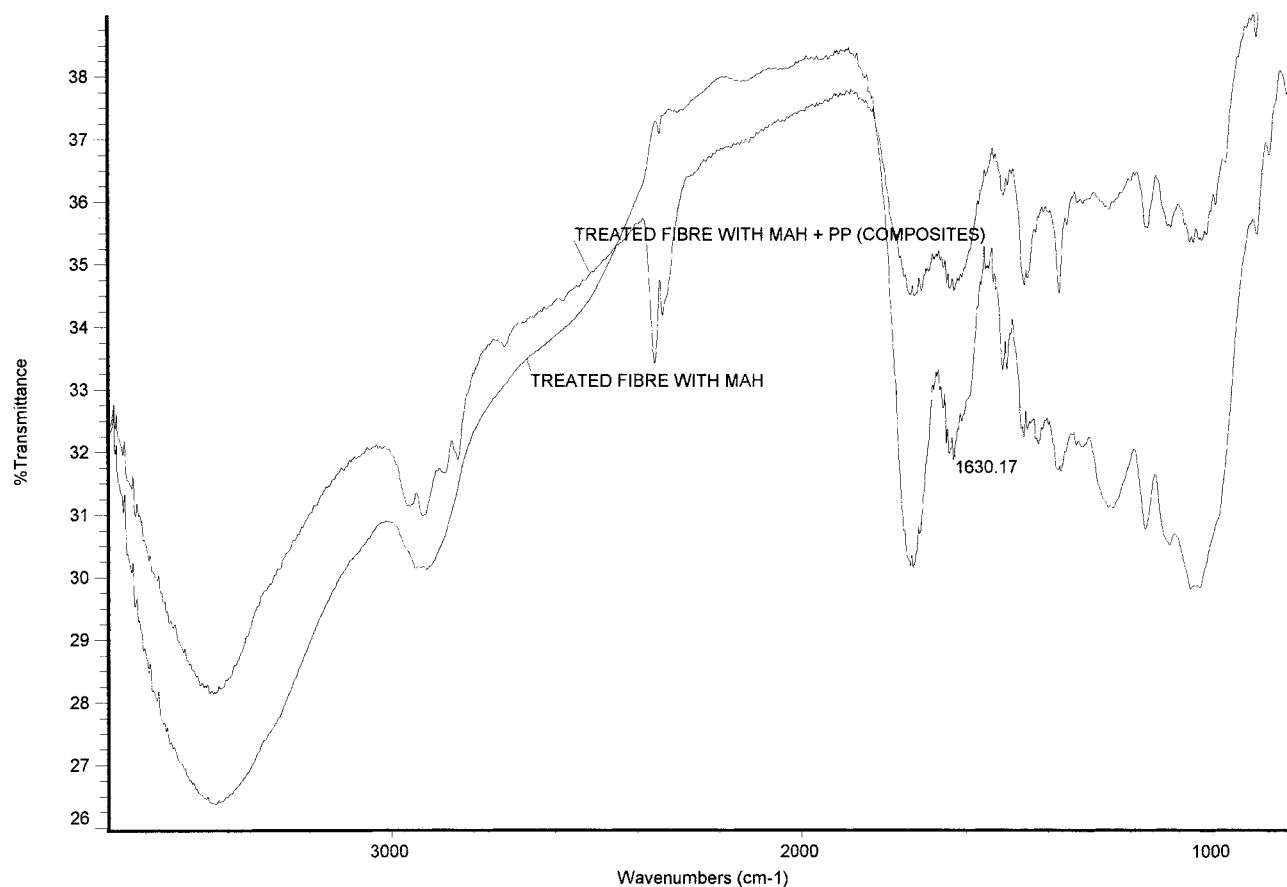


Figure 2 FTIR spectra for the MAH-treated filler before and after its incorporation with PP.

samples (15.0 cm long, 1.9 cm wide, and 0.3 cm thick). The test was carried out with a Universal testing machine (UK) at a crosshead speed of 5 mm/min.

Scanning electron microscopy (SEM)

The tensile fracture surfaces of the composite samples were studied with SEM (Leica Cambridge S-360, UK). The samples were mounted on an aluminum stub with double-sided tape and then gold-coated with a Polaron SEM coating unit (UK) to prevent electrical charging during the examination.

Dimensional stability test

Samples (20 mm × 15 mm × 3 mm) were used for the measurement of the water absorption and thickness swelling. After being oven-dried at 100°C to a constant weight, the specimens were immersed in deionized water. The specimens were periodically taken out of the water, surface-dried with absorbent paper, and reweighed; their thickness was remeasured, and they were immediately put back into the water. The water absorption and thickness swelling were calculated according to the following formulas:

$$\text{Water absorption (\%)} = \frac{M_2 - M_1}{M_1} \times 100$$

where M_1 and M_2 are the masses (g) of the sample before and after immersion and

$$\text{Thickness swelling (\%)} = \frac{t_w - t_0}{t_0} \times 100$$

where t_0 and t_w are the thicknesses (mm) of the sample before and after immersion.

Fourier transform infrared (FTIR) analysis

An FTIR spectroscopy analysis was carried out with a Nicolet FTIR spectrophotometer (Avatar system 360) with the KBr method. All spectra were recorded in the transmittance unit in the 4000–400-cm⁻¹ range, with a resolution of 4 cm⁻¹. There were 32 scans for each spectrum.

RESULTS AND DISCUSSION

FTIR spectra for the untreated and MAH-treated fillers are presented in Figure 1. There was some differ-

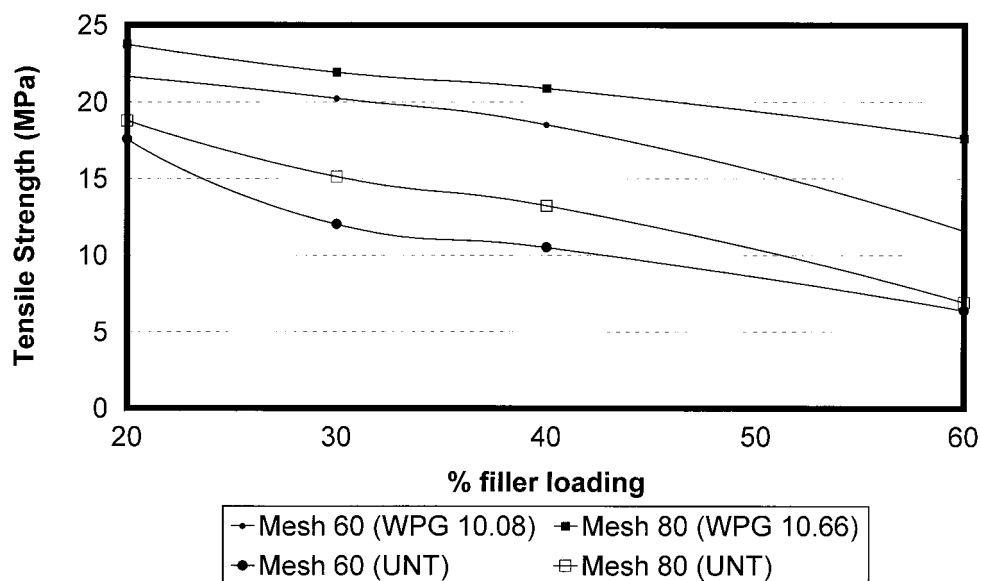


Figure 3 Effect of the filler loading on the tensile strength of untreated and MAH-treated samples.

ence for the peak at approximately 3420 cm^{-1} , which corresponded to the O—H stretching vibration. The MAH-treated sample showed a narrower peak than the untreated sample. The difference may be attributed to some changes that occurred as the result of the reaction between MAH and the filler. MAH, together with DMF (which served as a catalyst for the reaction and as a swelling agent for the lignocellulose material), swelled the cell wall and subsequently exposed lignocellulose OH groups ready to be reacted with MAH. Therefore, more OH groups were freed from the hydrogen bonding than for the untreated sample.⁵ The MAH-treated samples also showed an increased absorption in the carbonyl (C=O) region (ca. 1730 cm^{-1}). This proved that ester linkages were formed as

the result of the reaction between MAH and hydroxyl groups from EFBs. In addition, the MAH-treated samples also showed an increased absorption at 1630 cm^{-1} , which may be due to the presence of C=C bonds of MAH. Figure 2 shows spectra for an MAH-treated filler before and after its incorporation into PP for making board samples. The peak at approximately 1630 cm^{-1} shows a significant reduction in the transmittance. This indicates that the C=C groups of MAH (attached to EFBs) might have undergone a further reaction (in the presence of dicumyl peroxide) upon heating during mixing in the extruder and also during hot pressing.

The effects of the MAH chemical modification of the EFB fillers on the tensile properties of the EFB-PP

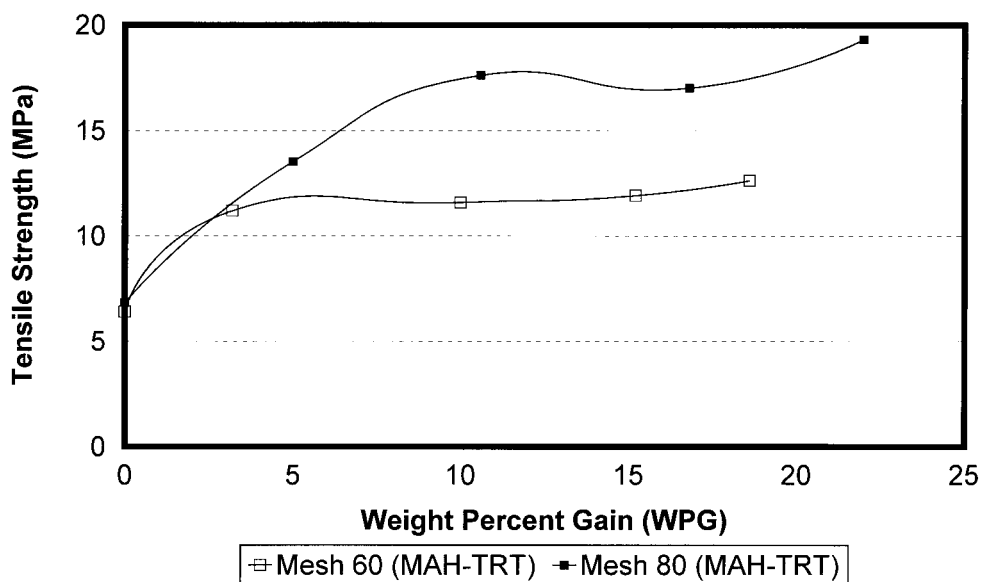


Figure 4 Effect of the MAH treatment on the tensile strength.

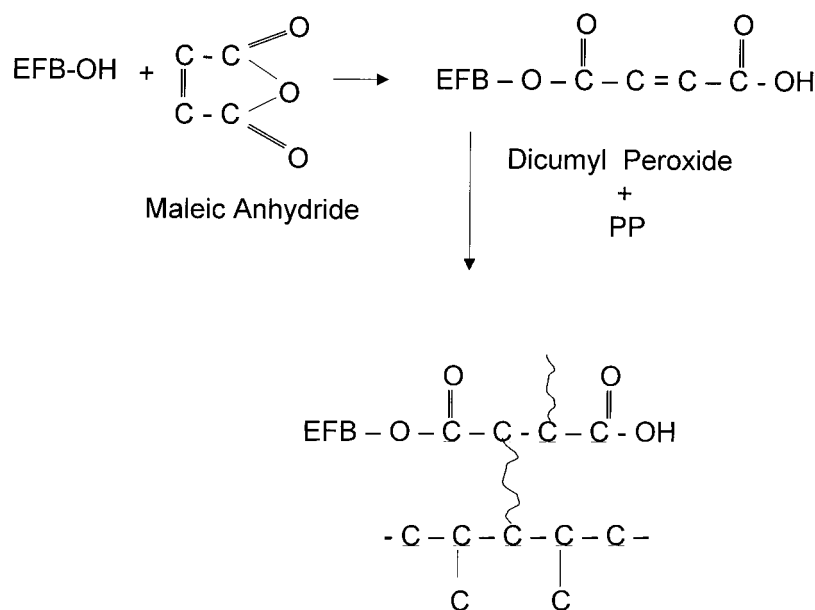


Figure 5 Schematic illustration of the reactions involved in producing the MAH-treated EFB-PP composite.

composites are shown in Figures 3–6. Generally, the tensile strength of the composites decreased with an increasing EFB filler loading (Fig. 3). This agreed with the trend observed in other lignocellulose-filled composites.^{6–10} Unlike fibers with a uniform cross section and a relatively high aspect ratio (the length-to-diameter ratio), the capability of irregularly shaped fillers such as EFBs to support stress transmitted from a thermoplastic matrix is rather poor. The effect is amplified if the proportion of EFBs is increased. The samples with the 80-mesh filler were marginally higher than those with the 60-mesh filler. This may be attributed to the greater interaction of the finer EFB fillers in the PP matrix, their better dispersion, or both.

A similar observation was reported by Rozman et al.⁷ for EFB/high-density PE composites. The results demonstrate that the composites with MAH-treated fillers had higher tensile strengths than those with untreated fillers. This indicates that the modification of the EFBs with MAH enhanced the transfer of stress from the matrix to the EFBs. Further evidence of the effect of the MAH treatment on the tensile strength is shown in Figure 4. The tensile strength of the MAH-treated composites increased as the WPG was increased. This shows that as the degree of the MAH modification of the EFBs was increased, the efficiency of stress transfer from the matrix to the filler was also improved. This might have come about as the result of better bridging

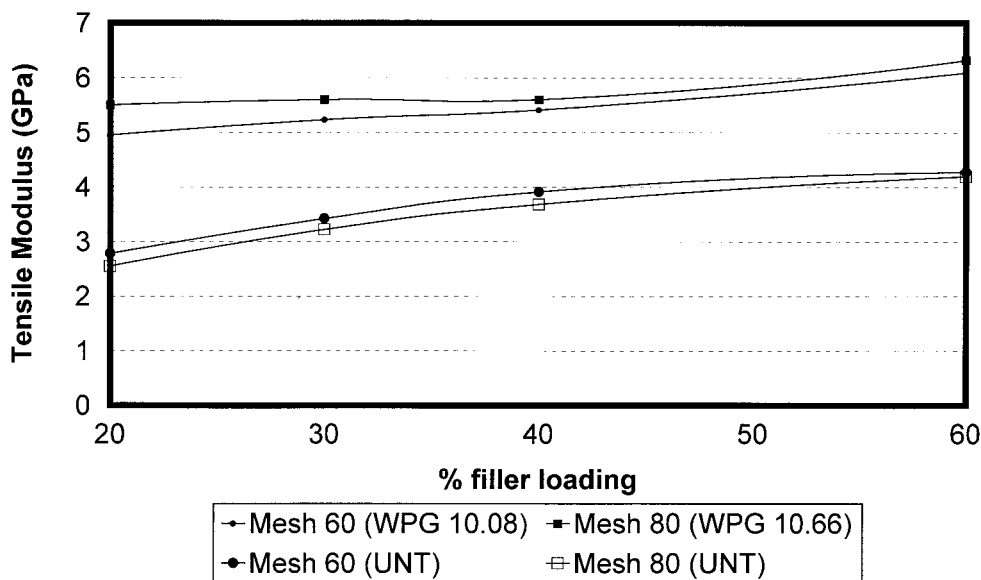


Figure 6 Effect of the filler loading on the tensile modulus of untreated and MAH-treated samples.

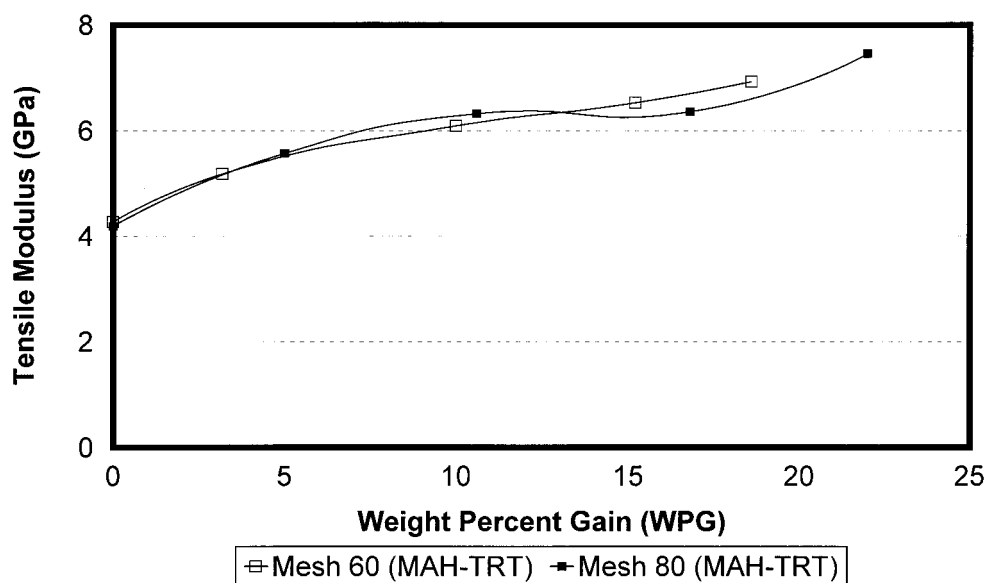


Figure 7 Effect of the MAH treatment on the tensile modulus.

between these two components at the interfacial region. The bridging might have been formed either by van der Waals interactions or covalent bonds between MAH and PP. Covalent bonding between MAH, which was attached to EFBs, and PP could have been possible through the opening of MAH C=C groups through a radical reaction of dicumyl peroxide (as indicated in FTIR spectra in Fig. 2). The possible mechanism is illustrated in Figure 5.

Figure 6 demonstrates the effect of the EFB loading on the tensile modulus. The results show that the tensile modulus increased as the percentage of the filler was increased. The composites with the MAH-treated filler showed significantly higher moduli than those with the untreated filler. Figure 7 shows that the

modulus increased as the WPG was increased. This indicates that the increased compatibility at the interfacial region might have increased the stiffness of the composites.

Generally, all samples showed a decreasing tensile toughness as the filler loading was increased (Fig. 8). Poor wetting was expected because there was a lack of compatibility between the polar functional groups of EFBs and nonpolar PP, and this gave way for weak interfacial regions. However, the results show that the toughness of the composites with MAH-treated fillers was higher than those with untreated fillers. Figure 9 shows that the toughness increased as the WPG was increased. Because toughness indicates the energy needed to bring a sample to failure, the results show

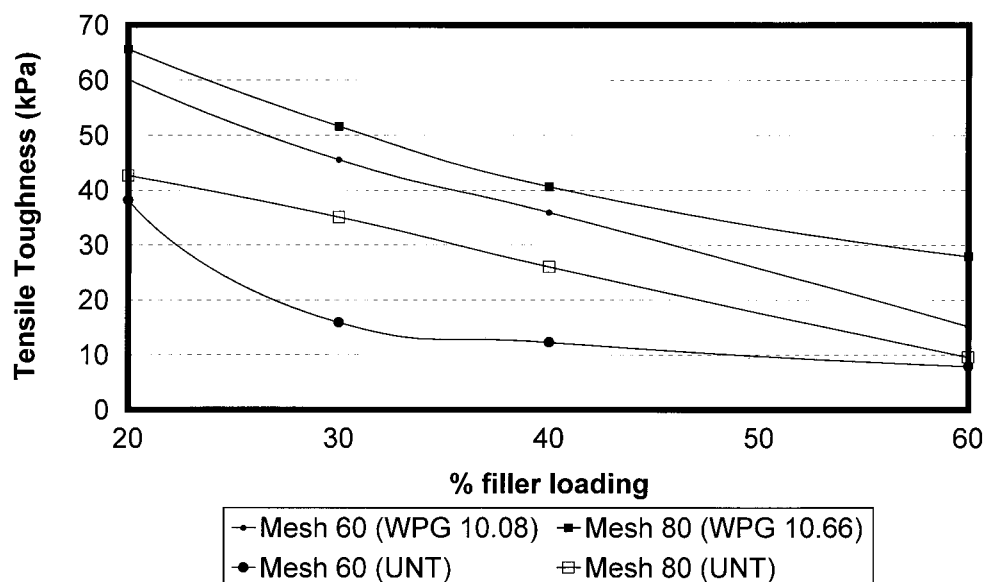


Figure 8 Effect of the filler loading on the tensile toughness of untreated and MAH-treated samples.

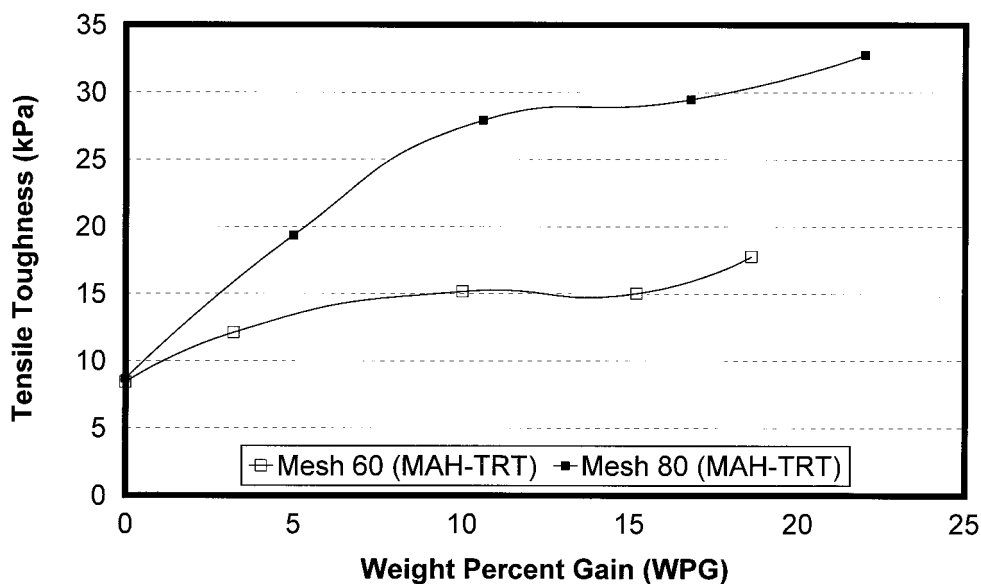


Figure 9 Effect of the MAH treatment on the tensile toughness.

that more energy was needed to break the MAH-treated composites than the untreated ones. Therefore, the MAH treatment enabled compatibility between the polar functional groups of EFBs and nonpolar PP to be improved. The results also demonstrate that the samples with smaller fillers displayed higher toughness than those with larger ones. According to the tensile strength results, this might have been due to the greater interaction of the finer EFB fillers in the PP matrix, their better dispersion, or both.

It is known that a lignocellulose material absorbs water by forming hydrogen bonds between water and hydroxyl groups of cellulose, hemicellulose, and lignin in the cell wall.¹¹ In general, the samples with MAH-treated fillers displayed lower water absorption

than those with untreated fillers (Fig. 10). This might have been due to (1) the replacement of hydrophilic OH groups from EFBs by more hydrophobic ester groups (as the result of OH from EFBs and anhydride groups from the MAH reaction) and (2) the formation of a protective layer on the interfacial zone, which prevented water molecules from penetrating into the cell wall of the lignocellulose. Thickness swelling of a lignocellulose material occurs when the cell wall is bulked by water.¹² The results for thickness swelling (Fig. 11) show a trend similar to that shown by water absorption. The MAH-treated samples showed significantly lower swelling than the untreated samples. Therefore, the results clearly indicate that MAH, chemically attached to EFBs, was able to prevent the

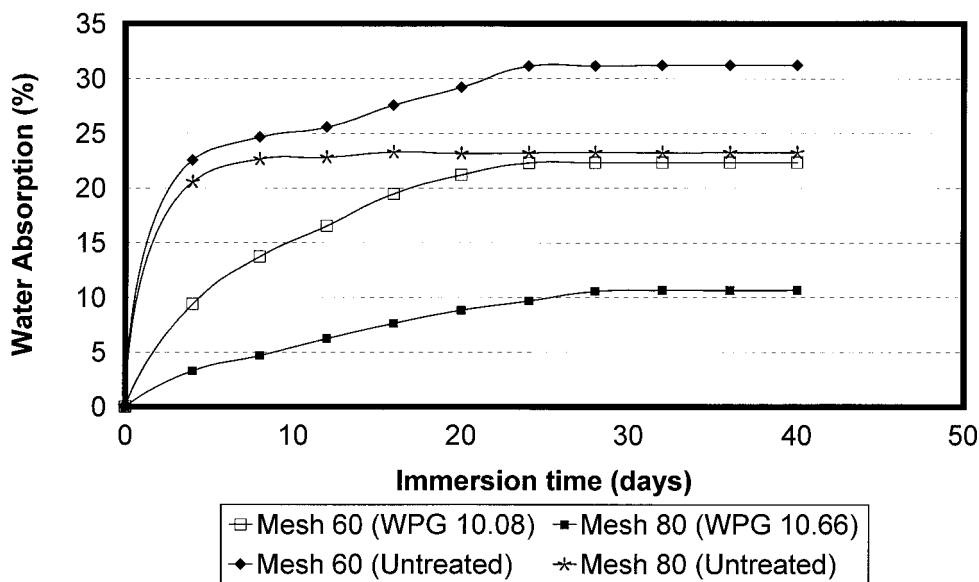


Figure 10 Water absorption results for untreated and MAH-treated samples.

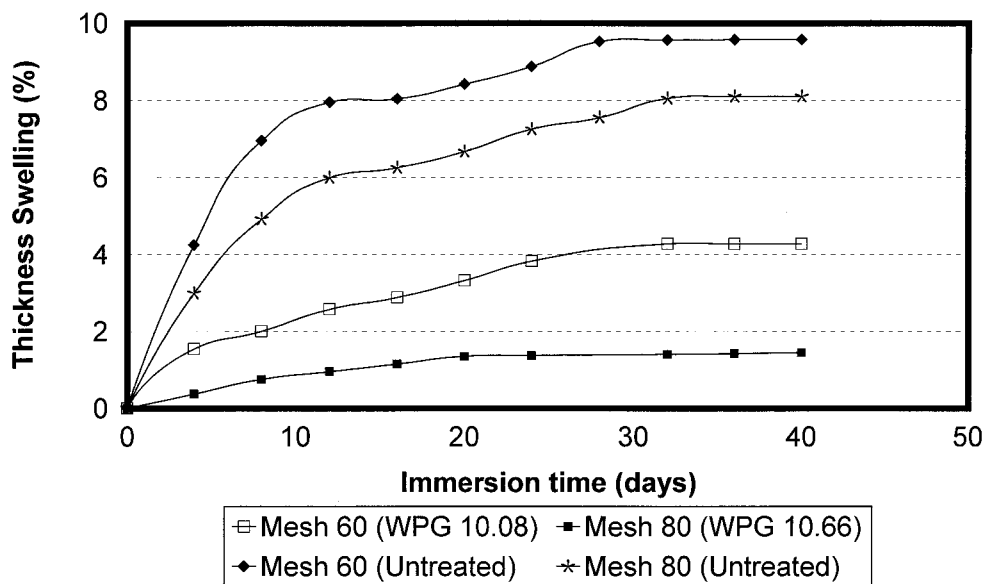
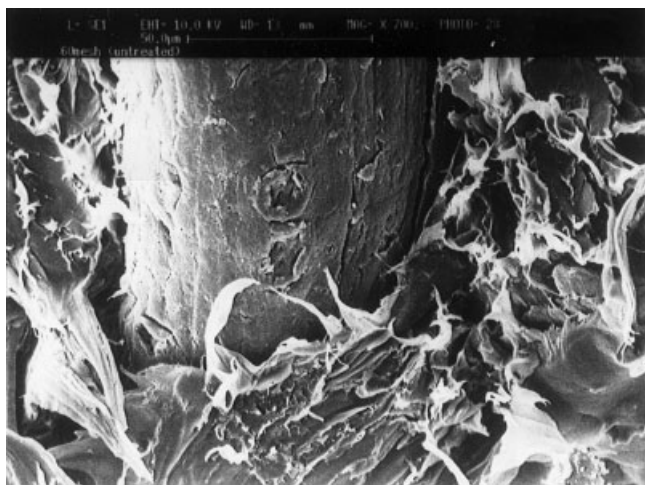
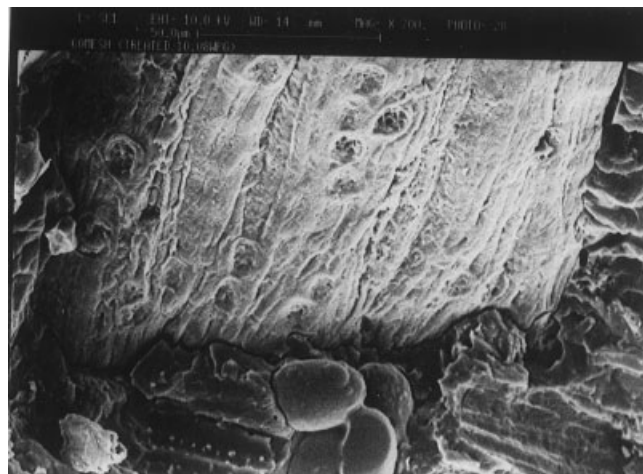


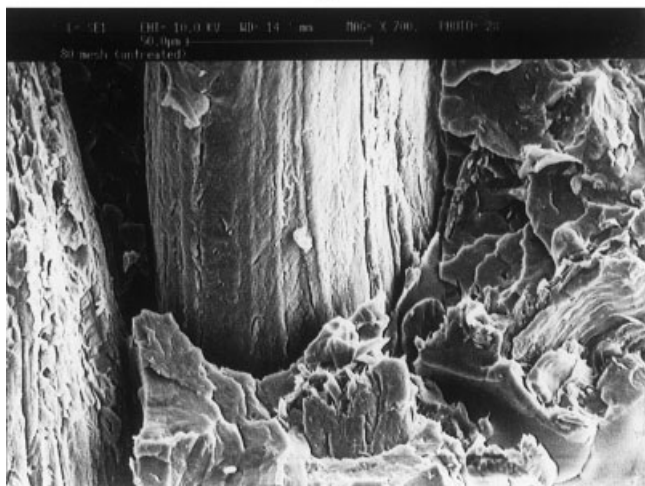
Figure 11 Thickness swelling results for untreated and MAH-treated samples.



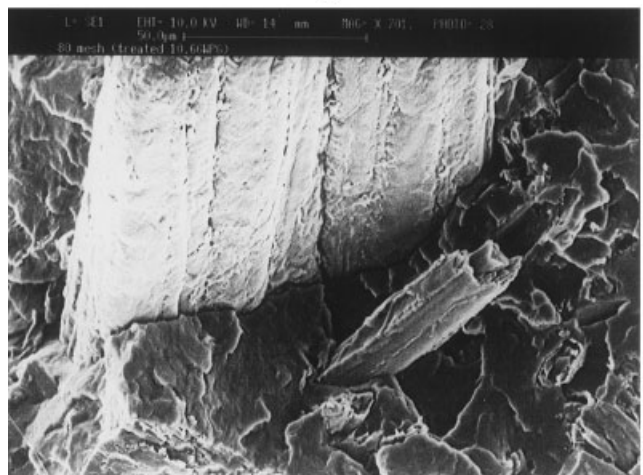
(a)



(a)



(b)



(b)

Figure 12 Micrographs of composites with untreated fillers: (A) 60-mesh filler and (B) 80-mesh filler.

Figure 13 Micrographs of composites with MAH-treated fillers: (A) 60-mesh filler and (B) 80-mesh filler.

water from going into the cell wall, and this resulted in less swelling. The results also demonstrate that the samples with smaller fillers absorbed and swelled less than those with bigger fillers. This can be attributed to the greater interaction of the finer EFB fillers in the PP matrix, their better dispersion, or both.

Figure 12 shows the micrograph of a composite with untreated EFBs. It is clear that the adhesion at the interfacial region was rather loose. However, for the samples with MAH-treated fillers (Fig. 13), better adhesion can be observed in the form of a more cohesive interface between the matrix and EFBs and a nicely embedded MAH-treated filler in the matrix.

CONCLUSIONS

Evidence for an MAH reaction with EFBs was observed through an FTIR analysis with the emergence of peaks characteristic of MAH in the EFB fillers. Composites with MAH-treated fillers displayed higher tensile and better dimensional stability properties. SEM showed evidence of better adhesion and compatibility between the EFBs and PP matrices as the

result of the chemical modification of the former with MAH.

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