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OIL PALM EMPTY FRUIT BUNCH–POLYPROPYLENE COMPOSITES: THE EFFECT MALEATED POLYPROPYLENE ON THE MECHANICAL PROPERTIES

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ABSTRACT

The production of oil palm empty fruit bunch (EFB) fibre–polypropylene (PP) composites with treated and non-treated maleated polypropylene (MAPP) was studied. Commercial MAPP (Epolene 43) and MAPP samples synthesized at the laboratory were used to determine MAPP's effectiveness as a coupling agent for EFB fibre-composites. Several analyses on MAPP-treated composites were carried out including FTIR spectra, acid number and G_d *tests to determine the action of the anhydride. The flexural and impact properties of the treated composite samples produced in the laboratory using both Epolene 43 and MAPP samples produced at laboratory were significantly better than those of the untreated composites.*

Keywords: Oil palm empty fruit bunches (EFB), polypropylene (PP), maleated polypropylene (MAPP), mechanical properties, coupling agents.

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INTRODUCTION

Cellulose fibre is little used as filler in thermoplastics compared to the inorganic fillers, such as talc, mica and glass fibre, despite its many advantages such as lower density, higher specific strength and modulus, renewable nature, lower fibre breakage during mixing and lower cost (Lightsey *et al*., 1981; Theberge *et al*., 1981). When cellulosic fibre is compounded with thermoplastic polymers, the main problem encountered is the poor interfacial adhesion between the hydrophobic polymer and hydrophilic filler. Coupling agents have been tested to improve the dispersion, adhesion and compatibility between the hydrophilic cellulose and hydrophobic matrix. These agents can improve the interface by interacting with both the fibre and its matrix, to form a stronger link between them (Gaylord, 1976). The coupling agents contain chemical groups which react with both the fibre and polymer, forming are covalent and hydrogen bonds which improve the interfacial adhesion. Maleated polypropylene (MAPP) has received considerable attention as a coupling agent because of its effectiveness in improving the mechanical properties of wood fibre-polypropylene composites (Kazayawoko *et al*., 1997).

EXPERIMENTAL WORK

Materials

Empty fruit bunch (EFB) fibre was obtained from Sabutek (M) Sdn Bhd. The polypropylene used was Propelinas 600 G (homopolymer), purchased from Polypropylene (M) Sdn Bhd with a density and melt index specified as 0.9 g cm^{-3} and 12 g 10 min^{-1}, respectively. Epolene-43 was purchased from Suka Chemicals (M) Sdn Bhd, it had a low molecular weight (M_n=3900 g mol^{-1} , M_w=9100 g mol^{-1}), density of 0.93 g cm^{-3} and acid number 47. Dicumyl peroxide, purchased from Komita (M) Sdn Bhd was used as the initiator in producing MAPP in the laboratory. Maleic anhydride (MAH) was purchased from Komita (M) Sdn Bhd.

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Preparation of Fibre

The EFB filler was delivered as long strands of fibre. The fibre was ground into small particles using a RetschMuhle grinding machine, and sieved through an Endicott sieve of mesh 35-60 (270-500 µm). The fibre was then extracted with a solution of toluene, ethanol and acetone (ratio 4:1:1, vol vol^{-1}) for about 3 hr and dried in an oven overnight at 105^{o}C.

Process of Producing MAPP in Laboratory

The production of MAPP was by using an internal mixer at 180^{o}C with 35 rpm rotor speed for about 20 min. Three compounds were produced - 25% MAH + 75% PP, 10% MAH + 90% PP and 5% MAH + 95% PP, - referred to as e3, e2 and e1, respectively. Approximately 2% dicumyl peroxide (based on the weight of MAH) as initiator was added. The compounds were ground to a fine powder using a RetschMuhle grinder.

Analysis of MAPP

Carbonyl Index

Analyses of Epolene 43 and MAPP (produced in the laboratory) by infra-red spectroscopy were carried out using a Nicolet FTIR spectrometer (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. Using these bands the carbonyl index (CI) was calculated:

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

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

Grafting Degree (G_d)

The grafting degree analysis (Zhou *et al*., 2000) was performed. A sample of the MAPP-composite (0.2 g) was dissolved in 50 ml toluene under reflux for half an hour. Then 100 ml hydrochloric acid were added and the mixture titrated with KOH (0.1 M) with phenolphthalein as indicator. A blank was carried out by the same method. The grafting degree (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 oven dry sample (g)
V = volume of KOH (ml) for the blank solutions
V_0 = volume of KOH (ml) for the MAPP solution

Acid Number

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

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

where,
A = acid number
W = weight of oven dry sample (g)
V′ = volume of KOH (ml) for sample solution
H = volume of KOH (ml) for blank solution
f′ = factor value of KOH solutions (0.1 M)
= concentration of KOH (M) solution

Compounding and Processing

Compounding of the materials and filler treatments were carried out using a Haake Rheocord 5000. The screw speed was set at 35 rpm with temperature zones of 165^{o}C (zone 1), 170^{o}C (zone 2), 175^{o}C (zone 3) and 180^{o}C (zone 4). The MAPP was loaded while compounding with: 1%, 3% 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 with dimensions of 170 x 170 x 3 mm^{3}. The pellets were pre-heated for 12 min at 180^{o}C and low pressure, followed by heating at the same temperature for 10 min with 8 t pressure and then cooled to 30°C for 12 min with the same pressure. Four ratios of the EFB-PP mixtures were produced: 20% - 80%, 30% - 70%, 40% - 60% and 60% - 40%.

Mechanical Testing

The flexural tests were conducted according to ASTM D790 (Anon, 1992a) on samples of 15 x 1.5 x 0.3 cm^{3} (length x width x thickness) using a Testometric machine (Model M500-25KN) at a crosshead speed of 4 mm min^{-1}. The flexural toughness was calculated from the area under the stress-strain curve. The flexural strength and flexural modulus were calculated by:

$$\text{Flexural strength} = \frac{3WL}{2bd^2}$$

$$\text{Flexural modulus} = \frac{L^3\, \Delta W}{4bd^3\, \Delta S}$$

where W = ultimate failure load (N), L = span between centres of support (mm)
b = mean width of sample (mm), d = mean thickness of sample (mm)
ΔW = increase in load (N), ΔS = increase in deflection (mm)

Impact tests were conducted according to ASTM D256 (Anon, 1992b). The Izod method was applied on unnotched samples of 6.0 x 1.5 x 0.3 cm^3 (length x width x thickness), using the Zwick Impact Pendulum Tester model 5101.

RESULTS AND DISCUSSION

Carbonyl Index

The contents of anhydride from the carbonyl index (CI) tests are shown in *Table 1*. Epolene 43 showed the highest CI. The absorption bands at (1740-1860) cm^{-1} corresponded to stretchings of anhydride group gives a higher number of CI by Epolene 43 than e1, e2, and e3. The commercial Epolene 43 had a higher anhydride content than the prepared samples. The processing of the MAPP produced was *in situ* resulting in less MAH grafted to PP than to Epolene 43. For the MAPP samples produced in the laboratory, e3 had a higher anhydride content than e2 followed by e1, as was to be expected. The results are qualitatively shown in the FTIR spectra (*Figure 1*) with increasing peaks at 1740-1860 cm^{-1} as the anhydride content increased. The qualitative differences showed that the MAH grafting to the PP chain was according to the MAH loading. Other researchers have reported similar results and attributed them to the same cause (Zhou *et al.,* 2000, Chuai *et al.,* 2000, Ha *et al.,* 2000).

Grafting Degree (G_d)

Table 2 shows that Epolene 43 had significantly higher G_d than to e1, e2, and e3. Since G_d indicates the percentage of MAH grafted to the PP backbone, the results indicated the most MAH-PP grafting for epolene 43 (*Figure 2*). In *Table 3,* e3 had higher G_d than e2 and e1. Thus, the G_d of e3 had increased with the MAH loading. The grafting degree is important because it provides the interactive sites for increased interaction between the filler and polyolefin matrix (Zhou *et al.,* 2000).

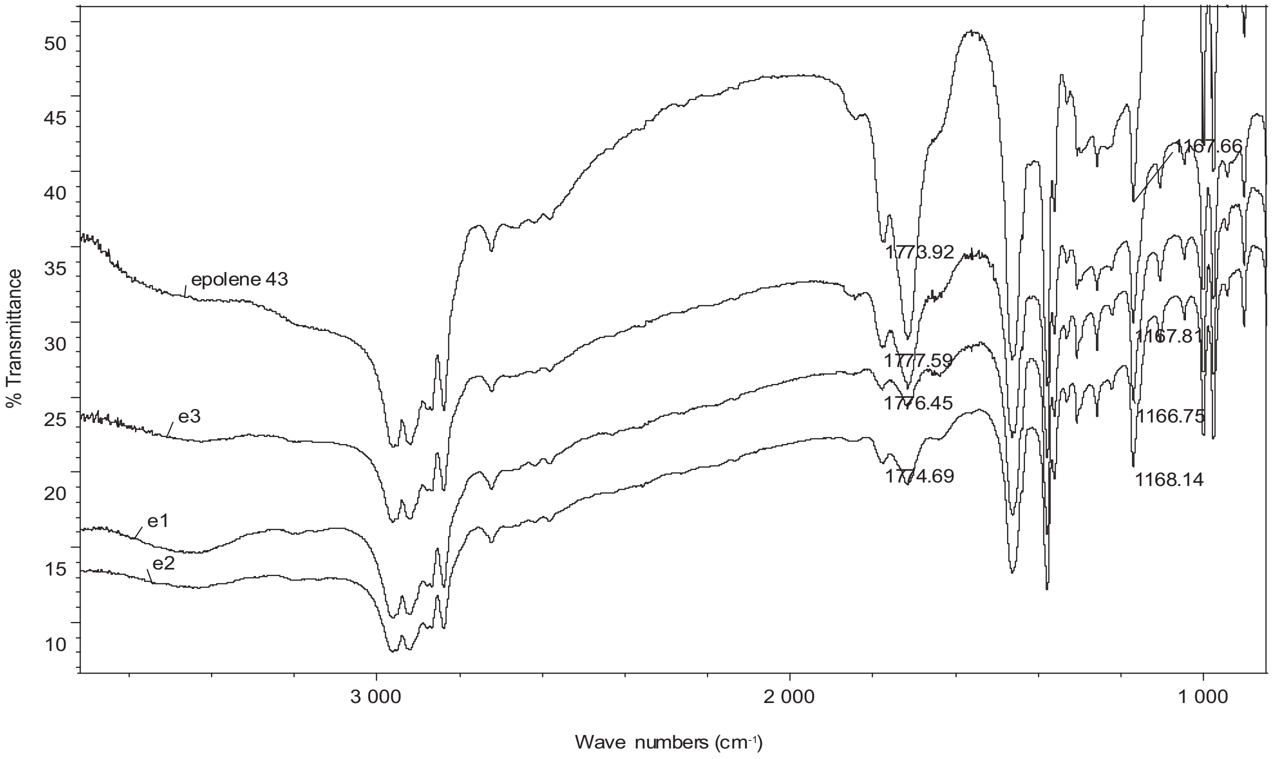

Figure 1. FTIR spectra for different maleated polypropylene (MAPP).

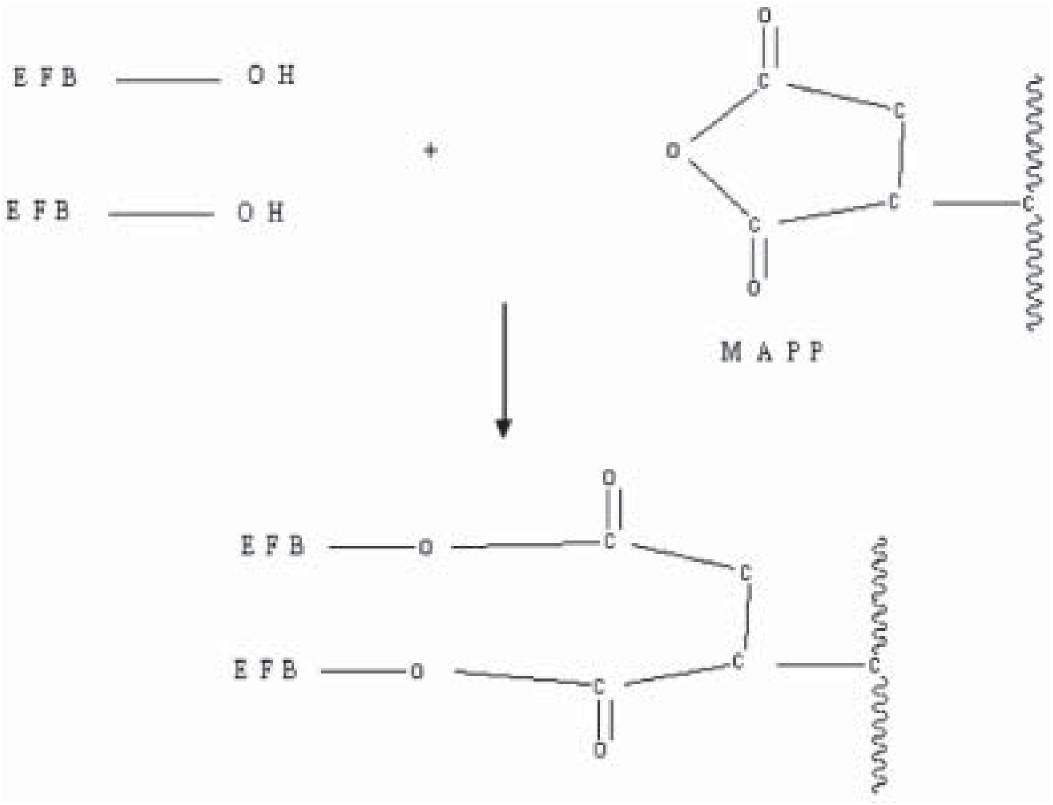

Figure 2. Reactions involved in producing the MAPP treated EFB-PP composites.

Acid Number

Table 3 shows the effect of MAH loading on the acid number. Generally, Epolene 43 had a higher acid number than the others. These results are in line with the G_d and FTIR results, and prove that the anhydride content is the main factor raising the acid number in the MAPPs. From *Table 3*, e3 with a higher MAH loading had a higher acid number than e1 and e2.

Mechanical Testing

In *Figures 3* to *5*, the composites with MAPP-treated fillers had higher flexural strength than that with the untreated filler. Thus, MAPP had enhanced the flexural strength of the composites. The Figures also show that using more MAPP increased the strength of the composites. The strength is believed to be conferred by the anhydride groups in MAPP which increase covalent and hydrogen bonding with the OH groups and oxygen from the carboxylic groups (*Figure 2*), respectively, improving the adhesion between the filler and matrix plastic. Good wetting of the filler by the matrix also created better reception of the filler by the matrix whenever stress applied. Other researchers using the same coupling agents have also reported similar results with composites of lignocellulose – plastic (Rozman *et al.*,

TABLE 1. CARBONYL INDEXS OF MALEATED POLYPROPYLENE (MAPP) SAMPLES

MAPP	Carbonyl Indices (CI)
e1	0.20
e2	0.32
e3	0.33
Epolene 43	0.97

TABLE 2. GRAFTING DEGREE (G_d) OF MALEATED POLYPROPYLENE (MAPP) SAMPLES

MAPP	Grafting Degree (G_d)
e1	0.50 (0.01)
e2	1.54 (0.01)
e3	2.02 (0.02)
Epolene 43	5.12 (0.03)

Note: Values in parentheses are the standard deviations.

TABLE 3. ACID NUMBER OF MALEATED POLYPROPYLENE (MAPP) SAMPLES

MAPP	Acid Number
e1	0.51 (0.03)
e2	0.57 (0.012)
e3	0.63 (0.01)
Epolene 43	0.78 (0.02)

Note: Values in parentheses are the standard deviations.

2000; 1998a, b). Mixing with Epolene 43 conferred higher strength than with e3, e2, and e1. The higher content of anhydride in Epolene 43 may be the main cause for the higher strength. Thus, in succession, the composite with e3 was stronger than that with e2 followed by than that with e1. The flexural strength of the treated as well as untreated composites decreased as the filler loading was increased (*Figures 3* to *5*). This relationship has also been reported by other authors (Rozman *et al.*, 1998a, Mohd Ishak *et al*., 2000). With more filler, more filler bundles are formed from the hydrogen bonding and the composite becomes less able to bear the stress transmitted from the matrix.

The flexural modulus of the composites with MAPP-treated and untreated fillers are shown in *Figures 6* to *8*. The treated composites had higher modulus than the untreated. Thus, MAPP enhanced the stiffness of the composites. In addition, the better modulus of composites can also be attributed to the better dispersion of filler within the matrix (Maldas *et al.*, 1992). Epolene 43 produced a better modulus than e3, e2 and e1. Thus, it conferred better stiffness than the others. The modulus increased as the percentage of filler increased. These relationships have also been found by other researchers (Rozman *et al.*, 2000; 1998b), although the inherent stiffness of EFB contributed more to the overall modulus than that of the matrix.

The effects of MAPP treatment of EFB filler on the flexural toughness of the EFB–PP composites are shown in *Figures 9* to *11*. All the Figures show greater toughness in the treated composites than the untreated sample. This suggests that of MAPP had improved the compatibility between filler and plastic matrix, possibly due to better bridging between the filler surface and matrix at the interfacial region. As the toughness corresponds to the energy needed to break the samples, the samples with MAPP would require more energy to break than the control ones. In general, the flexural toughness of the composites increased with the MAPP loading (from 1%, 3% and 5%). This was probably due to the anhydride groups which caused more ester bonds to be found between the OH groups of the EFB filler, and/or hydrogen bonding between the OH groups and oxygen of the carboxylic groups (related chemical reactions in *Figure 2*). The results corroborate the findings by other authors on lignocellulose-filled composites. Further, for the same reasons, the epolene 43 composites were tougher than the e3, e2 and e1 composites. The toughness decreased as the filler loading was increased. More EFB filler caused more filler bundles to form, weakening the composites as less energy would be required to break them.

Figures 12 to *14* show the impact strength of the MAPP-treated composites compared to the untreated. Adding MAPP to the composites improved the wetting of the EFB filler in the matrix resin. In the impact test, cracks proliferate through the polymer as well as the interfacial region, so a good interfacial region would improve the crack resistance and, consequently the impact strength. Basically, the impact strength increased with the MAPP loading probably due to the interfacial region becoming better in resisting cracking. This finding is in line with those by other researchers on lignocellulose-filled composites (Li *et al*., 2001, Rozman *et al*., 1998b). Chuai *et al.* (2000) reported that conifer fibre treated with Epolene 43 had better

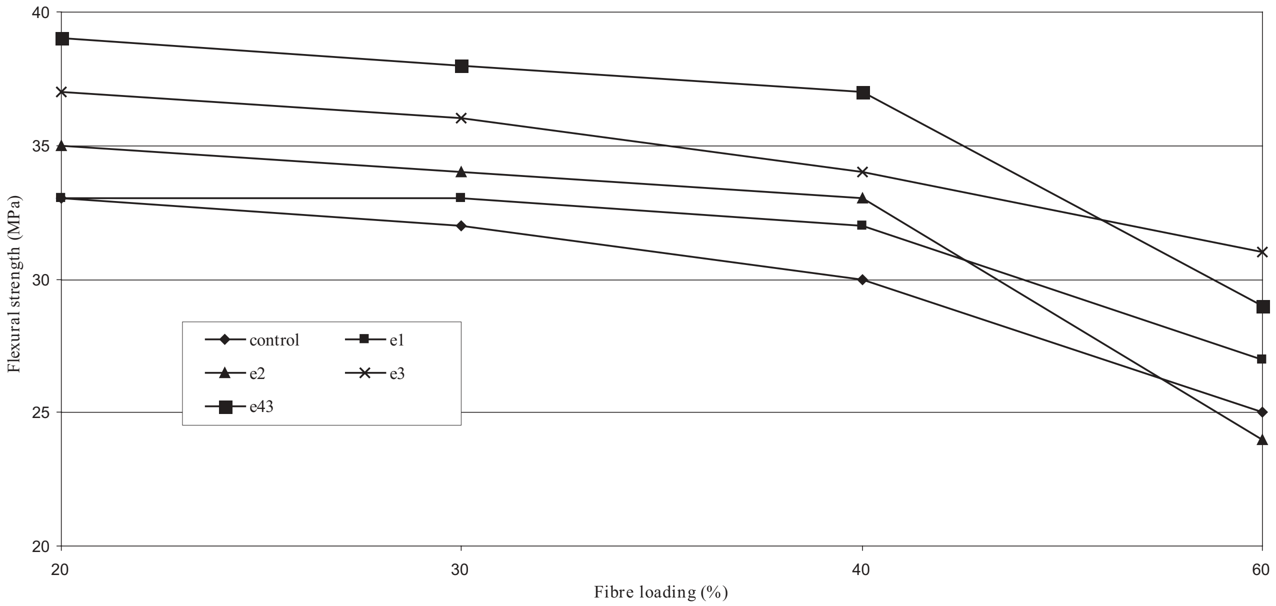

Figure 3. Effects of fibre loading on the flexural strength of maleated polypropylene (MAPP) treated (1% MAPP loading) and untreated samples.

impact strength than an untreated sample due to esterification of the fibre hydroxyl groups and anhydride in MAPP, chemically bridging the fibre and matrix and improving the transfer of stress from the matrix to the fibre.

Figures 12 to *14* show the higher impact strength in the Epolene 43 treated composite over the e3, e2 and e1 composites. The causes are probably the same as those for flexural toughness described earlier. The impact strength decreased with increasing filler content in both the treated and untreated composites. This observation was not unexpected for a filled plastic and has been made before by Kendall (1977) and Raj *et al*. (1989). The probable reason is agglomeration of the filler, weakening the interfacial regions and making them less resistant to crack propagation.

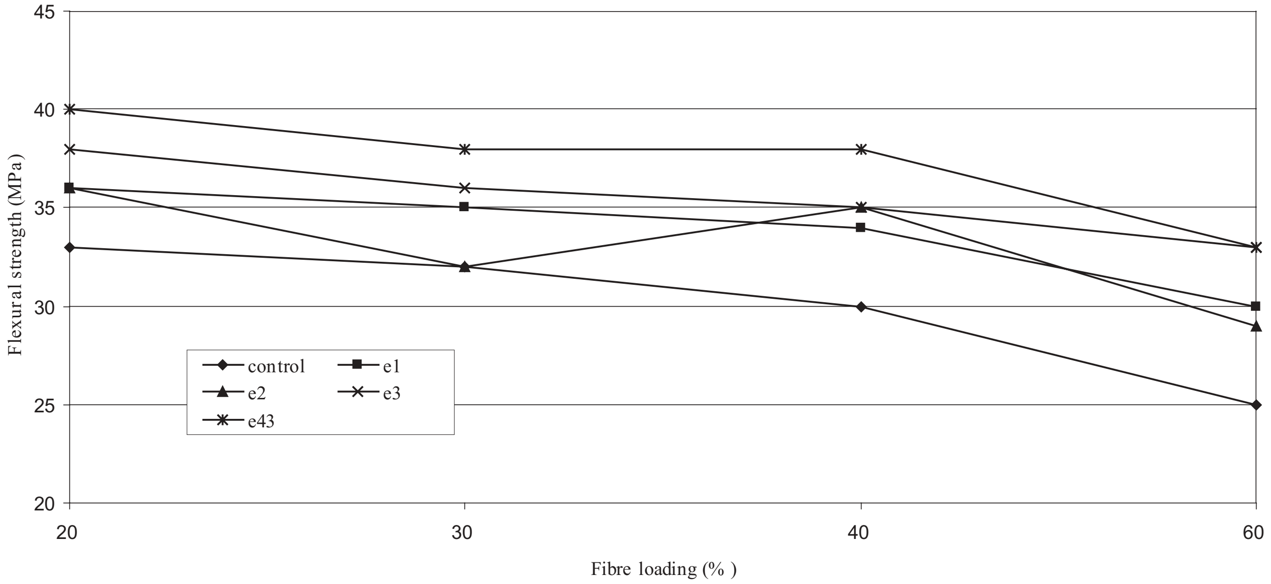

Figure 4. Effects of fibre loading on the flexural strength of maleated polypropylene (MAPP) treated (3% MAPP loading) and untreated samples.

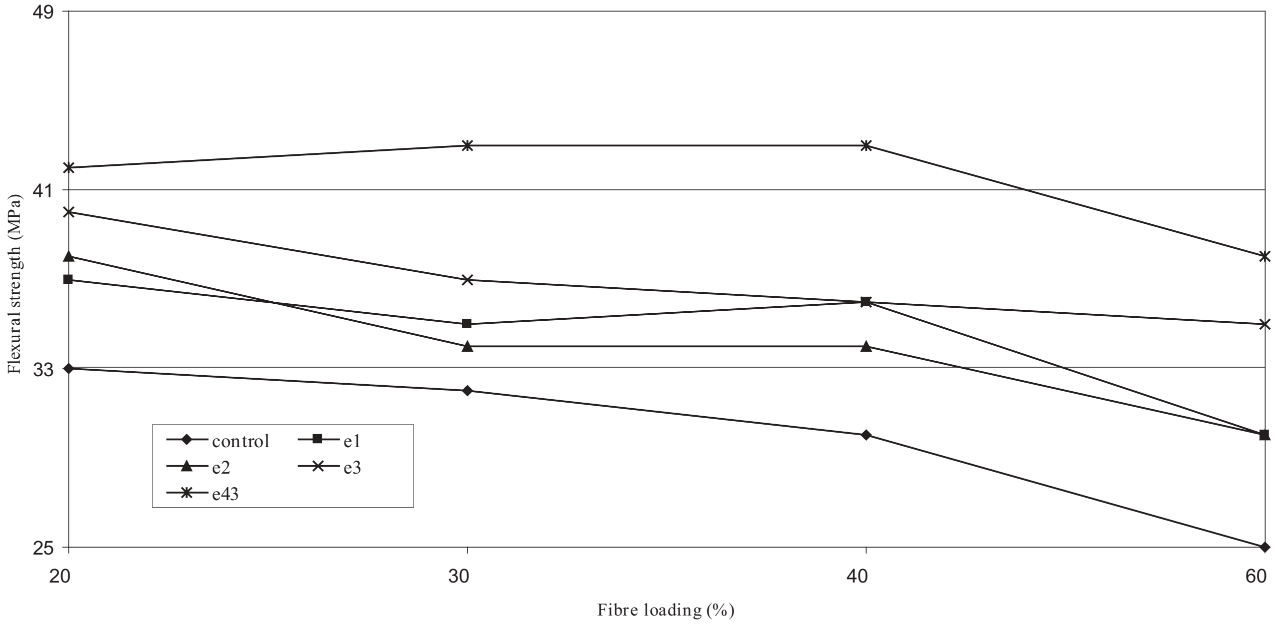

Figure 5. Effects of fibre loading on the flexural strength of maleated polypropylene (MAPP) treated (5% MAPP loading) and untreated samples.

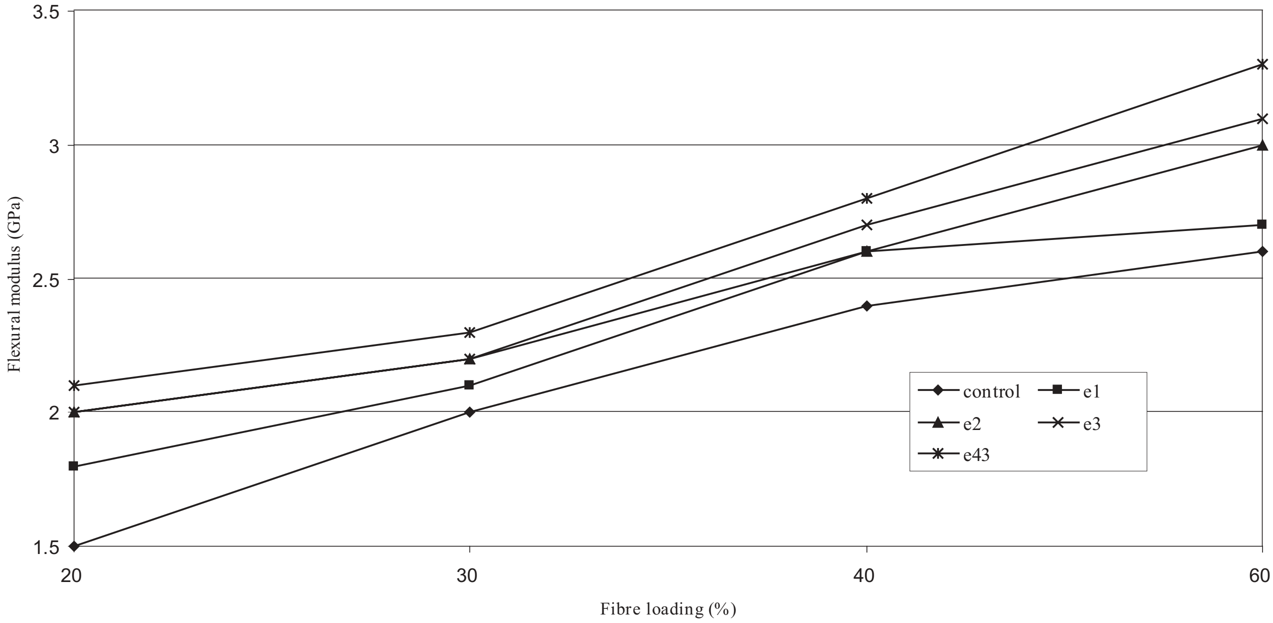

Figure 6. Effects of fibre loading on the flexural modulus of maleated polypropylene (MAPP) treated (1% MAPP loading) and untreated samples.

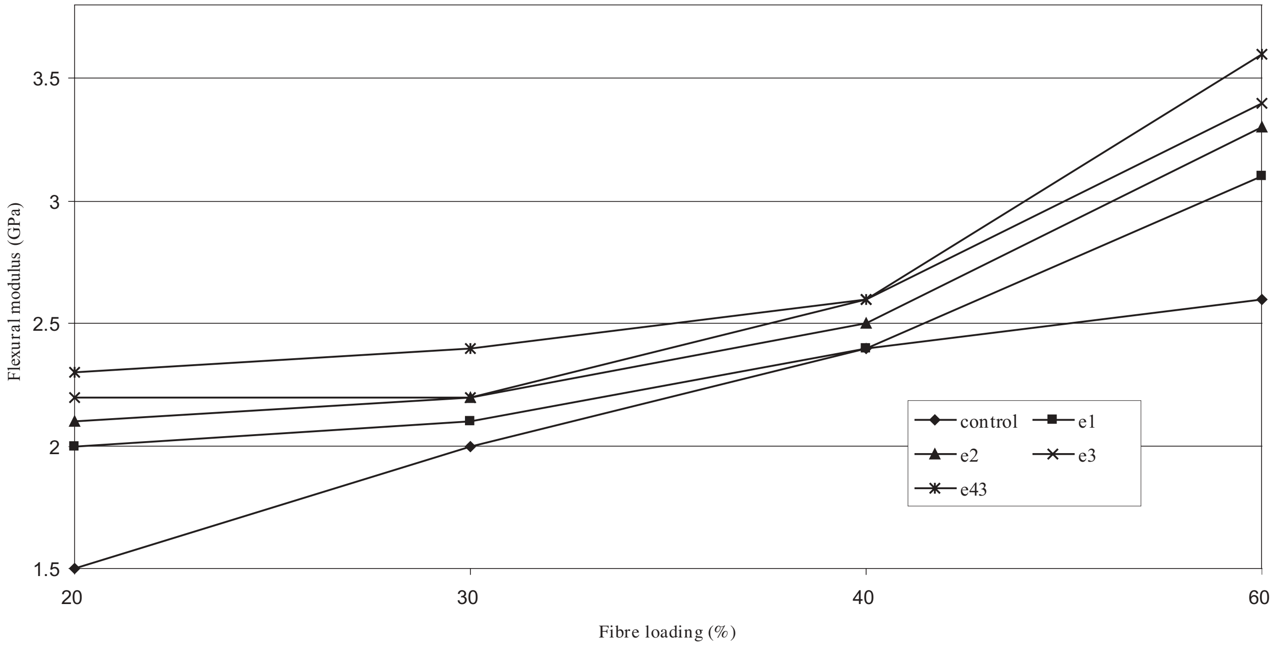

Figure 7. Effects of fibre loading on the flexural modulus of maleated polypropylene (MAPP) treated (3% MAPP loading) and untreated samples.

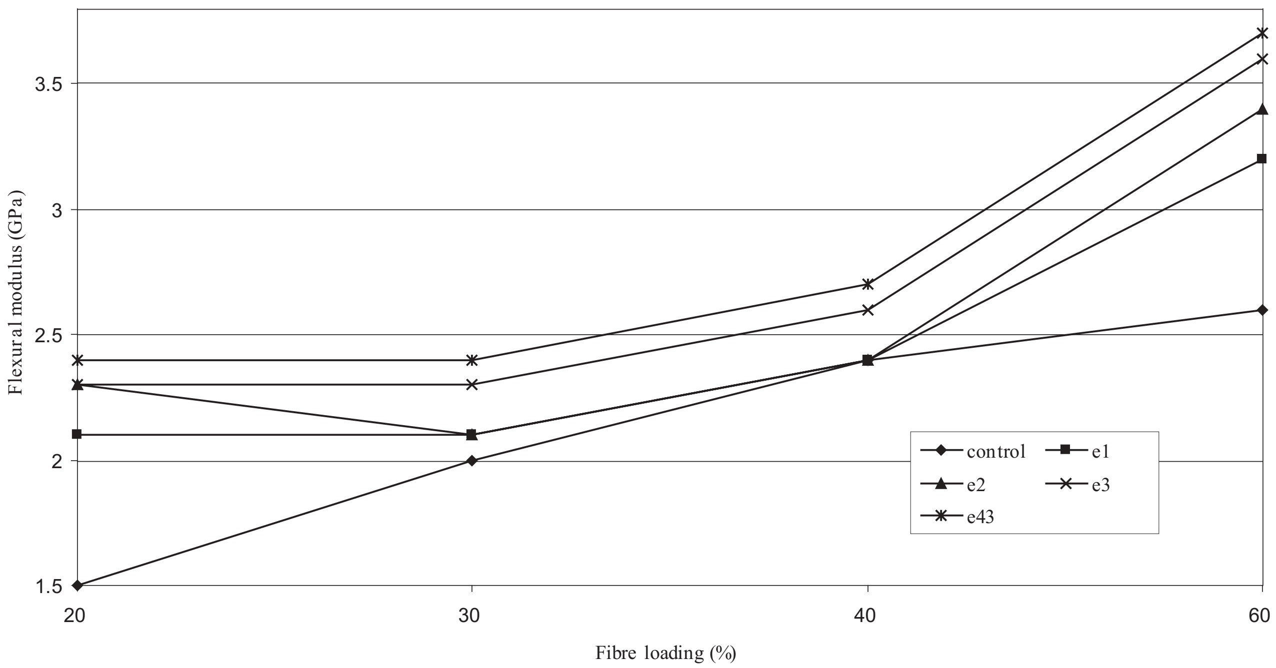

Figure 8. Effects of fibre loading on the flexural modulus of maleated polypropylene (MAPP) treated (5% MAPP loading) and untreated samples.

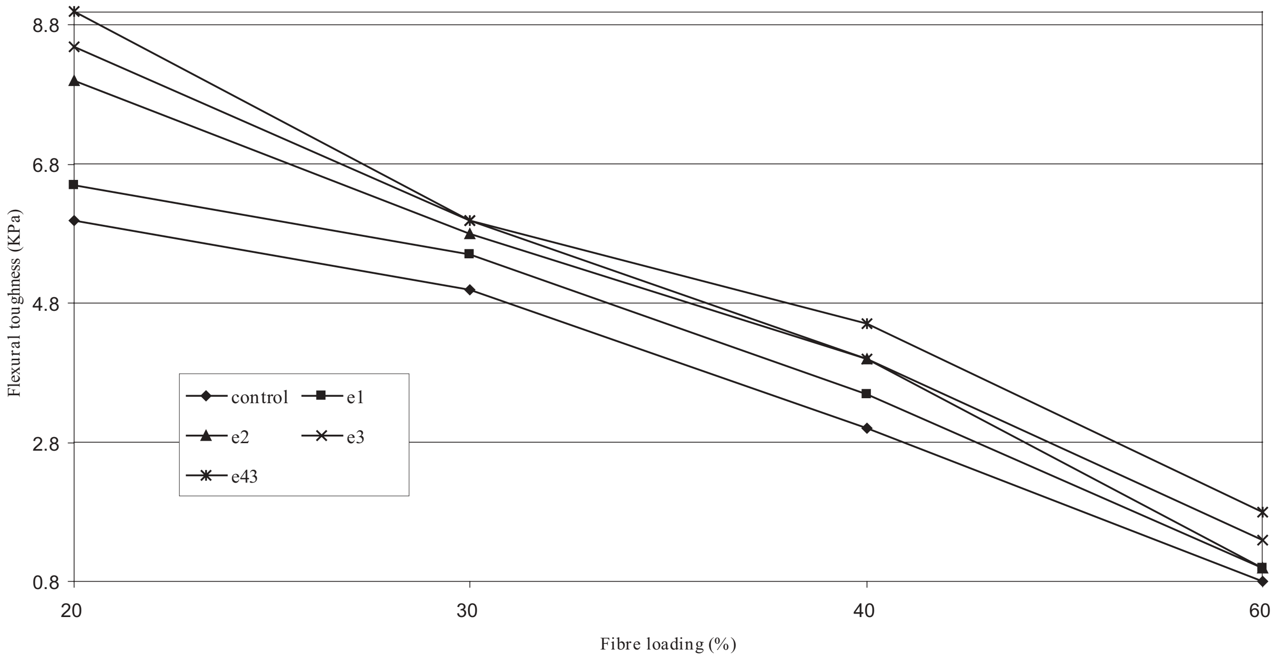

Figure 9. Effects of fibre loading on the flexural toughness of maleated polypropylene (MAPP) treated (1% MAPP loading) and untreated samples.

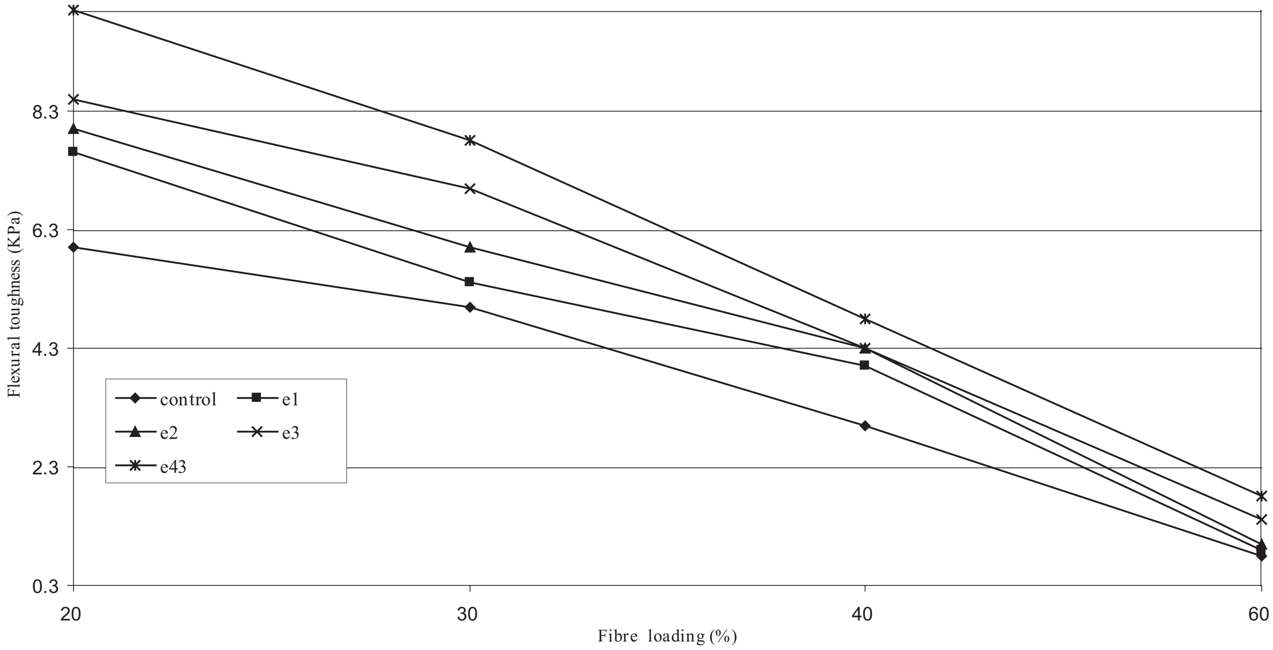

Figure 10. Effects of fibre loading on the flexural toughness of maleated polypropylene (MAPP) treated (3% MAPP loading) and untreated samples.

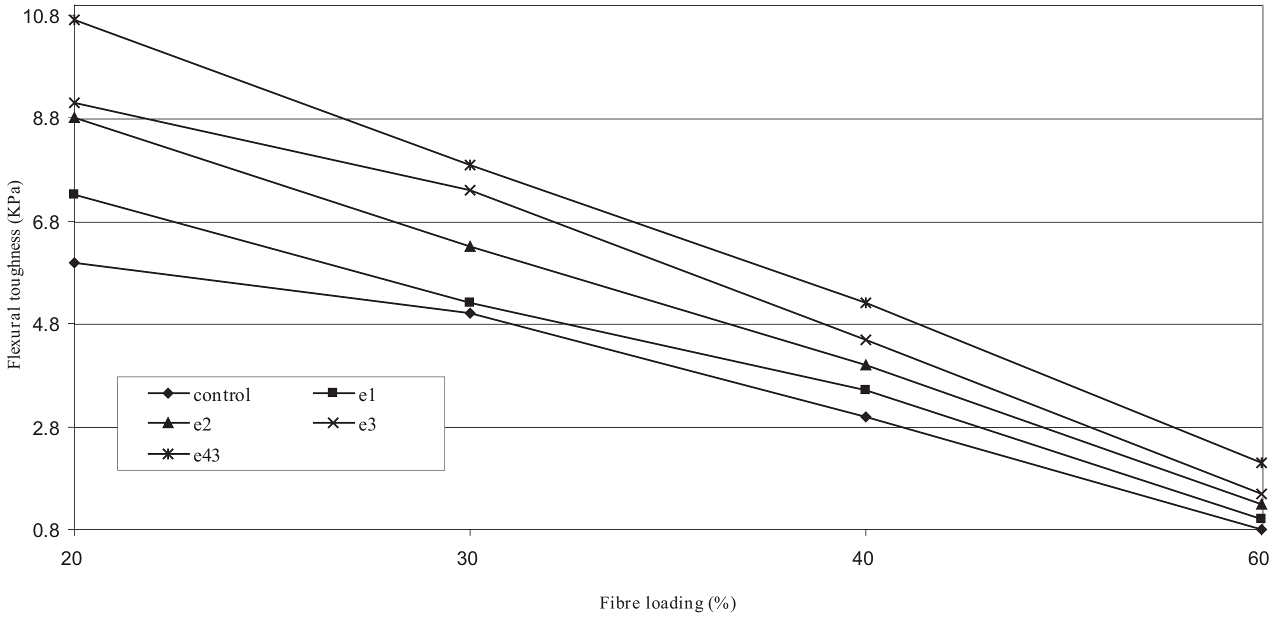

Figure 11. Effects of fibre loading on the flexural toughness of maleated polypropylene (MAPP) treated (5% MAPP loading) and untreated samples.

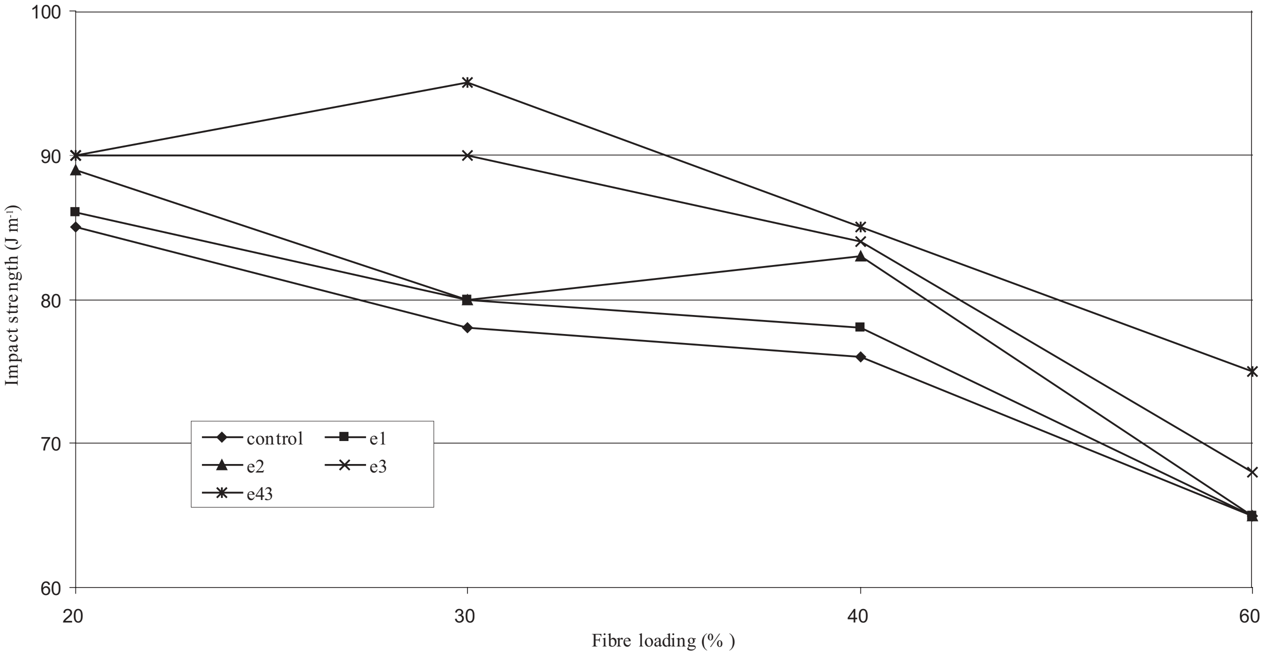

Figure 12. Effects of fibre loading on the impact strength of maleated polypropylene (MAPP) treated (1% MAPP loading) and untreated samples.

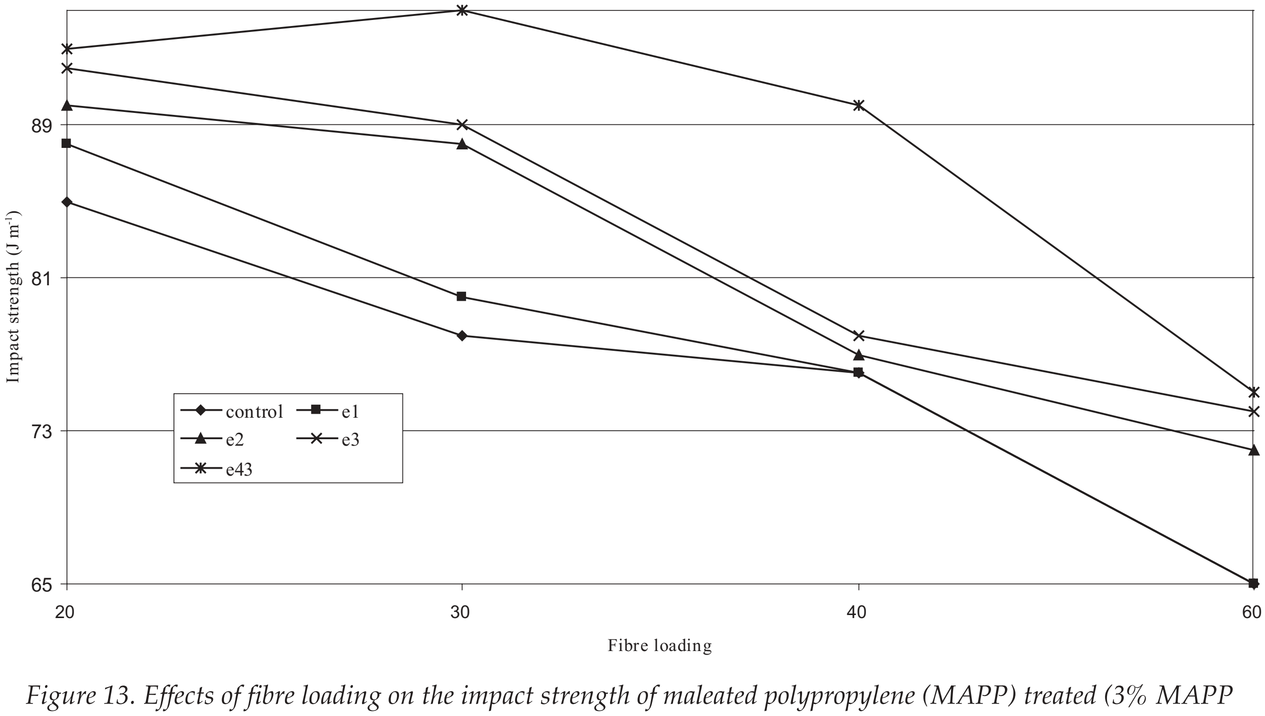

Figure 13. Effects of fibre loading on the impact strength of maleated polypropylene (MAPP) treated (3% MAPP loading) and untreated samples.

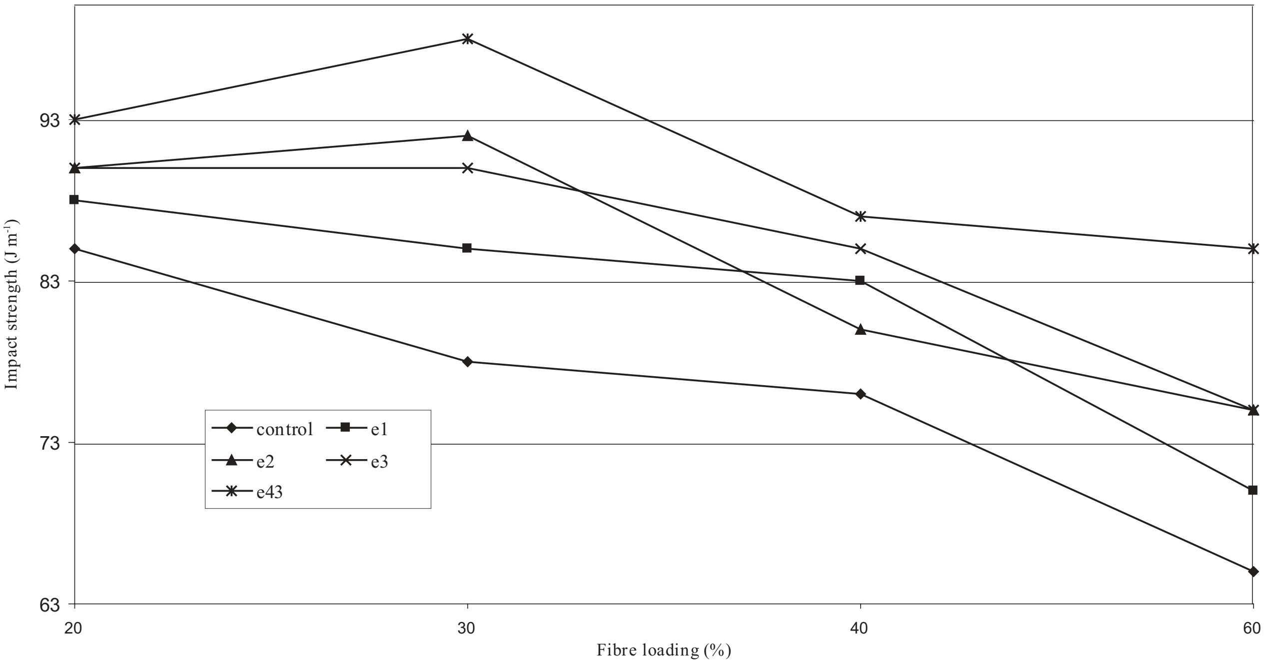

Figure 14. Effects of fibre loading on the impact strength of maleated polypropylene (MAPP) treated (5% MAPP loading) and untreated samples.

CONCLUSION

The study showed that the flexural and impact properties of composites were enhanced by adding the MAPP due to its anhydride content, and the higher the MAPP loading the better the properties. The mechanism involved was coupling by the anhydride group for better transfer of stress from the matrix to the lignocellulose.

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