Rubberwood–Polymer Composites Based on Glycidyl Methacrylate and Diallyl Phthalate

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ABSTRACT: Wood–polymer composites (WPC) of rubberwood (Hevea Brasiliensis) were prepared by impregnating the wood with glycidyl methacrylate (GMA), combinations of glycidyl methacrylate and diallyl phthalate (GMA–DAP), or diallyl phthalate (DAP) alone. Polymerization was carried out by catalyst-heat treatment. The results showed that WPC based on GMA exhibited greater dimensional stability (results of antishrink efficiency after six days of soaking) about five times than those based on DAP alone. Flexural [Modulus of Elasticity (MOE), Modulus of Rupture (MOR), and toughness], compressive, and impact properties for all the samples tested are improved, especially for those with higher chemical loading. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1221–1226, 1998

Key words: wood–polymer composites; rubberwood; diallyl phthalate; glycidyl methacrylate; catalyst–heat treatment

INTRODUCTION

Impregnation of wood with a suitable chemical that can react with cell wall components has been extensively reported to improve dimensional stability towards moisture and some mechanical properties. Impregnation of wood to produce wood–polymer composites (WPC) can be carried out with suitable chemicals, such as liquid-borne preservative[1] or monomers that can be polymerized *in situ* either by using a catalyst-heat technique[2] or an irradiation method.[3]

The most common monomers employed are styrene, methyl methacrylate (MMA), and other vinyl and acrylic monomers. Apart from difficulties encountered during machining of these types of WPC, such as clogging of abrasive grit along with saw dust, these types of WPC display a relatively low dimensional stability in water. This may be due to the fact that most monomers used are confined only in the lumen, not in the cell wall.[4] If a monomer can enter and bulk the cell wall, the dimensional stability of the WPC will be improved. Thus, a system is sought to impart effective dimensional stability, as well as to reduce the difficulties during machining. The system should consist of a monomer that has the ability to penetrate into the cell wall and copolymerize with other monomers that can provide reactive sites for crosslinking. The machining characteristics of such crosslinked polymeric systems in the WPC was studied by Meyer,[5] who reported that the loading of the sand paper was radically reduced and the sanding discs could be used much longer than was possible before.

Since the crosslinkable compositions in the preparation of WPC will lead to superior performance with respect to high temperature resistance during machining and sanding, investigations were taken up to make WPC based on glycidyl methacrylate (GMA) and diallyl phthalate. GMA is difunctional monomer, which consists of

Table I   Monomer Systems Used in Impregnation

Sample	Monomer Systems		
0.1	100% glycidyl methacrylate	+	2% benzoyl peroxide (by weight)
5/5	50% diallyl phthalate 50% glycidyl methacrylate	+	2% benzoyl peroxide (by weight)
1/0	100% diallyl phthalate	+	2% benzoyl peroxide (by weight)
UNT	Untreated wood (controls)		

a terminal C=C and an epoxy group. GMA was shown to be able to react with wood hydroxyl groups through its epoxy end.[6] Diallyl phthalate (DAP) is a tetrafunctional monomer and, therefore, provides reactive sites ideally suited for crosslinked structure. Rozman et al.[7] showed that the DAP system was able to produce WPC with improved mechanical properties as well as dimensional stability.

EXPERIMENTAL PROCEDURE

Rubberwood was obtained from Merbok MDF Sdn. Bhd., Merbok, Sungei Petani, Kedah, Malaysia. The monomers used are listed in Table I.

The samples used in this study were sawn into specimens of $20 \times 20 \times 30$ mm (radial $\times$ tangential, $\times$ longitudinal directions) for dimensional stability test and compression parallel to the grain tests (10 specimens for each type of test); $10 \times 10 \times 50$ mm for impact tests (five specimens); and $10 \times 10 \times 150$ mm for bending tests (six 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, which was evacuated to three levels of vacuum of about 635, 380, and 127 mm Hg and held 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 allowed to reach atmospheric pressure, and samples were held then 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 to determine volume increase after cure and weighed to determine the polymer loading.

Samples were tested for impact strength on a Zwick impact tester according to ASTM D256; and both compression and bending tests were carried out according to ASTM D790, by using a Universal Testing Machine Model STM-10 at a crosshead speed of 2 mm min.

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

RESULTS AND DISCUSSION

Dimensional stability results are presented in Table IIA–IID. The results show that WPG for various samples (0/1, 5/5, and 1/0) impregnated at 635 and 380 mm Hg are about the same, which are lower than the ones impregnated at 127 mm Hg. At 127 mm Hg, sample 5/5 shows the highest WPG. At about the same WPG, sample 0/1 (impregnated with GMA only) swells more than sample 1/0 (impregnated with DAP only). Sample 5/5 (impregnated with 50% GMA to 50% DAP solution) requires more WPG in order to reach the same level of swelling than the sample 0/1. These results show that the WPG obtained does not exactly reflect the increase in the volume of the sample after cure due to the impregnation. This probably shows that the impregnation conditions and reagents are not favorable to allow greater penetration into the cell wall. The major portion of the WPG constitutes the polymerized materials confined to the lumen. Nevertheless, the results indicate that GMA is able to penetrate into the cell wall more readily as compared to DAP due to advantageous molecular size. This suggestion is

Table IIA   Dimensional Stability Test Results: Chemical Loading (WPG) of Test Samples

Samples	Impregnation Pressure (mm Hg)		
	635	380	127
0/1	33.4	27.1	25.7
5/5	32.6	36.1	50.5
1/0	26.8	23.3	36.4

Table IIB   Dimension Stability Test Results: Chemical Loading (WPG) of Test Samples

WPG	Volume Increase after Cure (%)		
	0/1	5/5	1/0
23.3	—	—	3.6
25.7	5.2	—	—
26.8	—	—	3.2
27.1	8.1	—	—
32.6	—	7.4	—
33.4	6.52	—	—
36.1	—	8.2	—
36.4	—	—	3.6
50.5	—	6.6	—

Table IIC   Antishrink Efficiency (ASE) for Samples Impregnated at 127 mm Hg

Soaking Time (days)	0/1	5/5	1/0
1	67.5	57.9	33.4
2	—	—	—
3	34.1	28.9	9.7
4	27	20.4	9.4
5	24.1	7.5	5.5
6	24	7.1	4.9

Table IID   Water Absorption for Samples Impregnated at 127 mm Hg

Soaking Time (days)	Unt	0/1	5/5	1/0
1	48.5	8.2	7.5	13.4
2	—	—	—	—
3	59.1	18.1	16.6	24.6
4	63.2	21	20	28
5	65	23.4	20.6	31.1
6	65.8	25.3	21.9	33.1

further supported by antishrink efficiency (ASE) results. Samples impregnated only with GMA and the mixture of GMA and DAP show significantly higher ASE than the ones with DAP alone. This would mean that when the sample (GMA-based WPC) was soaked with water, the cell wall was not bulked to the same extent as in the untreated sample because it was already bulked by the poly-

Table III   Bending Test Results

Samples	Impregnation Pressure (mm Hg)		
	635	380	127
Chemical Loading (WPG) of Test Samples			
0/1	29.7	43.7	47.6
5/5	31.8	38.6	46.1
1/0	30.4	36.6	40.7
Modulus of Elasticity (MOE) (GPa)			
Unt	6.52		
0/1	6.9	7	7.9
0/5	6	6.8	7.4
1/0	5.9	6.9	7
Modulus of Rupture (MOR) (MPa)			
Unt	98.3		
0/1	126.5	134.8	128.6
5/5	100.4	122.2	128.1
1/0	92.2	116.2	113.1
Toughness (kPa)			
Unt	119.6		
0/1	125.4	120	163.2
5/5	127	125.5	148
1/0	105.7	110	147.3

mer.[4] In general, all the samples show a decrease in ASE upon soaking for six days. Samples impregnated with GMA show greater stability in ASE than those impregnated with a mixture of GMA and DAP. Samples impregnated with DAP alone show the least stability as compared to other types of sample. The results indicate that GMA is able to retain in the cell wall upon soaking in water better than DAP. Further, DAP alone has not possibly polymerized completely to a well-knit structure under the conditions employed but has remained as a weak gel incapable of contributing significantly either to mechanical strength and to the dimensional stability. It has been known that DAP forms a gel at a low conversion of about 35%.[8] Much of the monomer remains unreacted under these conditions, and the gel will therefore be in the swollen state in the monomer system. In fact, all the high performance shown by the DAP system is based on the prepolymer separated from the monomer system after polymerization. It is therefore obvious that the gel

formed by DAP polymerization does not possess good mechanical properties. On the other hand, the DAP–GMA system has obviously undergone copolymerization to provide higher cohesive strength, which is reflected in superior physical properties. GMA moieties may further interact with the wood hydroxyl group through glycidyl functionality. This is borne out by the fact that the GMA-impregnated sample is able to retain as high as 35% of its original ASE (one day soaking) after six day soaking as a result of reactions of the wood hydroxyl group and the epoxy group of GMA. In their study of copolymerization of GMA and MMA, Rozman et al. showed that GMA could react with wood hydroxyl groups.[6]

The results show that all treated samples absorb significantly less water than the untreated samples. Since DAP contains a benzene ring, it is expected that DAP would instill greater hydrophobicity to the specimen than the one without. Samples impregnated with GMA (sample 0/1 and 5/5) show lower absorption than the ones impregnated with DAP. This could be as the result of the same factor, as discussed earlier.

Bending test results are shown in Table III. Overall, MOE results correspond well with the level of WPG, where higher loading produces higher stiffness. The MOE for all impregnated samples fall within the same value as the untreated. MOR results show that samples impregnated with GMA exhibit higher ultimate flexural strength, as compared to the ones impregnated with DAP. At about the same WPG (approximately 30%), samples impregnated with GMA

Table IV   Compression Test Results

Samples	Impregnation Pressure (mm Hg)		
	635	380	127
Chemical Loading (WPG) of Test Samples			
0/1	24	25.4	53.6
5/5	26.8	38	51.5
1/0	17.2	24	47.3
Compressive Strength (MPa)			
Unt	56.3		
0/1	71.6	64.7	90.9
5/5	69.9	62.6	65.5
1/0	61.8	64.6	64.8

Table V   Impact Test Results

Samples	Impregnation Pressure (mm Hg)		
	635	380	127
Chemical loading (WPG) of Test Samples			
0/1		21.8	50.5	56.1
5/5		24.1	34.3	45.2
1/0		24.5	33.6	37.6
Impact Strength (J m)			
Unt	268.4		
0/1		463.9	529.8	953.4
5/5		293.3	413.5	446.7
1/0		357.9	464.6	532.7

show significantly higher MOR than the ones with 50% GMA to 50% DAP and DAP only. Toughness of the samples is improved only for the samples with higher WPG (impregnated at 127 mm Hg); however, there is no significant changes for the ones with lower WPG, regardless of the types of sample.

Most samples show some improvement in compressive strength as compared to the untreated samples, though, statistically, there is no significant difference (Table IV). However, samples impregnated with GMA with WPG of about 54% show significantly higher strength than the rest of the samples. As indicated by Siau et al.,[9] 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, which thickens them, thus greatly increasing their lateral stability.

Impregnated samples, especially the ones with higher WPG (approximately 30–60%; see Table V), showed significant improvements in the impact strength when compared with the controls. Overall, samples impregnated with GMA show higher impact strength than the other types of impregnated samples. It is, however, difficult to interpret since 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.[10] The process of crack initiations and propagations in WPC is perhaps sufficiently modified by the presence of polymer in the lumen; and

probably in the cell wall, as in the case of GMA-impregnated samples, the impact toughness is improved.

CONCLUSIONS

The results showed that WPC based on GMA exhibited greater dimensional stability than those based on DAP alone. This might be attributed to the greater ability of the GMA to penetrate the cell wall and react with wood hydroxyl groups and to copolymerize with DAP to form a crosslinked structure. Flexural (MOE, MOR, and toughness), compressive, and impact properties are improved, especially for those with higher chemical loading.

APPENDIX 1

$$\text{Chemical loading}\,(\%) = \frac{W_1 - W_0}{W_0} \times 100$$

where W_1 is the weight of WPC after curing, and W_0 is the weight of untreated wood (ovendry).

$$\text{Volume increase after cure}\,(\%) = \frac{V_c - V_i}{V_i}$$

where V_c is the wood volume after curing (oven-dried at 105°C), and V_i is the initial wood volume (oven-dried at 105°C).

$$\text{Anti-shrink efficiency}\,(\text{ASE})\,(\%) = \frac{S - S_0}{S_0} \times 100$$

where S is the volumetric swelling coefficient for the treated sample, and S_0 is the volumetric swelling coefficient for the untreated sample (control).

The volumetric swelling coefficient is as follows:

$$S = \frac{V - V_0}{V_0}$$

where V is the wood volume after soaking, and V_0 is the wood volume before soaking.

$$\text{Water absorption } (\%) = \frac{W - W_0}{W_0} \times 100$$

where W is the weight of the sample after soaking, and W_0 is the weight of the sample before soaking.

Modulus of elasticity (MOE) is as follows:

$$\text{MOE (Pa)} = \frac{L^3 \Delta W}{4bd^3 \Delta S}$$

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

Modulus of rupture (MOR) is as follows:

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

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

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