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THE EFFECT OF PP/MAPP BLENDS ON EFB FIBRES FOR IMPROVING TENSILE AND DIMENSIONAL STABILITY PROPERTIES

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ABSTRACT

Empty fruit bunch fibre – polypropylene composites with treated and untreated maleated polypropylene (MAPP) were produced. The MAPP used as coupling agents were Epolene-43 (commercial MAPP) and MAPP samples produced in laboratory. Analyses on the MAPP samples included FTIR, acid number and grafting degree (G_d) to determine the number of anhydride groups available in the MAPP. The MAPP-treated composites had better tensile results than the untreated ones. The dimensional stability of the MAPP- treated samples improved with water absorption and as the thickness swelling decreased. The scanning electron microscopy (SEM) of the interfacial regions between filler and matrix showed the treated composites to have better interaction than the untreated samples.

Keywords: empty fruit bunch (EFB), polypropylene (PP), maleated polypropylene (MAPP), tensile tests, dimensional stability.

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INTRODUCTION

The incorporation of plastic and natural fibres, such as hemp, kenaf, *etc*., offer many advantages such as (i) lower density, (ii) higher specific strength and modulus, (iii) use of a renewable resource, (iv) lower cost than the commonly used inorganic fillers (Lightsey *et al*., 1981; Theberge *et al*., 1981). When an untreated fibre is compounded with a thermoplastic polymer, the main problem usually encountered is the poor adhesion between the hydrophobic polymer and hydrophilic filler. Coupling agents can be used to modify the interface by interacting with both the fibre and the matrix to better link the two components (Gaylord, 1976). The coupling agents used would contain a chemical group that can react with both the fibre and polymer. The bonds formed covalent and hydrogen improves the interfacial adhesion. Maleated polypropylene (MAPP) has received considerable attention as a coupling agent because of its availability, low cost and effective in improving the mechanical properties of wood fibre-polypropylene composite (Kazayawoko *et al*., 1997). Wood polymer composite industry throughout the world that used PP as their matrix has been using MAPP to strengthen their products and some of the MAPP producer using the name of *Polybond*, *Dufon* and others are amongst of them. The purpose of the paper is to address the incompatible of wood and plastic PP problems by introducing coupling agents which is MAPP to improve the tensile and dimensional stability properties.

EXPERIMENTAL

Materials

Empty fruit bunch (EFB) fibre was obtained from Sabutek (M) Sdn Bhd, Teluk Intan, Perak. The polypropylene used was Propelinas 600G (homopolymer), purchased from Polypropylene (M) Sdn Bhd, Kuantan, Pahang with density and melt index specified as 0.9 g cm^{-3} and 12 g 10 min^{-1}, respectively. Epolene 43 with low molecular weight

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(M_n=3900 g mol^{-1}, M_w=9100 g mol^{-1}), density of 0.93 g cm^{-3} and acid number 47 was purchased from Suka Chemicals (M) Sdn Bhd, Pulau Pinang. Dicumyl peroxide was used as initiator in producing MAPP in the laboratory, and purchased from Komita (M) Sdn Bhd, Pulau Pinang.

Methods

Preparation of fibre. The EFB fibre was ground using a RetschMuhle laboratory grinder and sifted through a 35-60 mesh (270-500 μmm) before use. The fibre was extracted with a chemical solution of toluene, ethanol and acetone (4:1:1, v / v / v) for about 3 hr and dried in an electric oven overnight at 105ºC.

Laboratory preparation of maleated polypropylene. MAPP was produced using a mixer at 180ºC with rotor speed 35 rpm for about 20 min. Three compounds were produced with different ratios of maleic anhydride: polypropylene, *i.e.* 25:75% (e3), 10:90% (e2) and 5:95% (e1). Approximately 2% dicumyl peroxide (based on the weight of MAH) was added as initiator. The compounds were ground to become a fine form using a laboratory grinding machine, model RetschMuhle.

Analysis of Maleated Polypropylene

Carbonyl index. Infrared analyses of all the MAPPs (Epolene 43 and the laboratory-produced MAPP) were carried out using a Nicolet FTIR spectroscope, model Avatar System 360, with a resolution of 4 cm^{-1} and 32 scans per spectrum (Agnelli and Bettini, 2000). The wavelengths of interest were 1775 cm^{-1} (characteristic of anhydride groups) and 1167 cm^{-1} (characteristic of methyl groups). The carbonyl index (CI) was calculated as:

$$\text{Carbonyl index (CI)} = \frac{A_{1775\ \text{cm}^{-1}}}{A_{1167\ \text{cm}^{-1}}}$$

where:
$A_{1775\ \text{cm}^{-1}}$ is absorbance at 1775 cm^{-1}
$A_{1167\ \text{cm}^{-1}}$ is absorbance at 1167 cm^{-1}

Grafting Degree (G_d)

The grafting degree (G_d) was analysed according to Zhou *et al*. (2000). Approximately 0.2 g MAPP was dissolved in 50 ml toluene under reflux for 30 min. Then, 100 ml hydrochloric acid (0.1 M) was added to the solution prior to titration with KOH (0.1 M) using phenolphthalein as indicator. A blank titration was done by the same method. The G_d was derived by:

$$G_d = \frac{N\,(V_0 - V) \times 98.06}{2 \times W \times 1000}$$

where:
N = concentration of KOH (M)
W = weight of sample (g)
V = volume of KOH (ml) for the blank titration
V_0 = volume of KOH (ml) for the MAPP titration

Acid Number

The acid number of the MAPP solutions was also determined by titration (Matsuda *et al.*, 1998). A sample of 0.1 g was placed in a volumetric flask with 10 ml acetone, 10 ml hydrochloric acid (0.1 M) and 100 ml water. The solution was then titrated with 0.1 M KOH using phenolphthalein as indicator. A blank titration was also done. The acid number, A, was derived by:

$$A\ (\text{eq/kg}) = \left[\frac{(V' - H)}{W}\right] \times f'$$

where:
W = weight of sample (g)
V′ = volume of KOH (ml) for sample titration
H = volume of KOH (ml) for blank titration
f′ = factor value of KOH solution (0.1 M) = concentration of KOH (M) solution

Compounding and Processing

Compounding of the materials and filler was degree carried out using an extrusion machine, Haake Rheocord Model 5000. The screw speed was fixed at 35 rpm, with temperature zones of 165ºC (zone 1), 170ºC (zone 2), 175ºC (zone 3) and 180ºC (zone 4). The MAPP (commercial and laboratory made) was added while compounding at two different loadings - 1% and 5% (w/w). The compounds were extruded through a single 3 mm-rod die and cut into pellets using a Haake electronic rotating cutter. The pellets were transferred to a mould of 17 cm (length) x 17 cm (width) x 0.3 cm (thickness). The pellets were pre-heated for 12 min at 180ºC and low pressure, followed by heating at the same temperatures for 10 min at 8 t of pressure and then cooled for 12 min at the same pressure. Three EFB: PP mixtures were produced, *i.e.* 20:80%, 40:60% and 60:40%.

Mechanical Testing

Eight samples (15 cm long x 1.9 cm wide x 0.3 cm thick) were tested for their tensile strength according to ASTM D618 using a Testometric machine model M500-25KN at a cross-head speed of 5 mm min^{-1}. The tensile toughness was computed from the area under the stress-strain curve. The tensile strength and tensile modulus were calculated by:

$$\text{Tensile strength} = \frac{W}{bd}$$

$$\text{Tensile modulus} = \frac{m}{bd}$$

where:
W = ultimate failure load (N)
b = mean width of sample (mm)
d = mean thickness of sample (mm)
m = slope of the stress-strain curve

Dimensional Stability Testing

Eight samples of 3 cm (length) x 1.5 cm (width) x 0.3 cm (thickness) were tested for water absorption and thickness swelling. The specimens were immersed in deionized water at 25°C, and periodically taken out every four days over 40 days for measurement. For each measurement, the sample was dried using absorbent paper and its weight and thickness taken immediately. The water absorbed and thickness swelling were calculated by:

$$\text{Water absorption (\%)} = \left[\frac{M_2 - M_1}{M_1}\right] \text{x } 100$$

where:
M_2 = weight of the sample after immersion (g)
M_1 = weight of the sample before immersion (g)

$$\text{Thickness swelling (\%)} = \left[\frac{t_2 - t_1}{t_1}\right] \text{x } 100$$

where:
t_2 = thickness of the sample after immersion (mm)
t_1 = thickness of the sample before immersion (mm)

Scanning Electron Microscopy

The fracture surfaces of the composites from the tensile tests were examined under a Leica Cambridge S-360 Scanning Electron Microscope. The fractures were mounted on aluminum stubs and sputter coated with gold to avoid electrostatic charging during the examination.

RESULTS AND DISCUSSION

Carbonyl Index

The anhydride contents from the CI tests are shown in *Table 1*, where it is seen that Epolene 43 shows the highest CI. It means that Epolene 43 contains the most anhydride. The processing of MAPP played a crucial role, as the MAPP produced in laboratory is using *in situ* process contained less MAH grafted to the PP as compared to Epolene 43. Among the samples produced in laboratory, e3 was found to be of higher CI than e2 followed by e1. FTIR spectra (*Figure 1*) show the increasing peak intensities at (1740-1860) cm^{-1} region as the anhydride content increased. The differences are evident in the spectra as indicating the extent of MAH grafting to the PP chain according to the MAH loading. Similar results are also reported by other researchers (Zhou *et al.*, 2000; Chuai *et al.*, 2000; Ha *et al.*, 2000).

TABLE 1. CARBONYL INDICES, GRAFTING DEGREE (G_d) AND ACID NUMBER OF MALEATED POLYPROPYLENE (MAPP) SAMPLES

MAPP	Carbonyl index (CI)	Grafting degree (G_d)	Acid number
e1	0.20	0.50 (0.01)	0.51 (0.03)
e2	0.32	1.54 (0.01)	0.57 (0.01)
e3	0.33	2.02 (0.02)	0.63 (0.01)
Epolene 43	0.97	5.12 (0.03)	0.78 (0.02)

Note: Values in parentheses are the standard deviations.

Grafting Degree

Table 1 shows that Epolene 43 has significantly higher G_d than e1, e2 and e3. Since G_d indicates the percentages of MAH grafted to the PP backbone, the MAH-PP grafted for Epolene 43 was the highest. The data from *Table 1* also demonstrate that e3 displayed higher G_d compared to e2 and e1. The G_d of e3 had increased as the MAH loading increased. The G_d is important because it provides interactive site for increased interaction between filler and polyolefin matrix (Zhou *et al.*, 2000).

Acid Number

Table 1 demonstrates the effect of MAH loading on the acid number. Generally, it can be seen that Epolene 43 displayed higher acid number than the prepared samples. The results complement the G_d and FTIR measurements. Anhydride content is the main factor in the resulting higher acid number for various samples of prepared MAPP. From *Table 1*, e3 with a higher MAH loading, had a higher acid number than e1 and e2.

Mechanical Testing

The effects of the different MAPP on the tensile strength of the composites are shown in *Figures 3* and *4*. The composites with MAPP had higher tensile strength than the untreated composites. The increased tensile strength with MAPP may be due to better compatibility between the filler and matrix. A good filler-matrix interaction can derive from the formation of ester bonds between the anhydride groups of MAPP and the hydroxyl groups at the surface of the EFB filler (*Figure 2*). Furthermore, as MAPP is derived from PP, it should be compatible with the PP matrix. Other researchers have reported a similar result in EFB-PP composites (Rozman *et al.*, 1998a). Generally, the composites treated with Epolene 43 displayed better strength than those treated with e1, e2 or e3 (*Figures 3* and *4*). The higher content of anhydride groups in Epolene 43, could have been the main reason. The more the anhydride groups, the more will be the ester bonds formed between the MAPP and hydroxyl groups on the EFB surface. For the composites treated with the laboratory MAPP, e3 had the best strength, followed by e2 and e1. This is the same as for Epolene 43. The strength of the composites decreased as the filler content increased. This agrees with the trends in other lignocellulosic-filled composites (Rozman *et al.*, 1998a, b). Unlike fibre, which has a uniform cross-section and a relatively high aspect ratio, the capability of irregularly-shaped fillers, such as EFB, to support stress transmitted from the thermoplastic matrix is rather poor.

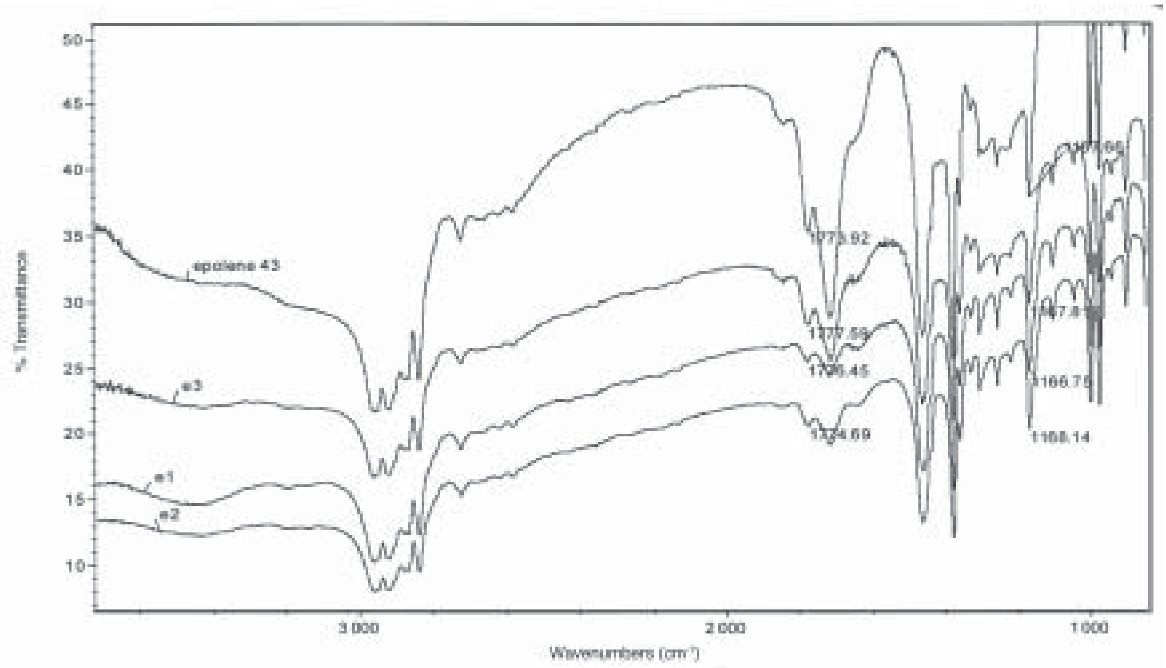


Figure 1. FTIR spectra for the different maleated polypropylene (MAPPs).

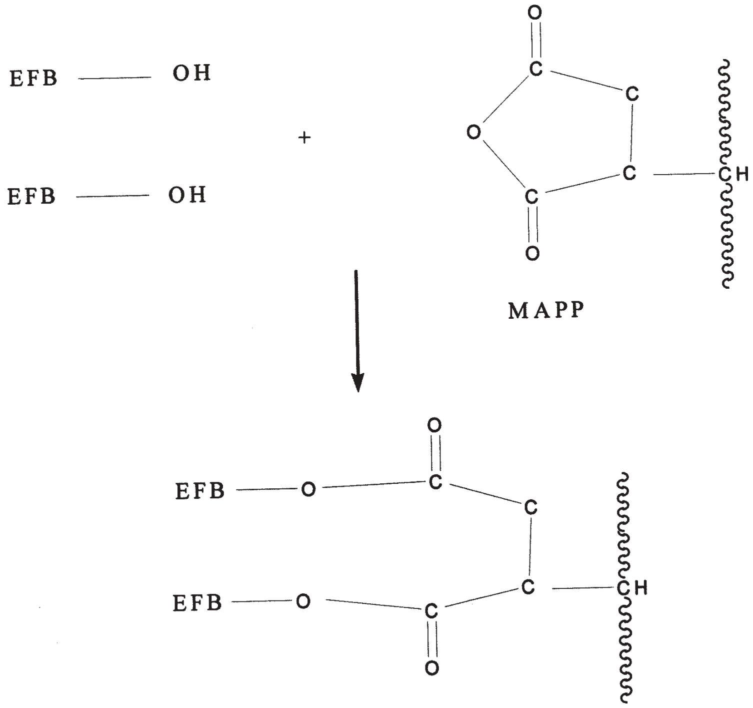


Figure 2. Schematic illustration of the reactions involved in producing the maleated polypropylene (MAPP)-treated EFB-PP composites.

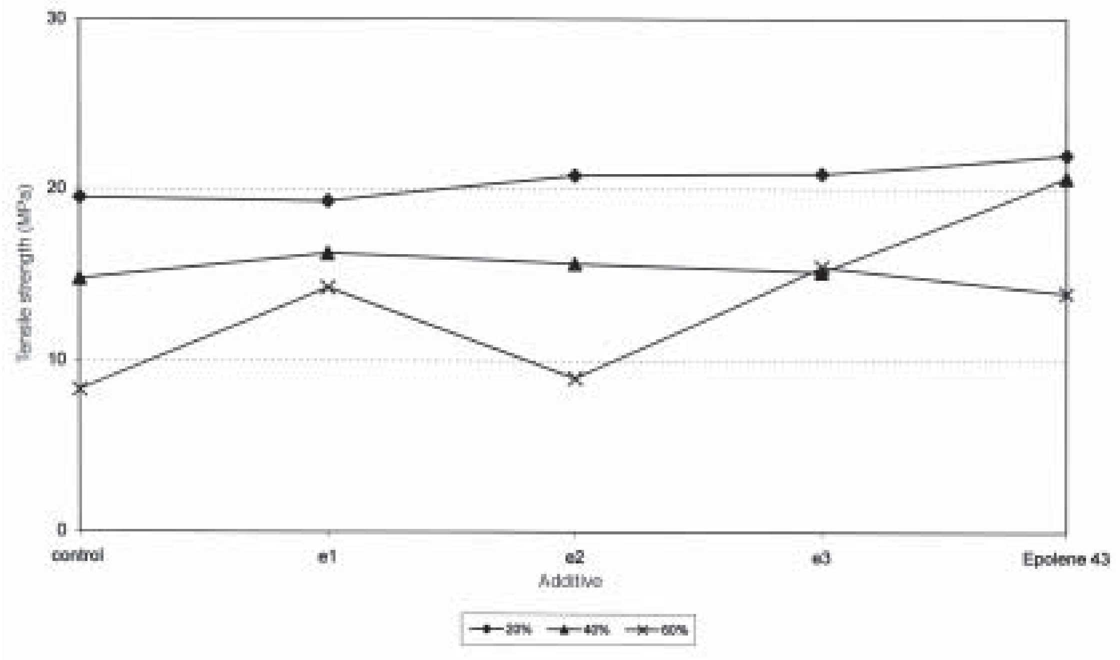


Figure 3. Tensile strength of the EFB-PP composites at 1% maleated polypropylene (MAPP) loading.

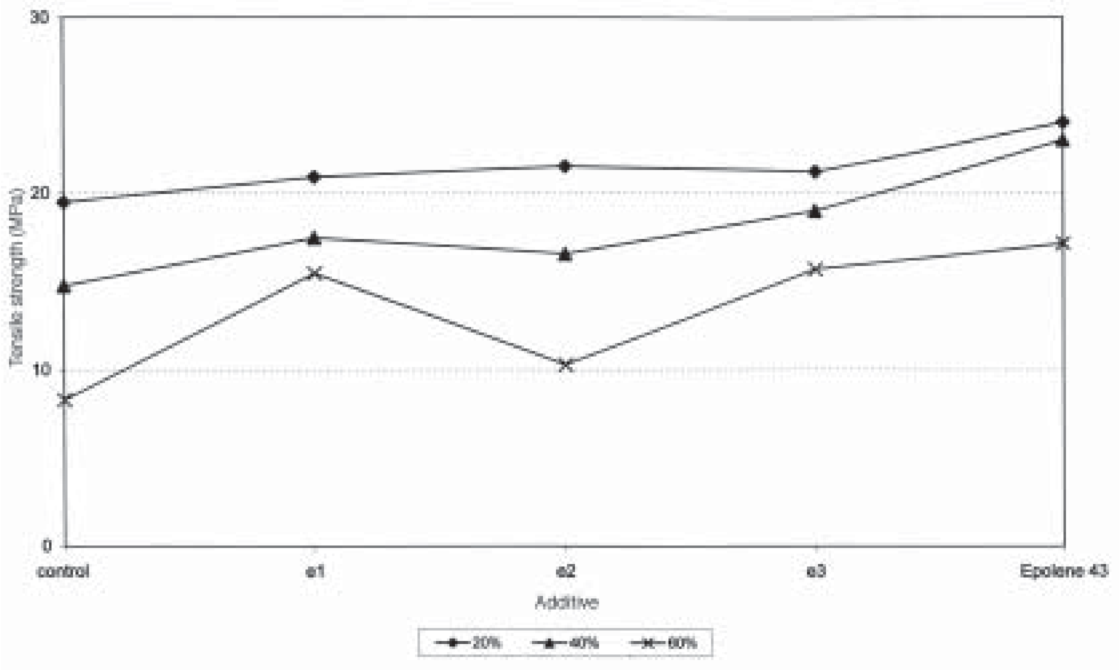


Figure 4. Tensile strength of the EFB-PP composites at 5% maleated polypropylene (MAPP) loading.

The tensile module of the MAPP-treated composites were higher than those of the untreated composites (*Figures 5* and *6*). Hence, MAPP enhanced the stiffness of the composites. Epolene 43 imparted the greatest stiffness to the composites, followed by e3, e2 and e1. These results are in line with reports by other researchers (Rozman *et al.*, 1998a). From *Figures 5* and *6*, the modulus increased with the filler loading. This seems a common phenomenon, which has already reported for other lignocellulosic-filled composites. Since the EFB filler is stiffer than the matrix, any increase in filler loading would have increased the stiffness of the composite.

Figures 7 and *8* show the tensile toughness of the composites with MAPP to be higher than those of the untreated composites. Thus, more energy would be needed to break the composites with MAPP. This, in turn, indicates that MAPP imparted greater compatibility between the EFB fibre and PP matrix, due to covalent bonding between the anhydride groups of MAPP and hydroxyl groups of EFB. The Epolene 43-treated composites had the highest tensile toughness followed by e3, e2 and e1. Scanning Electron Microscopy (SEM) analysis showed the better interaction at the interfacial regions with Epolene 43 (*Figure 15b*) than in those samples treated

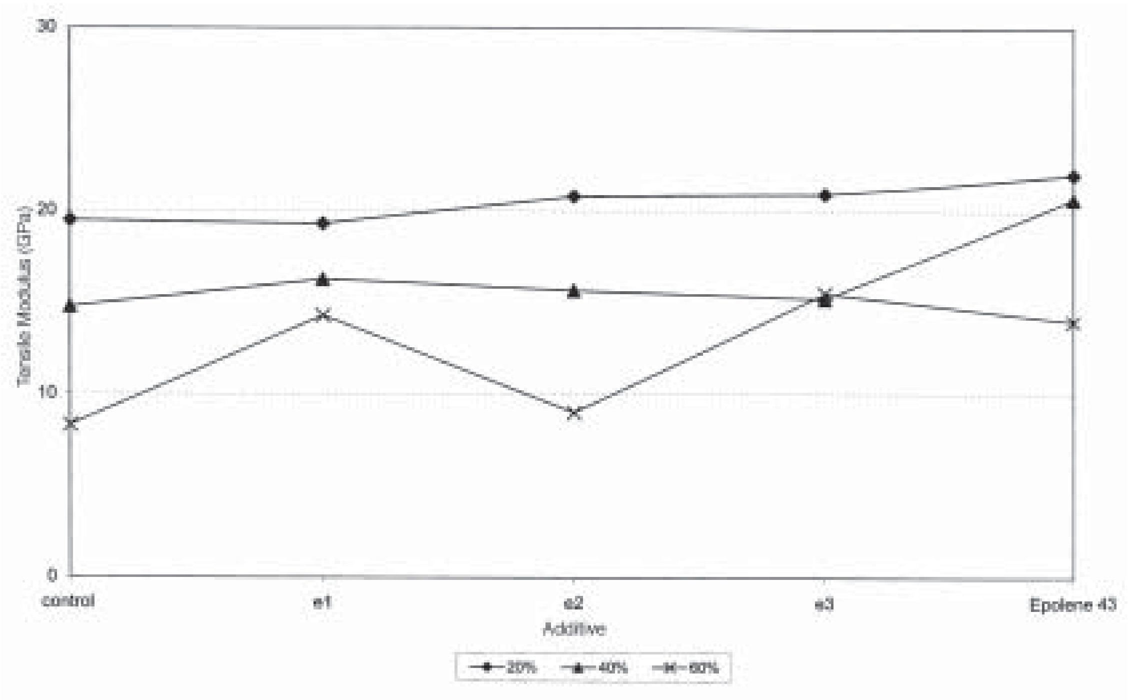


Figure 5. Tensile modulus of the EFB-PP composites at 1% maleated polypropylene (MAPP) loading.

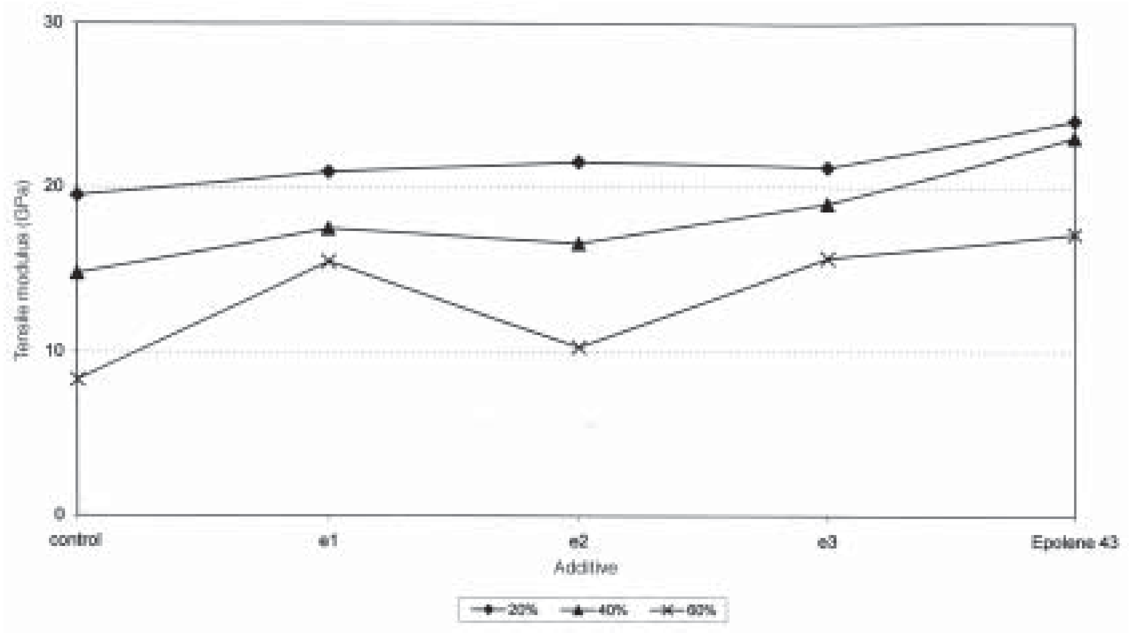


Figure 6. Tensile modulus of the EFB-PP composites at 5% maleated polypropylene (MAPP) loading.

with laboratory MAPP (*Figure 15c*). The anhydride groups seemed to be the main factor enhancing the toughness of the composites as Epolene 43 had more anhydride groups than the other samples of MAPP prepared as discussed earlier. In general, the tensile toughness decreased as the filler loading increased (*Figures 7* and *8*). Poor wetting is expected because of the lack of compatibility between the polar functional groups of EFB and the non-polar PP, giving rise to weak interfacial regions. However, due to treatment of the filler, the tensile toughness of the composites with MAPP was higher than those of the untreated filler as the filler loading increased.

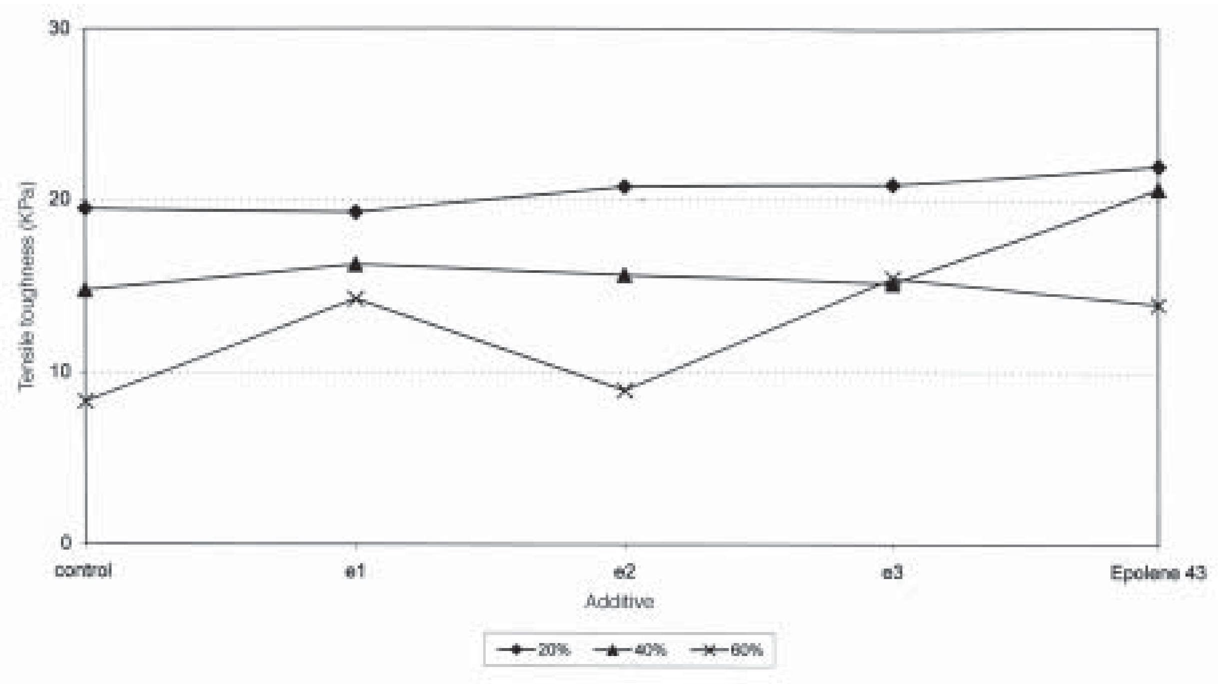


Figure 7. Tensile toughness of the EFB-PP composites at 1% maleated polypropylene (MAPP) loading.

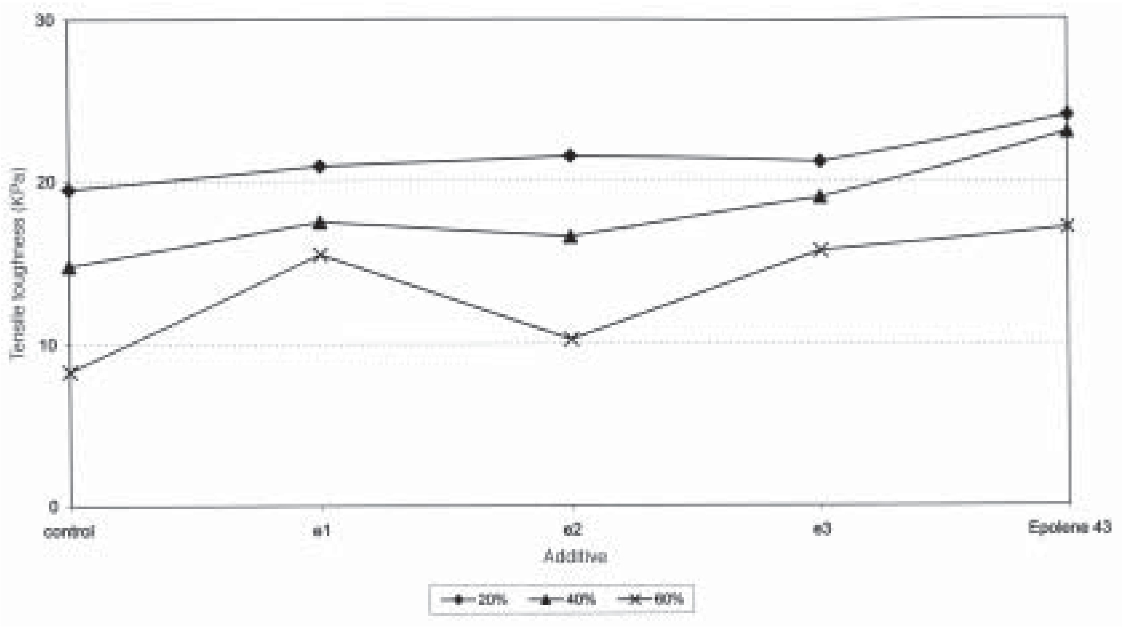


Figure 8. Tensile toughness of the EFB-PP composites at 5% maleated polypropylene (MAPP) loading.

Dimensional Stability

Figures 9 to *11* show water absorption by the composites (with different levels of filler loading) with and without MAPP. The treated composites (with MAPP) had lower water absorption than those untreated. Lignocellulose materials absorb water by hydrogen bonding between their hydroxyl groups and water in the cell wall region (Rowell *et al*., 1976). For the treated composites, there would have been less hydrogen bonding due to the chemical layer formed on the filler surface preventing water from coming into contact with the OH groups in the EFB. The water absorption by the composites with MAPP decreased as the chemical loading increased. The figures also demonstrate the increasing water absorption with filler loading. Swelling of lignocellulosic materials occurs when the absorbed water bulks the cell wall.

The thickness swelling (*Figures 12* to *14*) followed a similar trend to water absorption. The MAPP samples swelled significantly less than the untreated samples. Hence, the formation of ester bonds between the anhydride groups of MAPP and OH groups of EFB was able to prevent water penetrating into the cell wall, resulting in less swelling.

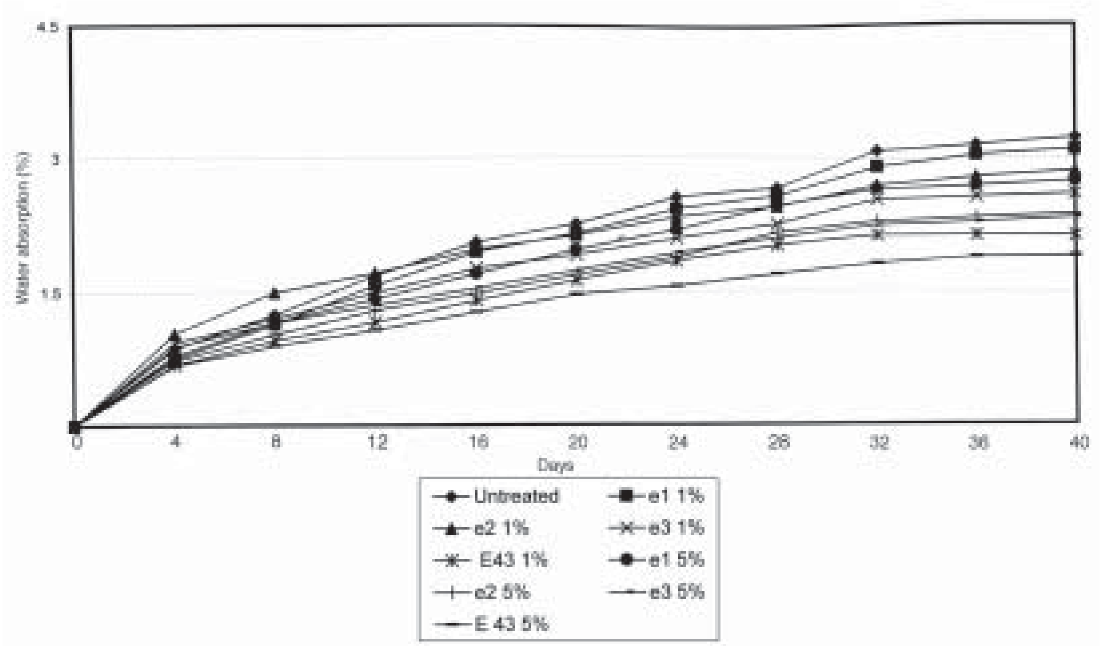


Figure 9. Effect of maleated polypropylene (MAPP) on water absorption at various MAPP loadings at 20% fibre content.

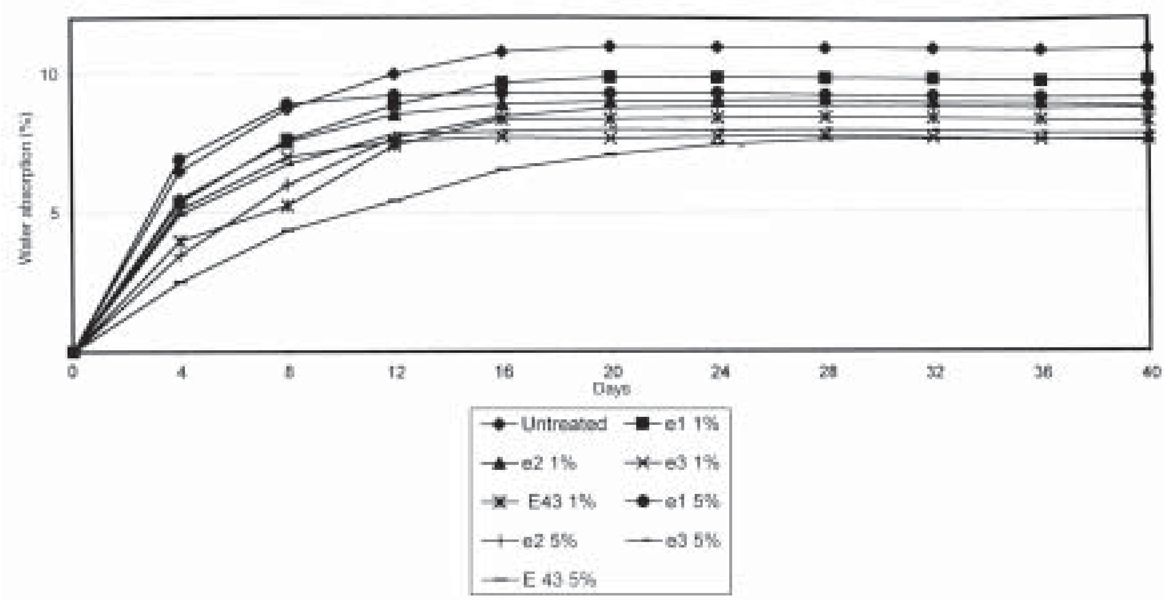


Figure 10. Effect of maleated polypropylene (MAPP) on water absorption at various MAPP loadings at 40% fibre content.

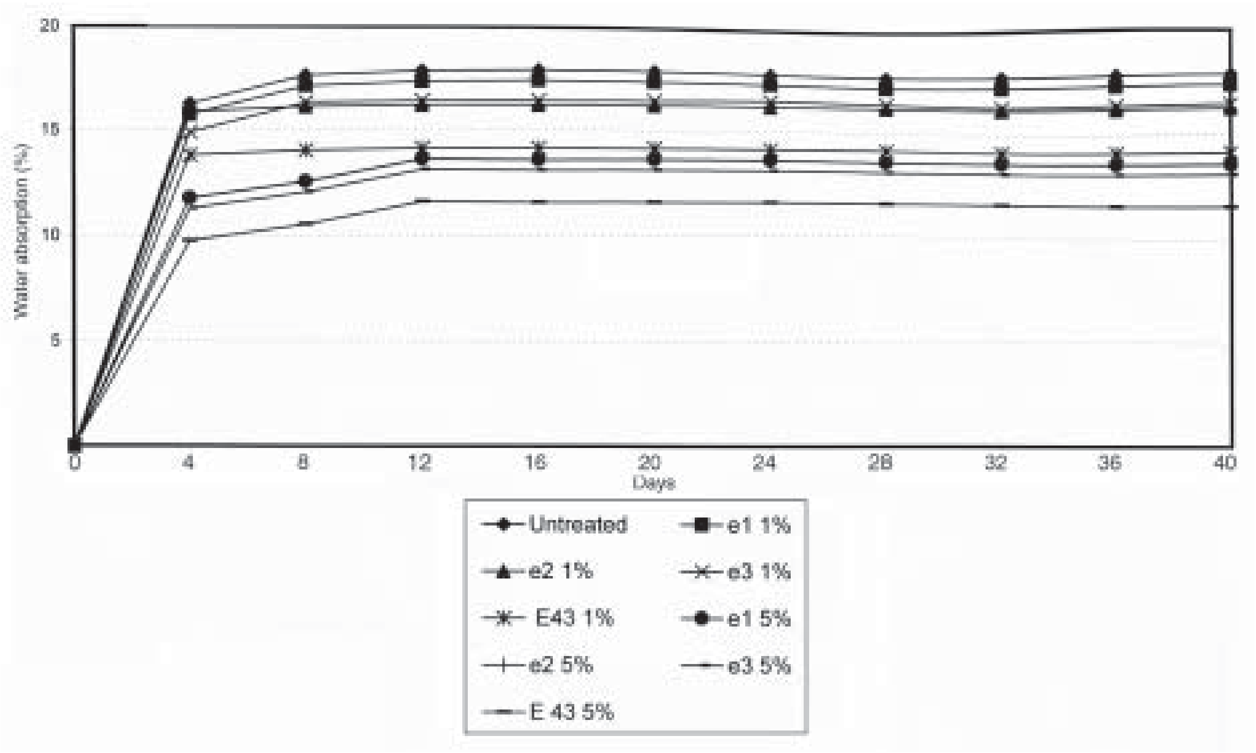


Figure 11. Effect of maleated polypropylene (MAPP) on water absorption at various MAPP loadings at 60% fibre content.

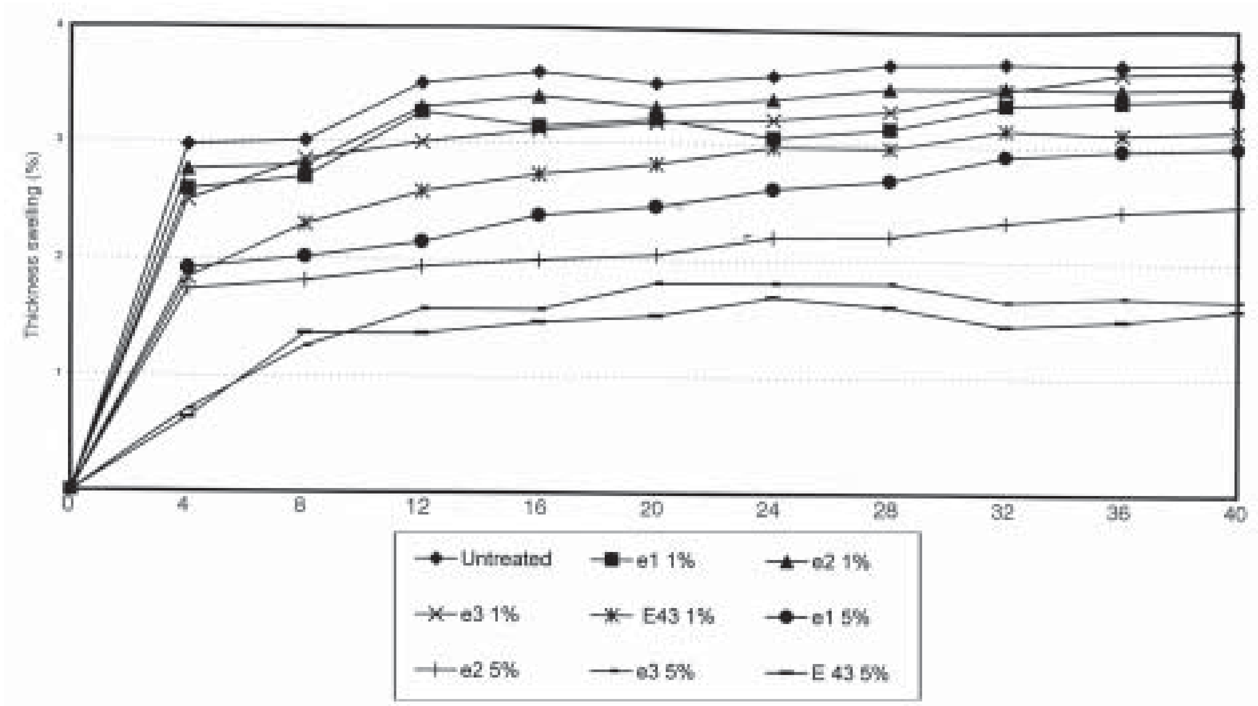


Figure 12. Effect of maleated polypropylene (MAPP) on thickness swelling at various MAPP loadings at 20% fibre content.

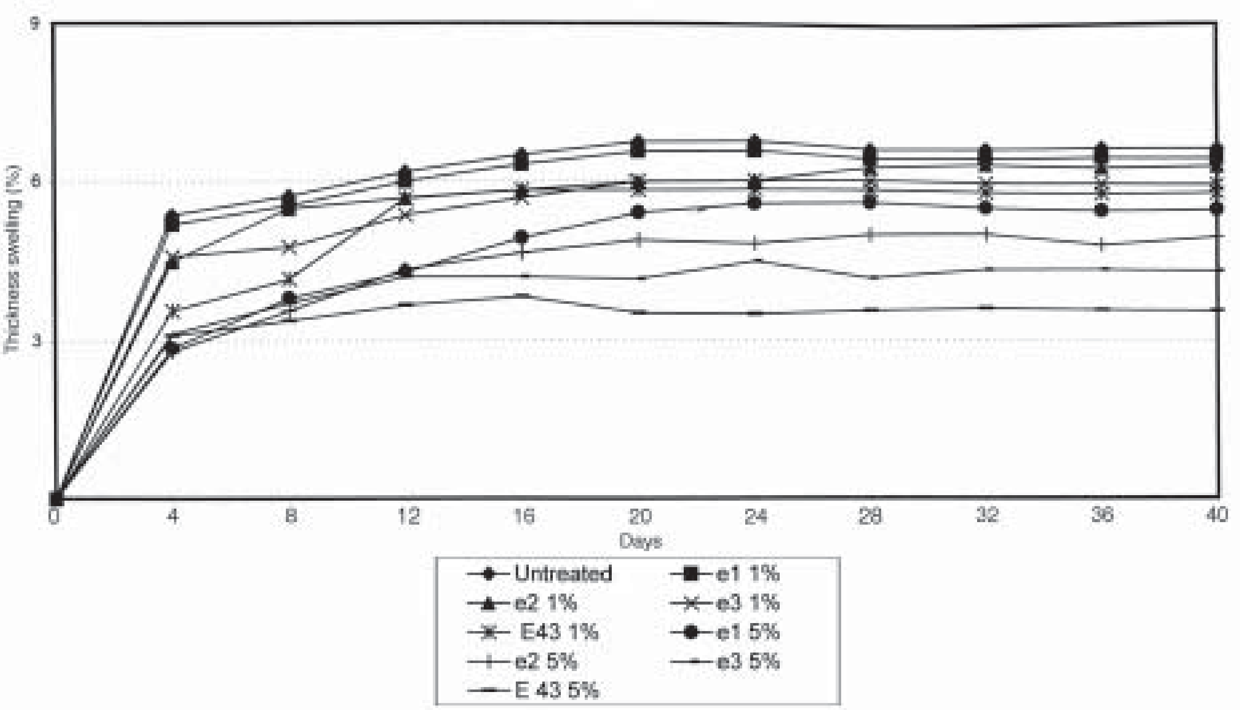


Figure 13. Effect of maleated polypropylene (MAPP) on thickness swelling at various MAPP loadings at 40% fibre content.

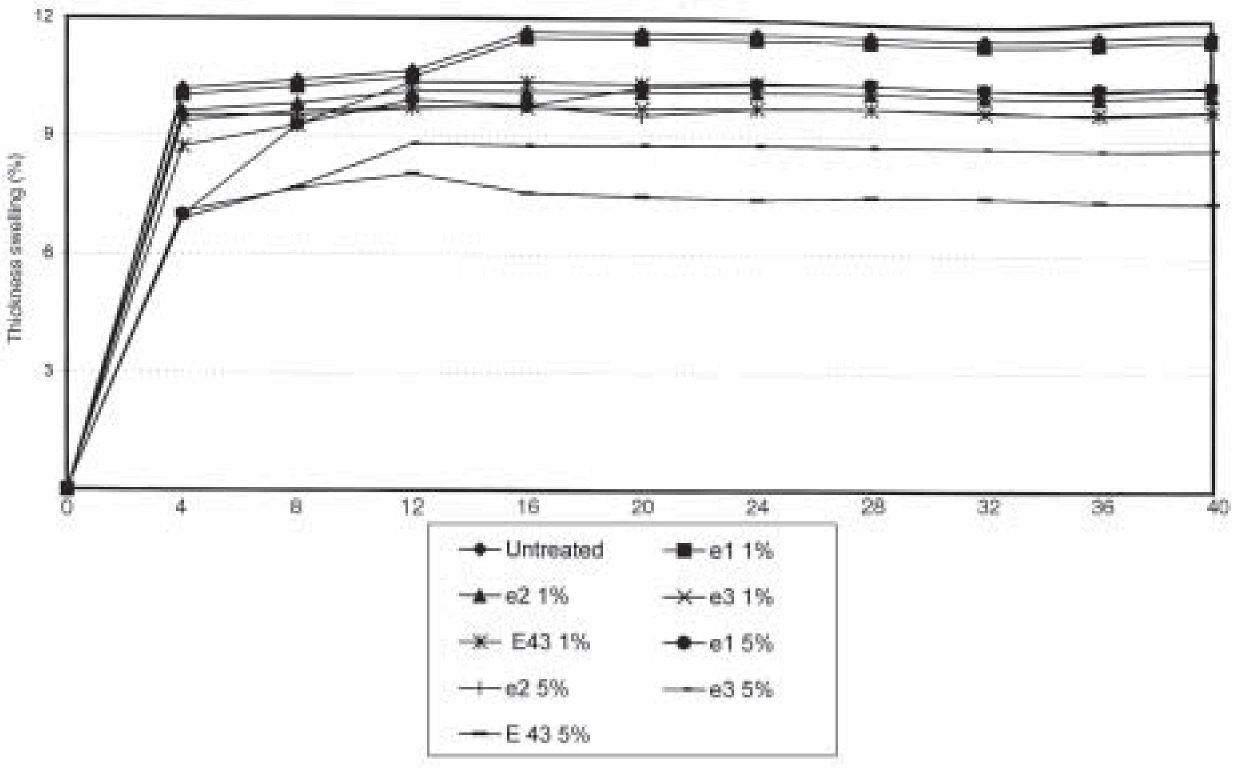


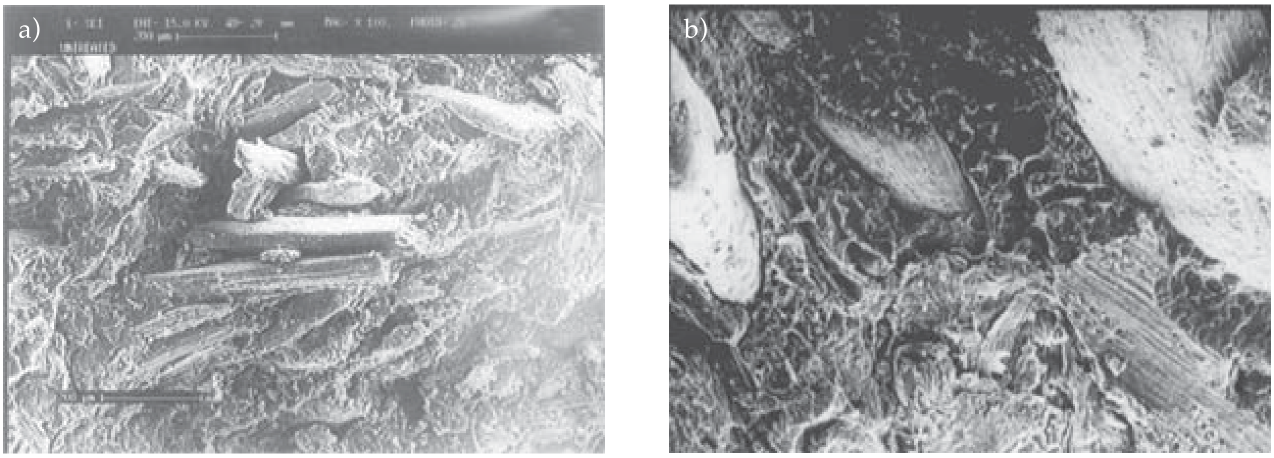
Figure 14. Effect of maleated polypropylene (MAPP) on thickness swelling at various MAPP loadings at 60% fibre content.

Scanning Electron Microscopy (SEM)

Figure 15a is a micrograph of a composite with untreated filler. It shows the weak interaction between filler and PP matrix by the loose adhesion formed. Since the interaction between them is important for withstanding the stress imposed in tests, the weak adhesion resulted in lower tensile strength. In addition, the filler occurs in bundles from hydrogen bonding within the filler itself, thus, further decreasing the strength of the composite. *Figures 15b* and *c* shows that the composites with MAPP-treated filler had better adhesion between the filler and matrix. Further, the composite treated with Epolene 43 (*Figure 15b*) showed better adhesions than that with e1 (*Figure 15c*) which looked looser. The SEM proved the outstanding mechanical and physical properties of the composite with Epolene 43 over those with the laboratory MAPP as explained in previous chapter.

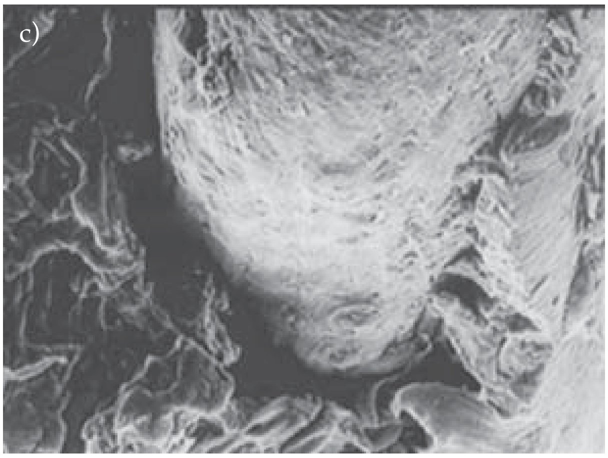
CONCLUSION

The analysis of MAPP (FTIR, G_d and acid number) has shown chemical bonding between MAH and PP backbone. Composites with MAPP treated fillers (oil palm EFB fibres) had higher tensile strength and dimensional stability than the untreated samples. The composite with Epolene 43-treated filler gave the best mechanical and physical properties, followed by that with e3, then e2 and e1. This was probably due to Epolene 43 having more anhydride groups than the others. SEM showed the better compatibility and adhesion between the PP matrix and fibre with MAPP than untreated fibre.



Micrograph of an untreated composite.

Micrograph of an epolene 43-treated composite.



Micrograph of a epolene el-treated composite.

Figure 15.

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REFERENCES

AGNELLI, J A M and BETTINI, S H P (2000*). Polymer Testing*. Vol. 19. p. 3-15.

CHUAI, C; ALMDAL, K; POULSEN, L and PLACKETT, D (2000). *J. Applied Polymer Science Vol., 80*: 2893-2841.

GAYLORD, N G (1976*). Introduction Copolymers, Polyblends and Composites* (N Platzer, ed.). Academic, New York. p. 76.

HA, C S; CHO, Y W; GO, J H and CHO, W J (2000*). J. Applied Polymer Science Vol., 77*: 2777-2784.

KAZAYAWOKO, M; BALATINECZ, J J; WOODHAMS, R T and LAW, S (1997). *J. Reinforced Plastic and Composites Vol., 16*: 1383-1406.

LIGHTSEY, G R (1981). *Polymer Science and Technology*. Vol. 17. p. 193.

MATSUDA, H; UEDA, M and MORI, H (1998). *Wood Science and Technology Vol., 22*: 21-32.

ROZMAN, H D; PENG, G B and MOHD ISHAK, Z A (1998a). *J. Applied Polymer Science Vol., 70*: 2647-2655.

ROZMAN, H D; KON, B K; ABUSAMAH, A; KUMAR, R N and MOHD ISHAK, Z A (1998b). *J. Applied Polymer Science Vol., 69*: 1993-2004.

ROWELL, R M; GUTZMER, D I and KINNEY, R E (1976). *Wood Science Vol., 9*: 51.

THEBERGE, J E and HOHN, E (1981*). Polymer Plastic Technology Engineering*. Vol. 16. p. 41.

ZHOU, X; DAI, G; GUO, W and LIN, Q (2000). *J. Applied Polymer Science Vol., 76*: 1359-1365.