

# FTIR Characterization of Tropical Wood-Polymer Composites

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## SYNOPSIS

Wood-polymer composites (WPC) of Geronggang (*Cratoxylon arborescens*), a light tropical hardwood, impregnated with methyl methacrylate (MMA), methyl methacrylate-co-acrylonitrile (1 : 1; MAN), and styrene-co-acrylonitrile (3 : 2; STAN), were prepared by *in situ* polymerization using gamma radiation or the catalyst-heat treatment. The FTIR spectra of the three types of WPC, with polymer loadings ranging from 10 to 70%, were compared with that of the wood itself and the respective polymers. Characteristic peaks due to C=O vibration of MMA, C≡N stretching of acrylonitrile, and ring stretching and bending of styrene monomers, were prominent in the samples that had higher polymer loadings. For the copolymeric systems, quantitation of the FTIR spectra of these characteristic peaks enabled calculations of incorporated acrylonitrile and styrene monomers in the composites to be made. The FTIR spectra of the residues remaining, after exhaustive extraction to remove homopolymer, showed that graft copolymerization of wood components with acrylonitrile and styrene monomers was possible, but not with MMA. Composites prepared by the two methods, gamma radiation and the catalyst-heat treatment, were shown to be chemically very similar.

## INTRODUCTION

The impregnation of wood with vinyl monomers followed by *in situ* polymerization by either gamma radiation or the catalyst-heat treatment, results in composite materials known generally as wood-polymer composites (WPC). WPC exhibited improved strength properties, dimensional stability, and resistance to biodeterioration.<sup>1-5</sup> The extent of improvement in property was directly related to the polymer content, which, in turn, was dependent on the type of wood, the nature of the polymer, and the processing applied.

Infrared spectroscopy is widely used to elucidate chemical structures, enabling functional groups and linkages to be identified. Greatly improved spectra of wood and wood products have been reported using Fourier transformed infrared (FTIR) spectropho-

tometers compared to the conventional dispersive IR instruments. FTIR was used by Faix<sup>6</sup> as a rapid method for determining lignin in woody materials and in pulps, and Michell<sup>7</sup> studied the chemical changes in wood during pulping by FTIR.

This study on the characterization of WPC using FTIR complements other investigations on the behavior and properties of WPC prepared from a wide range of Malaysian tropical hardwoods and various vinyl monomers.<sup>8-12</sup> In this study, three types of Geronggang-polymer composites, with polymer loadings ranging from 10 to 70%, were prepared and their FTIR spectra compared with that of wood and the bulk polymer. FTIR spectra of residues remaining, after exhaustive extraction of the composites to remove homopolymer, were also determined. The purpose was to obtain information, which would indicate the nature of wood-polymer interactions, i.e., specifically, to determine if chemical linkages between wood cell wall components and the impregnated monomers existed, indicating graft copolymerization.

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## EXPERIMENTAL

### Preparation of Composites

The impregnation system for WPC preparation is shown in Figure 1. Oven-dried wood specimens were evacuated in the impregnation chamber, followed by the introduction of the monomer or monomeric mixture at atmospheric pressure and immersion of the wood for various periods of time. For the gamma radiation process, the samples were individually wrapped in foil and irradiated using a Co-60 source.<sup>13</sup> In the catalyst-heat treatment, the catalyst, azobisisobutyronitrile at 0.25% by weight based on the monomeric system, was introduced with the monomeric system. The samples were wrapped in foil and cured in a 60°C oven for 24 h.

The monomeric systems used for preparing the composites were methyl methacrylate (MMA), methyl methacrylate-*co*-acrylonitrile (1 : 1; MAN), and styrene-*co*-acrylonitrile (3 : 2; STAN). The polymer loading for the composites was calculated as follows:

$$\% \text{ Polymer loading} = \frac{100(W - W_0)}{W}$$

where  $W$  = weight of WPC and  $W_0$  = weight of oven-dried wood.

### Preparation of Samples for FTIR

Geronggang (GE) and the Geronggang composites (GE-MMA, GE-MAN, and GE-STAN) were oven-dried, carefully ground to fine powder, and dried again at 105°C for 24 h before being used for FTIR determinations. For comparison, the FTIR of the bulk polymers (PMMA, PMAN, and PSTAN), prepared by polymerization of monomers by gamma radiation, were also determined.

In another set of experiments, GE-MMA, GE-MAN, and GE-STAN were individually Soxhlet extracted with 300 mL chloroform in excess of 60 h. This was to remove the homopolymer present in the composites. FTIR spectra of the respective residues were then determined.

One milligram of the samples prepared as described above was dispersed in 400 mg dry KBr and further ground to a fine mixture in a mortar, before pressing to form moisture-free KBr pellets. A Perkin-Elmer 1710 FTIR spectrophotometer was used to obtain the IR spectra.

## RESULTS AND DISCUSSION

### FTIR of GE

In spite of the highly opaque nature of wood, a FTIR spectrum of GE with good resolution was obtained, as shown in Figure 2(i), which enabled the identi-

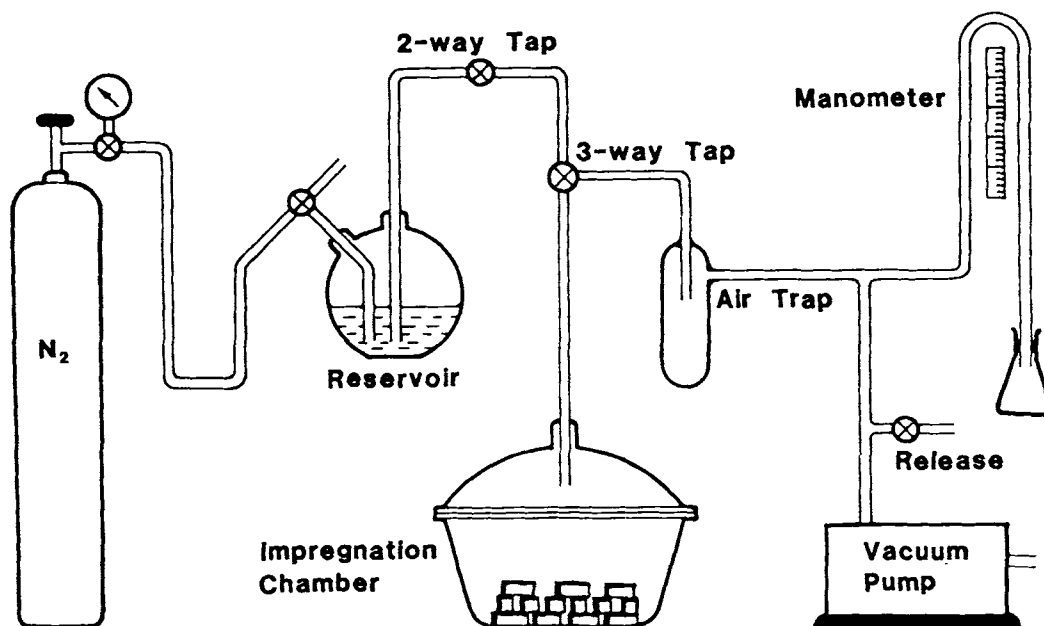


Figure 1 Setup for WPC preparation.

**Table I Assignment of FTIR Peaks for Geronggang**

Frequency (cm <sup>-1</sup> )	Assignment
3600–3200	H-bonded OH stretching; water
2940–2890	C—H stretching
1735	C=O stretching of acetyl groups in hardwood xylans
1670	Stretching of conjugated aryl carbonyl
1505	Aromatic skeletal vibrations
1460	Asymmetric C—H deformation in methyl and methylene groups
1425	Aromatic skeletal vibrations coupled with C—H in-plane deformation
1375	C—H bending
1325	Aromatic ring breathing with C—O stretching in syringyl unit
1240	C—O stretching of acetyl group
1160	Antisymmetric bridge oxygen stretching
1125	Aromatic C—H in-plane deformation of guaiacyl and syringyl units
900	$\beta$ -Linkage vibration

fication of absorption bands associated with the major wood components such as cellulose, hemicelluloses, and lignin. The assignment of absorption bands for GE, tabulated in Table I, have been made by consulting available literature of IR assignments for wood in general.<sup>14–17</sup>

The phenylpropane units in lignin were characterized by the absorption bands at 1125 cm<sup>-1</sup>, attributed to aromatic C—H in-plane deformation of the guaiacyl and syringyl units and the asymmetric C—H deformation at 1460 cm<sup>-1</sup> due to methyl and methylene groups. Vibrational modes, associated with the aromatic skeleton of lignin, were also observed at 1425 and 1505 cm<sup>-1</sup>, together with aromatic ring breathing with C—O stretching in syringyl units at 1325 cm<sup>-1</sup> and the stretching of conjugated aryl carbonyl groups at 1670 cm<sup>-1</sup>.

Absorption bands due to hemicelluloses and cellulose were indicated by the broad band at 3200–3600 cm<sup>-1</sup> due to H-bonded OH stretching, but which can also be attributed to the presence of water; C—H stretching and bending observed at 2890–2940 cm<sup>-1</sup> and 1375 cm<sup>-1</sup>, respectively; and the absorption

band at 900 cm<sup>-1</sup>, considered characteristic of  $\beta$ -linkage between glucose units in cellulose. The absorption peaks at 1735 and 1240 cm<sup>-1</sup> were attributed to acetylated xylans, which are typical of hardwoods. However, it should be noted that C=O stretching of uronic acids of hemicelluloses and unconjugated keto groups in lignin also absorb at around the 1700 cm<sup>-1</sup> region.

#### FTIR of PMMA, PMAN, and PSTAN

The FTIR spectra of poly(methyl methacrylate) (PMMA), poly(methylmethacrylate-*co*-acrylonitrile) (PMAN), and poly(styrene-*co*-acrylonitrile) (PSTAN) are shown in Figures 2(v), 3(v), and 4(v), together with the detailed assignments of absorption bands tabulated in Tables II–IV, respectively.<sup>18</sup>

The absorption bands of PMMA can be assigned to those due to the presence of the ester functional group and those related to the methyl group. Two prominent peaks at 3000 and 2960 cm<sup>-1</sup> can be attributed to the C—H stretching of the methyl group, with the latter peak receiving some contribution from the C—H stretching of the methylene group. The deformation of C—H bonds in the methyl group, on the other hand, accounted for the three peaks in the region 1390 to 1490 cm<sup>-1</sup>. The characteristic C=O stretching of the ester carbonyl in PMMA occurred at 1735 cm<sup>-1</sup>, whereas a group of four peaks in the region 1150–1275 cm<sup>-1</sup> can be attributed to the C—O—C stretching of the ester group. A group of peaks located between 750 and 950 cm<sup>-1</sup> have not been assigned, but represented a kind of “fingerprint” region characteristic of PMMA.

The FTIR spectrum of the copolymer PMAN showed absorption peaks at 3000, 2960, and 1735 cm<sup>-1</sup>, which were characteristic of PMMA. However, the former two peaks were observed to be much larger in proportion to the latter peak than in the FTIR spectrum of PMMA. The ratios of the peaks at 2960 cm<sup>-1</sup> to that at 1735 cm<sup>-1</sup> for the pure PMMA and that for the copolymer PMAN were 0.25 as compared to 0.51. From this quantitation of the FTIR spectra, the ratio of MMA : acrylonitrile in the copolymer PMAN was calculated to be 1 : 1, which is the mixture used to prepare the copolymer. The above calculations were made on the assumption that both monomers contributed equally to the absorption at 2960 cm<sup>-1</sup> but only MMA absorbed at 1735 cm<sup>-1</sup>.

Characteristic absorptions that can be attributed to the acrylonitrile component were a prominent

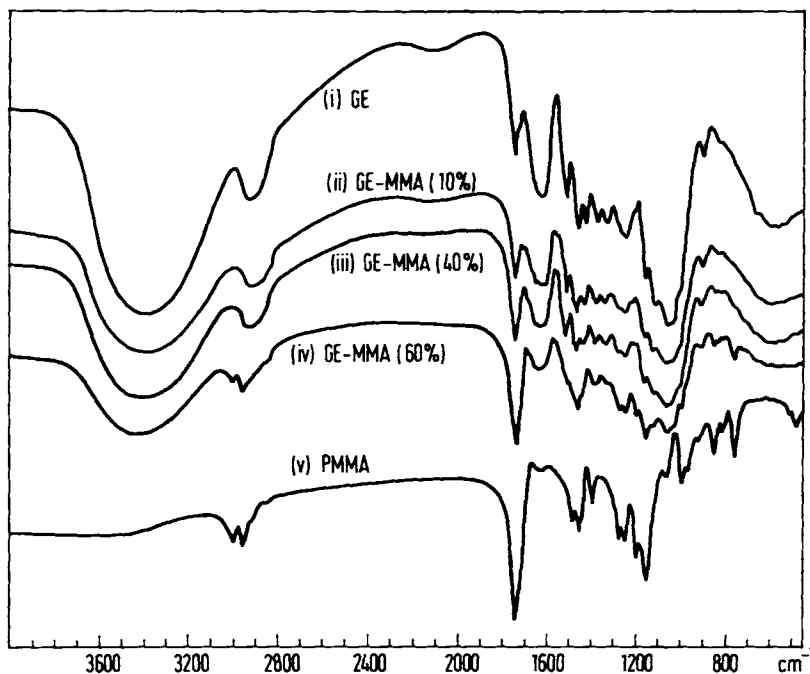


Figure 2 FTIR spectra of GE, GE-MMA composites, and PMMA.

peak at  $2230\text{ cm}^{-1}$ , due to  $\text{C}\equiv\text{N}$  stretching, decoupled from the rest of the peaks and therefore very useful in analyses of copolymers, and a small peak at  $2850\text{ cm}^{-1}$  assigned as the antisymmetric C-H stretching of methylene groups.

The major absorption peaks for PSTAN were clearly those characteristic of the acrylonitrile component discussed previously and peaks attributable to the aromatic ring of styrene. These were peaks assigned to aromatic C-H stretching ( $3030\text{--}3085$

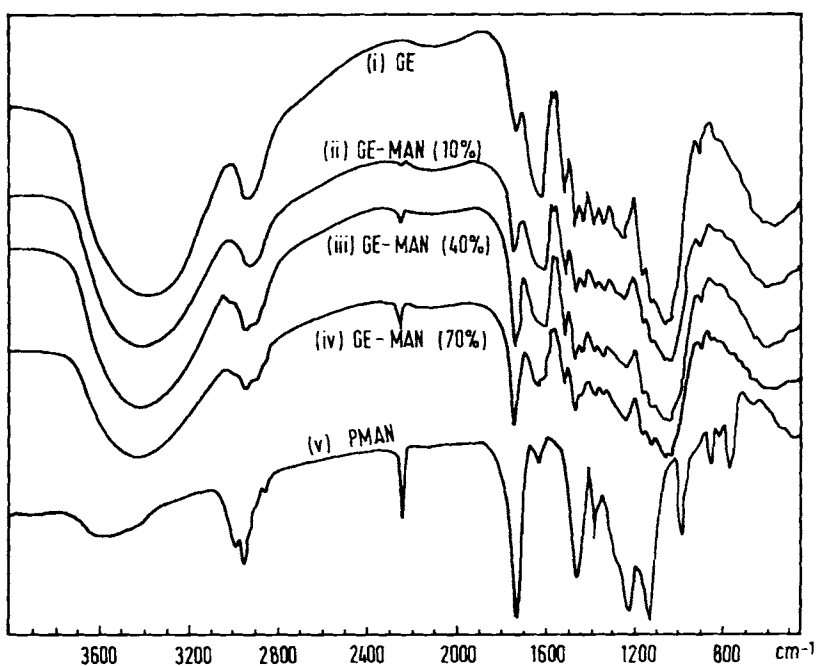


Figure 3 FTIR spectra of GE, GE-MAN composites, and PMAN.

**Table II Assignment of FTIR Peaks for PMMA**

Frequency (cm <sup>-1</sup> )	Assignment
3000	C—H stretching of methyl group
2960	C—H stretching of methyl group and symmetric CH <sub>2</sub>
1735	C=O stretching of ester carbonyl group
1490 } 1450 } 1390 }	C—H deformation of methyl group
1275 } 1245 } 1195 } 1150 }	C—O—C ester stretching band ("regularity band")

cm<sup>-1</sup>) and aromatic ring vibrations mixed with C—H in-plane bending (between 1000 and 1605 cm<sup>-1</sup>; and two prominent peaks were at 1500 and 1450 cm<sup>-1</sup>): aromatic C—H wagging at 760 cm<sup>-1</sup> and aromatic ring bending at 700 cm<sup>-1</sup>. The latter two peaks were particularly useful in copolymer analyses.

#### FTIR of GE-MMA, GE-MAN, and GE-STAN

The FTIR spectra of GE-MMA, GE-MAN, and GE-STAN at various polymer loadings are shown in Figures 2(ii)–(iv), 3(ii)–(iv), and 4(ii)–(iv),

**Table III Assignment of FTIR Peaks for PMAN (1 : 1)**

Frequency (cm <sup>-1</sup> )	Assignment
3000	C—H stretching of methyl group
2960	C—H stretching of methyl group and symmetric CH <sub>2</sub> stretching
2850	Antisymmetric CH <sub>2</sub> stretch
2230	C≡N stretching
1735	C=O stretching of ester carbonyl group
1460 } 1395 }	C—H deformation of methyl group
1245 } 1145 }	C—O—C ester stretching band ("regularity band")

**Table IV Assignment of FTIR Peaks for PSTAN (3 : 2)**

Frequency (cm <sup>-1</sup> )	Assignment
3085 } 3065 } 3030 }	Aromatic C—H stretching
2930	Symmetric CH <sub>2</sub> stretching
2860	Antisymmetric CH <sub>2</sub> stretching
2240	C≡N stretching
1605 } 1585 }	Aromatic ring stretching
1500 } 1455 } 1070 } 1030 }	Semicircular aromatic ring stretching mixed with C—H inplane bending
760	Aromatic C—H wagging
700	Aromatic ring bending

respectively. As the polymer loading increased, characteristic peaks of the different polymers became more prominent. In the case of GE-MMA, the C=O vibration at 1735 cm<sup>-1</sup> increased substantially as the polymer loading increased from 10 to 60%. Other peaks also became observable: The most obvious were those at 2960 and 3000 cm<sup>-1</sup>, attributed to C—H stretching of methyl groups, and the "fingerprint" region between 750 and 950 cm<sup>-1</sup>. There was also a concomitant decrease in some of the GE peaks, notably that at 1670 cm<sup>-1</sup>.

For GE-MAN and GE-STAN composites, the peaks that became most prominent as polymer loading increased were the C≡N peak for both GE-MAN and GE-STAN and that due to C=O stretching for the GE-MAN and those due to the aromatic ring of styrene in the region 3030–3085 cm<sup>-1</sup>, 700 cm<sup>-1</sup>, and 760 cm<sup>-1</sup> for GE-STAN.

For the two copolymeric systems GE-MAN and GE-STAN, an attempt was made to look at the FTIR peaks quantitatively to determine the proportion of each monomer that was incorporated into the composites during *in situ* polymerization. For GE-MAN, incorporation of acrylonitrile can be represented by the C≡N peak. Calculations showed that for the GE-MAN composites that had 10, 40, and 70% polymer loadings, although the MMA : acrylonitrile monomeric mixture used for copolymerization was 1 : 1, the MMA : acrylonitrile ratio in the above composites were 1 : 0.40, 1 : 0.40, and

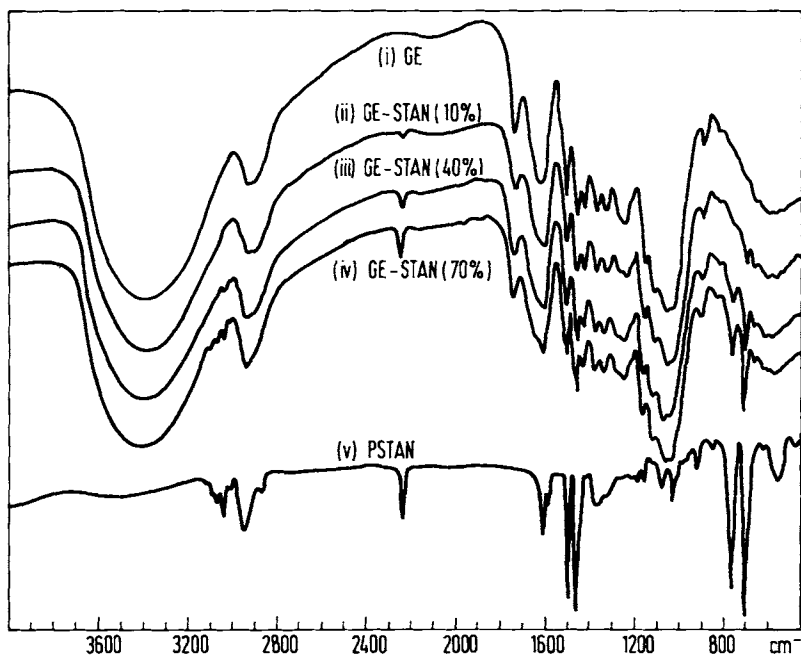


Figure 4 FTIR spectra of GE, GE-STAN composites, and PSTAN.

1 : 0.53, respectively. This observation can be attributed to the difficulty in polymerization of acrylonitrile compared to MMA.

In the case of GE-STAN, the acrylonitrile incorporation was calculated as for GE-MAN, based on the  $C\equiv N$  peak, whereas for styrene incorporation, it was based on the absorption peak at  $700\text{ cm}^{-1}$ . Calculations based on these peaks showed that

for the 40 and 70% GE-STAN composites, although the ratio of the monomeric mixture used for polymerization was styrene : acrylonitrile 1 : 0.66 (i.e., 3 : 2), the incorporation of the two monomers were, respectively, 1 : 1 and 1 : 1.12. These results seem to indicate that the uptake rate or the polymerization of styrene proceeds with greater difficulty than that of acrylonitrile in wood.

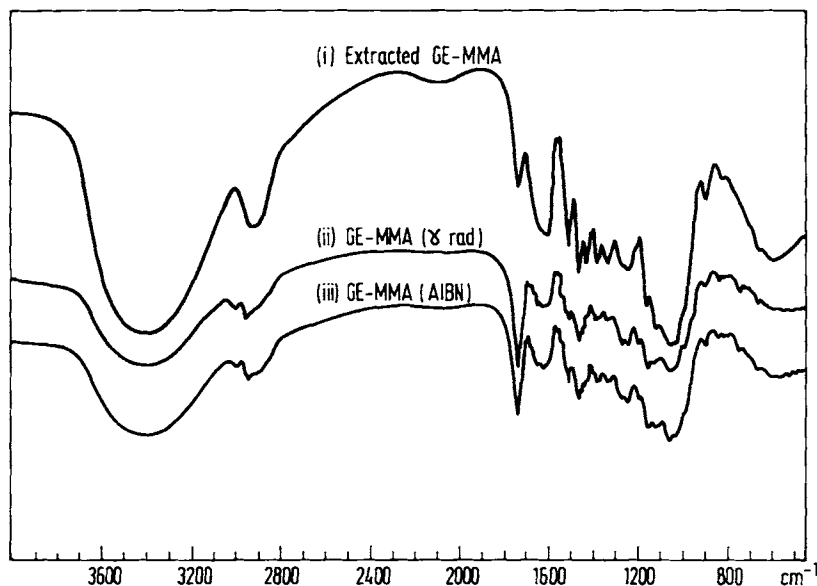
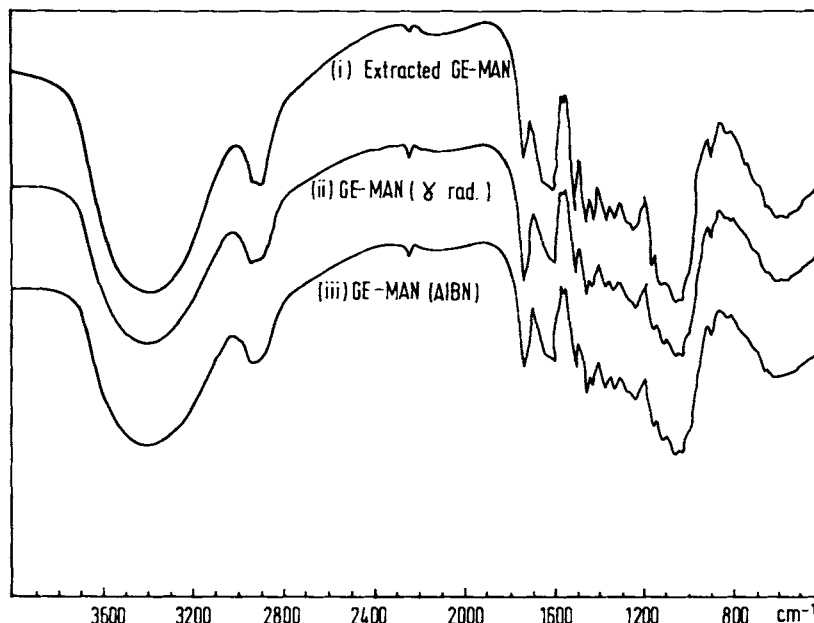


Figure 5 FTIR spectra of extracted GE-MMA, GE-MMA ( $\gamma$ -radiation), and GE-MMA (AIBN).



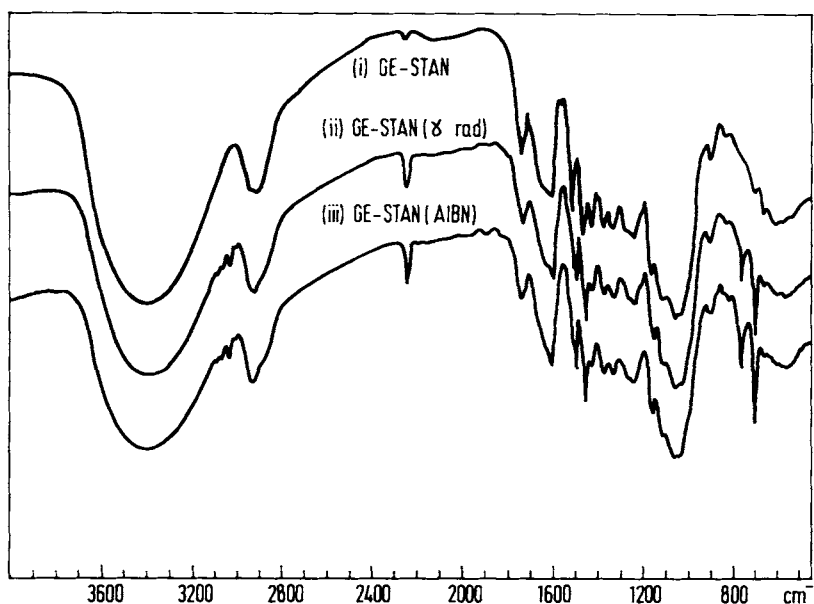
**Figure 6** FTIR spectra of extracted GE-MAN, GE-MAN ( $\gamma$ -radiation), and GE-MAN (AIBN).

#### Grafting in GE Composites

The gamma irradiation of impregnated wood with vinyl monomers results in the formation of free radicals on the monomers as well as on wood components, particularly cellulose. Different possible cellulose radicals have been proposed by Hebeish and Guthrie<sup>19</sup> and Arthur and Mares.<sup>20</sup>

To investigate whether graft copolymerization of

wood cell wall components and the respective monomers had taken place, the homopolymer fraction of composites (polymer loadings 60–70%) was removed by exhaustive Soxhlet extraction with chloroform. The FTIR spectra of the residues of GE-MMA, GE-MAN, and GE-STAN remaining after extraction are shown in Figures 5(i), 6(i), and 7(i), respectively.



**Figure 7** FTIR spectra of extracted GE-STAN, GE-STAN ( $\gamma$ -radiation), and GE-STAN (AIBN).

The FTIR spectrum for extracted GE-MMA showed no trace of the more prominent characteristic peaks of PMMA, but was very similar to the FTIR spectrum of GE. This strongly indicated that no grafting had taken place for the GE-MMA composite and that the impregnated polymer was essentially a homopolymer of MMA. This was not surprising, since for grafting of wood components and monomer to occur, the monomer needs to penetrate the wood cell wall. MMA is known to be nonpolar and has been shown in our laboratory to swell wood by only 1%, as compared to STAN, which caused wood to swell by about 10% by volume.<sup>21</sup> Acrylonitrile has been reported to swell wood by 7%.<sup>22</sup>

On the other hand, the FTIR spectra of the extracted GE-MAN and GE-STAN showed the presence of peaks that indicated the presence of the respective monomers. The C≡N peak was present in both the extracted GE-MAN and GE-STAN FTIR spectra, suggesting the grafting of acrylonitrile monomer to wood for both composites. In the case of the extracted GE-STAN, the characteristic peaks of styrene at 700 and 760 cm<sup>-1</sup> were observable, even though they were rather small, indicating the concomitant grafting of styrene to wood components.

Although acrylonitrile and styrene are nonpolar, they have been shown to cause wood to swell, as previously discussed, allowing for penetration of these monomers into the cell wall. This accounted for the present observation that graft copolymerization of wood components and these monomers can occur. This direct evidence of the presence of grafted copolymer in STAN composites confirmed earlier studies that showed STAN composites possessing superior dimensional stability properties, which was attributed to grafting.<sup>21</sup> Furthermore, thermal characterization of WPC also indicted the presence of grafting for STAN composites.<sup>23</sup>

#### Radiation-Induced/Catalyst-Heat Composites

Comparison of the FTIR spectra of composites, prepared either by gamma irradiation or by the catalyst-heat treatment, shown in Figures 5(ii)-(iii), 6(ii)-(iii), and 7(ii)-(iii), indicated that the composites were chemically very similar, since the corresponding spectra were identical. This supports the similarity in bulk properties such as strength, hardness, and abrasive resistance observed by other researchers<sup>24</sup> and also in our studies on WPC properties.<sup>25</sup>

#### REFERENCES

1. J. F. Siau, J. A. Meyer, and C. Skaar, *Forest Prod. J.*, **15**(4), 161 (1965).
2. J. E. Langwig, J. A. Meyer, and R. W. Davidson, *Forest Prod. J.*, **18**(7), 33 (1968).
3. J. A. Kent, G. B. Taylor, A. Winston, and W. Boyle, *Chem. Eng. Prog. Symp. Ser. 83*, **64**, 136 (1968).
4. R. L. Calleton, E. T. Chong, and R. C. McIlhenny, *Wood Sci. Technol.*, **4**, 216 (1970).
5. S. Katsurada and K. Kurahashi, Br. U. K. Pat. Appl. GB 2141753 (Cl B27K3/15) (January 3, 1985); *Chem. Abstr.*, **102**, 115426K (1983).
6. O. Faix, *Mikrochim. Acta*, **1**, 21 (1988).
7. A. J. Michell, *Cellulose Chem. Tech.*, **22**(1), 105, (1988).
8. L. H. L. Chia and H. K. Kong, *J. Macromol. Sci. Chem.*, **A16**(4), 803 (1981).
9. L. H. L. Chia, P. H. Chua, and E. E. N. Lee, *Radiat. Phys. Chem.*, **26**(4), 423 (1985).
10. L. H. L. Chia, V. L. S. Lim, and M. G. S. Yap, *Radiat. Phys. Chem.*, **29**(4), 303 (1987).
11. K. Y. Chan, M. G. S. Yap, L. H. L. Chia, and S. H. Teoh, *Radiat. Phys. Chem.*, **33**(3), 205 (1989).
12. M. G. S. Yap, L. H. L. Chia, and S. H. Teoh, *Wood Chem. Technol.*, **10**(1), 1 (1990).
13. H. K. Kong, MSc Thesis, University of Singapore, 1979.
14. K. V. Sarkanen and C. H. Ludwig, *Lignins*, Wiley Interscience, New York, 1971.
15. S. Z. Chow, *Wood Sci.*, **5**(1), 27 (1972).
16. R. H. Marchessault, *Pure Appl. Chem.*, **5**, 107 (1962).
17. M. G. S. Yap and M. Wayman, *Can. J. Chem.*, **57**(19), 2603 (1979).
18. W. Klopffer, *Introduction to Polymer Spectroscopy*, Springer-Verlag, Berlin, 1984.
19. A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, Berlin, 1981.
20. J. C. Arthur, Jr. and T. Mares, *J. Appl. Polym. Sci.*, **9**(7), 2581 (1965).
21. K. Y. Chan, MSc Thesis, National University of Singapore, 1988.
22. W. E. Loos and G. L. Robinson, *Forest Prod. J.*, **18**(9), 109 (1968).
23. K. Y. Chan, M. G. S. Yap, L. H. L. Chia, and K. G. Neoh, *Radiat. Phys. Chem.*, **33**(3), 197 (1989).
24. J. F. Siau and J. A. Meyer, *Forest Prod. J.*, **16**(8), 47 (1966).
25. Y. T. Que, MSc Thesis, National University of Singapore, 1990.

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