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# Properties of Boards Produced from Methacrylated Fibers and Subsequent Copolymerization with Various Vinyl Monomers

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Wood fiber of thermo-mechanical pulp type was extracted with neutral organic solvent, dried, and reacted with an electrophilic reagent, ie glycidyl methacrylate (GMA). The adduct formed was reacted in hot press with three types of vinyl monomers (methyl methacrylate, styrene, and butyl methacrylate) in the presence of a free radical initiator (benzoyl peroxide). Modified boards showed significant reduction in thickness swelling as well as improved strength compared to control phenol-formaldehyde boards. GMA-modified methyl methacrylate boards showed the most stability towards wet and dry exposure cycles, whereas GMA-modified butyl methacrylate boards showed the greatest degradation in strength and dimension among the modified boards.

**KEY WORDS** Thermo-mechanical pulp, chemical modification, glycidyl methacrylate, methyl methacrylate, styrene, butyl methacrylate, fiberboards, copolymerization, water absorption, thickness swelling, Modulus of rupture, Modulus of elasticity.

## 1.0 INTRODUCTION

Various studies have been done on the chemical modification of solid wood, and the subject has been reviewed extensively by Rowell and Banks.<sup>1,2</sup> The success of the modification of solid wood, especially in improving the dimensional stability, enable the technique to be applied on wood composites. More recently interest has developed in the use of di- or poly-functional reagent so that the product is left attached to the cell wall.<sup>3–5</sup> The attached functional groups are then used in secondary reactions. These secondary reactions could provide greater variations and choice of the desired properties, whether by copolymerization to give stable

covalent bonding or provide better physical bonding or entanglements. The purpose of this work is to chemically modify wood fiber so that the dimensional stability of product would be improved, and, furthermore, to produce active sites for reactions with thermoplastics. This would allow the development of wood composites with the desired properties incorporated by the thermoplastics and also the possibility of the products being molded and extruded.

## 2.0 MATERIALS AND METHODS

Thermo-mechanical pulp (TMP) fiber (a mixture of softwood species such as Corsican pine and Scots pine) refined at high temperatures for medium density fiberboard (MDF) production was acquired from the Caberboard Company (Stirling, Scotland). The fiber 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 fiber and residual solvent was removed by evaporation at ambient temperature and finally by heating at 105°C in an oven for several hours. The fiber was then reacted at 90°C in batches of around 30 g with an approximately 3 fold excess (based on the estimated hydroxyl content of wood fiber<sup>6</sup>) of glycidyl methacrylate (GMA) (concentration of 0.72 M) diluted in 9:1 v:v with pyridine as swelling agent/base catalyst. To minimize the risk of free radical reaction at the unsaturated ends of the molecule, the reactions were carried out in the dark, in an inert atmosphere (argon gas), and in the presence of radical inhibitor (hydroquinone). Reaction time was adjusted to produce adducts with approximately 10, 15, and 20 weight percent gain (WPG).

After reaction, the modified wood fiber was separated from the liquid reagents by filtration, washed with acetone, and refluxed with excess fresh acetone for about 2 hours to ensure removal of solvent, unreacted reagent, and any homopolymers formed during the reaction. The fiber was then oven-dried for several hours at 105°C.

The modified fibers were then blended with monomer (methyl methacrylate (MMA), styrene, or n-butyl methacrylate (BMA)). The fibrous samples were hand mixed into a "dough" with an equal mass of monomer containing about 6 percent benzoyl peroxide as free radical initiator. The doughs were laid as mats between aluminum foil covered platens and heated under pressure at 70°C for about 1 hour and then for a further 20 minutes at 120°C. The edges of each board produced were cut off to dispose of the unhomogeneous sections.

Two types of control board were made by mixing 10 percent and 55 percent (percent of the dry weight of the fibers) phenol formaldehyde (PF) resin with oven-dried fibers. The amount of fibers used was varied depending on the amount of PF used to obtain the desired density (0.7–0.8 g/cm<sup>3</sup>). The purpose of using 55 percent of PF was to compare the properties of the board with monomer blended boards where the actual amount of the binder was about the same.

Three rectangular samples of dimensions approximately 9.0 × 1.5 × 0.50 cm (length × width × thickness) were cut from each board to be used for static bending tests, water absorption, and thickness swelling measurements. All test

samples were of the same density range (0.70 to 0.80 g/cm<sup>3</sup>). Before being tested, all test samples were conditioned at 20°C ± 2°C and 65 percent ± 5 percent relative humidity until constant mass was achieved.

Test samples were subjected to soak and dry cycles. The conditioned samples were weighed and the dimensions were measured, followed by mechanical testing to measure initial properties, modulus of elasticity (MOE) initial. The samples were then immersed in cold water for 24 hours. On removal, the samples were allowed to drain for a few minutes, surface dried with absorbent paper, and the mass and dimensions of each sample were measured. This was followed by the MOE measurement for cycle 1 in wet condition. The samples were then dried in an oven at 75°C overnight and reconditioned (at 65 percent relative humidity and 20°C) until constant mass was achieved. After the samples were conditioned, the weight and dimensions were measured followed by mechanical testing to measure MOE for cycle 1 in the dry condition. These procedures were repeated through the sixth cycle. Initial modulus of rupture (MOR) was measured from the conditioned samples (without any wetting), whereas the final MOR was measured from conditioned samples after subjecting to six cycles of soak and dry.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Thickness Swelling and Water Absorption

Dimensional changes occurring after six water soak and dry cycles are presented in Table I. The results suggest that the samples blended with styrene and BMA, with and without modification with GMA, exhibit lower reversible swelling than those blended with MMA. Because the reversible swelling relates to the hygroscopicity of the sample,<sup>7</sup> the results may be due to the higher hydrophobicity of styrene and BMA compared with that of MMA. This is likely because styrene has no hydrogen bonding group associated with it, and butyl methacrylate has a longer carbon chain per ester group than does methyl methacrylate. Hence, the matrix formed by reaction with styrene and BMA have less hydrogen bonding capacity per unit mass of adduct than does the MMA matrix. The results indicate no significant improvement in reversible swelling due to GMA modification as shown by the results of unmodified monomer and GMA-modified monomer samples at different GMA chemical loadings WPG. Generally, all unmodified monomer blended and GMA-modified monomer blended samples show lower reversible swelling than the controls (PF boards). However, there was no statistically significant difference among the samples.

The results of irreversible swelling show that both unmodified monomer blended and GMA-modified monomer blended samples display significantly lower irreversible swelling than the control boards. Irreversible swelling is virtually absent in the GMA-modified, MMA blended boards. The GMA-modified styrene blended boards display swelling of about 10 percent and the ones blended with BMA range from 17 percent to 52 percent.

Irreversible swelling is probably associated with the relaxation of stresses imposed in the composite during manufacture.<sup>8</sup> For low irreversible swelling, it could be

TABLE I  
Thickness swelling

Types of sample	Reversible (%)	Irreversible (%)	Total (%)
Unmodified/PF 10%	12.3 (7.4)	153 (6.2)	165.3 (13.5)
Unmodified/PF 55%	11.9 (0.7)	51.4 (6.8)	63.3 (7.2)
Unmodified/MMA	9.1 (0.1)	7.3 (1.0)	16.4 (0.9)
Unmodified/STY	5.2 (0.7)	30.4 (2.0)	35.6 (1.4)
Unmodified/BMA	5.6 (0.5)	11.4 (6.0)	17.0 (5.8)
10 WPG GMA/MMA	9.3 (2.9)	0.7 (4.3)	10.0 (2.1)
15 WPG GMA/MMA	10.8 (0.5)	-1.9 (1.6)	8.9 (1.4)
20 WPG GMA/MMA	8.0 (2.3)	0.5 (1.9)	8.5 (4.0)
10 WPG GMA/STY	5.5 (0.8)	11.4 (1.7)	16.9 (2.4)
15 WPG GMA/STY	5.8 (0.3)	10.4 (1.7)	16.1 (2.0)
20 WPG GMA/STY	5.6 (0.6)	10.8 (0.4)	16.4 (0.5)
10 WPG GMA/BMA	7.1 (2.3)	52.1 (11.3)	59.2 (9.2)
15 WPG GMA/BMA	4.4 (1.2)	24.7 (6.5)	29.1 (5.4)
20 WPG GMA/BMA	3.9 (0.7)	17.0 (1.8)	20.9 (1.1)

\* All data are the average of 3, taken from independent boards. Figures in brackets are standard deviations. The measurements were carried out during the sixth cycle of soak and dry.

$$\text{Reversible swelling} = \frac{t_w - t_e}{t_o}$$

$$\text{Irreversible swelling (springback)} = \frac{t_e - t_o}{t_o}$$

Total swelling = reversible swelling + irreversible swelling

$t_o$  = initial thickness of the sample (conditioned)

$t_w$  = thickness of wetted sample

$t_e$  = thickness of the sample after soaking and reconditioned at 65% relative humidity and 25°C.

that the process applied in making the test boards allows stress relief as the board is forming, or the bonds holding the fibers into the formed shape are sufficient to resist any stress relaxation tendency. It is likely that both effects may play a part in enhancing the dimensional stability. This is because, the chemical modification of wood with GMA may introduce a degree of thermoplasticity into the fiber that will encourage stress relaxation during board formation, and the attached methacrylic group—allowing chemical reaction to occur between fiber and matrix—introduces strong fiber-matrix bonds, which are able to resist the stress relaxation forces. Rozman indicated that GMA reacted with wood fiber through its epoxide

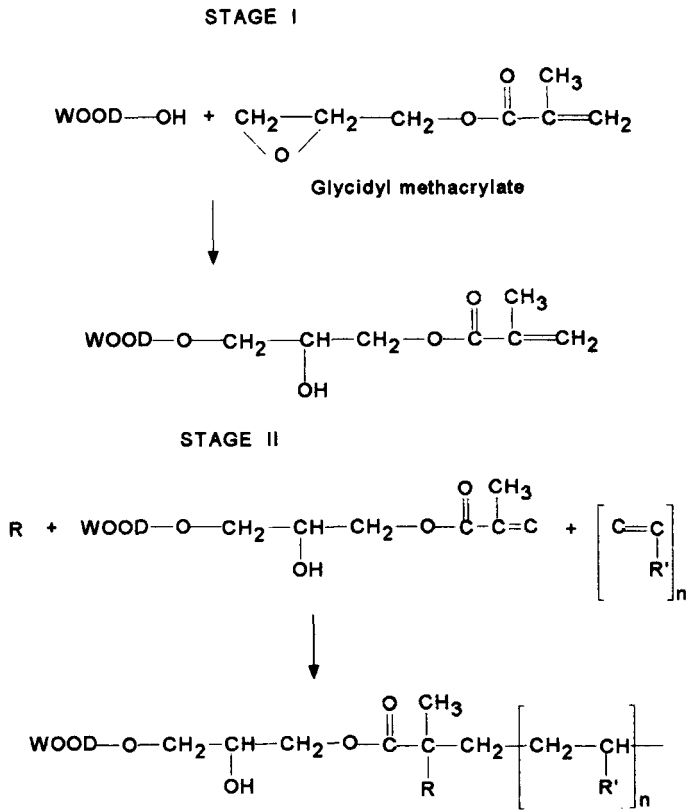


FIGURE 1 Proposed reaction wood and GMA, and between methacrylated fiber and vinyl monomer.

end,<sup>9</sup> leaving its terminal double bond for copolymerization with vinyl monomer. The proposed chemical reaction is shown in Figure 1.

Inspection of the BMA blended samples and Table I show that the unmodified monomer blended samples exhibited lower irreversible swelling than the GMA-modified/monomer blended samples. There are two possible explanations for this: (i) BMA with a longer butyl chain might give a more flexible polymer allowing more stress relief during board formation with unmodified fibers, thus giving less irreversible swelling during the cyclic process, and (ii) there is not sufficient bonding formed in the GMA-modified BMA blended samples to resist the relaxation process. The results probably indicate that BMA is less reactive than MMA towards GMA-modified fibers in the composite.

Total swelling results show the contribution of reversible and irreversible swelling toward the overall swelling. Generally, all the unmodified monomer blended and GMA-modified monomer blended samples display lower swelling compared with the controls. Among the GMA-modified samples, those blended with MMA show the lowest total swelling, followed by those blended with styrene and those blended with BMA. The lower total swelling displayed by the GMA-modified MMA blended samples is largely contributed by their greater stability toward permanent degra-

dation (irreversible swelling), whereas the higher total swelling for the samples blended with BMA is largely contributed by their higher irreversible swelling.

Overall, all the unmodified monomer blended and GMA-modified monomer blended samples exhibit lower water absorption than the controls (see Table II). Generally, there is little improvement in the GMA-modified samples compared with the unmodified samples. In fact, a majority of modified samples show higher absorption than the unmodified. The reaction of GMA with wood fibers produces new hydroxyl groups and also introduces carboxylic ester groups on the fibers. Therefore, these functional groups might contribute to the water absorption of all the GMA-modified samples. Among the vinyl binders used, BMA gives a composite that has lower water absorption properties than those blended with styrene or MMA. This may be due to the longer hydrophobic chain of the BMA molecule. However, it must be recognized that the styrene molecule might be expected to be even more hydrophobic. More work is needed to establish where the adducts formed by reaction with the various reagents are located. This may play a vital role in determining the effectiveness of the modifications.

TABLE II  
Water absorption

Types of sample	Water absorption (%)
Unmodified/PF 10%	255.3 (12.3)
Unmodified/PF 55%	92.9 (12.0)
Unmodified/MMA	28.9 (3.8)
Unmodified/STY	26.7 (1.7)
Unmodified/BMA	13.4 (1.1)
10 WPG GMA/MMA	26.6 (3.4)
15 WPG GMA/MMA	38.8 (3.8)
20 WPG GMA/MMA	42.7 (4.2)
10 WPG GMA/STY	13.2 (2.0)
15 WPG GMA/STY	24.2 (1.0)
20 WPG GMA/STY	21.3 (3.1)
10 WPG GMA/BMA	14.5 (1.6)
15 WPG GMA/BMA	14.3 (0.9)
20 WPG GMA/BMA	14.3 (0.6)

\* All data are the average of 3, taken from independent boards. Figures in brackets are standard deviations. The measurements were carried out during the sixth cycle of soak and dry.

$$\text{Water absorption} = \frac{M_2 - M_1}{M_1} \times 100$$

$M_2$  = mass of the sample after immersion (g)

$M_1$  = mass of the sample before immersion (g)

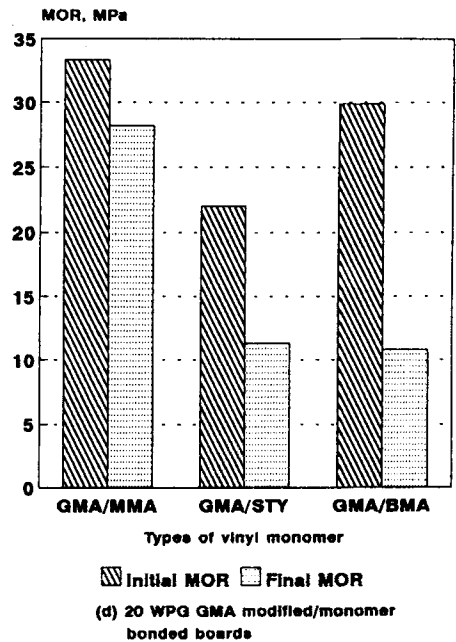
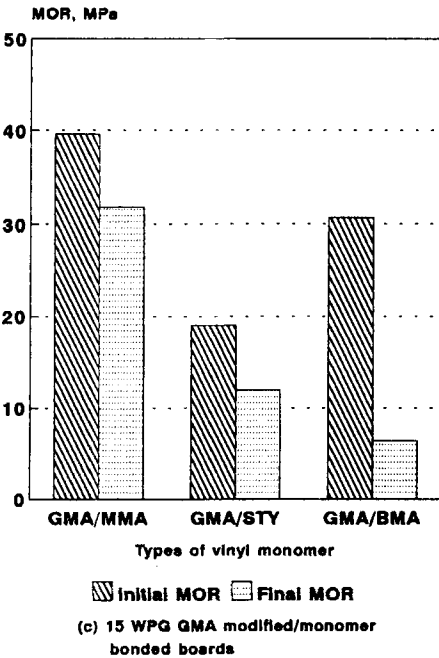
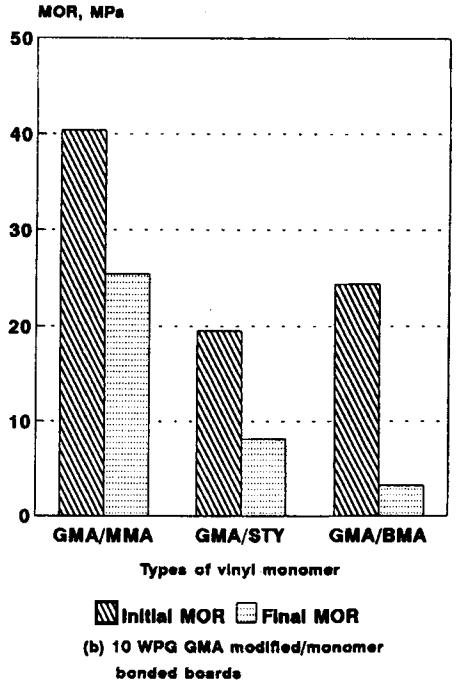
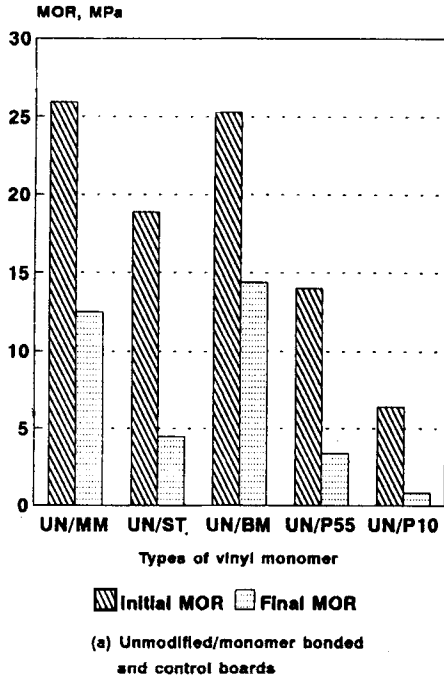


FIGURE 2 Results of MOR. Values were obtained from dry (conditioned) samples before (initial) and after 6 sets of water soak and dry cycles (final).



### 3.2 Results of Modulus of Rupture and Modulus of Elasticity

Modulus of rupture results are presented in Figure 2. The data show that unmodified MMA bonded and unmodified BMA bonded samples retain their dry MOR more effectively after soaking and conditioning than the unmodified styrene samples. Both PF bonded boards (controls) containing 55 percent and 10 percent phenol formaldehyde show significantly lower initial MOR and higher fractural strength loss than the test boards.

For samples with 10 WPG, GMA-modified fibers that bonded with MMA show the highest initial MOR, about 40 MPa; followed by BMA, 24 MPa; and styrene, 20 MPa. GMA-modified MMA bonded samples also show the highest final MOR, 25 MPa; followed by GMA-modified styrene bonded samples, 8 MPa; and GMA-modified BMA bonded samples, 3 MPa. Thus, the results illustrate that at 10 WPG, GMA modified MMA samples retain their initial MOR much better than the GMA modified styrene samples. The samples bonded with BMA show the greatest strength reduction due to water soaking.

For samples made with 15 and 20 WPG GMA-modified fibers, the initial MOR results show the same trend as do the samples with 10 WPG GMA-modified fibers. That is, MMA bonded samples show the highest initial MOR followed by BMA bonded and styrene bonded samples. MMA bonded samples also show the highest final MOR, followed by styrene bonded and finally BMA bonded samples. Again, the strength retention is best for MMA bonded boards and poorest for the BMA bonded boards, with the styrene boards occupying an intermediate position.

Overall, the results show significant improvement in MOR of all the GMA-modified vinyl-monomer bonded samples over the PF control boards. This suggests that the bonding formed in these samples—in which covalent bonding contributes, *ie*, copolymerization of GMA on the GMA-modified fiber surfaces and vinyl monomers—can withstand the stresses produced during soaking and drying process better than the controls.

Thus, bonding with BMA seems to be less effective than with MMA, as shown in the swelling results where the GMA-modified fibers bonded with BMA samples show greater dimensional degradation than the ones bonded with MMA. The reason for this difference has not been investigated. However, it may be associated with the  $T_g$  of the poly(*n*-butyl methacrylate) formed. The  $T_g$  of the polymer is about 20°C, so it is very likely to release stress, especially during 75°C drying. Whereas PMMA and polystyrene have glass transitions around 100°C and should be much stiffer. The difference may also be associated with reduced fiber-resin interaction due to the larger size of the BMA molecule or due to the larger butyl chain allowing particles to relax more and swell, to an extent where effective hydrogen bonds cannot reform on reconditioning.

Generally, the data show that of the binder systems used, styrene and MMA give better initial wet stiffness properties than does BMA (Figure 3). However, during cycling, wet MOE is retained better by the MMA bonded boards than by those blended with styrene. The good initial wet strength of boards blended with styrene may be associated with the strongly hydrophobic character of polystyrene. High wet stiffness retention by the MMA bonded boards is probably another reflection of covalent bonding between the activated fibers and this matrix resin.

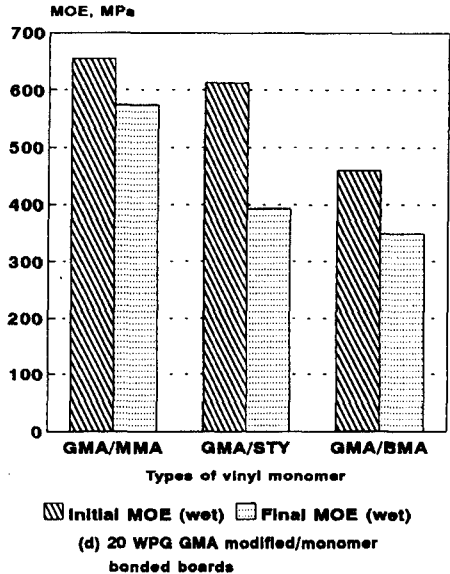
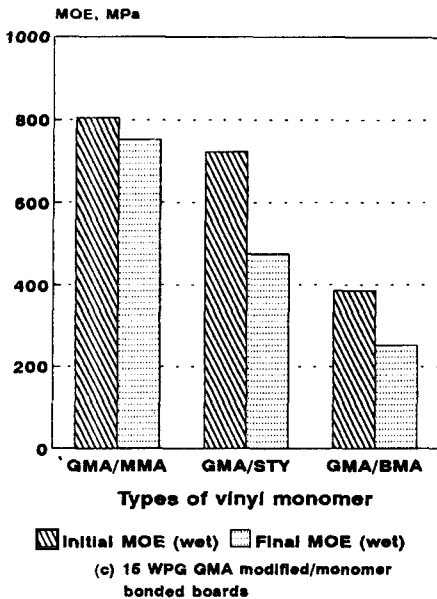
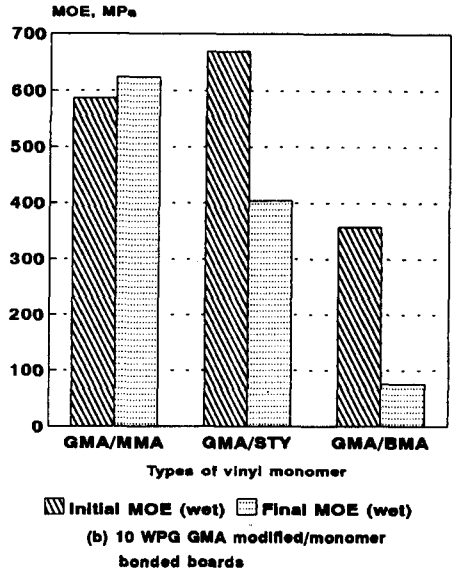
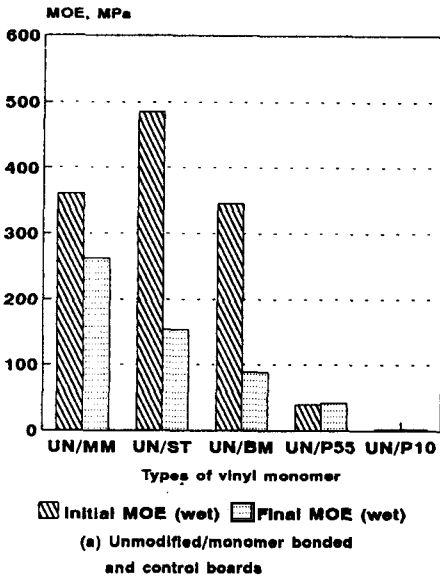
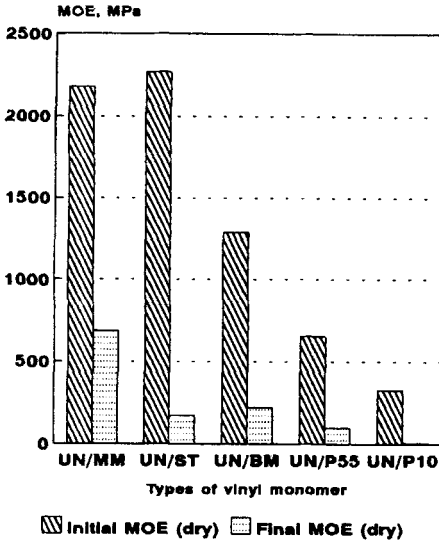


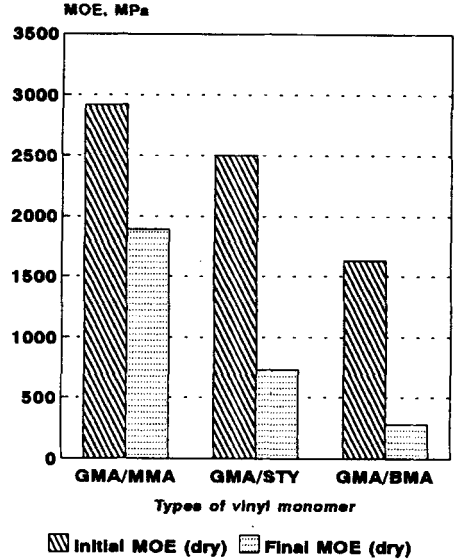
FIGURE 3 Results of MOE in wet condition. Values were obtained after the first (initial MOE wet) and the sixth water soak and dry cycles (final MOE wet).

It is most noticeable that the chemically-modified, vinylic bonded boards all show better wet stiffness retention than do the control (PF bonded) material. As in the case of MOR, the BMA bonded material is least effective of the three vinyl system tested. This may be for reasons similar to those presented in the MOR discussion.

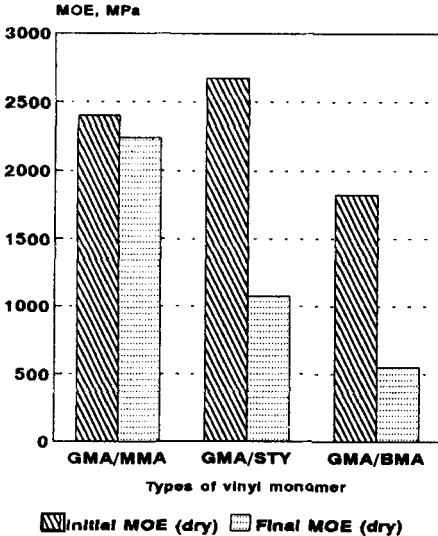
The results of MOE in dry condition also show significant improvements over



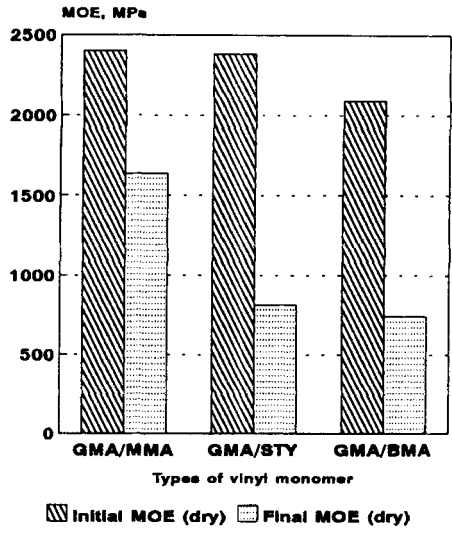
(a) Unmodified/monomer bonded and control boards



(b) 10 WPG GMA modified/monomer bonded boards



(c) 15 WPG GMA modified/monomer bonded boards



(d) 20 WPG GMA modified/monomer bonded boards

FIGURE 4 Results of MOE in dry condition. Values were obtained before (initial MOE dry) and after 6 sets of water soak and dry cycles (final MOE dry).

PF control boards. Among the unmodified samples, those blended with BMA show lower initial and final MOE than the ones blended with MMA and styrene (Figure 4). The same applies to the modified ones. The GMA modified MMA bonded samples show a significantly higher final MOE—with a lower MOE loss—than either the styrene or BMA blended specimens.

## CONCLUSIONS

The work demonstrates that chemical modification of wood fibers followed by copolymerization with vinyl monomers considerably improve the physical and mechanical properties of the boards compared with the control PF boards. Boards made from GMA-modified fibers copolymerized with MMA display greater stability in dimensional stability, MOR, and MOE toward soak and dry cycles than boards blended with styrene and BMA. BMA blended boards show greater dimensional degradation, which, in turn, affects their MOR and MOE after six cycles of soaking and drying.

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