

Rubberwood–Polymer Composites Based on Diallyl Phthalate and Methyl Methacrylate

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SYNOPSIS

Wood–polymer composites (WPC) of rubberwood (*Hevea brasiliensis*), were prepared by impregnating the wood with methyl methacrylate (MMA), and the combinations of MMA and diallyl phthalate (MMA/DAP). Polymerization was carried out by catalyst heat treatment. Impregnated samples showed significant improvements in compressive and impact strengths, hardness, and dimensional stability (toward water) over that of the untreated rubberwood. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Structural wood, despite its valuable properties, is known to display undesirable properties, such as poor dimensional stability toward moisture and a high moisture absorption. These effects are especially pronounced in tropical areas where wood suffers from continuous exposure to sunlight and high humidity. One convenient way to reduce these deficiencies is to impregnate the wood with a suitable chemical such as liquid borne preservative¹ or a monomer that can be polymerized *in situ* either using a catalyst heat technique² or an irradiation method³ to give a wood–polymer composite (WPC).

This technique is of growing interest in developing countries and considerable efforts are being made to produce WPCs from tropical woods.⁴ However, when monomers such as methyl methacrylate (MMA), styrene, and other vinyl and acrylic monomers are employed for making WPC, difficulties can be encountered during machining. For instance, when WPC is sanded the heat of sanding can melt the polymer and the sandpaper can be rapidly loaded with the fine particles and become essentially useless. The melted polymer clogs the abrasive grit along with the saw dust and cannot be removed from the sandpaper by simply shaking or vibrating. But

by copolymerizing the vinyl monomers with monomers that can provide reactive sites for crosslinking, this problem can be mitigated to a considerable degree. The machining characteristics of such crosslinked polymeric systems in the WPC was studied by Meyer⁵ who reported that the loading of the sandpaper was drastically reduced and the sanding discs could be used much longer than it was possible before.

Because the crosslinkable compositions in the preparation of WPC will lead to superior performance, investigations were taken up to make WPC based on diallyl phthalate (DAP) and MMA. DAP is a tetrafunctional monomer and therefore provides reactive sites ideally suited for crosslinked structure. DAP based moldings have an established reputation for excellent dimensional and thermal stability in the electronic component industry. Apart from three patents^{6–8} on the development of WPC and bulk copolymers based on the DAP–MMA system by gamma radiation processing, there has been no published work on this system.

EXPERIMENTAL

Rubberwood was obtained from Pan Malaysian Wood Mill, Butterworth, Malaysia. The monomers used are listed in Table I.

The samples used in this study were sawn into specimens of 20 × 20 × 30 mm (radial × tangential

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CHEMICAL LOADINGS

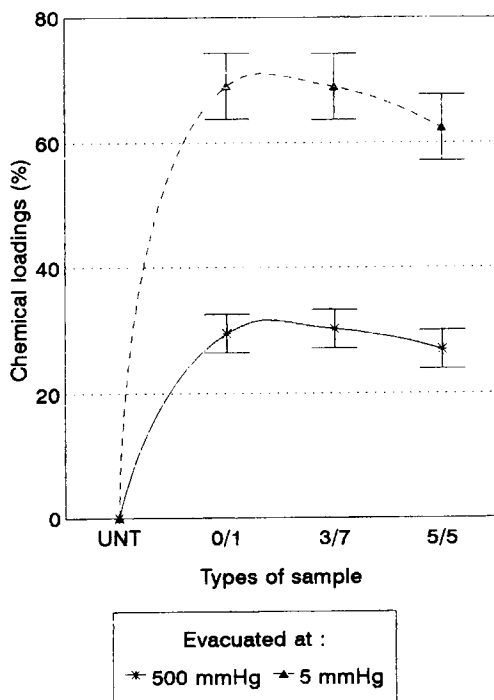


Figure 1(a) Chemical loadings of samples for swelling and water absorption tests; impregnated at 500 and 5 mm Hg.

× longitudinal directions) for the dimensional stability test and compression parallel to the grain tests (10 specimens for each type of test); 10 × 10 × 50 mm for impact and hardness tests (5 specimens for each type of test); and 10 × 10 × 150 mm for bending tests (6 specimens). All samples were oven dried to constant weight at 105°C, and the dimensions and weight were then measured. Samples were placed into an impregnation chamber that was evacuated to two levels of vacuum pressure of about 500 and 5 mm Hg, and held in excess for about 5 min. The appropriate monomer system was then introduced, and the specimens were left immersed until atmospheric pressure was attained. The chamber was left at atmospheric pressure at room temperature for 4 h to obtain further impregnation. The specimens were removed from the chamber, wiped free of excess impregnant, and weighed immediately to determine the monomer uptake. They were wrapped in aluminum foil and sealed to minimize loss of monomer by evaporation, and then placed in an oven at 90°C for 24 h to polymerize the monomer. After impregnation, the samples were again oven dried at 105°C for 24 h. The specimens were then measured and weighed to determine the polymer loading.

Table I Monomer Systems Used in Impregnation

Sample	Monomer Systems
0/1	100% Methyl methacrylate + 2% Benzoyl peroxide (by weight)
3/7	30% Diallyl phthalate + 2% Benzoyl peroxide (by weight)
5/5	70% Methyl methacrylate 50% Diallyl phthalate + 2% Benzoyl peroxide (by weight)
UNT	50% Methyl methacrylate Untreated wood (controls)

Samples were tested for impact strength on a Charpy impact tester, and both compression and bending tests were carried out in a Universal testing machine (Instron) at a crosshead speed of 2 mm/min. Hardness was tested on a Rockwell hardness tester.

For the dimensional stability and water absorption tests, samples were placed in a water bath at room temperature for 24 h. The dimensions and weight were measured before and after soaking.

ANTI-SHRINK EFFICIENCY (ASE)

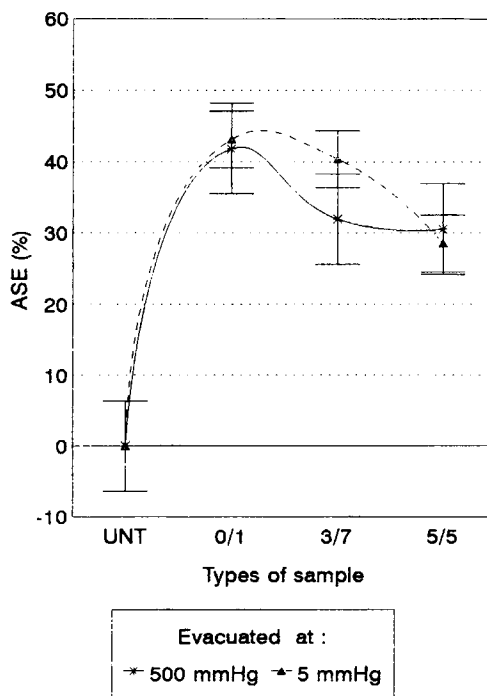


Figure 1(b) Swelling test results of samples impregnated at 500 and 5 mm Hg.

WATER ABSORPTION RESULTS

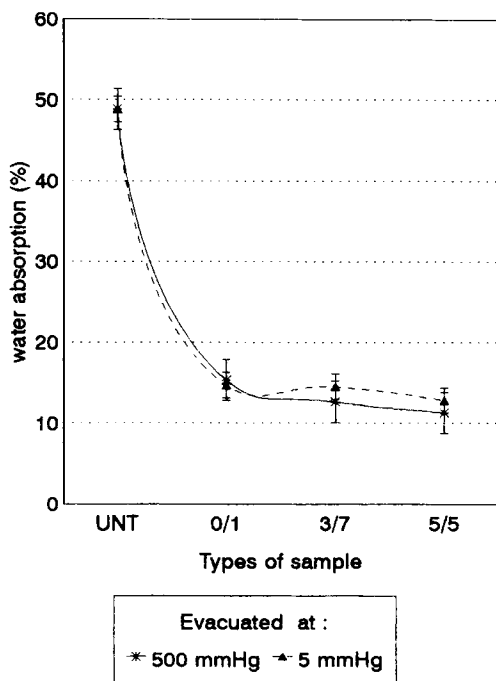


Figure 1(c) Water absorption test results of samples impregnated at 500 and 5 mm Hg.

RESULTS AND DISCUSSION

Swelling and water absorption results are shown in Figures 1(b) and 1(c), respectively, and the chemical loadings for the test samples are shown in Figure 1(a). For the samples impregnated at 500 mm Hg, the chemical loadings obtained were about the same, that is, 27–30%. The antishrink efficiency (ASE) obtained was about 42, 32, and 31%, for sample 0/1, 3/7, and 5/5, respectively [Fig. 1(b)]. However, there was no significant difference (at 95% confidence interval) among them. At 5 mm Hg, the loadings obtained were higher than the one impregnated at 500 mm Hg, that is from 62 to 69%. The ASE obtained was comparable with the one impregnated at 500 mm Hg (lower loadings). The results show the same trend, where the ASE decreases as the proportion of MMA in the system is lowered.

Water absorption of the rubberwood was significantly reduced upon impregnation with the monomer [Fig. 1(c)]. The water absorptions of all impregnated samples were about the same. The results show that the degree of chemical loading does not influence the absorption behavior and water absorption remains the same regardless of the proportion of the monomers used.

Generally, the results show that samples impregnated with MMA alone exhibit lower swelling upon soaking in water. Because DAP contains a benzene ring, it is expected that DAP would instill greater hydrophobicity to the specimen than the one without. Yap et al.,³ in their work using FTIR to analyze the penetration of PMMA into the wood cell wall, showed that there were prominent peaks attributed to PMMA in the impregnated samples (after exhaustive extraction with chloroform to wash out the homopolymers), especially at chemical loadings of 40 and 60%. Because in these experiments the loading achieved was about 30–70%, these results may indicate that there is some possibility that MMA enters and bulks the cell wall. This would mean that when the sample was soaked in water, the cell wall was not bulked to the same extent as in the untreated sample, because it was already bulked by the polymer.⁹ This phenomenon may explain why there was less swelling in the treated sample as opposed to the controls.

Modulus of elasticity (MOE) and modulus of rupture (MOR) results are shown in Figures 2(b) and 2(c), respectively, and the chemical loadings for the test samples are shown in Figure 2(a). Both

CHEMICAL LOADINGS

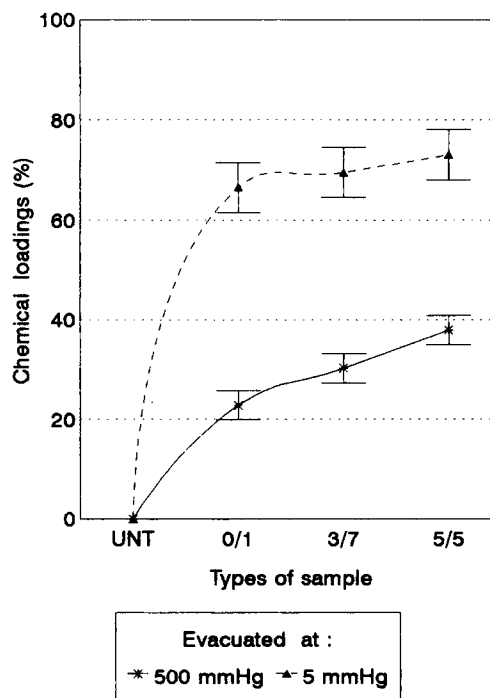


Figure 2(a) Chemical loadings of samples for bending tests; impregnated at 500 and 5 mm Hg.

MODULUS OF ELASTICITY (MOE)

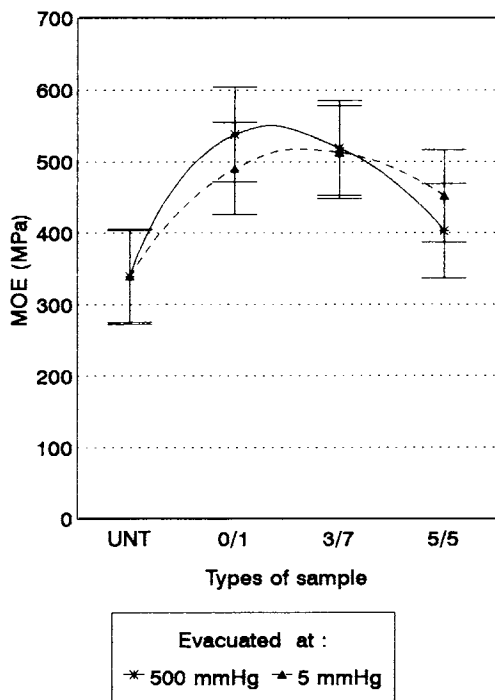


Figure 2(b) Results of modulus of elasticity (MOE).

CHEMICAL LOADINGS

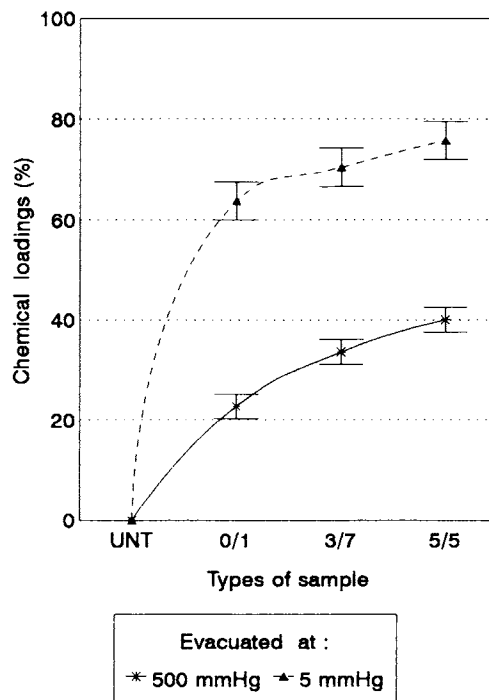


Figure 3(a) Chemical loadings for compression test samples; impregnated at 500 and 5 mm Hg.

MODULUS OF RUPTURE (MOR)

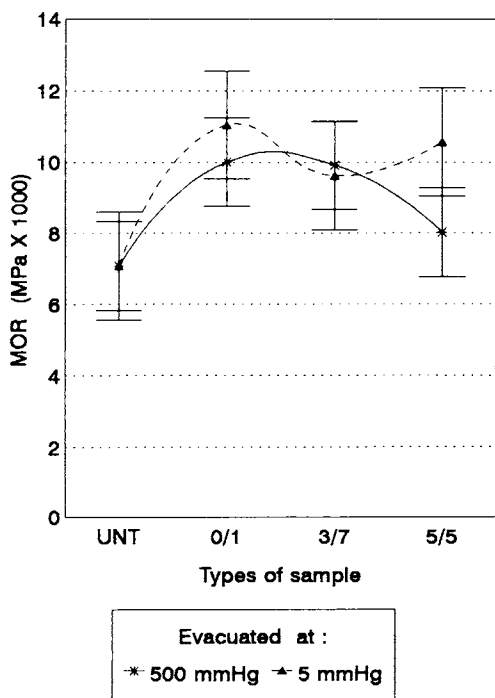


Figure 2(c) Results of modulus of rupture (MOR).

types of sample, 0/1 and 3/7, impregnated at 500 and 5 mm Hg showed significant improvement in MOE (about 45–60%) compared with the controls. However, there was no significant difference between sample 5/5 and the controls at both pressures. Generally, all samples showed improvement in MOR except samples with lower loading and lower proportion of MMA.

The chemical loadings of the compression test samples and the compression test results are shown in Figures 3(a) and 3(b), respectively. Samples impregnated at 500 mm Hg showed a slight improvement in compressive strength over that of the untreated wood. With a greater degree of loading, impregnation at 5 mm Hg, treated samples showed much greater compressive strength than the controls. As indicated by Siau et al.,¹⁰ untreated wood probably fails in compression due to the buckling of relatively thin cell walls because of a long-column type of instability. The addition of polymer places a coating on the cell walls that thickens them, thus greatly increasing their lateral stability.

Impregnated samples with various levels of chemical loadings [Fig. 4(a)] showed significant improvements in the impact strength when com-

pared with the controls [Fig. 4(b)]. Generally, samples with higher loadings showed greater strength than the ones with lower loadings. However, it is difficult to interpret because wood by itself exhibits a high degree of impact resistance due to its complex microstructure and submicroscopic ultrastructure. Similar results have been reported by Subramaniam et al.¹¹ The process of crack initiations and propagations in WPC is perhaps sufficiently modified by the presence of polymer in the lumen that the impact toughness is greatly improved.

The hardness of the samples also improved upon impregnation (Fig. 5). The improvement was greater for samples containing higher polymer loading. The chemical loadings of the hardness test samples are tabulated in Table II.

CONCLUSIONS

The results showed that impregnation of rubberwood with MMA and MMA/DAP monomer systems improved dimensional stability toward water as well as mechanical properties. In general, com-

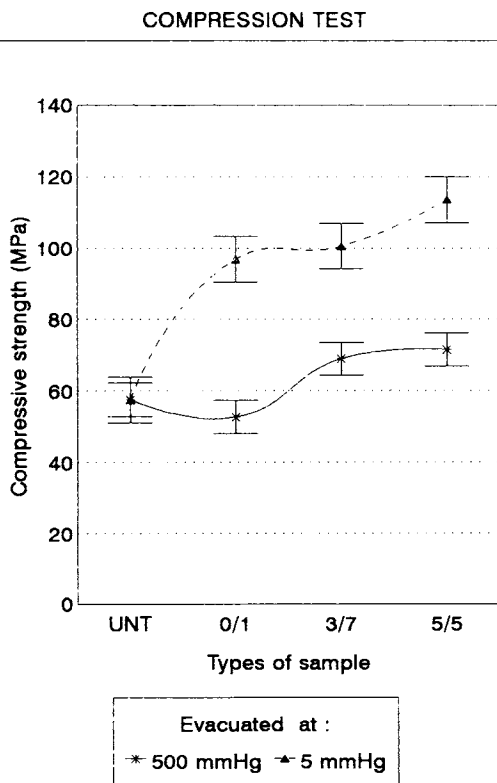


Figure 3(b) Compression test results of samples impregnated at 500 and 5 mm Hg.

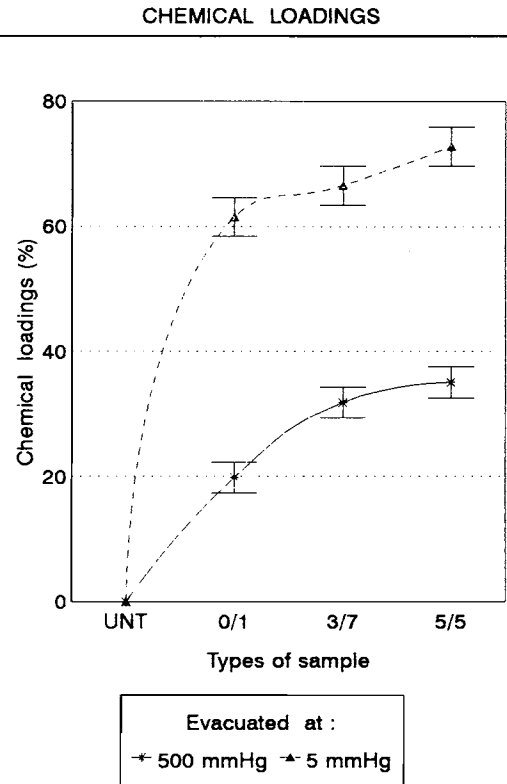


Figure 4(a) Chemical loadings for impact test samples; impregnated at 500 and 5 mm Hg.

pressive strength, impact strength, and hardness improve to a greater extent than the MOE and MOR. The systems do not impart any difference in the water absorption (among the impregnated samples). However, the swelling ability is affected by the proportion of the monomers used.

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APPENDIX

Chemical

$$\text{loading (\%)} = \frac{W_1 - W_o}{W_o} \times 100$$

W_1 = weight of WPC after curing

W_o = weight of untreated wood (oven dry)

Antishrink efficiency (ASE)

$$\text{(\%)} = \frac{S - S_o}{S_o} \times 100$$

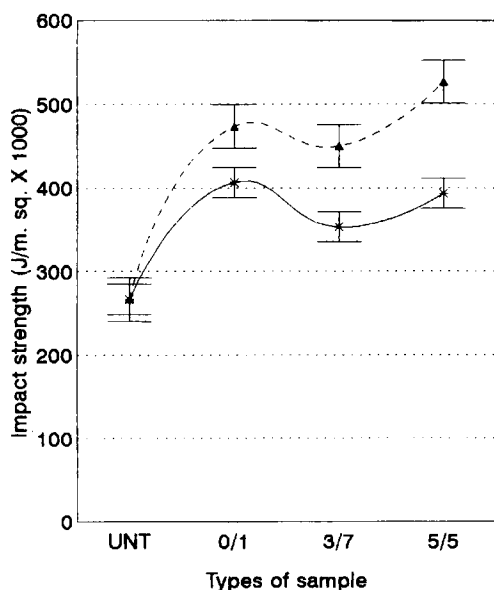
volumetric swelling coefficient for

S = treated sample

volumetric swelling coefficient for

S_o = untreated sample (control)

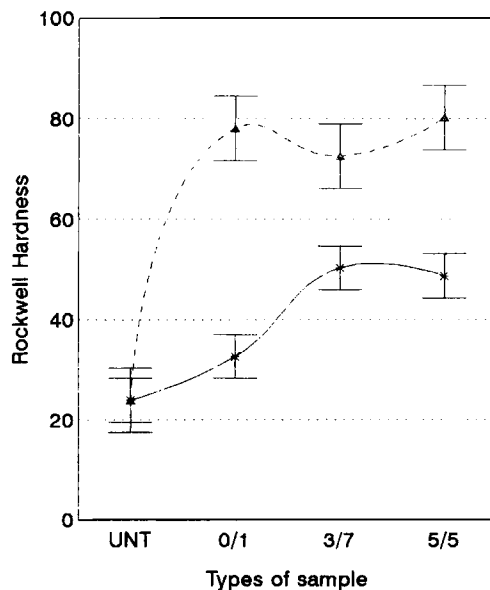
IMPACT STRENGTH



Evacuated at :
 * 500 mmHg ▲ 5 mmHg

Figure 4(b) Impact test results of samples impregnated at 500 and 5 mm Hg.

ROCKWELL HARDNESS



Evacuated at :
 * 500 mmHg ▲ 5 mmHg

Figure 5 Hardness test results for samples impregnated at 500 and 5 mm Hg.

Volumetric swelling coefficient, $S = V - V_o / V_o$

V = wood volume after soaking
 V_o = wood volume before soaking

Water absorption (%) = $(W - W_o) / W_o \times 100$

W = weight of the sample after soaking
 W_o = weight of the sample before soaking

Modulus of elasticity MOE

$$(Pa) = L^3 \Delta W / 4bd^3 \Delta S$$

Table II Chemical Loadings of Samples (for Hardness Testing)

Sample	Chemical Loadings (%)
500 mm Hg	
0/1	32.67
3/7	50.30
5/5	48.70
5 mm Hg	
0/1	78.07
3/7	72.57
5/5	80.20

the span between the centers of support
 L = ports (m)
 ΔW = the increment in load (N)
 the mean width (tangential direction) of the sample (m)
 b = the mean thickness (radial direction) of the sample (m)
 d = of the sample (m)
 ΔS = the increment in deflection (m)

Modulus of rupture

$$MOR = 3WL / 2bd^2$$

W = the ultimate failure load (N)
 the span between centers of support
 L = (m)
 the mean width (tangential direction) of the sample (m)
 b = the mean thickness (radial direction) of the sample (m)
 d = of the sample (m)

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