

Rubberwood–High-Density Polyethylene Composites: Effect of Filler Size and Coupling Agents on Mechanical Properties

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ABSTRACT: Composites were made from rubberwood in the form of fibers (RWF) and powder (RWP) and high-density polyethylene (HDPE). The RWP–HDPE composites showed higher tensile strength than those of the fibers. The inferior properties of the RWF-filled composites were believed to be attributed to the agglomeration of the fibers. Two types of coupling agents, that is, 3-(trimethoxysilyl)propyl methacrylate (TPM) and 3-aminopropyltriethoxysilane (APE), were employed in an attempt to improve the mechanical properties of the composites. The former was able to significantly improve the modulus of elasticity (MOE) and impact strength of the RWF-filled composites. Treatment with TPM resulted in the reduction of the tensile modulus and increase in the elongation at break (EB) for both RWF and RWP-filled composites. APE produced RWP-filled composites with a higher tensile strength and modulus. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1993–2004, 1998

Key words: high-density polyethylene; rubberwood; thermomechanical fiber; coupling agent; filler

INTRODUCTION

The utilization of lignocellulosic material as a reinforcing component in polymer composites has received increased attention particularly for price-driven/high-volume applications. This development has been brought about since reinforcement by lignocellulosic fillers offers several advantages over their inorganic counterparts, that is, lower density, greater deformability, less abrasiveness to expensive molds and mixing equipments, and, of course, lower cost. Moreover, lignocellulosic-based fillers are derived from a renewable resource.

Generally, most lignocellulosic fillers used in thermoplastic composites are ground into fine particles with relatively low aspect ratios. These

fillers have been shown to increase the stiffness of the composites, but the strength, however, suffers a setback.¹ On the other hand, lignocellulosic materials in fibrous form with a greater aspect ratio could be used to impart greater strength as well as stiffness to the composites.

Various lignocellulosic materials in fibrous form have been used as reinforcing agents in thermoplastic composites. These include sisal,² newsprint paper,³ chemithermomechanical pulp (CTMP),⁴ and bamboo.⁵ In the present work, an effort was made to use wood pulp in fibrous form, which has a greater aspect ratio than in powder or meal form, as a means of reinforcing polyethylene resin and reducing material costs. Thermomechanical pulp (TMP) fiber from rubberwood which is indigenous to Malaysia can also be used as a reinforcing agent in thermoplastic composites. TMP, which is produced for the production of the medium-density fiberboard (MDF) through mechanical pulping and a refining process at a high temperature of the wood, still re-

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tains most of its lignin. The lignin has been reported to aid fiber dispersion and improve interfacial adhesion with nonpolar hydrocarbon polymers.⁶ The effects of two of the main parameters, namely, the size of the reinforcing agents (fiber and powder form) and the addition of coupling agents, affecting the properties of reinforced thermoplastics were studied. With regard to coupling agents, two types of chemicals were studied. Improvements in interfacial adhesion were sought by the pretreatment of the filler with 3-(trimethoxysilyl)propyl methacrylate (TPM) and 3-aminopropyltriethoxysilane (APE).

EXPERIMENTAL

Materials

Rubberwood fibers in the form of thermomechanical pulp (TMP) were obtained from Hume Fibreboard Seremban, Malaysia. Rubberwood meal was produced by grinding untreated wood obtained from Merbok, Malaysia. The polyethylene used was high density polyethylene (HDPE), purchased from The Polyolefin Co. (Singapore; melt index of 0.7 g/min and density of 0.96 g/cm³). The coupling agents 3-(trimethoxysilyl)propyl methacrylate (TPM) and 3-aminopropyltriethoxysilane (APE) were supplied by Bumi Sains Selangor, Malaysia. The fiber and powder size-distribution data are given in the Appendix.

Filler Treatment

The coupling agents (TPM and APE) were delivered in liquid form, and prior to application, the coupling agent was diluted in ethanol to make a 20% solution. The amount of the coupling agent used in this study was 1, 3, and 5% by weight of the filler. The filler was charged into a benchtop tumbler mixer and the solution was added slowly to ensure uniform distribution of the coupling agent. After completion of the silane addition, the filler was continuously mixed for another 30 min. The treated filler was then dried at 100°C for about 5 h to allow complete evaporation of the ethanol.

Preparation of Composite

The filler (in fiber or powder form) and HDPE were mixed using a Haake Rheocord System consisting of a Haake Rheodrive 5000 (drive unit)

and a Haake Rheomix 600 with a roller blade (mixer). The filler (with or without pretreatment with coupling agents) and HDPE pellets were dry-mixed prior to feeding them in the mixer. The loading of the filler was varied from 20, 30, and 40% by weight of the whole mixture (HDPE, filler, and coupling agent). The mixing was carried out at 160°C for 20 min at a rotor speed of 25 rpm. The compound was then transferred to a mold with the dimensions of 160 × 160 × 3 mm. The compound was preheated for 10 min at 160°C followed by hot-pressing at the same temperature for another 10 min. Cooling was carried out for 5 min under pressure.

Testing

The sheet produced was cut into three types of test samples, that is, flexural, tensile, and impact tests. Tensile tests were carried out according to ASTM D618 on samples with the dimensions of 15 × 1.9 × 0.3 cm (length × width × thickness), using an Instron machine Model 1114 at a crosshead speed of 0.5 cm/min. The flexural test was conducted according to ASTM D790, that is, a three-point bending system, using a Universal testing machine Model STM-10. The samples with dimensions of 15 × 1.5 × 0.3 cm were tested at a crosshead speed of 2.0 mm/min. The Izod impact test was carried out according to ASTM D256 on unnotched samples with dimensions of 6.5 × 1.5 × 0.3 cm, using a Zwick impact pendulum tester Model 5101. A minimum of six samples was tested in each case. Toughness was calculated from the area under the stress-strain curve. The calculations for the modulus of rupture (MOR) and modulus of elasticity (MOE) are given in the Appendix.

The fracture surface of the composites from the tensile test were investigated with a Leica Cambridge S-360 scanning electron microscope. The objective was to obtain some information regarding the fiber dispersion and the bonding quality between the fiber and matrix and to detect the presence of microdefects if any. The fracture ends of the specimens were mounted on an aluminum stub and sputter-coated with a thin layer of gold to avoid electrostatic charging during examination.

RESULTS AND DISCUSSION

Effects of Filler Form on the Mechanical Properties of Composites

The results of the modulus of rupture (MOR) are shown in Figure 1. The MOR for both the rub-

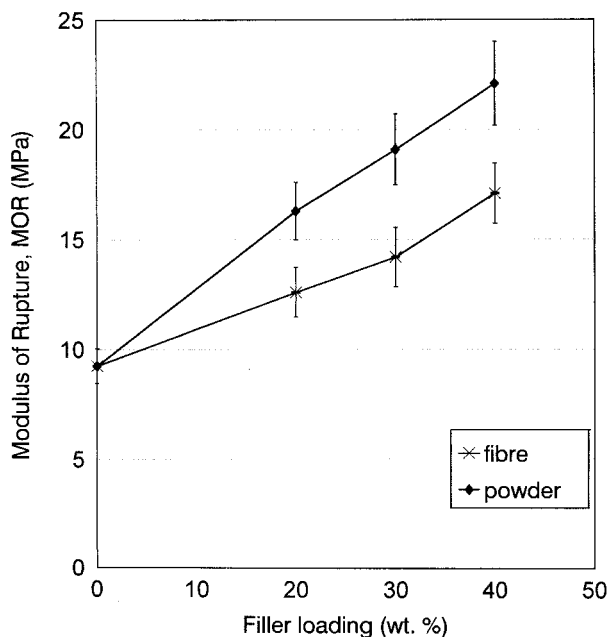


Figure 1.

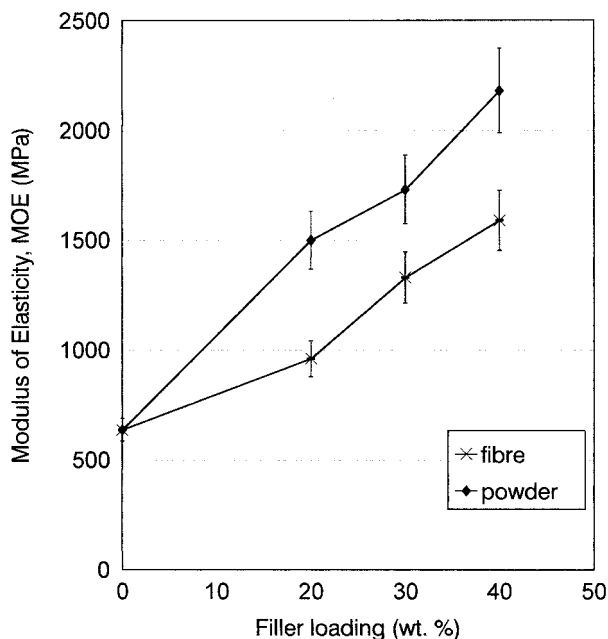


Figure 2.

berwood fiber (RWF) and powder (RWP)-HDPE composites increase as the percentage of filler is increased. Several workers also found that the flexural strength of a composite filled with wood powder increased as the the percentage of filler was increased.⁷⁻⁹ RWP-HDPE composites show a significantly higher MOR than does the RWF counterpart. Thus, the results show that although TMP RWF have a higher aspect ratio than that of RWP, the composites filled with fibers do not show superior flexural strength as compared with the ones filled with powder. This may be due to better and uniform dispersion of particulate matter (RWP) in the polymer matrix. The particulate fillers tend to form a continuous morphological domain in the matrix so that regions of discontinuities which are possible with a fibrous matrix are absent. The TMP fiber with a higher degree of lignin (which contains polar hydroxyl groups) on its surface may have the tendency to agglomerate through the formation of hydrogen bonding. The agglomeration may then produce discontinuity in the matrix which subsequently creates stress concentration points in the composite samples. The subject will be exemplified further with the qualitative evidence obtained from the SEM study.

Both types of composites show an increasing stiffness as filler loading is increased (Fig. 2). A

similar trend was also observed by other workers.^{6,10,11,12} Again, the RWP-HDPE composites show significantly higher stiffness than that of the RWF composites. The higher flexural properties of the RWP-filled composites may be attributed to better dispersion of the RWP in the HDPE matrix.

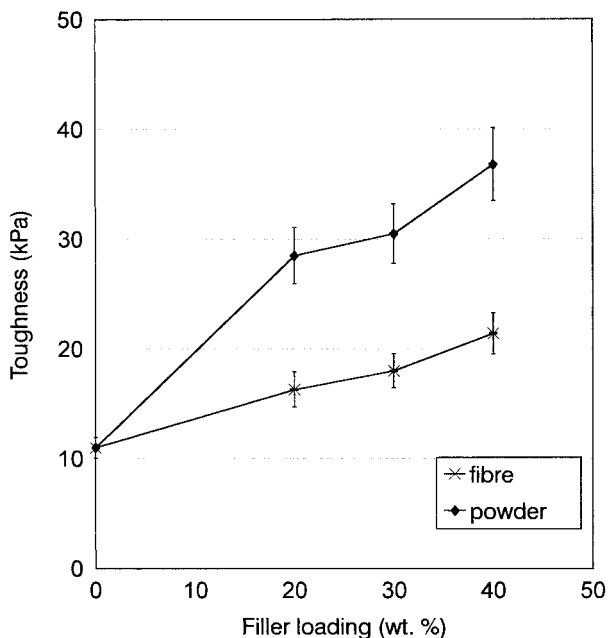


Figure 3.

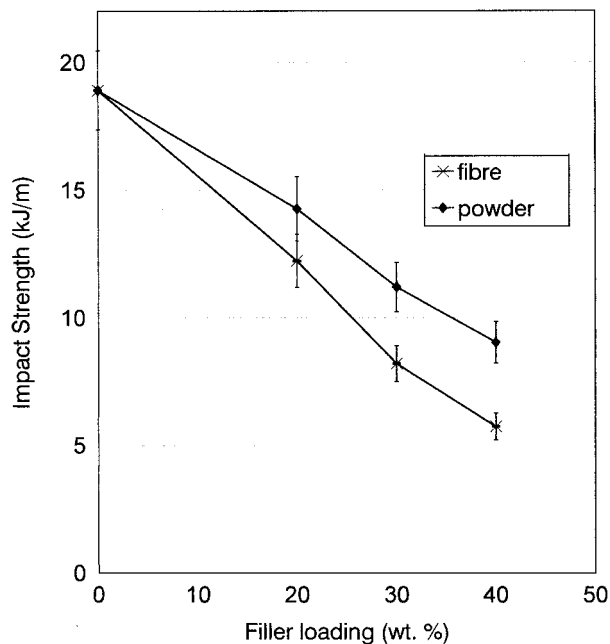


Figure 4.

The fine nature of the RWP will give rise to better filler-matrix interactions and may facilitate a better transfer of stress than that of RWF. This statement is in agreement with the results of flexural toughness which are shown in Figure 3, where the RWP composites show significantly higher toughness than that of the RWF-HDPE composites. As toughness is a measure of the energy needed to break a material, the results show that more energy is required to break RWP-filled composites than the ones filled with RWF. The fine size (hence, higher cross-sectional area) and uniform distribution of RWP is believed to provide greater hindrance to the failure process.

The impact strength of both RWP and RWF composites decreases as the filler content increases (Fig. 4). This observation is quite expected for filled composites and has been commonly observed.¹³⁻¹⁵ RWP-filled composites show a superior impact strength than that of the RWF-filled ones. This again may be attributed to the higher surface area of RWP than of RWF, which may produce better hindrance to crack propagation.

The results of the tensile strength (Fig. 5) show that the strength decreases as the percentage of filler is increased. Similar results have been observed by several workers.^{16,17} The RWP-filled composites display higher tensile strength than

that of the ones filled with RWF, although the difference not too obvious. This may again indicate the influence of the higher surface area of RWP, which leads to more contact surface with the matrix. The RWF with a relatively higher aspect ratio than that of RWP coupled with hydrogen bonding between the fiber surfaces tend to agglomerate in the matrix, which, consequently, lowers the area of contact with the matrix. Klason et al.¹⁵ also stated that the aspect ratio of lignocellulosic fibers did not necessarily result in the improvement of the strength of a composite, especially if there was widespread fiber agglomeration in the polymer matrix. However, the length and aspect ratio of the fibers could enhance the stiffness of a composite, as shown by Figure 7 later in the discussion.

The incorporation of both fillers, that is, RWP and RWF, in the HDPE matrix resulted in a drastic reduction in the elongation at break (EB) (Fig. 6). This may be contributed by the decreased deformability of a rigid interface between the filler and matrix component. Composites filled with RWP show a higher elongation at break (EB) than that of the ones filled with RWF. As the elongation is reciprocal to the stiffness of a material,⁴ the results, thus, show that the fiber imparts a greater stiffening effect than that of the powder.⁹ The results are further supported by the tensile

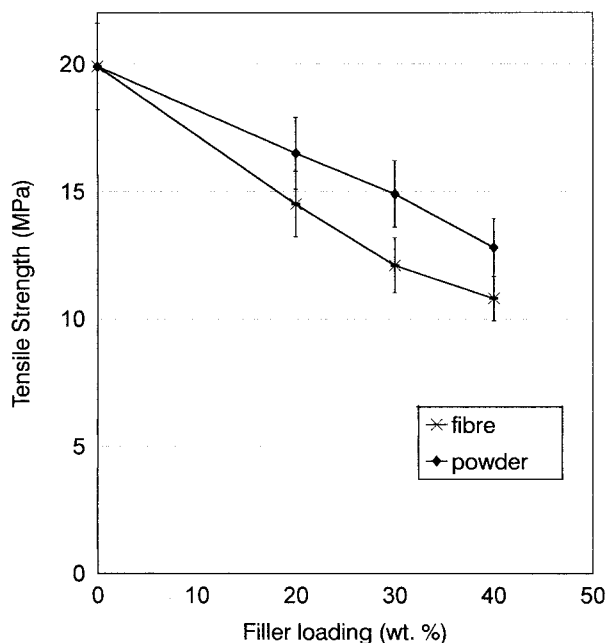


Figure 5.

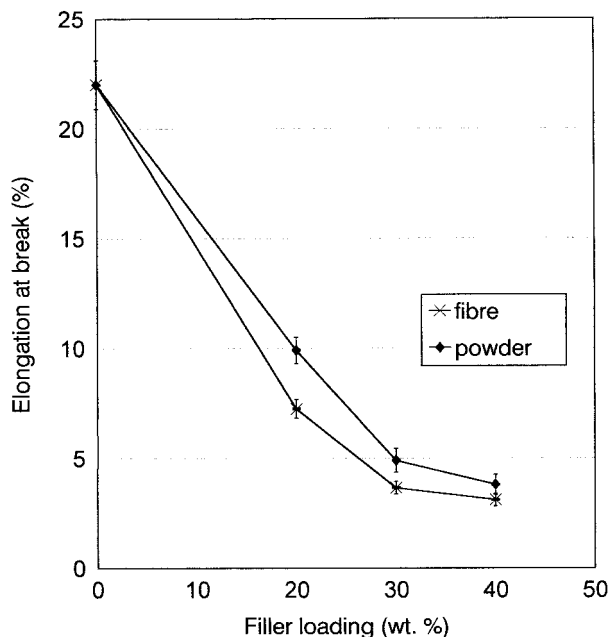


Figure 6.

modulus properties (Fig. 7) which show that the modulus of the RWF-filled composites are higher than that of the RWP-filled composites. The overall increase in the tensile modulus for both types of composites shows the ability of the filler either in powder or fiber form to impart greater stiffness to the composite. This is in agreement with the trend observed in other lignocellulosic-filled thermoplastics.¹⁸⁻²¹

Scanning electron microscopy (SEM) was employed to study the tensile fracture surfaces of composite samples based on 20 and 40% filler. SEM micrographs of the fracture surfaces of an RWF-filled HDPE composite are shown in Figure 8(A) and (B) for 20% fiber content and in Figure 8(C) and (D) for 40% fiber content, with magnifications of $\times 100$ and $\times 300$, while SEM micrographs for RWP-filled composites are shown in Figure 9(A) and (B) for 20% powder content with magnifications of $\times 100$ and $\times 300$, respectively. Figure 9(C) and (D) are micrographs for the composites with 40% powder content with magnifications of $\times 100$ and $\times 200$, respectively.

It is known that composite materials with satisfactory mechanical properties could only be achieved if there is a good dispersion and wetting of the fibers in the matrix that will give rise to strong interfacial adhesion. However, this is not

the case when wood fillers are used in PE. The polarity of the wood filler is obviously not capable of forming good filler-matrix interactions with the nonpolar PE. On the contrary, due to hydrogen bondings, these fillers, especially in fiber form, have a greater tendency to agglomerate among themselves into fiber bundles. Although the micrographs are rather difficult to interpret, generally it is observed, especially as shown in Figure 8(A,C), that the fibers tend to cling together in bundles and resist dispersion of the individual fibers as fiber content increases. These fiber bundles can be observed by SEM to be distributed unevenly throughout the matrix. Clean and smooth traces of indentation can be seen in Figure 8(B). These indicate the lack of adhesion between the fibers and polymer matrix, a major reason for the poor tensile strength. Figure 8(D) shows that more pullout occurs as the fiber content increases.

Figure 9(A) - (D) shows the distribution of the RWP of different shapes in the matrix. It is obvious that as the powder content increases [Fig. 9(C,D)] more fiber pullout and debonding are observed. Perhaps a significant improvement in the strength properties can be achieved if the efficiency of the filler dispersion can be enhanced by using coupling agents to improve the bonding quality between the filler and the polymer matrix.

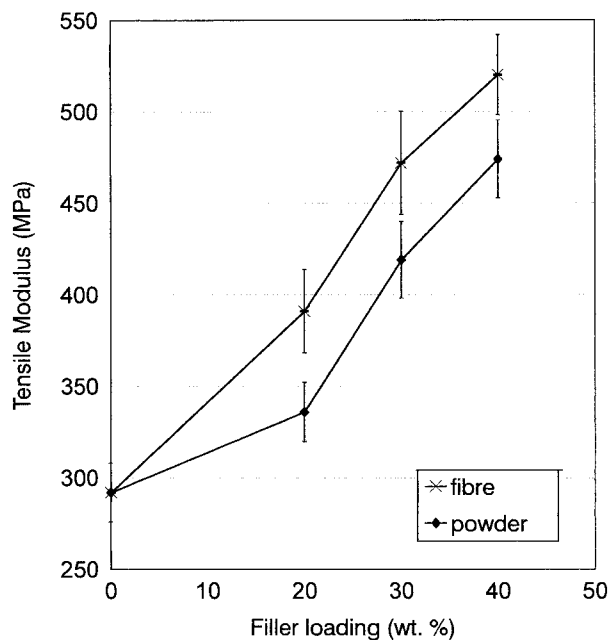
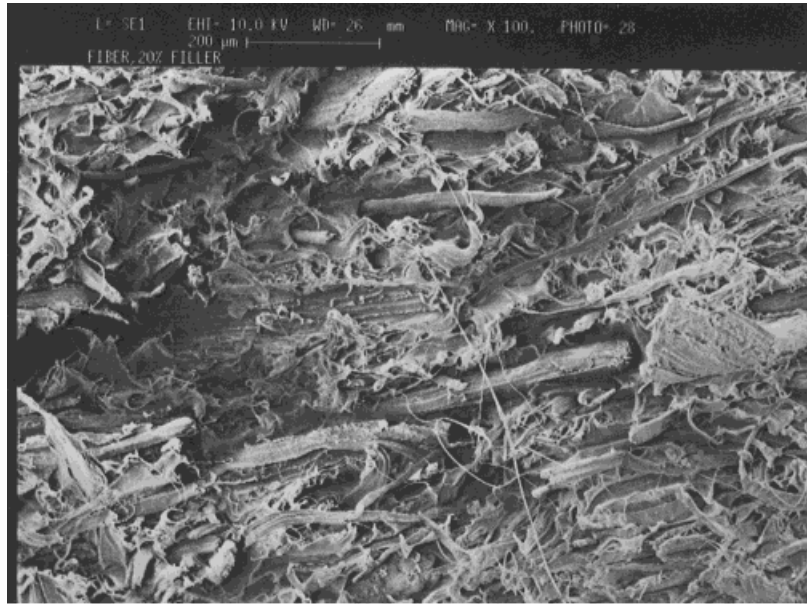


Figure 7.



(A)



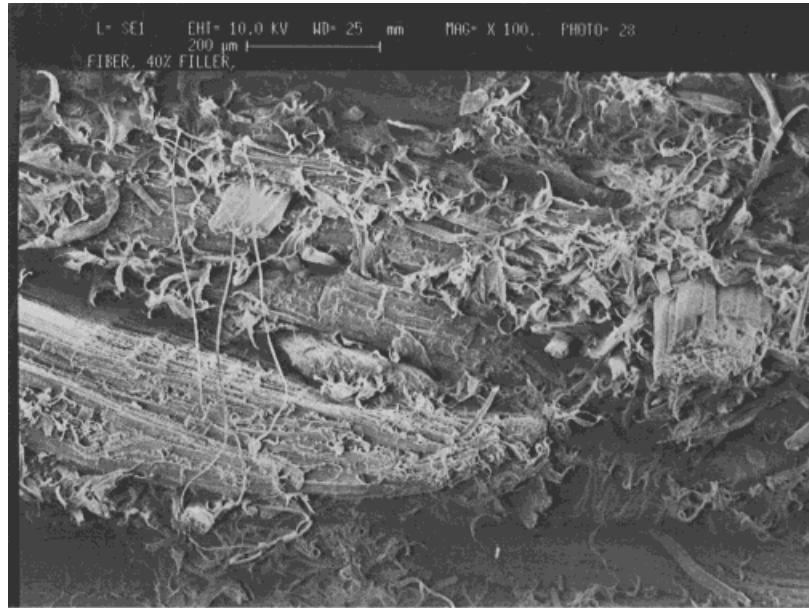
(B)

Figure 8.

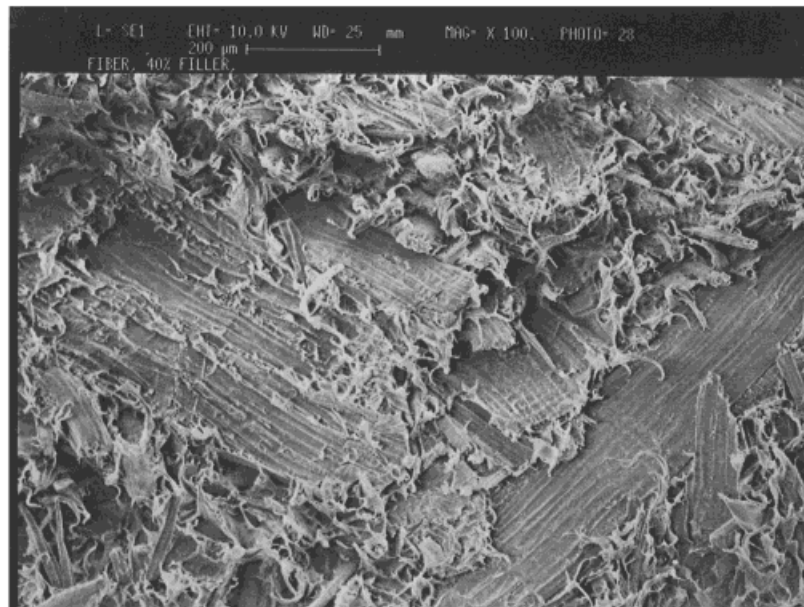
Effect of Coupling Agents on the Mechanical Properties of Composites

The effect of coupling agents on the flexural stiffness (MOE) is shown in Figure 10. Addition of both TPM and APE does not result in the improvement of the stiffness of the RWP-filled composites.

However, TPM is able to impart greater stiffness in the RWF-filled composite, while APE can only manage to improve the stiffness at 1% loading. Thus, the results indicate that incorporation of TPM may improve the dispersion of the fiber in the composite more efficiently than can APE, which, however, resulted in an improved stiffness.



(C)

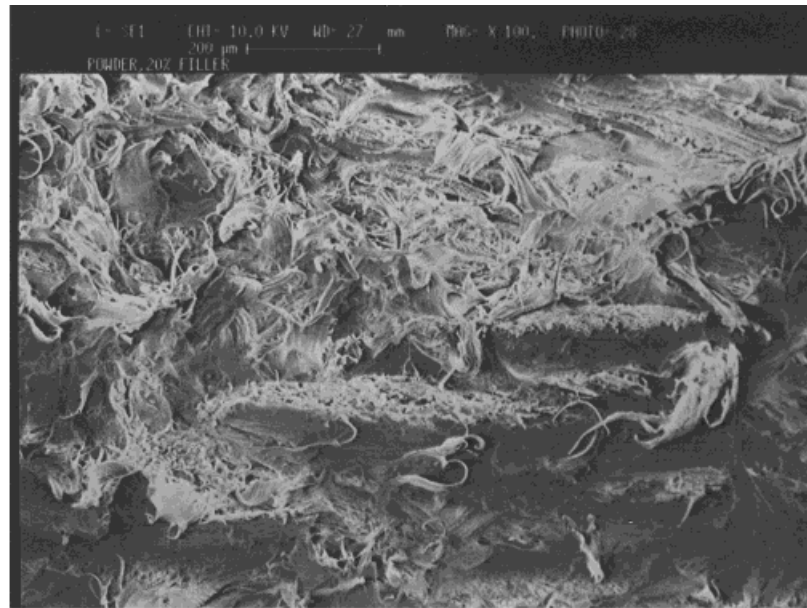


(D)

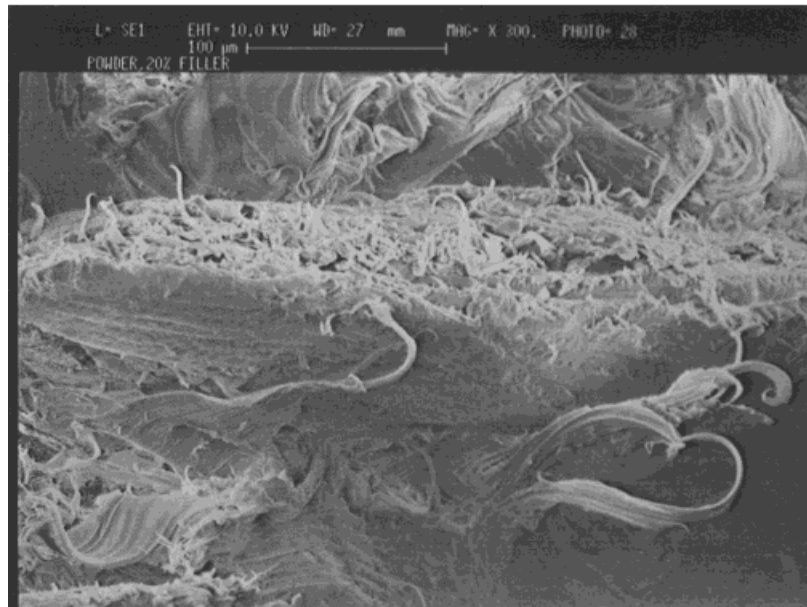
Figure 8. (Continued from the previous page)

The impact strength of the RWF-filled composites is significantly improved by TPM (Fig. 11). However, with APE, the improvement in the impact strength is rather marginal. The results indicate the presence of improved adhesion as the result of the addition of TPM. It can also be observed that there is an increase of about 20% in impact

strength by the addition of TPM. This can be attributed to an increase in adhesion between the matrix and fiber together with the role played by the coupling agent to improve the dispersion of the fiber with the matrix and reduction in the tendency for the fibers to agglomerate. However, both APE and TPM have not produced any sig-



(A)



(B)

Figure 9.

nificant improvement for the RWP-filled composites.

The effect of the coupling agent on the tensile strength of the HDPE composites is shown in Figure 12. The incorporation of coupling agents has resulted in significant improvement in the tensile strength of RWP-filled composites. The higher

tensile strength of TPM-treated RWP clearly indicates that TPM is more efficient in improving the filler–matrix interaction. This may be attributed to better interaction of the methacrylic group in TPM with the polymer matrix as opposed to the amino group in APE. However, both TPM and APE do not show significant improvement for the



(C)



(D)

Figure 9. (Continued from the previous page)

RWF-filled composites. As in the RWP-filled composites, TPM again resulted in higher strength compared to APE in the RWF-filled composites.

The tensile modulus results are shown in Figure 13. The results show that APE in both types of composites resulted in a higher modulus compared to the ones with TPM. As mentioned earlier,

the stiffness of a sample is a reciprocal of the elongation at break. Stiffer composites, as can be seen for the ones treated with APE, show a lower elongation at break as compared to TPM which is lower in stiffness (Fig. 14). All samples show greater elongation at break, especially at 1% loading.

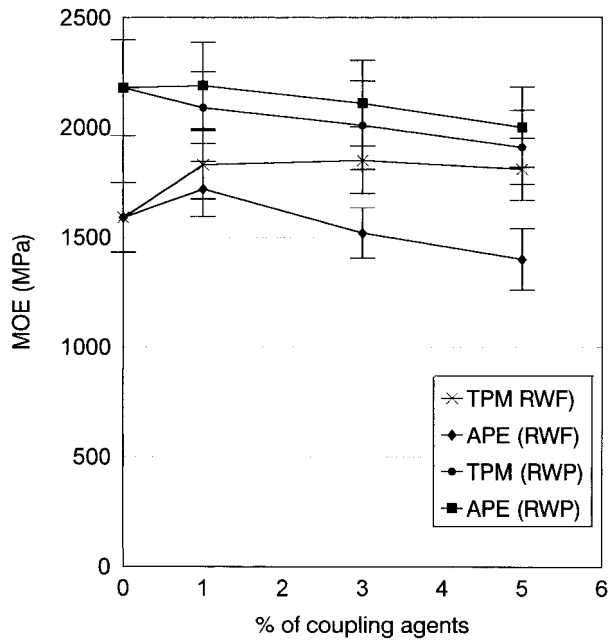


Figure 10.

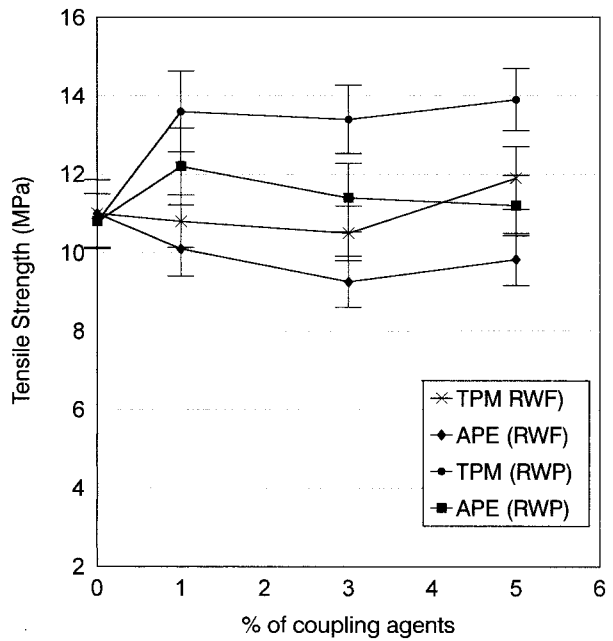


Figure 12.

CONCLUSIONS

RWP composites yield a higher tensile strength than those of RWF. The lower properties of the RWF-filled composites are believed to be attributed to the agglomeration of the fibers. TPM as a

coupling agent is able to significantly improve the MOE and impact strength of the RWF-filled composites. The treatment with TPM resulted in a decrease in tensile modulus and increase in EB for both RWF and RWP-filled composites. On the contrary, APE did not produce any significant im-

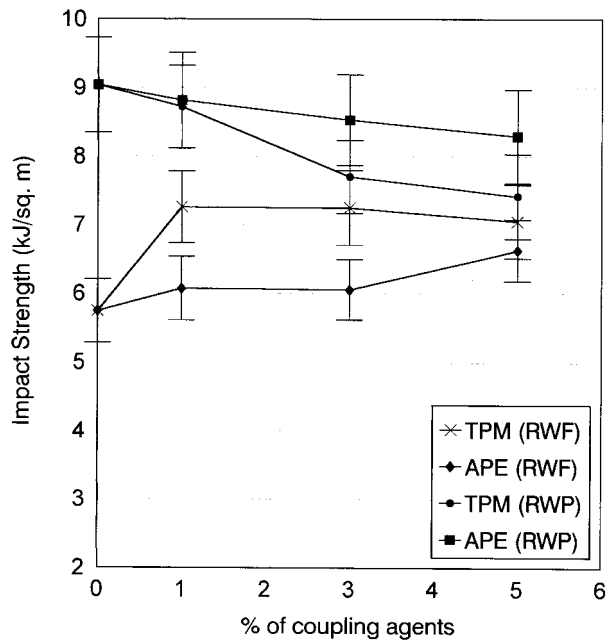


Figure 11.

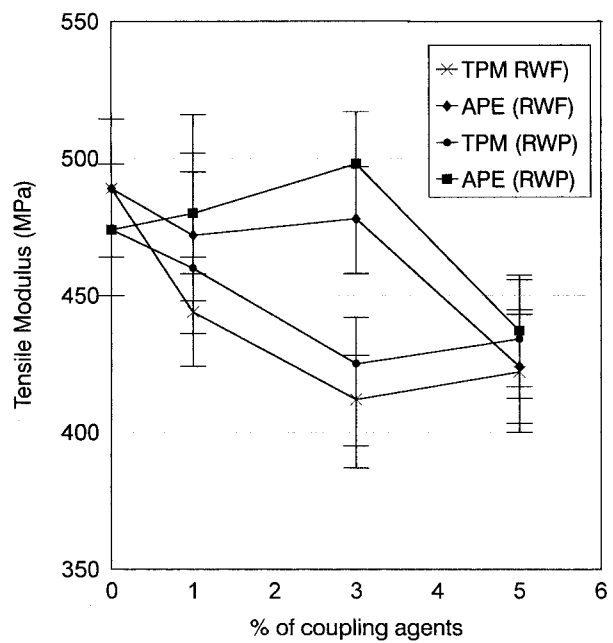


Figure 13.

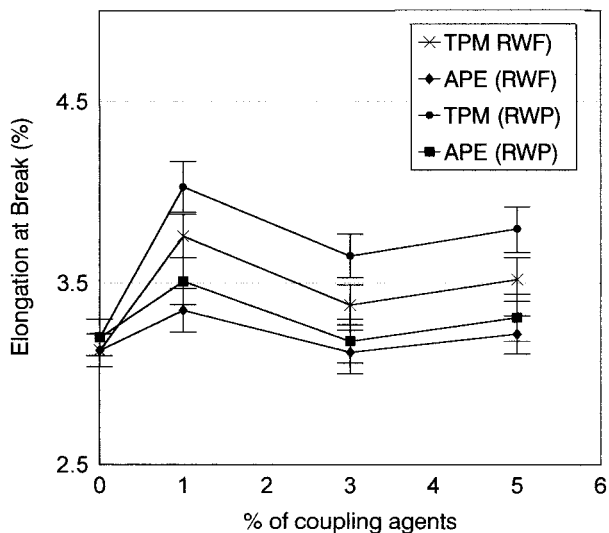


Figure 14.

provement in the MOE for the RWP-filled composites. However, APE produced RWP-filled composites with a higher tensile strength and modulus.

APPENDIX

Fiber and Powder Size-distribution Data

Calculations for Modulus of Rupture and Modulus of Elasticity

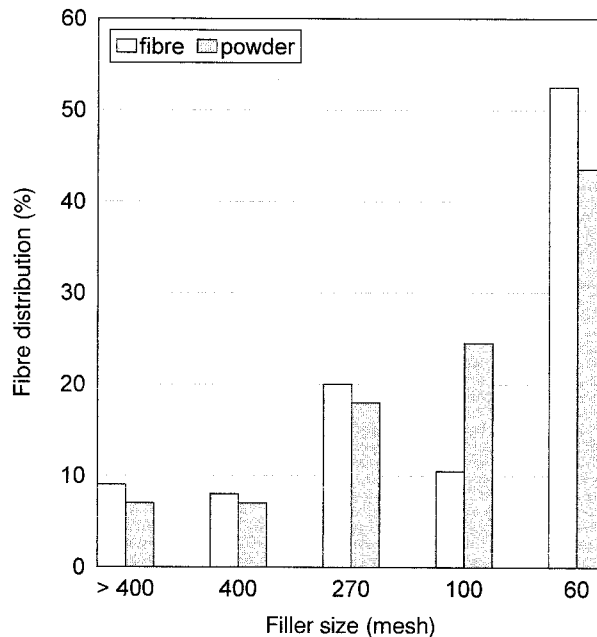
The modulus of elasticity (MOE) was calculated according to the formula given below:

$$MOE = \frac{L^3 \Delta W}{4bd^3 \Delta S}$$

where L is the span between the centers of supports (m); ΔW , the increment in load (N); b , the mean width (tangential direction) of the sample (m); d , the mean thickness (radial direction) of the sample (m); and ΔS , the increment in deflection (m).

The modulus of rupture (MOR) was calculated according to the given formula:

$$MOR = \frac{3WL}{2bd^2}$$



Appendix 1.

where W is the ultimate failure load (N); L , the span between centers of support (m); b , the mean width (tangential direction) of the sample (m); and d , the mean thickness (radial direction) of the sample (m).

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