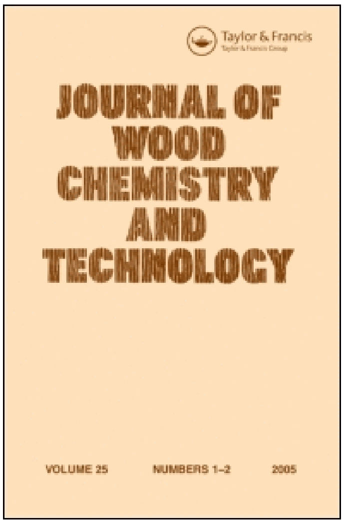

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CHEMICAL MODIFICATION OF WOOD WITH MALEIC ANHYDRIDE AND SUBSEQUENT COPOLYMERIZATION WITH DIALLYL PHTHALATE

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ABSTRACT

Rubberwood meal was reacted with maleic anhydride (MAH). The treated sample was mixed with diallyl phthalate (DAP) prior to hot pressing. Generally, all modified samples performed well in all tests conducted. Modified samples showed greater stability in water than the untreated. Infra-red spectroscopy indicated that the unsaturated maleate components reacted with DAP.

INTRODUCTION

Various works have been done on the chemical modification of solid wood, and it has been reviewed extensively by Rowell[1] and Banks.[2] Interest has been shown in recent time on the use of di or polyfunctional reagents in the chemical modification of wood.[3-6] It involves interaction with the cell wall components of wood on one hand and provides reactive sites on the other which are available for secondary reactions. A variety of secondary reactions could provide greater variations and choice of the desired properties, whether by copolymerization to give stable covalent bonding or to provide better physical bonding or entanglements. One area of immense interest is to convert these materials into thermoflowable products which could be moulded into various articles. Studies on the thermoplasticization of wood have been reported by Shiraishi.[7] Various methods have been employed to confer thermofluidity to wood. Wood has been shown to display thermoflowable properties through esterification.[4] Thermofluidity of wood has also been shown to be improved by the addition of synthetic polymers as external plasticizers.[8] Other methods involve the grafting of vinyl monomers subsequent to acetylation.[9] It has been shown that the grafting technique was superior to blending in producing high degree of compatibility of acetylated wood and synthetic polymers.[10] The chemical modification by appropriate polyfunctional reagents can impart internal plasticization and this technique has been the subject of an earlier publication.[11] It is however interesting to develop a thermoflowable material which has a crosslinking potential. Further investigations were taken up to achieve this objective. The following sequence of process treatment was adopted:

1. chemical modification of wood meal by treatment with maleic anhydride.
2. treatment of chemically-modified wood meal with a multi-functional monomer, dially phthalate.
3. compression mould the mixture (dough moulding coumpund) at elevated temperature in a hydraulic press.

The above process was believed to ensure both cohesion within the matrix resin as a result of crosslinking, as well as adhesion between wood and the resin through the intermediate chemical linkage contributed by maleic unsaturation. Otherwise, the matrix resin does not have natural affinity to the wood components.

EXPERIMENTAL

Air-dried rubberwood obtained from Merbok MDF Sdn. Bhd. was ground and screened to obtain 75-180μm meal. The meal was extracted with a 1:1:4 part mixture of acetone:ethanol:toluene to remove organic soluble material. After extraction, the solvent was drained from the meal and the residual solvent was removed by evaporation at ambient temperature and then finally by heating at 105°C in an oven for approximately 20 hours. The meal was then reacted at various temperatures (60, 80, 100 and 120°C) in batches of around 12g with maleic anhydride (MAH)/dimethylformamide (DMF) solution; 3:7, vol:vol. After reaction, the modified fibre was separated from the liquid reagents by filtration, washed with acetone, and refluxed with excess fresh acetone for about 3 hours to ensure removal of the solvent, the unreacted reagent, and homopolymers if any, formed during the reaction. The modified meal was then hand-mixed into a "dough" with diallyl phthalate (DAP) (50% weight of meal) and benzoyl peroxide (BPO) (6% weight of DAP) as radical initiator. The dough was placed in a mould with dimensions of 12 cm X 1.5 cm X 1 cm (length X width X thickness) and heated at 150°C for 30 minutes.

The bending tests were conducted using a Universal Testing Machine at a strain rate of 2mm/min. The bending test samples with dimensions of 12 cm X 1.5 cm X 1 cm (length X width X thickness) were conditioned at 23 ± 2°C and 55 ± 5 % relative humidity for about 72 h. before being tested. The modulus of Rupture (MOR) and modulus of elasticity (MOE) (based on BS 373:1957) were calculated as shown below.

The modulus of rupture (MOR);

$$\text{MOR} = \frac{3 \text{ X } W \text{ X } L}{2 \text{ X } b \text{ X } d^2}$$

where *W* is the ultimate failure load; *L*, the span between centres of support; *b*, the mean width of the sample; and *d*, the mean thickness of the sample.

The modulus of elasticity (MOE);

$$\text{MOE} = \frac{L^3 \text{ X } \Delta W}{4 \text{ X } b \text{ X } d^3 \text{ X } \Delta S}$$

where *L* is the span between the centres of supports; ΔW, the increment in load; *b*, the mean width of the sample; *d*, the mean thickness; and ΔS, the increment in deflection corresponding to *W*.

Samples with approximate dimensions of 5.0 cm X 1.5 cm X 0.5 (length X width X thickness) were tested for impact strength on a Charpy impact tester. Samples of approximate dimensions of 2.0 cm X 1.5 cm X 0.5 cm were used for the measurements of water absorption and thickness swelling. After being vacuum-dried at 70°C to a constant weight, the specimens were immersed in deionized water. The specimens were periodically taken out of the water, surface dried with absorbent paper, reweighed and remeasured the thickness, and immediately put back into the water. Water absorption and thickness swelling were calculated according to the following formula;

Water absorption (WA);

$$\underset{(\%)}{\text{WA}} = \frac{M_2 - M_1}{M_1} \text{ X } 100$$

M_2 is the mass of the sample after immersion (g)

M_1 is the mass of the same before immersion (g)

Thickness swelling was measured as follows:

$$\text{Thickness swelling (\%)} = \frac{t_w - t_o}{t_o} \times 100$$

t_o = initial thickness of the sample (conditioned)

t_w = thickness of wetted sample

$$\text{Weight Percent Gain (WPG, \%)} = \frac{W_f - W_o}{W_o} \times 100$$

W_f = final weight after reaction followed by washing (oven-dried)

W_o = initial weight before reaction (oven-dried)

All samples for IR spectroscopy were milled to a fine flour and refluxed with acetone for 3 hours to ensure removal of unreacted reagents and homopolymers. They were then examined in transmission (as KBr discs) using Fourier Transform Infra-Red spectroscopy (FTIR).

RESULTS AND DISCUSSION

Figure 2 shows the effect of reaction time on the WPG of the MAH-reacted samples. For samples reacted at 60 and 80°C, WPG gradually increases as the reaction time is increased. However, at 100 and 120°C, WPG values reach maximum at about 25 and 47 WPG for 1 hour reaction time, respectively, and decrease to about 10-13 WPG. In the initial period of reaction, the process is believed to be predominantly controlled by a fast reaction between wood particles and MAH. As the duration of reaction is increased,

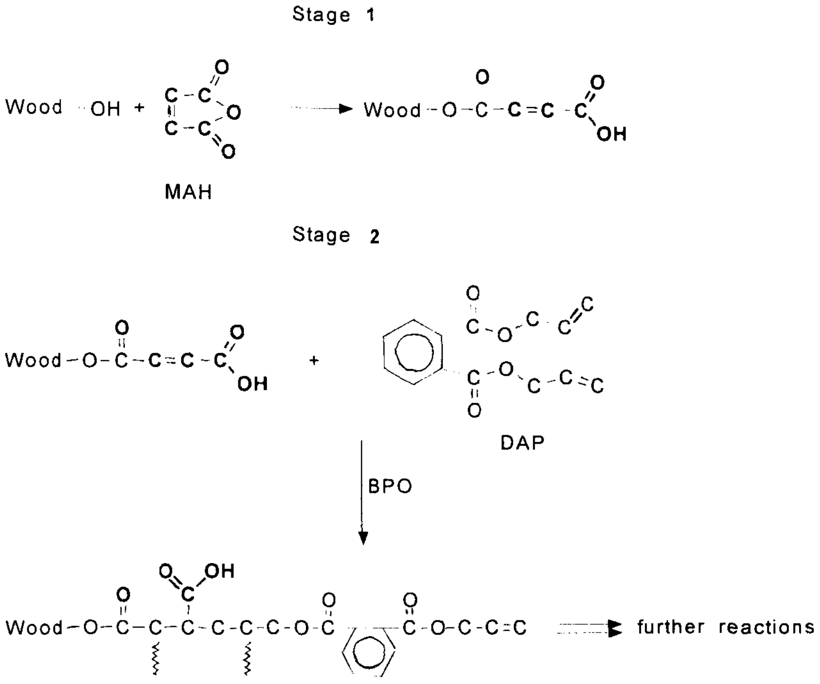

FIGURE 1 - Possible reactions between wood, MAH and DAP

there is a possibility that the degree of swelling of wood particles is also increased which may result in the formation of highly porous structure. Consequently, this may cause leaching of extracts which subsequently reducing the WPG. This phenomenon is particularly significant at high temperatures (100 and 120°C) as shown in Fig. 2.

The effect of MAH modification on the modulus of rupture (MOR) of MAH/DAP samples is shown in Fig. 3. Samples reacted at 120 and 100°C show higher MOR than the ones reacted at 60 and 80°C for 1 hour reaction time, which corelate well with their degree of chemical loadings (Figure 2). Samples with DAP alone (without modification with MAH) give a MOR value of only about 9 MPa, since DAP per se does

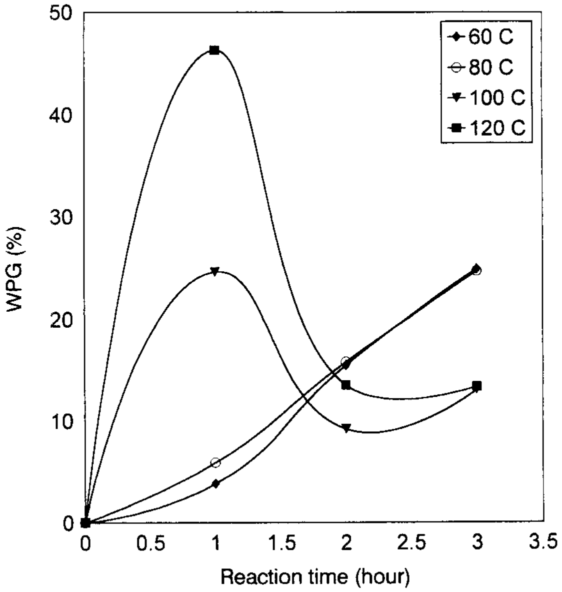

FIGURE 2 - Reaction profile of wood and MAH

not react with wood cell wall components. It is obvious that the MOR is increased significantly when the meal is modified with MAH. Maleic unsaturations present on the treated wood surfaces could provide reactive sites suitable for copolymerization with DAP. The wood meal pre-treated with MAH and mixed with DAP into a dough, displays outstanding flowability with tendency to flow into mould cauls with ease. On continued hot pressing, the material is transformed into a dense, well consolidated composite. The copolymerization of MAH and DAP (as proposed in Figure 1) could result in an interpenetrating polymeric structure with improved properties.

The results of modulus of elasticity (MOE) in Fig. 4 again show the same trend as MOR. The results of impact strength which are shown in Fig. 5, also exhibit similar trend

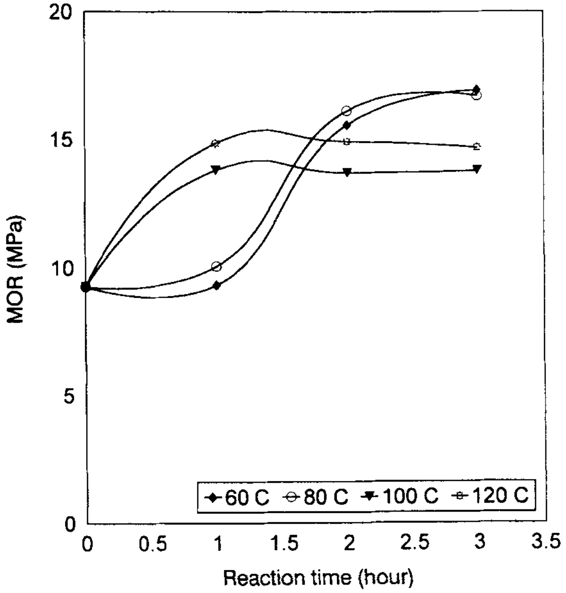

FIGURE 3 - Results of Modulus of Rupture (MOR)

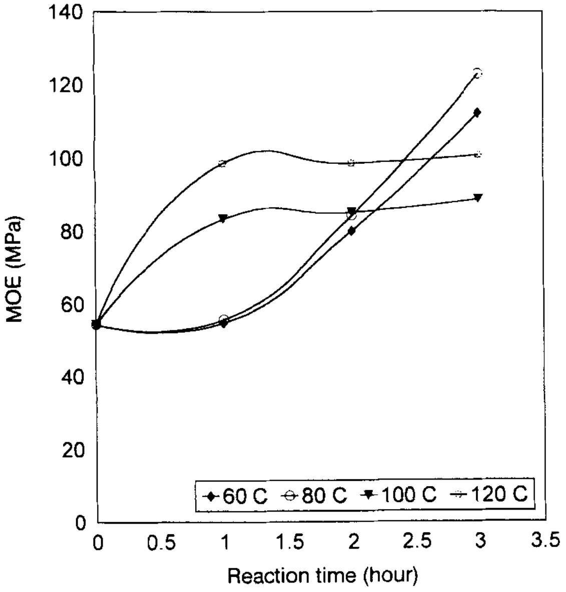

FIGURE 4 - Results of Modulus of Elasticity (MOE)

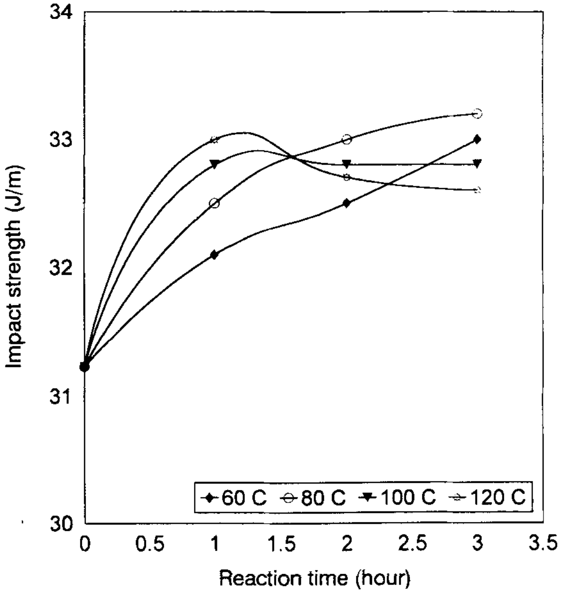

FIGURE 5 - Results of Impact Strength

to those shown by MOR and MOE results, where the strength is increased with the increase of MAH modification. This may be attributed by the same factor as discussed in the case of MOR.

Results of water absorption are shown in Fig. 6. All modified samples display lower rate of absorption compared with the untreated. After 7 days soaking, all treated samples show significantly lower water absorption (about 16-20%) than the untreated (about 87%). However, there is no clear distinction shown by the level of modifications on water absorption.

Results of thickness swelling (Fig. 7) show similar trend as shown by water absorption. All modified samples show significantly lower swelling than the untreated,

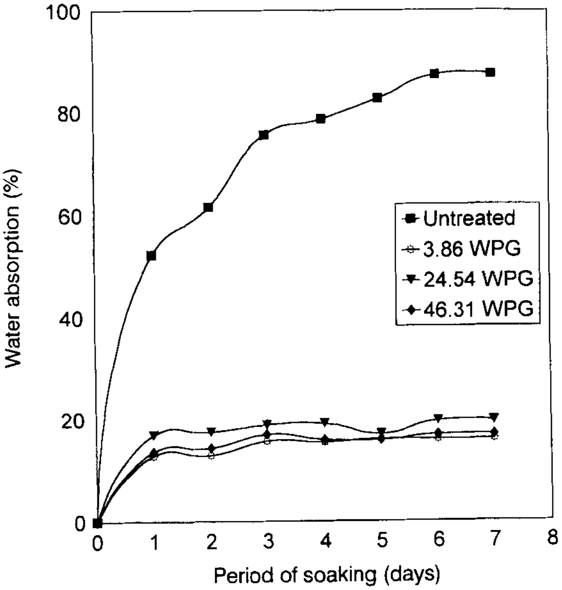

FIGURE 6 - Results of Water Absorption

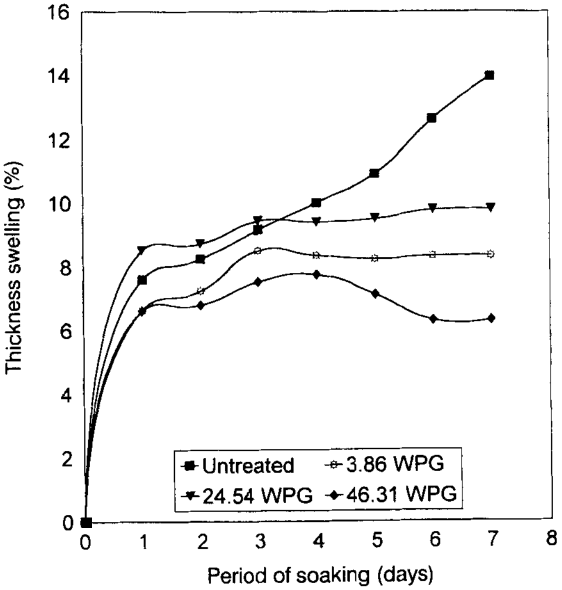

FIGURE 7 - Results of Thickness Swelling

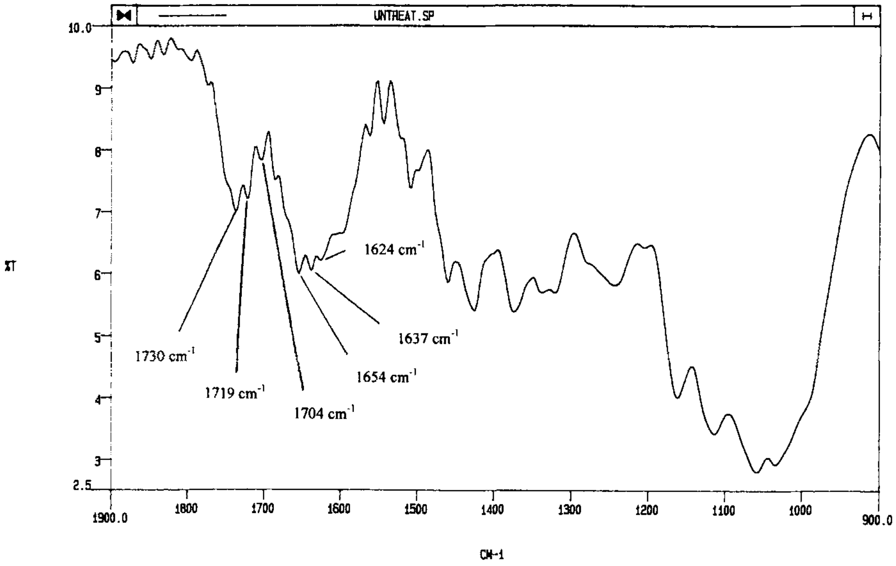

FIGURE 8 - IR Spectrum of untreated wood

starting from the 4th. day of soaking. The data presented are in line with the idea of covalent bonding between matrix and wood. Rozman et al[12] and Banks et al[13] showed indications that MAH reacted with methyl methacrylate (MMA) monomer, through the double bond of the former.

Infra-red spectra for the solvent extracted untreated and MAH chemically treated samples are presented in Figures 8 and 9, respectively. In the treated sample there is an increased absorption in the carbonyl regions (about 1712 cm^{-1}), suggesting ester carbonyl content. This suggests the formation of ester with cellulosic hydroxyl. There is also evidence of increased absorption at 1647 and 1630 cm^{-1}, which may be due to the presence of C=C bonds contributed by maleic anhydride. Careful inspection of Figure 9 (MAH-treated sample) shows growth of a peak at about 1415 cm^{-1}. This is in the area

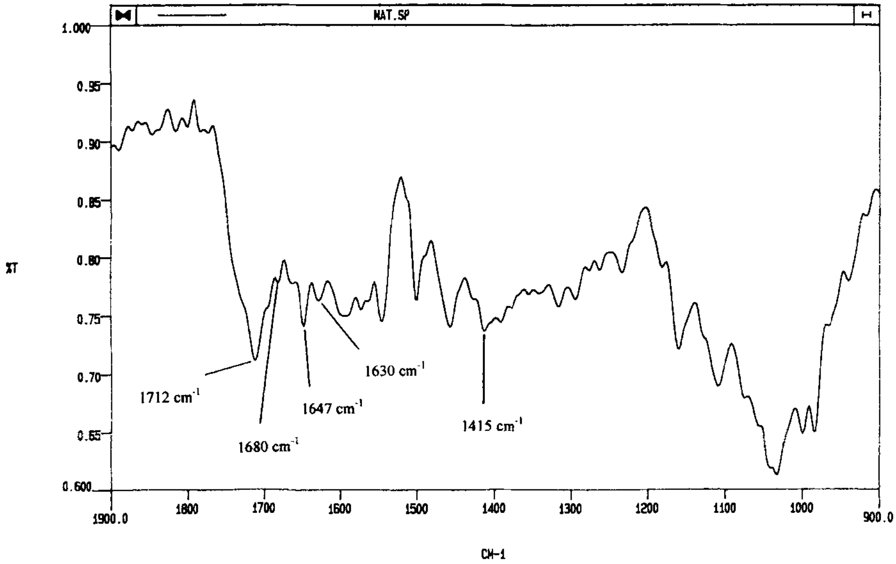

FIGURE 9 - IR Spectrum of MAH-treated wood

associated specifically with cis disubstituted vinyl derivative rocking vibrations (the trans derivatives absorp at significantly lower wavenumber).[13] Overall, the observed changes are consistent with the attachment of maleic anhydride to wood.

From Figure 10, it is clear that there is an overall reduction in unsaturation at about 1647 and 1630 cm^{-1}, after the treated wood are further processed with DAP. This shows that the unsaturated bond of DAP reacts rather extensively with unsaturated sites of maleic anhydride and wood.

This work supports the work of Matsuda et al.,[4-5] in which the mixed reagent system leads into a coherent board. It suggests that the weight increases reported are due to the chemical bonding between wood and activating reagent and the activated sample is then able to react with the reactive unsaturated monomers to form grafted or crosslinked

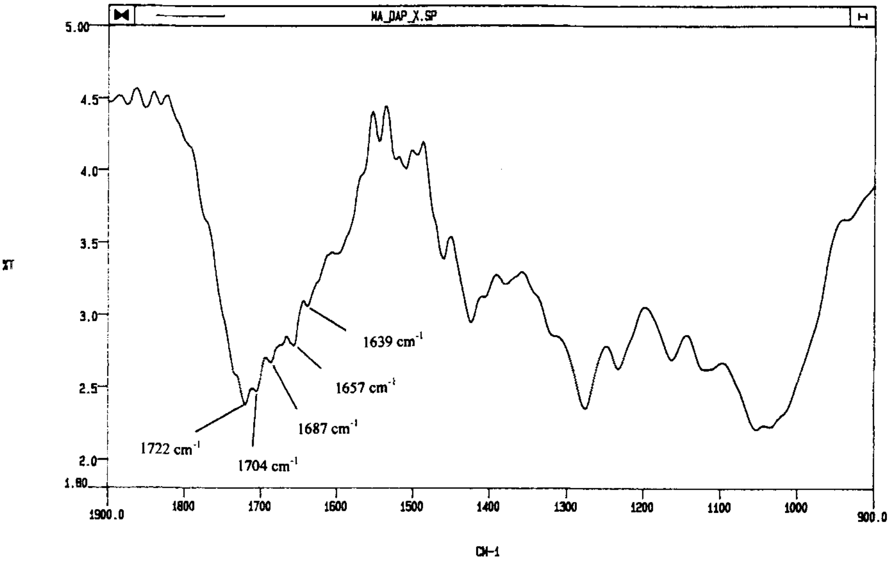

FIGURE 10 - IR Spectrum of MAH-treated/DAP sample

polymer chains attached to the fibre. Bonding may occur, (i) by simple physical interaction between oligomer modified fibre surfaces and homopolymer from DAP, or (ii) by crosslinking between free radical active adjacent modified wood surfaces. The extent to which such crosslinking occurs is uncertain. This is a topic to be addressed in future work.

CONCLUSIONS

The work demonstrates that by chemically modifying rubberwood meal with MAH and followed by DAP, the meal could be plasticized and pressed to a well conformed board with enhanced properties. All the modified samples performed well in all the tests conducted. All modified samples also show greater stability than the untreated samples in water. The work demonstrates that maleic anhydride could react with wood fibre to form ester attachments. Furthermore, the studies, through careful application of infra-red spectroscopy indicate clearly that the unsaturated adducts so formed will react with unsaturated monomers (DAP) to form grafted chains or crosslinked networks. The extent of polymerization is not yet known and is the subject of further study.

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