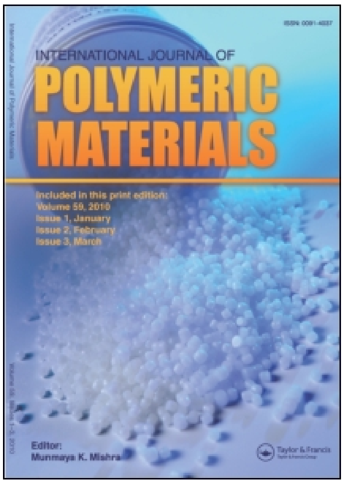

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FTIR Characterization of Chemically Modified Fiberboard

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FTIR Characterization of Chemically Modified Fiberboard

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High temperature refined thermo-mechanical pulp (MDF fiber) was dried, extracted with neutral organic solvent and reacted with an electrophilic reagent, i.e. glycidyl methacrylate (GMA). The adducts formed were characterized by infra-red spectroscopy and further reacted in a hot press with a series of vinyl monomers in the presence of a free radical initiator (benzoyl peroxide). Well conformed boards were produced by the process. Samples of these boards were ground to a fine flour, extracted with acetone/toluene to remove the polymers and again characterized by infra-red spectroscopy. The spectral evidence suggests that some copolymerization occurs between GMA-modified fiber and the polymer.

KEY WORDS MDF fiber, chemical modification, glycidyl methacrylate, polymerization, infra-red spectroscopy

1. 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] The success of the modification on 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 surface.[3–5] 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 co-polymerization to give stable covalent bonding or provide better physical bonding or entanglements. The purpose of this work is to assess the feasibility of modifying wood fiber so that it is physically and chemically compatible with thermoplastic resin or reactive resin precursor. This might allow the development of wood/plant fiber based composite products bonded together by meltable resins attached chemically or perhaps simply physically to the modified fiber.

2. MATERIALS AND METHODS

2.1 Glycidyl Methacrylate-Modified Sample

Thermomechanical pulp (TMP) fiber refined at high temperature for medium density fiberboard (MDF) production was acquired from the Caberboard Co. in Scotland. The fiber was extracted with a 1:1:4 part mixture of acetone:ethanol:toluene (vol:vol) 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)[6] of glycidyl methacrylate (GMA) (concentration of 0.72 M) diluted in 9:1 (vol:vol), with pyridine as swelling agent/base catalyst. To minimize the risk of free radical reaction at the unsaturated ends of the molecules, the reactions were carried out in the dark and inert atmosphere (argon gas) and in the presence of free radical inhibitor (hydroquinone). Reaction time was adjusted to produce adducts with approximately 15 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 products cleaned up in this way were weighed to assess extent of reaction and small samples were withdrawn, milled to a fine flour and examined in transmission as KBr discs using Fourier Transform Infra-red Spectroscopy (FTIR).

2.2 Reactions with Monomers

The modified fiber sample was then treated with methyl methacrylate (MMA), butyl methacrylate (BMA) and styrene, separately. The fibrous sample was hand mixed into a "dough" with an equal mass of monomer containing about 6% benzoyl peroxide as free radical initiator. The dough was laid as mat 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. Small samples were cut from the hardened products and milled to a fine flour using a vibratory disintegrator. These flours

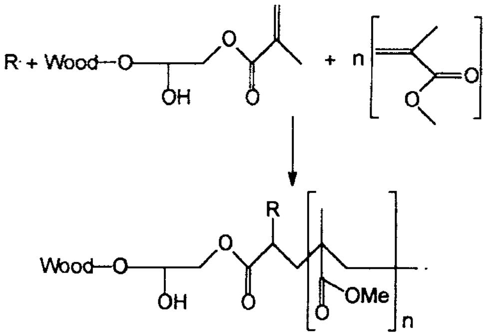

FIGURE 1 Proposed reaction between methacrylated fiber and methyl methacrylate.

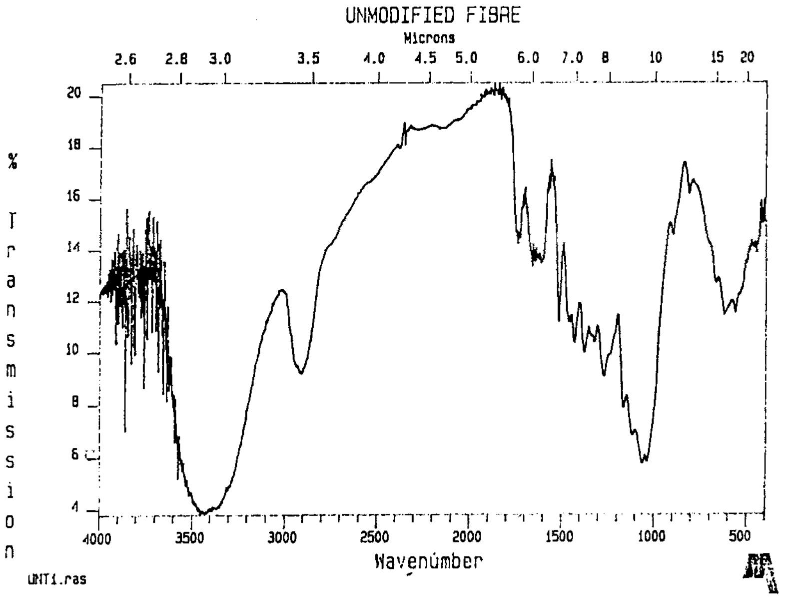

FIGURE 2 Infra-red spectrum of unreacted TMP fiber.

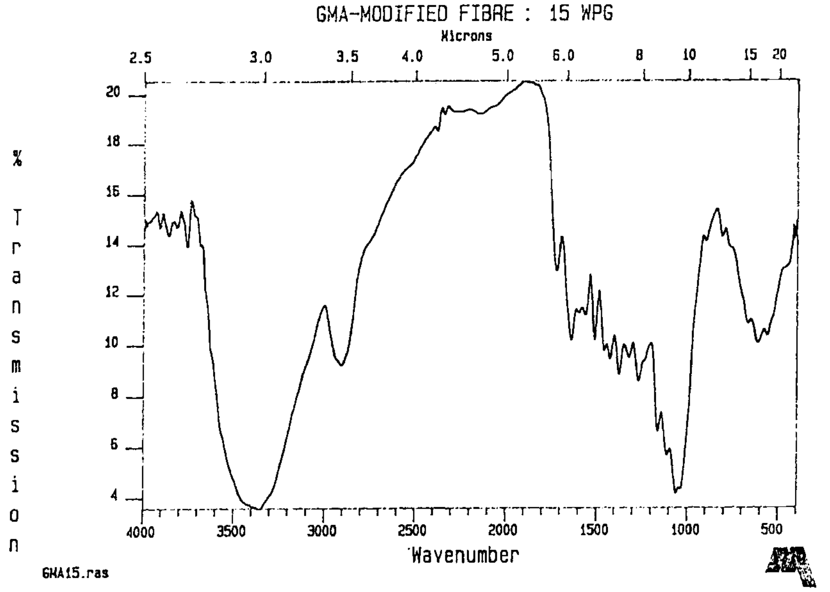

FIGURE 3 Infra-red spectrum of TMP fiber reacted with glycidyl methacrylate (GMA).

were then extracted by reflux with acetone/toluene to remove free monomers and any homopolymers derived from them. The extractive solvent was removed by filtration and finally after rinsing with clean acetone, by evaporation at 105°C until acetone free. As for the GMA-modified sample, infra-red spectra were acquired by the KBr disc method.

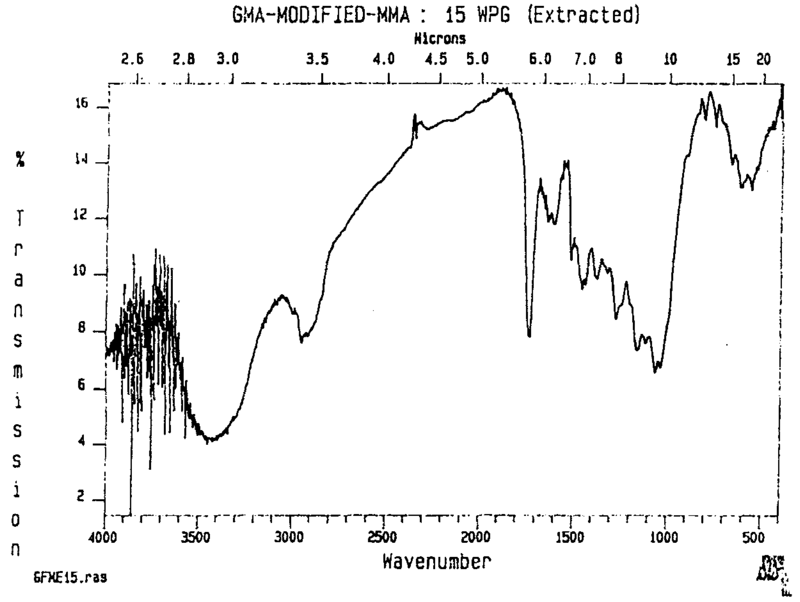

FIGURE 4 Infra-red spectrum of GMA-modified/MMA bonded fiber.

3. RESULTS AND DISCUSSION

3.1 Reaction of Glycidyl Methacrylate (GMA) with Fiber

Comparison of Figures 2 and 3 (unmodified fiber and GMA-modified fiber), shows that in the reacted fiber there is increased absorption in the C=C region (at about 1630 cm^{-1}). This is probably due to the absorption of C=C unsaturated groups of GMA. Since the samples for infra-red study were extracted exhaustively with solvent to remove free reagent and homopolymer, this suggests that GMA reacts with wood fibers and introduces terminal C=C on the surfaces.

Infra-red spectra for the GMA-modified fiber blended and heated with different monomers are presented in Figures 4–6. Comparison of Figures 3 and 4 (reaction with GMA only and reaction GMA/MMA) shows a large increase in carboxyl region (1730 cm^{-1}) after blended with MMA. This is in line with addition methacrylic ester to the fiber. There is also some loss of absorption in the C=C region (1630 cm^{-1}) which is consistent with attachment of MMA to the fiber by addition across the C=C bond, (see Figure 1).

For the GMA-modified/styrene bonded fiber (Figure 5), new prominent bands appeared compared to the GMA-modified fiber at 1600 and 1500 cm^{-1}, which are characteristics of benzene ring. In addition, a characteristic band at 1630 cm^{-1} due to the C=C unsaturated groups of GMA is still observed. As with the GMA-modified/MMA bonded fiber (Figure 4), its intensity is diminished in comparison to that of GMA-modified fiber. This suggests that the double bond in the GMA-modified fiber has reacted with styrene.

Infra-red spectra of the GMA-modified/BMA bonded fiber (Figure 6) also shows a decrease in the intensity at 1630 cm^{-1} (characteristics of C=C ester groups of

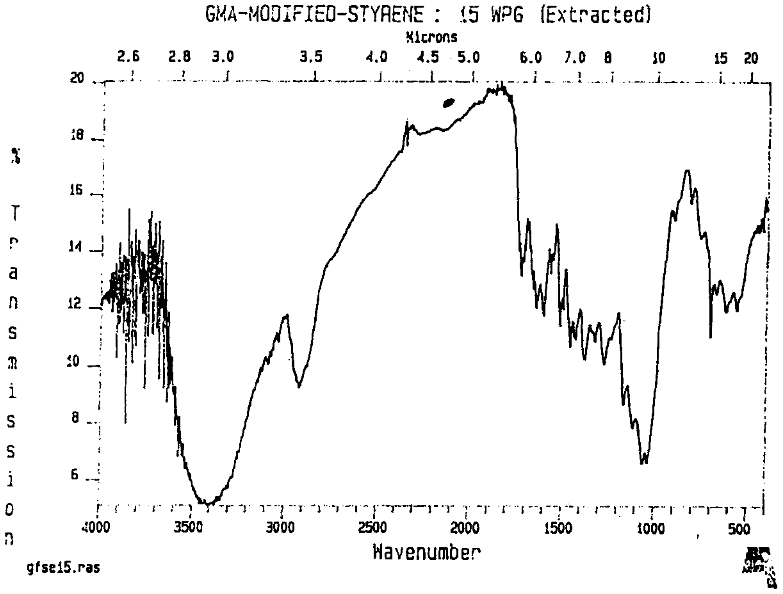

FIGURE 5 Infra-red spectrum of GMA-modified/styrene bonded fiber.

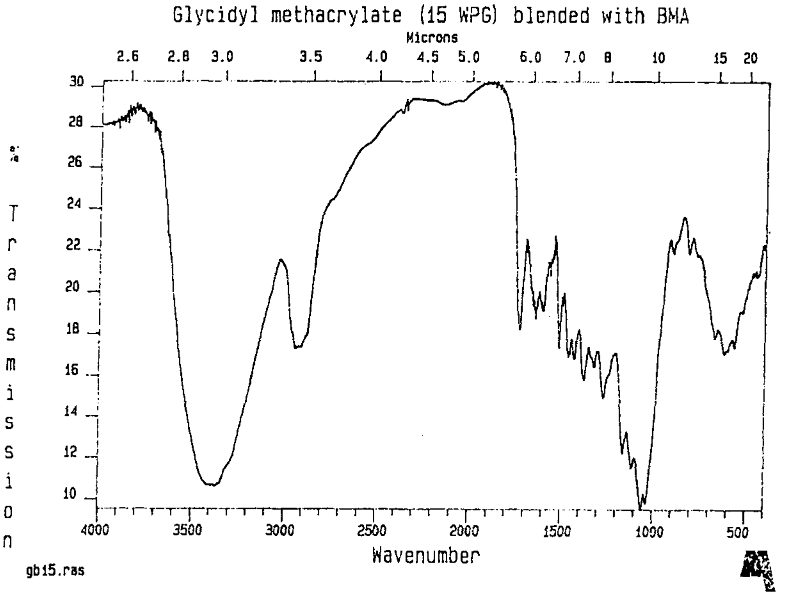

FIGURE 6 Infra-red spectrum of GMA-modified/BMA bonded fiber.

GMA) and an increase at 1720 cm^{-1} (due to an increase inC=O ester groups from PBMA) as compared to the GMA-modified fibers (Figure 3). By looking at the extent of the decrease and increase of the bands intensities, at 1630 cm^{-1} and 1730 cm^{-1}, respectively, it can be seen that GMA-modified/BMA bonded fibers tend to show a lesser decrease (at 1630 cm^{-1}) and increase (at 1730 cm^{-1}) than the ones blended with MMA. Though these results are not inclusive, it may indicate that there is a lower degree of interaction of GMA-modified fibers with BMA than with MMA.

These results support the work of Nakagami and Yokota,[7] and Matsuda, *et al.*[4] who showed that chemical bonding occurred between wood and activating agent and the activated fiber was able to react with unsaturated monomers to form grafted polymer attached to the fiber.

The bonding formed in the board may be contributed by: i) physical entanglement between methacrylated fiber and homopolymer, or (ii) by crosslinking between the adjacent activated surfaces. If crosslinking does occur it may lead to significantly improved dimensional stability towards exposure to water of moisture. However, if the degree of crosslinking becomes excessive, it may lead to embrittlement.

CONCLUSIONS

The work demonstrates that unsaturated epoxide may be reacted with wood fiber to form ether linkages. Through careful application of infra-red spectroscopy, this demonstrates clearly that the unsaturated adducts so formed may be further reacted with vinyl monomers to form grafted chains. The extent of crosslinking and polymerization is not yet known and is the subject of further study.

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