Combined Styrene/MMA/Nanoclay Cross-linker Effect on Wood-Polymer Composites (WPCs)

Md. Rezaur Rahman,[a] Josephine Lai Chang Hui,[a,*] Sinin Hamdan,[b] Abu Saleh Ahmed,[b] Rubiyah Baini,[a] and Shanti Faridah Saleh [a]

In the present study, batai wood (*Paraserianthes moluccana*) was impregnated with a combination of styrene, methyl methacrylate, and nanoclay in order to improve compression strength, thermal stability, and surface morphology. Styrene (ST) and methyl methacrylate (MMA) cross-linker introduced a co-polymerization reaction with cellulose in the wood cell wall and produced wood polymer composites (WPCs), as confirmed by Fourier Transform Infrared (FT-IR) Spectroscopy. The mechanical properties of the WPCs were significantly increased compared to the raw wood. Thermal properties of both raw wood and WPCs were evaluated by thermogravimetric analysis (TGA). WPCs exhibited higher thermal stability relative to the raw wood due to the co-polymerization reaction. The surface morphologies of the fracture surface for both the raw wood and WPCs were recorded using scanning electron microscopy (SEM). The SEM micrographs reveal that after polymerization, WPCs show smoother texture and adhesion compared to that of raw wood.

Keywords: Crosslinker; Batai wood; Mechanical properties; Thermal properties

Contact information: a: *Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia;* b: *Department of Mechanical Engineering, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia;*
** Correspondent author: Josephine Chang-Hui Lai, E-mail: josephinelai91@hotmail.com*

INTRODUCTION

Wood is a natural material that is made of cellulose, hemicellulose, and lignin. It is a remarkable material of great value and importance in the world's economy (Zabel and Morrell 1992). Increased attention on wood in the 21st century will be favored by demands for materials that are renewable, sustainable, and eco-friendly (Mohanty *et al*. 2002; Bledzki *et al*. 2007; Nishino 2004). The excellent material properties and desirable environment characteristics ensure that wood is applicable to many usages and there is an abundant availability of wood worldwide. Raw wood has contributed to great environmental benefits over other building materials because of its low cost and biodegradable properties (Tawakkal *et al.* 2012). Wood can be used to produce a variety of wood materials such as plywood, wood plastic composites, and wood composites *etc.* On the other hand, motor fuels and lubricants can be produced from the conversion of wood. Besides, wood serves as a great insulator and uses less energy to process compared to steel, concrete, aluminum, or plastic. Also, the emissions of carbon dioxide from wood are three times lower than from steel. One of the important characteristics of wood is its renewability.

Batai soft wood is abundantly available in the Borneo Islands due to its growth characteristics (Islam *et al.* 2012). Although wood is environmentally friendly, there are some drawbacks to softwood species. Softwood species do not easily withstand drastic changes in temperature. Moreover, softwood species are more susceptible to attack by fungi and termites due to their hydrophilic nature. Softwood species have low dimensional stability and durability due to their low densities. In order to overcome the aforementioned drawbacks of softwood species, wood specimens in this study were impregnated with ST/MMA/Clay co-polymer crosslinker to produce wood polymer composites (WPCs).

Nowadays, the two most common processes available for improvement of solid wood properties are acetylation and thermal modification (Segerholm *et al.* 2012). Acetylation can be defined as a single-site reaction in which acetic anhydride reacts with the wood hydroxyl groups. Rowell (2006) stated that the resulting wood material by acetylation is fixed in a swollen state, and it has good dimensional stability with high resistance to decay by fungi and microorganisms.

In the present work, wood specimens were impregnated with a combination of ST/MMA/nanoclay to produce wood polymer composites (WPCs). Mechanical, thermal, and morphological properties were investigated.

MATERIALS AND METHODS

Materials

The wood specimen dimensions were 6 cm x 2 cm x 2 cm. The chemicals used to produce WPCs were styrene (ST), methyl methacrylate (MMA), and benzoyl peroxide and were supplied by Merck, Germany. Nanoclay, Nanomer 1.31PS was supplied by Sigma-Aldrich. Catalogue number of the clay was 682632-500G. It was montmorillonite clay surface modified with 15-35 wt.% octadecylamine and 0.5-5 wt.% aminopropyltriethoxysilane. The bulk density of the clay was 200 to 500 kg/m^3 and average particle size was around 20 microns.

Monomer Preparation

The monomer system was prepared using ST/MMA/nanoclay in the presence of benzoyl peroxide. Benzoyl peroxide acts as an initiator to influence the reaction between styrene and methyl-methacrylate. Two grams of benzoyl peroxide and 5 g of nanoclay were added into each monomer system. The mixtures were covered with aluminum foil and put in an autoclave for 15 min to complete the reaction. Styrene, methyl-methacrylate, and the nanoclay monomer system were mixed with different ratios as shown in Table 1.

Table 1. Preparation of Monomer System at Different Ratio

Volume of Styrene (mL)	Volume of Methyl-methacrylate (mL)	Amount of Nanoclay (g)
20	80	5
30	70	5
40	60	5
50	50	5

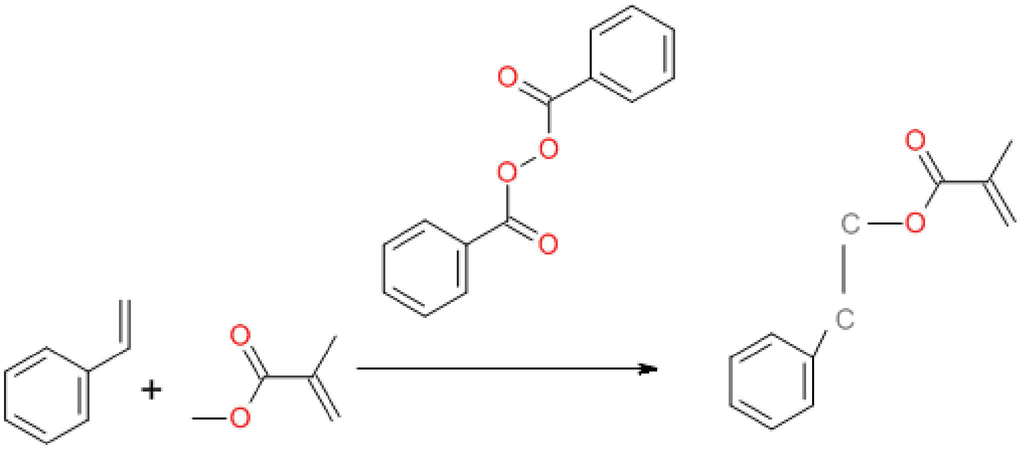

Fig. 1(a). The reaction scheme for synthesis of ST/MMA/nanoclay cross-Linker

Impregnation of Wood Specimens/Co-Polymerization Reaction with Cellulose in Wood Cell

Wood specimens were prepared according to ASTM D1037 and weighed using an electronic balance. The specimens were immersed into different monomer systems and were subjected to a vacuum process for 1 h. After 1 h, the samples were taken out, covered with aluminum foil, and put in an oven for 48 h at 70 ˚C to polymerize and produce wood polymer composites (WPCs). After 48 h, the WPCs were taken out of the oven and the unreacted chemicals were removed.

The weight percent gain (WPG) of the samples was then measured using Eq. 1,

$$\mathrm{WPG} = \frac{m_{\mathrm{treated}} - m_{\mathrm{untreated}}}{m_{\mathrm{untreated}}} \times 100\% \qquad (1)$$

where m_{treated} and $m_{\mathrm{untreated}}$ are the over-dried weight of the untreated and treated wood samples, respectively.

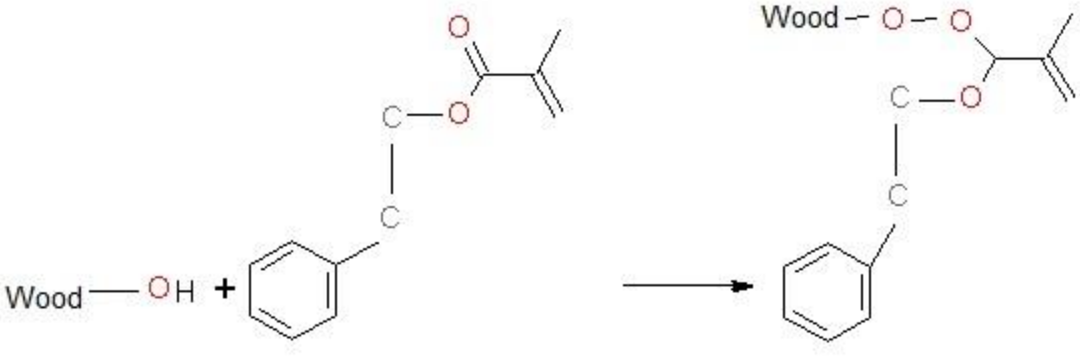

Fig. 1(b). Coupling reaction of wood with ST/MMA/Nanoclay

Microstructural Analysis

Fourier Transform Infrared Spectroscopy (FT-IR)

The infrared spectra of the raw wood and WPCs were recorded on a Shimadzu IRAffinity-1. The transmittance range of the scan was 700 to 4000 cm^{-1}.

Compression test

In order to carry out the mechanical tests, the test samples prepared were of 6 cm x 2 cm x 2 cm dimensions. Before the mechanical tests, the prepared samples were stored at a temperature of 85 ˚C inside a cool incubator for 4 days. The mechanical properties of the samples, including modulus of rupture (MOR) and modulus of elasticity (MOE), were tested using a compression machine branded Shimadzu according to ASTM D-143 (1996).

A Shimadzu Universal Testing Machine having a loading capacity of 300 kN was used for the test with a cross head speed of 10 mm/min. The MOE and MOR were measured using the compression test and were calculated using the following equations, respectively:

$$\text{MOE} = \frac{L^3 m}{4bd^2} \tag{2}$$

$$\text{MOR} = \frac{1.5PL}{bh^2} \tag{3}$$

Thermogravimetric analysis (TGA)

The TGA testing was started by weighing a finely ground sample and exposing it to a heated chamber in the presence of oxygen. The sample was suspended on a sensitive balance that measured the weight loss of the sample as the system was heated. The change in weight of the sample was recorded as a function of time at constant temperature ranging from 20 ˚C to 700 ˚C set in an isothermal TGA. After setting up, the rate of weight loss as a function of time and temperature could be measured with the use of a derivative computer.

After the data was obtained, curve smoothing and other operations were done to find the exact points of inflection. With this method, temperature increased slowly as weight loss increased.

Scanning Electron Microscopy (SEM)

The wood specimens were first fixed with Karnovsky’s fixative. The interfacial bonding between the cell wall and monomer was examined using a scanning electron microscope (SEM) (JSM-6710F) supplied by JEOL Company Limited, Japan. The specimens were first fixed with Karnovsky’s fixative and then taken through a graded alcohol dehydration series.

Once dehydrated, the specimen was coated with a thin layer of gold before being viewed microscopically. The micrographs were taken at a magnification of 250x and 1500x.

RESULTS AND DISCUSSIONS

Weight Percent Gain (WPG %)

The values of WPG for both raw wood and WPCs were measured before and after treatment, as given in Table 2. Results indicate that WPG significantly increased due to the ratios of the ST/MMA. This was expected because the monomer system reacted with OH groups of cellulose in the wood's cell wall and removed all of the impurities from the wood fiber surfaces, thus increasing the adhesion between wood fibers and polymer, resulting in a higher WPG.

According to the findings, the 50:50 ST/MMA/clay system had the highest WPG when compared with the other monomer systems.

Table 2. Average Weight Percent Gain, WPG (%)

ST/MMA/Clay	Average weight for Raw (g)	Average weight for WPCs (g)	Weight Percent Gain (WPG %)
20:80	9.399	11.301	20.24
30:70	8.149	10.928	34.10
40:60	7.805	11.860	51.95
50:50	7.378	11.858	60.72

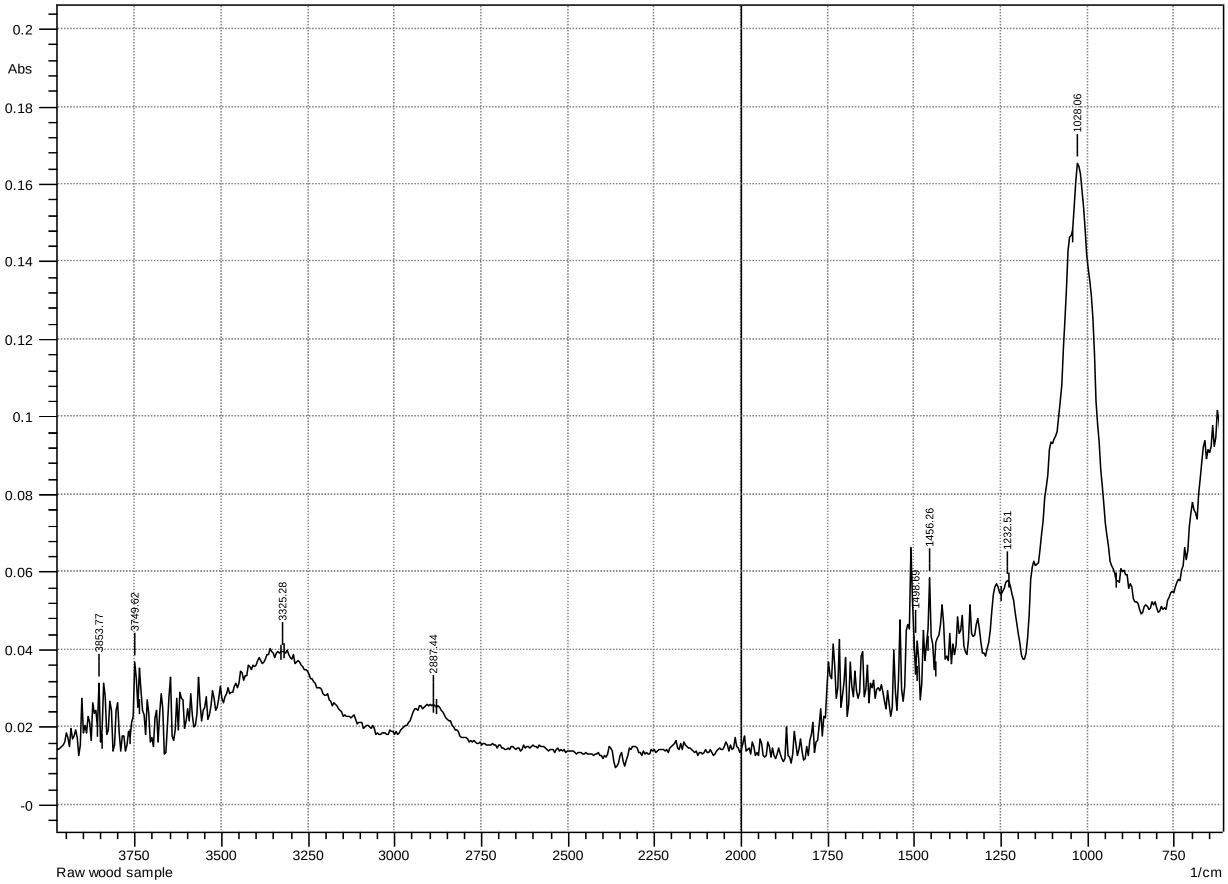

Fig. 2 (a). FT-IR Spectra of raw wood specimens

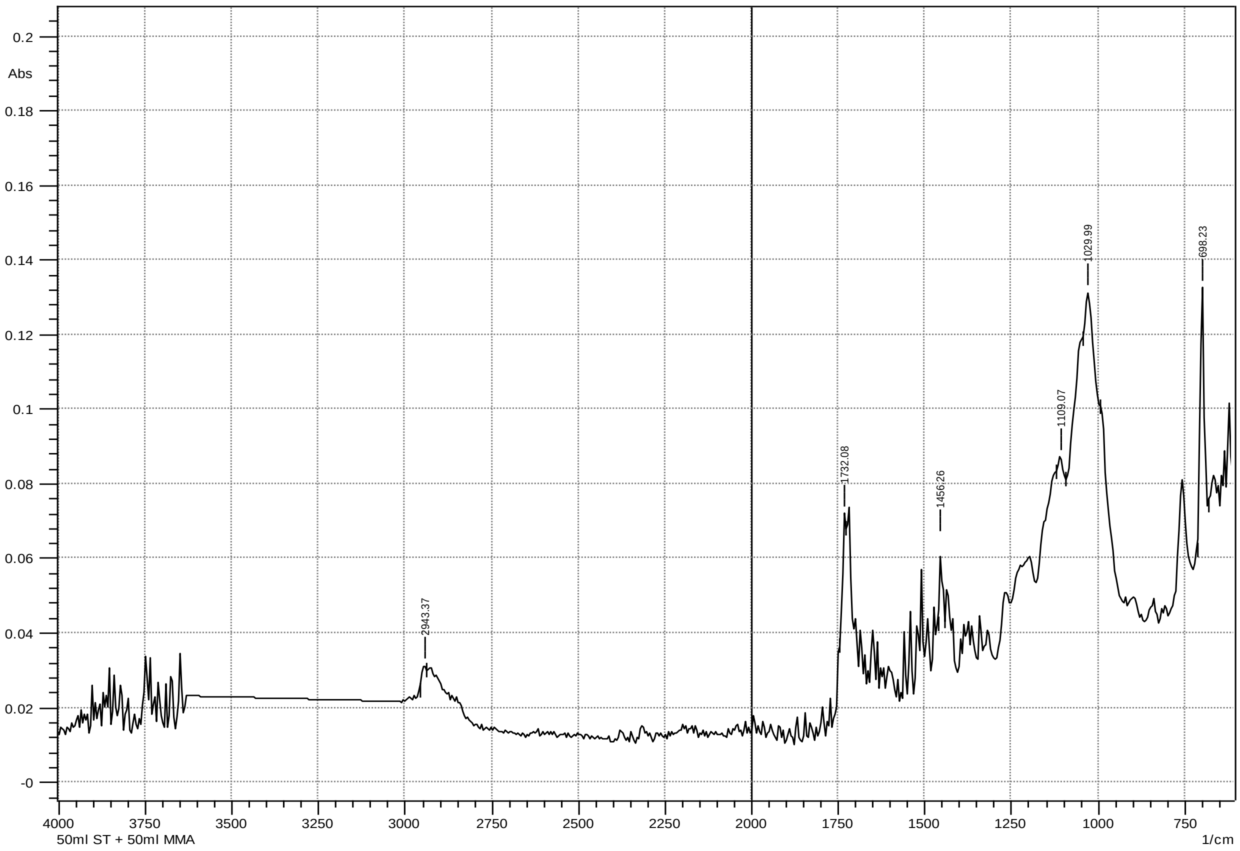

Fig. 2 (b). FT-IR Spectra of WPCs

Fourier Transform Infrared Spectroscopy (FT-IR)

Figures 2 (a) and (b) show the FT-IR spectra for both the raw wood and WPCs. The FT-IR results indicated that ST/MMA/clay not only impregnated the wood specimens but also reacted with hydroxyl groups of the cellulose in the wood's cell wall and produced a co-polymerized wood-ST/MMA/Clay product. This was confirmed by the FT-IR spectroscopic analysis.

It was found that there was a significant difference in absorption bands. This is due to the differences in structural and chemical composition within the raw wood and treated wood specimens (Islam *et al.* 2011a,b). The FT-IR spectrum of the raw wood specimens clearly show absorption bands in the region of 3325 cm^{-1}, 1028 cm^{-1}, and 1730 cm^{-1} due to O-H stretching vibration, C-H stretching vibration, and C=O stretching vibration, respectively.

For WPCs, the FT-IR spectrum clearly show that there were no absorption bands due to O-H stretching vibration, 1109 cm^{-1} due to C-H stretching vibration, and 1732 cm^{-1} due to C=O stretching vibration, respectively. This indicated that after ST/MMA/clay interacted with the wood, the OH groups in the wood specimens were reduced (Islam *et al.* 2012).

Mechanical Properties

Effects on MOE and MOR of the polymerized wood specimens and raw wood specimens are shown in Figs. 3(a) and (b), respectively. The ST/MMA/clay impregnation on the batai wood was investigated. The increment in MOR for WPCs was significantly higher than that of raw wood. From Fig. 3, it can be seen that the higher the polymer loading, the better the elasticity of the wood specimens. Polymer-filled wood yielded higher MOE compared to raw wood because of the co-polymerization of the wood's cell wall, which was in accordance with other research (Hamdan *et al*. 2010a, b; Yildiz *et al*. 2005; Adams *et al*. 1970). During impregnation, wood specimens coupled with monomers and filled the void spaces, which led to the increase in stiffness. The increments of MOE and MOR for 50:50 ST/MMA/Clay systems were higher than that of others.

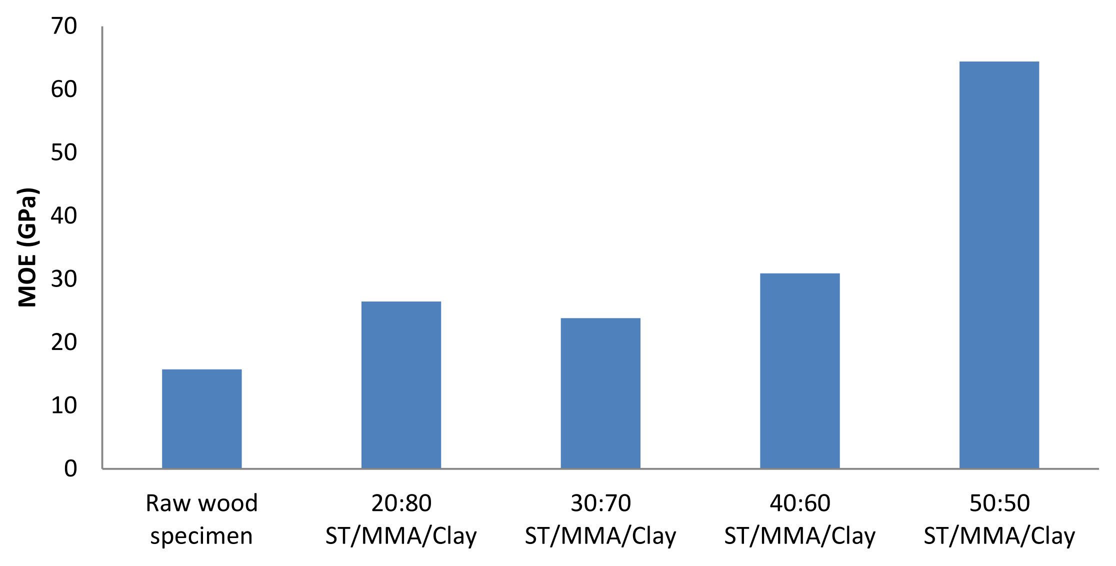

Fig. 3 (a). MOE of raw wood and WPCs

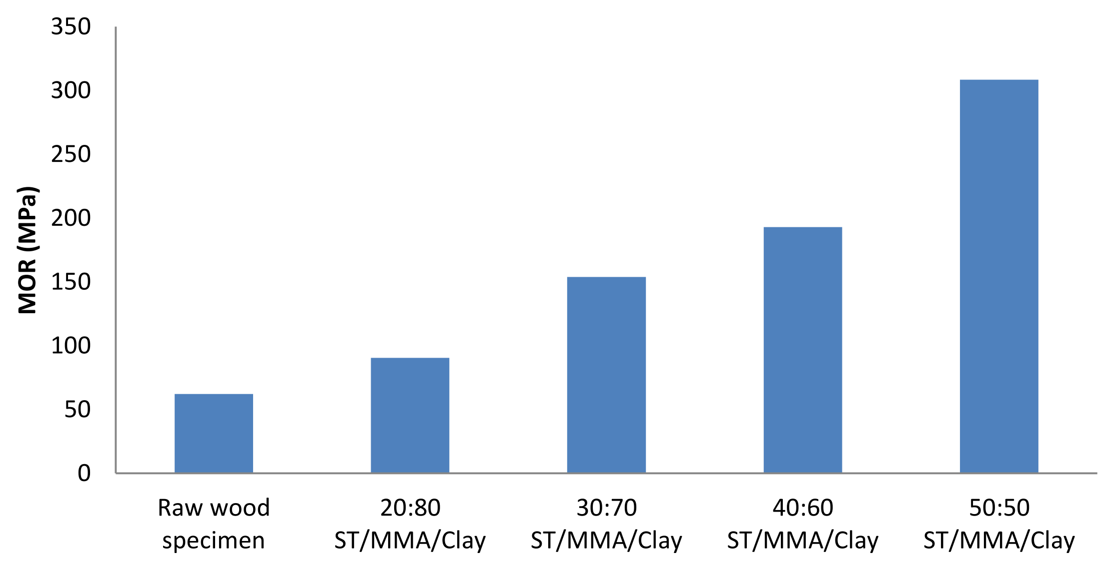

Fig. 3 (b). MOR of raw wood and WPCs

Thermogravimetric Analysis (TGA)

Thermal stability of wood is a very important parameter in the production of wood polymer composites. Figure 4 represents the TGA curves of raw wood and WPCs. According to Wielage *et al.* (1999), there is no degradation up to 160 ˚C. Thermal stability gradually decreases and decomposition takes place after 160 ˚C. As shown in Fig. 4, the weight loss of raw wood started at 248.08 ˚C and ended at 379.89 ˚C, while for WPCs, the weight loss range was between 274.45 ˚C and 431.6 ˚C. For the raw wood specimens, both the starting and ending temperature of degradation was lower compared to WPCs. Due to monomer impregnation, the residue of WPCs ended the degradation at a higher temperature compared to that of raw wood because monomer with clay impregnation of wood involves bond formation between the reagents and polymeric constituents of wood cell wall.

Modification with both thermosetting resin as well as thermoplastic brings out significant changes in the chemical, physical, thermal, and mechanical properties of the wood to a great extent. However, the synthesized combined monomer system significantly improved the thermal properties as well as the mechanical properties, which were reflected in the MOE and MOR results. The results show that the thermal stability of WPCs was higher than that of the raw wood due to the coupling reaction with cellulose and new chemical bonding between styrene and methyl methacrylate with the aid of benzoyl peroxide and nanoclay. This new bonding allows the thermal energy to be distributed over many bonds (Ramiah 1976; Wielage *et al.* 1999). In this monomer system, the layered silicate nanoclays act as *in situ* reinforcement, which enhances the thermal and mechanical properties (Tohmura *et al*. 2001). Overall, the 50:50 ST/MMA/clay monomer systems showed better thermal stability among the impregnated wood specimens when compared to the others.

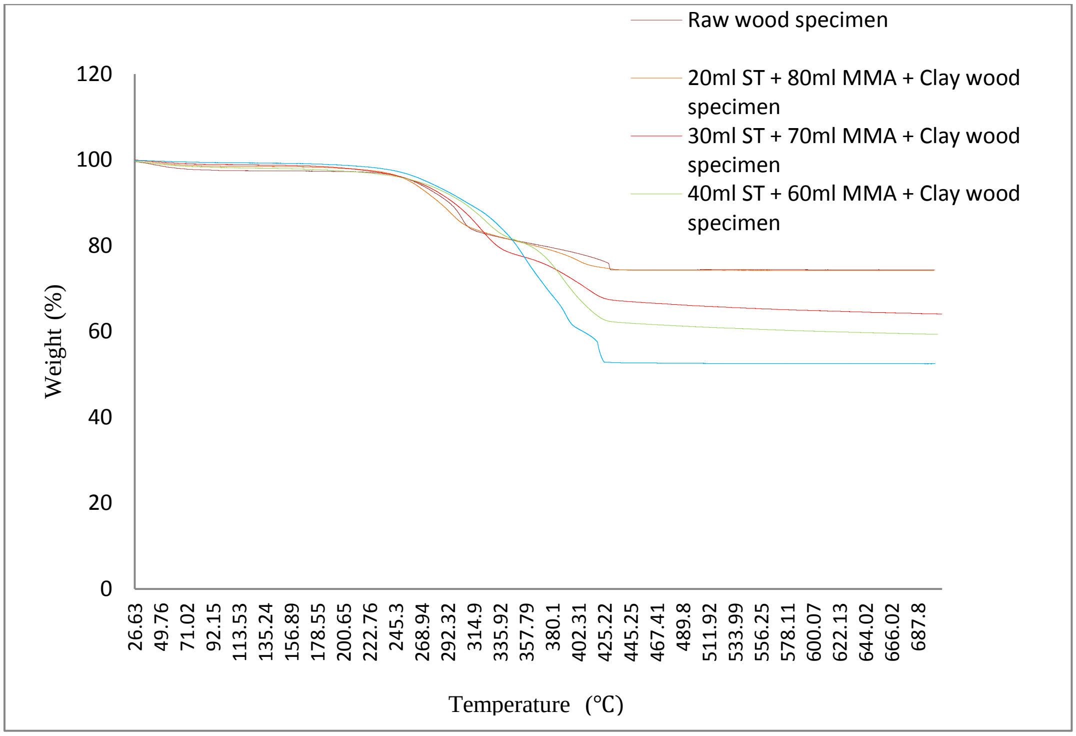

Fig. 4. TGA curves of raw wood and WPCs

Scanning Electron Microscopy (SEM)

Morphology of the fracture surface shows phase information reflecting reasons why the mechanical properties of the composites fabricated under different conditions are different. The SEM images of the raw wood and WPCs are shown in Figs. 5 (a-b).

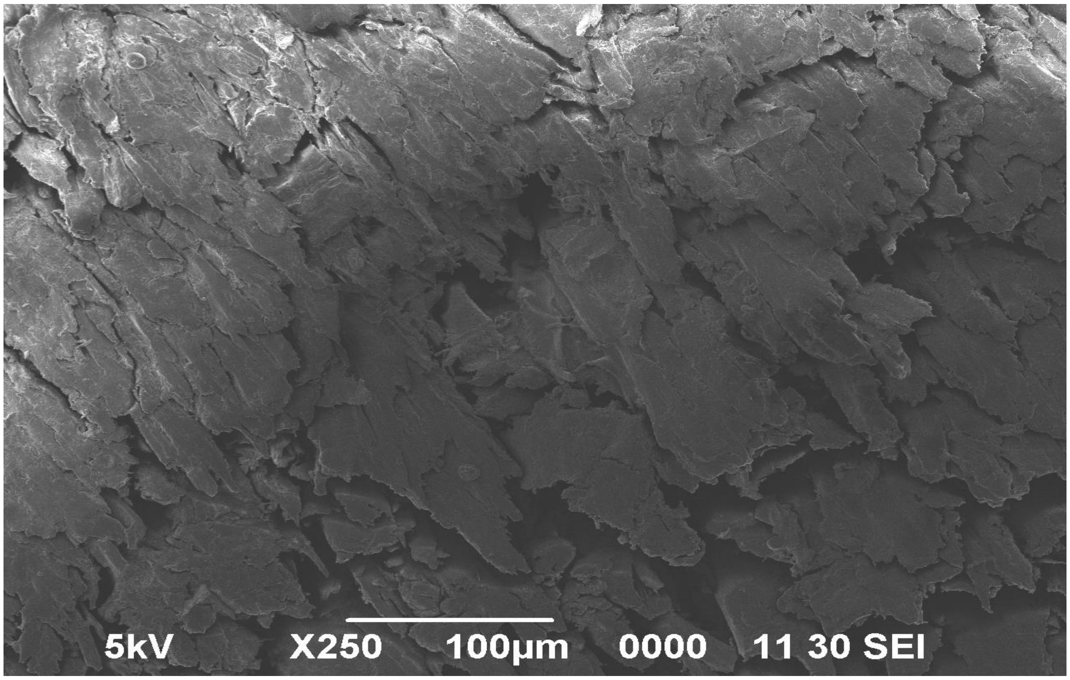

Fig. 5 (a). SEM for raw wood specimens

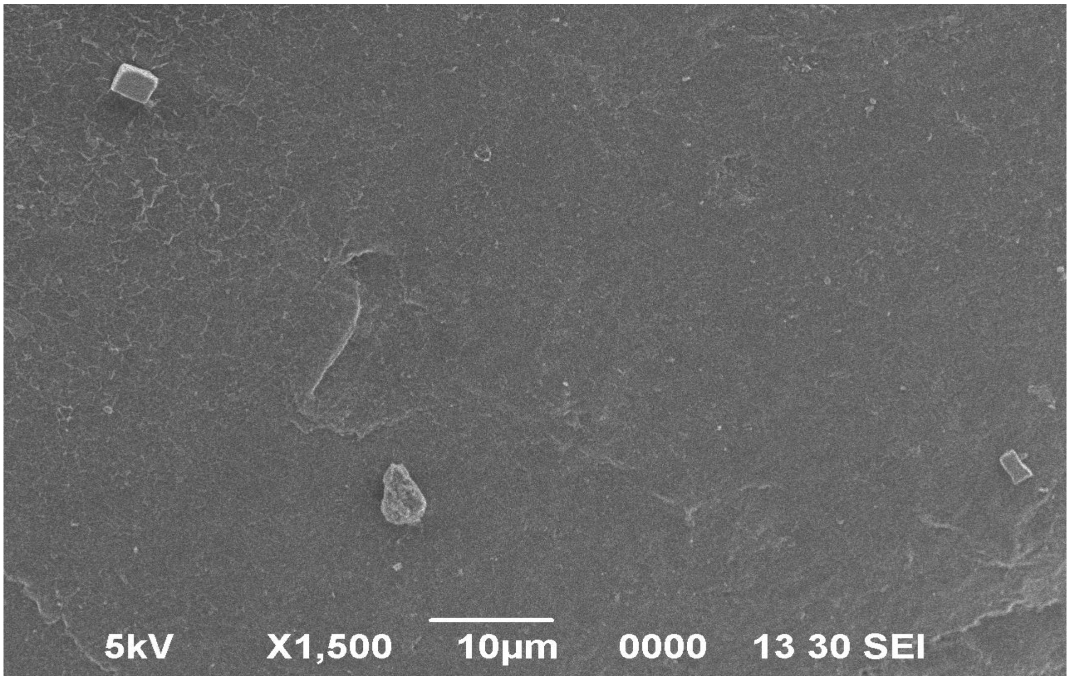

Fig. 5 (b). SEM for WPCs

Figure 5 (a) shows that there was no interfacial bonding between the filler and the matrix because there was no monomer impregnation. On the other hand, WPCs showed better interfacial adhesion between the filler and the matrix because of ST/MMA/clay crosslinking with the wood cell wall (Rahman *et al.* 2010a, b). The outcome of the better interfacial bonding between the filler and the matrix is reflected in the improvement of the mechanical properties of the WPCs (Islam *et al.* 2010). The result indicates that crosslinking filled the void spaces in wood cell walls and removed the waxy substances.

CONCLUSION

In this study, raw wood specimens were impregnated with ST/MMA/nanoclay to produce WPCs. In order to improve the mechanical, thermal, and morphological properties, wood specimens were polymerized with ST/MMA/clay to reduce the number of hydroxyl groups in the wood. The weight percent gain (WPG) for WPCs in 50:50 ST/MMA/clay systems was highest compared with other monomer systems. The FT-IR analysis confirm the coupling reaction with cellulose in wood in characteristic peaks at about 1109 cm^{-1} due to C-H stretching vibration and 1732 cm^{-1} due to C=O stretching vibration, respectively. Both MOE and MOR for WPCs were higher than the raw wood. Thermogravimetric analysis (TGA) revealed that decomposition temperature and exotherm peaks increased after impregnation. Scanning electron microscopy (SEM) of WPCs showed a smoother surface texture than the raw wood.

ACKNOWLEDGEMENT

The authors would like to acknowledge the Faculty of Engineering, University Malaysia Sarawak for their financial support, Grant no. FPI(F02)/134/2013(03).

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Article submitted: March 22, 2013; Peer review completed: May 27, 2013; Revised version received and accepted: June 25, 2013: Published: July 2, 2013.