

# IR Studies of Wood Plastic Composites

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## SYNOPSIS

Wood plastic composites (WPC) of simul were prepared by gamma radiation using butylacrylate (BA) and methylmethacrylate (MMA) as the monomer and methanol as the swelling agent at 9 : 1 (v/v) ratio. IR spectra of simul, bulk polymer of BA (or MMA) film, and WPC of different polymer loadings ranging from 18 to 115% were studied. Increase of the characteristic peak intensity at 1735 cm<sup>-1</sup> (C=O vibration for acetyl groups) over that of 1620 cm<sup>-1</sup> (conjugated aryl carbonyl groups) along with the increase of polymer loading of simul with the monomer indicates that the graft copolymerization took place between the monomer and the simul wood matrix. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Recently many authors reported on the wood plastic composites formation using different monomers. Synergistic yields of polymer loading were also reported in the presence of additives.<sup>1,2</sup> Analysis of composites by X-ray diffraction and scanning electron microscope (SEM) revealed the graft copolymerization of the monomer methylmethacrylate (MMA) with the wood matrix.<sup>3</sup> IR spectroscopy is known to elucidate functional groups and linkages in any chemical structure analysis. Recently wood polymer composites of Geronggang, a tropical hard wood of Malaysia were analysed by FTIR spectroscopy.<sup>4</sup> It was observed that graft copolymerization occurred with the wood components and acrylonitrile and styrene, but not with MMA. The purpose of the present work is to study the IR spectra of the simul, a soft wood of Bangladesh, and its composites with *n*-butylacrylate (BA) and MMA in order to determine, in further support of X-ray diffraction and SEM analysis, the extent of copolymerization of simul with BA and MMA.

## EXPERIMENTAL

### Preparation of Composite

Wood samples were prepared from long-grained planks of simul (*Salmalia malabarica*), having density 0.40 gm/cm<sup>3</sup> under oven dry conditions. They were uniformly polished with sandpaper. The container of wood samples was placed in a desiccator that was then evacuated for 1 h at 50 mmHg. Without interrupting the vacuum, a solution of the monomer BA or MMA and methanol at ratio of 9 : 1 (v/v) was introduced. All the samples were kept completely immersed in the solution for 15 h. The samples were then taken out of the solution, wiped with tissues, encapsulated with polyethylene bags, and placed in irradiation. Samples were irradiated at room temperature by gamma rays from Co-60 source (50 Kci) of Bangladesh Atomic Energy Commission for 3 Mrad at a dose rate of 0.8 Mrad/h. Untreated monomer was completely removed from the irradiated samples by heating them at 60°C under vacuum (50 mmHg). The treated wood was then converted into sawdust (about 60 mesh) that was extracted in a Soxhlet apparatus for 72 h with hot benzene. The polymer loading (PL), an index for the composite formation, was determined from the percentage of weight increase of the composite

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sample extracted in benzene under the similar condition of the wood.

### Preparation of Samples for IR

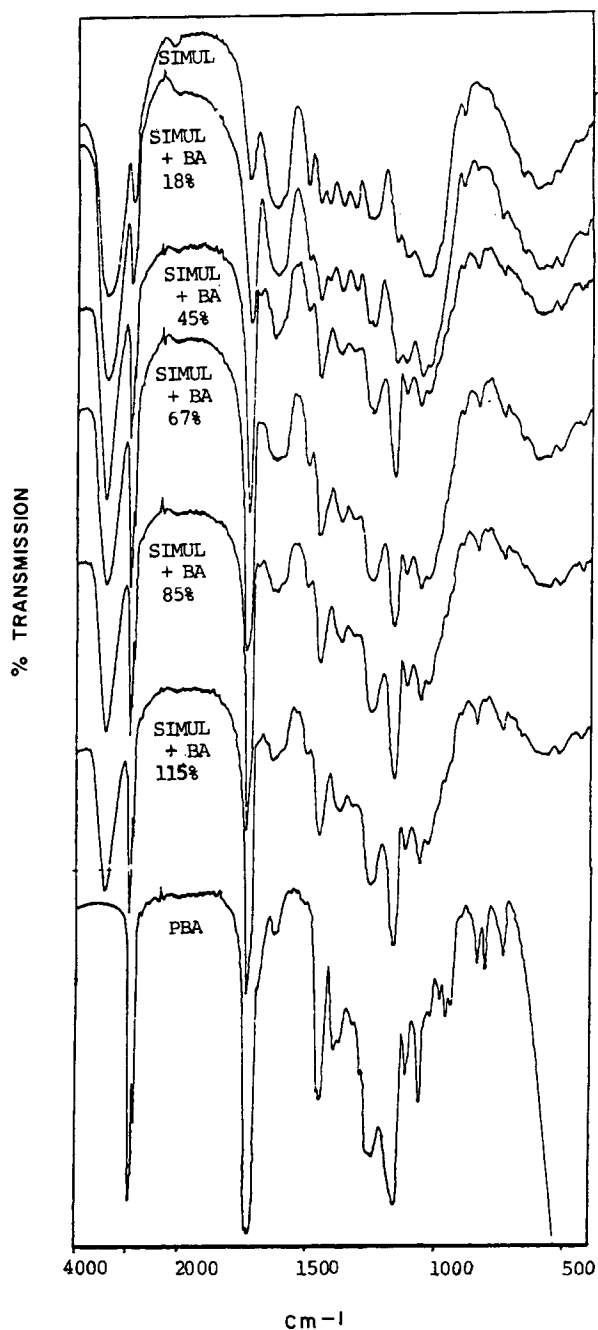
The benzene extracted sawdusts of wood and WPC were dried at 105°C for 24 h before the IR (IR 470 from Shimadzu) spectra were obtained. For comparison purposes, the IR of the bulk polymers polybutylacrylate (PBA) and polymethylmethacrylate (PMMA), (prepared by polymerization of monomer BA or MMA, respectively) by gamma radiation at 0.5 Mrad was also determined. The sawdust sample (1 mg) was dispersed in dry KBr (300 mg) and the mixture was ground to fine particles in a mortar and then pressed to form moisture free KBr pellets.

## RESULTS AND DISCUSSION

### IR Spectra of Simul

The IR spectrum of simul was obtained with good resolution as shown in Figure 1. This enabled the identification of absorption bands associated with the major wood components such as cellulose, lignin, and hemicellulose. The assignment of absorption bands for the simul was made considering the viewpoints given.<sup>5-8</sup> Results are given in Table I. Absorption bands obtained for hemicellulose and cellulose are indicated by the broad band at 3200–3600  $\text{cm}^{-1}$  and this is caused by H-bonded OH stretching, but this can also be attributed to the presence of water. The characteristic linkages between glucose units present in the cellulose can be attributed to C—H stretching and bending observed respectively at 2890–2940  $\text{cm}^{-1}$  and 1375  $\text{cm}^{-1}$  as well as the absorption band at 900  $\text{cm}^{-1}$  in the cellulose.<sup>4</sup> The absorption peaks at 1735  $\text{cm}^{-1}$  and 1240  $\text{cm}^{-1}$  are caused by the acetylated xylans. However, it is worth mentioning that the C=O stretching of uronic acid present in the hemicellulose and unconjugated keto groups in the lignin can also absorb at around the 1700  $\text{cm}^{-1}$  region.

The absorption band at 1120  $\text{cm}^{-1}$  can be assigned to the phenylpropane units of the lignins. This is attributed to the aromatic C—H in the plane deformation mode of the guaiacyl/syringyl units of the lignin. The aromatic C—H deformation at 1455  $\text{cm}^{-1}$  is observed because of the methyl and methylene groups. The aromatic skeleton of lignin was also obtained at 1420  $\text{cm}^{-1}$  and 1500  $\text{cm}^{-1}$  through the vibration modes together with an aromatic ring



**Figure 1** IR spectra of simul, simul + BA composite, and PBA.

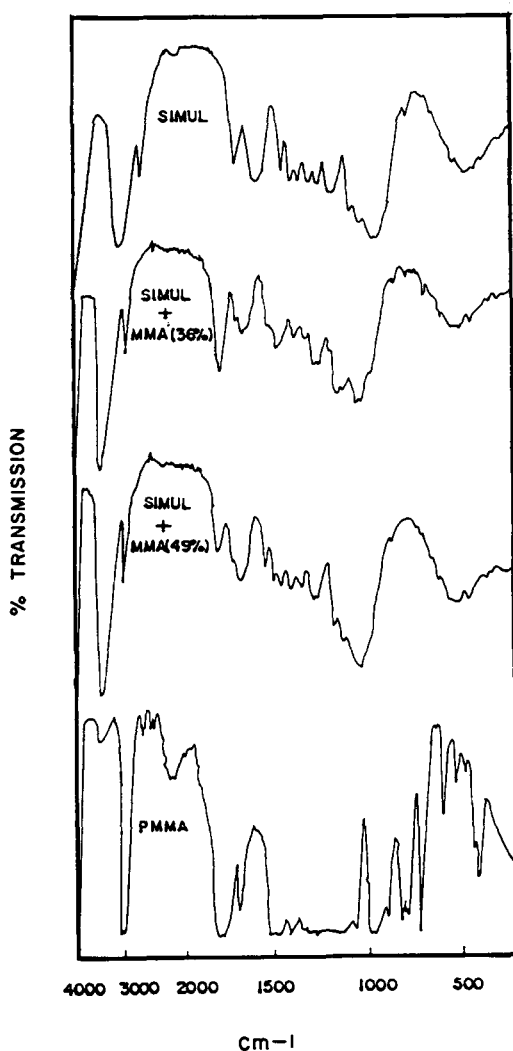
breathing via C—O stretching in the aryl carbonyl groups at 1655  $\text{cm}^{-1}$ .

### IR Spectra of PBA and PMMA

The IR spectra of PBA are shown in Figure 1 and those for PMMA are given in Figure 2; the detailed assignments of the absorption bands of PBA and

**Table I** Characteristic IR Peaks for Simul and Peak Assignment

Frequency (cm <sup>-1</sup> )	Vibration
3600–3200	H-bonded OH stretching;
2940–2890	C—H stretching
1735	C=O stretching of acetyl groups in wood xylans
1655	Stretching of conjugated aryl carbonyl
1500	Aromatic skeletal vibrations
1455	Asymmetric C—H deformation in methyl and methylene groups
1420	Aromatic skeletal vibrations coupled with C—H in plane deformation
1375	C—H bending
1320	Aromatic ring breathing with C—O stretching in syringyl unit
1240	C—O stretching of acetyl group
1160	Antisymmetric bridge oxygen stretching
1120	Aromatic C—H in plane deformation of guaiacyl and syringyl units
900	Linkage vibration

**Figure 2** IR spectra of simul, simul + MMA composite, and PMMA.

PMMA are given in Table II. The absorption bands of PBA can be assigned to those caused by the presence of the ester functional groups and to the butyl units. Two prominent peaks at 3000 cm<sup>-1</sup> and 2960 cm<sup>-1</sup> can be attributed to the C—H stretching of the methyl group; the 2940 cm<sup>-1</sup> peak may have some contribution from C—H stretching of the methylene group. However, the deformation of the C—H bond in the methyl group can be accounted for in the three peaks in the region of 1390 cm<sup>-1</sup> to 1490 cm<sup>-1</sup>. The characteristic C=O stretching of the ester carbonyl in PBA occurs at 1735 cm<sup>-1</sup> and a group of four peaks between 1150 cm<sup>-1</sup> and 1275 cm<sup>-1</sup> can be attributed to the C—O—C stretching of the ester group.<sup>4</sup> A group of peaks observed between 750 cm<sup>-1</sup> and 950 cm<sup>-1</sup> could not be assigned at this stage; but it may be similar to a “fingerprint” that is a characteristic band region of PBA. Similarly a characteristic fingerprint band is also observed with PMMA. The main difference between spectra of PBA and PMMA is due to CH<sub>2</sub>-groups present in them.

#### IR Spectra of Simul + BA

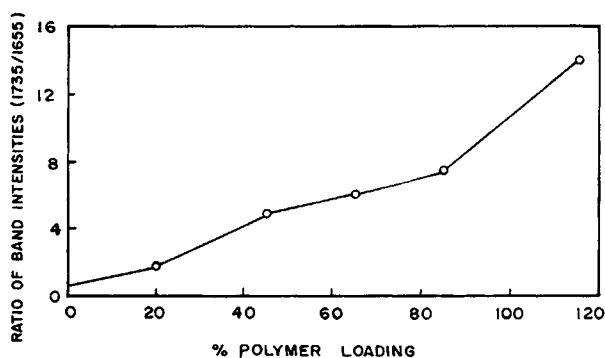
The IR spectra of simul + BA at various polymer loadings are shown in Figure 1. As the polymer loading is increased, characteristic peaks of the polymers become more prominent. The C=O vibration at 1735 cm<sup>-1</sup> increases substantially as the polymer loading increases from 18 to 115%. The most obvious peaks are at 2940 and 3000 cm<sup>-1</sup> and these are attributed to C—H stretching of the methyl groups; however, peaks of simul at 1655 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> are, respectively, caused by conjugated aryl carbonyl

**Table II** Characteristic IR Peaks for PBA and PMMA

Frequency (cm <sup>-1</sup> )	Vibration
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	C—H deformation of methyl group
1440	
1390	
1275	
1245	C—O—C ester stretching band (regularity band)
1195	
1150	

and aromatic ring skeleton (Table I). These two peaks slowly decrease as the polymer loading increases indicating a prohibition on the vibration of the conjugated aryl ring and the aromatic ring with the increase of polymerization of BA with simul (Fig. 1).

The increase of the peak intensity at 1735 cm<sup>-1</sup> for C=O vibration and decrease of that at 1655 cm<sup>-1</sup> with increase of polymer loading can be shown graphically (Fig. 3). The ratio of the intensities of 1735 cm<sup>-1</sup> to 1655 cm<sup>-1</sup> is plotted against percent polymer loading (Fig. 3). The value of the ratio is increased with the increase of polymer loading. On the other hand, the ratio of the peak intensities of 3450 cm<sup>-1</sup> for the OH group and 2940 cm<sup>-1</sup> for the methyl group, plotted against the percent polymer loading is found to decrease with the increase of polymer loading (Fig. 4). These observations indicate that the presence of monomer BA in simul, that is, the concomitant grafting of BA to the wood components. It is a clear indication that graft copolymerization of the wood component and the monomer has occurred. This is direct evidence of graft copolymer in BA + simul composite.

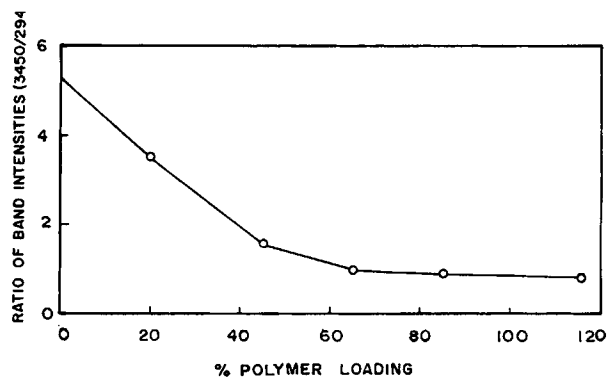


**Figure 3** Ratio of peaks at 1735/1620 (cm<sup>-1</sup>) against percent polymer loading.

### IR Spectra of Simul + MMA

The ratio of the intensities of the peaks at 1735 cm<sup>-1</sup> and 1655 cm<sup>-1</sup> present in the simul + MMA system increases like that in the simul + BA; but the amount of this increase in simul + MMA is quite small compared to that in the simul + BA system. It is reported that the Malaysian wood could not produce any grafting with MMA. However, Bangladeshi wood simul, has been able to produce, to some extent, copolymerization with MMA. This was also proved by X-ray diffraction and SEM studies.<sup>3</sup>

Figure 5 shows the IR spectra of the treated and untreated samples of simul and simul + BA, which were hydrolyzed in acid solutions. The ratio of the intensities of peaks at 1735 cm<sup>-1</sup> and 1655 cm<sup>-1</sup> of the hydrolyzed treated sample is about three times higher than that of the hydrolyzed untreated simul. However, Figure 3 shows that the ratio of the same peaks (1735 cm<sup>-1</sup> and 1655 cm<sup>-1</sup>) is about 1.5 times higher for the treated simul over the untreated; but in the latter case the samples were not hydrolyzed. This is possibly caused by the decomposition of the untreated wood portion present in simul and its



**Figure 4** Ratio of peaks at 3450/2960 (cm<sup>-1</sup>) against percent Polymer loading.

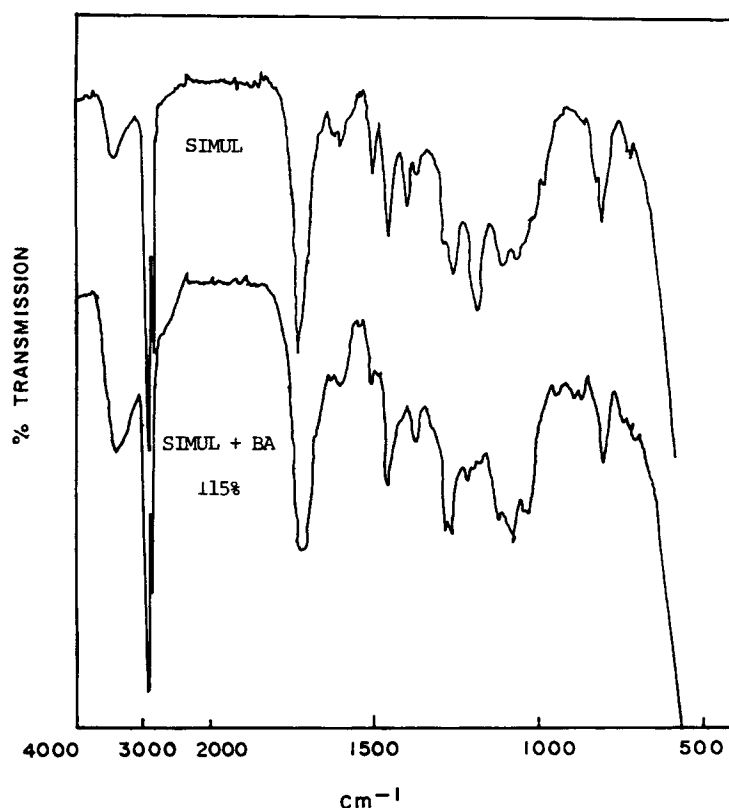


Figure 5 IR spectra of simul and simul + BA composite hydrolyzed in acid solution.

composites under the acid hydrolysis. This can also be considered as an indication of the graft copolymerization between BA and simul.

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