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Study on Thermal and Biodegradation Resistance of Tropical Wood Material Composites

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ABSTRACT: Thermal stability and decay resistance properties of tropical wood polymer composites (WPCs) were investigated in this study. WPCs were prepared from several selected tropical wood species by impregnating the woods with methyl methacrylate (MMA) which was combined with a crosslinker, hexamethylene diisocyanate (HMDIC). The impregnation of wood with the monomer systems and polymerization were accomplished by vacuum-pressure method. Thermal properties of manufactured WPC in terms of thermogravimetric analysis and differential scanning calorimetry were evaluated, and an improvement in thermal stability was found for fabricated WPC. The wood was then exposed to two types of fungi; white-rot (*polyporous versicolor*) and brown-rot (*postia placenta*), for 12 weeks. Decay was assessed through percentage (%) of weight loss. A significant improvement was found in the treated woods compared to the untreated ones. The improvement in properties was observed as more potential with the MMA/HMDIC combination. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Wood is a renewable resource and one of the most enthralling materials because of its complex structure, physical resilience physical strength, aesthetically pleasant characteristics, and superior material properties. However, structural wood has a few drawbacks which limit its use, including dimensional instability caused by changing moisture content, biodegradation, and thermomechanical property changes with environmental variations.[1–3] These defects are due to the presence of numerous hydroxyl groups (—OH) in the three major wood components (cellulose, hemicellulose, and lignin) and their various cavities. The —OH groups in wood attract water molecule through hydrogen bonding, thus making it dimensionally unstable, which in turn promotes physical, mechanical, and chemical properties changes. Modification of cell wall polymer through suitable chemical treatment is a promising method to improve wood properties. More precisely, modification using suitable chemical treatments such as the formation of wood polymer composites (WPCs) has shown some potential in improving wood properties.[4–6] Impregnating wood with polymerizable monomer formulation and then polymerizing it in place produces a WPC. WPC is produced by impregnating wood with polymerizable monomer formulation before polymerizing it in place. WPC is more convenient as a product material compared to plain wood as it is less susceptible to moisture-induced swelling, shrinking, and thermal degradation. Consequently, it has a longer life-span. Moreover, the WPC exhibited enhanced physical and mechanical strengths.

Of late, interest has been manifested in wood impregnation with a variety of monomers such as styrene, epoxy resins, urethane, phenol formaldehyde, methyl methacrylate (MMA), vinyl, and acrylic monomer to improve the negative properties in wood.[7,8] WPC created with combinations of monomers such as hexadiol, diacrylate, hydroxyethyl methacrylate, glycidyl methacrylate, and anhydride has been shown to improve dimensional and thermal stability.[9] However, it has also been established that most monomers do not form bonds with hydroxyl groups of cell wall polymer. As most monomers are nonpolar, there is little interaction between the monomer and the hydroxyl groups in the wood component. Poor chemical and

physical interfacial interactions between the wood surface and chemical are two of the most important causes of bond failure. Consequently, the polymer component in the WPC simply bulks the wood structure by filling the capillaries, vessels, and other void spaces within the wood. It can therefore be deduced that if there is a bond between the impregnated monomers and the hydroxyl groups of wood, the physical and mechanical properties of WPC may be improved further. It has been noted that adhesion, interaction, and compatibility between wood component and polymer can be enhanced by using varieties of chemicals and crosslinker monomers such as alcoxysalin coupling agents, diazonium salt, sodium perchlorate, Glycidyl Methacrylate, trimethylol propanetriacrylate, trivinylisocyanurate, ethylene glycol dimethacrylate, etc.[10,11] The crosslinking of material in wood samples provides better physical and mechanical strengths in WPC.[9] The properties of a wood composite are significantly improved by the addition of an isocyanate compound to the vinyl or acrylic monomer treating mixture.

The isocyanate compounds are most often used as an adhesive for wood bonding because of their reactivity with groups that contain reactive hydrogen, such as amine and alcohol groups, at room temperature. Wood modification with MMA and hexamethylene diisocyanate (HMDIC) as the crosslinker monomer has shown improvements in physical and mechanical properties.[12,13] HMDIC is a class of polymeric compound which has significant reaction ability with wood −OH groups and crosslinking to other monomer. HMDIC modification of wood relies on modifying the predominant wood cell wall polymer by reacting wood hydroxyl groups with a diisocyanate group to form a wood–urethane derivatives.[14] The formation of wood–urethane compounds is more potential for bonding green solid wood. Nevertheless, the isocyanate group of HMDIC can be exploited for reaction with −OH groups in wood component and for copolymerization with vinyl or acrylic type monomers. This reaction can also create new structures in the WPC which can influence morphology, crystallization, mechanical, thermal, biological, and other properties of wood. A number of studies have been carried out on thermal stability and decay resistance properties of various wood and their composites.[15,16] Little research work, however, have been made in this regard.

Motivated by our earlier study,[12,13] the current investigation was carried out to determine the thermal and decay resistance properties of MMA/HMDIC treated WPC. Five species of selected tropical light hardwood species, namely jelutong, terbulan, batai, rubberwood, and pulai were used as starting materials as they are abundantly available in the tropical region. The major drawbacks of using these species are their high moisture uptake, thermal instability, and high probability of deterioration by biological organisms. These effects are especially pronounced in tropical areas where wood suffers from exposure to sunlight and high hygroscopicity which cause swelling and deformation. To overcome these problems and to improve the interaction and compatibility of polymer to the cell wall component of wood, the wood samples were impregnated with MMA and combined with the crosslinker monomer HMDIC. This study examines the thermal and biodegradation to decay resistance properties of WPCs impregnated with MMA and MMA/HMDIC combination.

EXPERIMENTAL

Wood Materials

In this study, five types of selected tropical light hardwood species–Jelutong (*Dyera costulata)*, Terbulan *(Endospermum diadenum*), Batai (*Paraserianthes moluccana)*, Rubberwood (*Hevea brasiliensis)*, and Pulai (*Alstonia pneumatophora*) were collected from a local forest in Sarawak, Malaysia. The specific gravity of jelutong, terbulan, batai, rubberwood, and pulai were 0.46, 0.48, 0.38, 0.60, and 0.45, respectively. All the wood species were felled and cut into three bolts measuring 1.2 m in length. Each bolt was quarter-sawn to produce planks of 4 cm thickness. The bolts were subsequently conditioned to air-dry in a room with relative humidity of 60% and ambient temperature of around 25°C for 6 month before testing.

Monomer Solutions

Each specimen was impregnated with MMA and MMA/HMDIC(1 : 1 ratio) for the production of WPCs. The mixture contained 2% benzyl peroxide catalyst as a polymerization initiator. Immersion mixture volume was −1000 mL monomer mixture solution/10 wood specimen. Methyl Methacrylate and Hexamethylene Diisocaynate, was used to possess densities of 0.942–0.944 g/mm^3 and 1.046–1.047 g/mm,^{3} respectively. All chemicals were analytical grade products of Merck, Germany.

Specimen Preparation

Clear, defect-free planks were ripped and machined to a measurement of 20 mm (L) × 20 mm (T) × 20 mm (R) for decay resistance test and grounded powder samples for thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests, respectively.

Manufacturing of WPC

For WPC manufacturing, oven-dried raw wood specimens were placed in an impregnation vacuum chamber at a vacuum pressure of 10 kPa for 30 min. The respective monomer system and the 2% benzyl peroxide acting as a polymerization initiator were introduced into the chamber as the vacuum pressure was released. The specimens were kept immersed in the monomer mixture solution for 6 h at ambient temperature and pressure to obtain further impregnation. These were then removed from the chamber and wiped of excess impregnate. Specimens were wrapped with aluminum foil and placed in an oven for 24 h at 105°C for polymerization to take place. Weight percentage gain (WPG) of the samples was then measured using eq. (1);

$$\text{WPG } (\%) = \left(W_i - W_f\right)/W_i \times 100 \qquad (1)$$

where W_i and W_f are oven-dried weight of raw wood and fabricated WPC samples, respectively.

Thermal Analysis

Preparation of Samples. Treated and untreated wood samples were grounded to finer mesh and passed through a 250 Micron Sieve for controlling mesh size at 60. Then this powder samples (mesh size 60) were used for TGA and DSC test.

Thermogravimetric Analysis. TGA measurements were carried out on 5–10 mg of WPC and raw wood at a heating rate of 10°C/min in a nitrogen atmosphere using a Thermogravimetric

Analyzer (TA Instrument SDT Q600). WPC and raw wood were subjected to TGA in high purity nitrogen under a constant flow rate of 5 mL/min. Thermal decomposition of each sample occurred in a programmed temperature range of 30–800°C. The continuous weight loss and temperature were recorded and analyzed to determine the following TGA parameters: thermal degradation rate (% weight loss/min), initial degradation temperature, and residual weight (RW) at 800°C.

Differential Scanning Calorimetry. The WPC samples and the raw wood samples were analyzed using a Perkin Elmer thermal analyzer. All measurements were made under a nitrogen flow (30 mL/min), keeping a constant heating rate of 10°C/min and using an alumina crucible with a pinhole.

Decay Resistance Test

The decay resistance test was carried out using the Standard Method of Accelerated Laboratory test of natural decay resistance of wood ASTM D2017 (2001).[17] The specimens were first air-dried before conditioned to constant weight. They were then weighed accurately in the laboratory and transferred into a large, totally dark container which was maintained at 20 ± 1°C and a relative humidity of 65 ± 4%. Two types of fungus, white-rot (*polyporous versicolor* L.ex. Fr.) ATCC No. 12679 and brown-rot (*postia placenta)* (Fr). Cke. ATCC No. 11538, were used to test the resistance of WPC against decay. Reference blocks were made of sweet gum. There were eight replications for each specimen. The decay test was terminated after 12 weeks when the reference blocks obtained a weight loss of 60%. Mycelium was brushed off and test specimens were air-dried before once again conditioned to constant weight. The weight was recorded for each specimen. Weight loss was determined for individual samples using eq. (2).

$$\%\,\text{Weightloss} = \left[\left(W_0 - W_f\right)/W_0\right] \times 100 \qquad (2)$$

where W_0 is oven-dried weight of samples before exposure, and W_f is the oven-dried samples after exposure to fungus.

RESULTS AND DISCUSSION

Weight Percentage Gain

The values of WPGs for jelutong, terbulan, batai, rubberwood, and pulai after the impregnation with MMA were 14, 9, 17, 7, and 11, whereas with MMA/HMDIC, the gains were 50, 35, 55, 18, and 47, respectively. This result reveals that MMA and MMA/HMDIC were successfully incorporated in all wood species and that MMA/HMDIC monomer system exhibited higher percentage gain compared to MMA in all selected tropical wood species.

Thermal Analysis

Thermogravimetric Analysis. Figure 1(a,b) demonstrates the typical TGA and DTG thermograms of raw wood and WPC samples. Important data calculated from TGA thermograms and are tabulated briefly in Table I. It can be seen from Figure 1 and Table I, the initial decomposition temperature (T_i) for the typical thermal properties of wood, in which pyrolysis of wood components took place below 250°C. The previous researcher observed that pyrolysis of hemicellouse, lignin, and cellulose

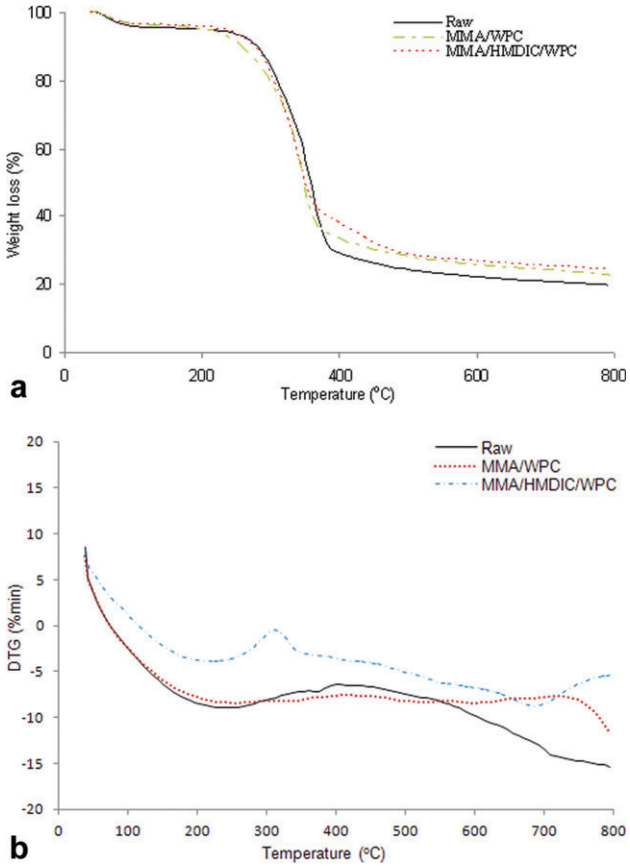

Figure 1. (a) Typical TGA curves of raw wood and MMA and MMA/HMDIC-treated WPC samples. (b) Typical DTG curves of raw wood and MMA and MMA/HMDIC-treated WPC samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

usually occur at 200, 220, and 250°C, respectively.[18,19] In contrast, the initial decomposition temperature (T_i) and the maximum pyrolysis temperature (T_f) values for MMA/HMDIC impregnated WPC samples were appreciably higher than MMA impregnated and raw samples. Furthermore, the RW at 800°C of MMA/HMDIC impregnated WPC samples displayed significant increase compared to the MMA impregnated and raw samples. The result indicates that a WPC sample impregnated with MMA/HMDIC was more thermally resistance than an MMA impregnated and a raw sample. Similar results have also been accounted by other researchers.[20,21] These results are expected and may be due to the strong interactions between HMDIC, wood and MMA, and the formation of wood composites. Microstructural studies by the FTIR and SEM analysis in our earlier study showed that the HMDIC as a crosslinker reacted with cell wall hydroxyl groups of wood and formed wood-O—C(=O)—NH—R compound, which in turn created a rigid linking bridge with wood fiber and MMA, thus enhancing the thermal stability.[12]

As seen in Table I, the maximum rate of mass loss (T_m) values of MMA/HMDIC impregnated WPC samples were lower than raw and MMA impregnated samples. It can also be observed that the TGA therograms of MMA/HMDIC/WPC samples

Table I. TGA Results of Raw Wood, MMA, and MMA/HMDIC-Treated WPC Samples

Wood species and sample particulars		[a]T_i(°C)	[b]T_m(°C)	[c]T_f(°C)	[d]T_{ii}(°C)	RW (%), at 800°C
Jelutong	Raw	242.71	375.78	391.60	-	19.10
	MMA/WPC	273.55	336.05	359.61	-	26.16
	MMA/HMDIC/WPC	281.36	332.12	468.75	359.61	28.93
Terbulan	Raw	242.19	359.50	383.16	-	21.12
	MMA/WPC	265.93	344.14	351.99	-	26.51
	MMA/HMDIC/WPC	273.49	336.12	484.62	367.30	30.11
Batai	Raw	242.24	367.00	390.68	-	18.90
	MMA/WPC	258.54	351.76	375.30	-	22.18
	MMA/HMDIC/WPC	265.95	336.19	476.56	359.57	25.86
Rubberwood	Raw	250.00	359.38	390.82	-	19.80
	MMA/WPC	234.80	352.05	375.02	-	22.75
	MMA/HMDIC/WPC	281.71	344.35	484.38	367.74	25.20
Pulai	Raw	242.34	351.73	381.11	-	23.29
	MMA/WPC	242.60	336.30	367.62	-	24.11
	MMA/HMDIC/WPC	258.20	320.73	484.32	367.62	27.90

[a]T_i values for initial decomposition temperature.
[b]T_m values for the maximum rate of mass loss.
[c]T_f values for the maximum decomposition temperature.
[d]T_{ii} values for the second step decomposition temperature.
RW values for residual weight.

exhibited three-step decomposition, whereas the raw and MMA/WPC samples showed two-step decomposition following the temperature range. The explanations may be due to the elimination of small molecules from the wood component and the formation of crosslinking, which acted as an infusible support and provided thermal resistance to the wood composites. It is believed that, the main source of this resistance is the elemental orientations, crosslinking, and a new chemical bonding which allow thermal energy to be distributed over many chemical bonds.[22] All these, as stated above, confirmed HMDIC crosslinker significantly increased the thermal resistance of WPC.

Differential Scanning Calorimetry. The DSC thermograms of raw and WPC samples are shown in Figure 2, while crystallization enthalpy ($-\Delta H$) and exotherm peaks are tabulated in Table II. From Figure 2, a broad endotherm peak was observed in the temperature range of approximately 50–150°C for raw samples, which indicated a high amount of water molecules in the wood fibers. On the contrary, significant reduction on endotherm peak was observed in both treated WPC samples, indicating a smaller amount of water molecules in the samples. A similar result was obtained in our previous study by the moisture content and water absorption measurements.[23,13] More often than not, decomposition for wood fiber begins at approximately 200 to 360°C.[24] As can be seen from the figure, untreated wood showed a single endothermic peak at 260°C due to thermal decomposition of wood fibers. Wood treated with MMA also showed one endothermic peak at around 228°C. On the other hand, MMA/HMDIC impregnated WPC samples exhibited two endothermic peaks at 228 and 275°C. The double endothermic peaks obtained in DSC thermograms were due to the thermal decomposition of wood fibers and filled polymer in the wood.[25] This observation can be explained on the basis of prominent changes occurring in the structure and morphology of wood components due to MMA/HMDIC combined treatment.[12]

It can be established from Table II that the first decomposition temperature of all treated wood samples showed a lower value than the raw wood samples. In addition, WPC samples treated with MMA/HMDIC exhibited a second exotherm peak in the temperature range of 249–257°C, whereas no second exotherm peak was observed in untreated and MMA impregnated samples. According to the exotherm, the WPC sample infused with MMA/HMDIC was more thermally stable than untreated and MMA impregnated samples.[26] Similar observation for thermal stability was reported by Hamdan and his coauthors for

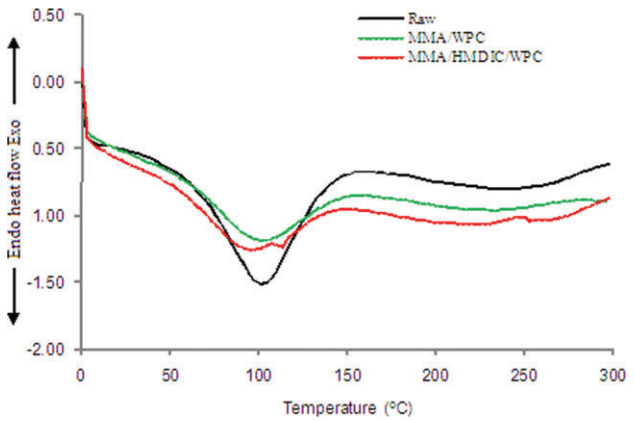

Figure 2. Typical DSC thermograms of raw wood, MMA, and MMA/HMDIC-treated WPC samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Crystalline Enthalpy and Exotherm Peaks of Raw Wood, MMA, and MMA/HMDIC-treated WPC Samples

Wood species	Sample particulars	First exotherm peaks (°C)	Second exotherm peaks (°C)	Crystalline enthalpy, $-\Delta H$ (J/gm)
Jelutong	Raw	158.06	-	287.24
	MMA/WPC	154.90	-	288.12
	MMA/HMDIC/WPC	142.21	249.77	290.04
Terbulan	Raw	161.16	-	270.24
	MMA/WPC	151.73	-	272.11
	MMA/HMDIC/WPC	148.57	252.96	275.30
Batai	Raw	148.54	-	204.10
	MMA/WPC	145.41	-	206.39
	MMA/HMDIC/WPC	145.37	259.28	209.43
Rubberwood	Raw	158.05	-	207.42
	MMA/WPC	154.89	-	209.82
	MMA-HMDIC/WPC	154.83	256.92	210.30
Pulai	Raw	151.75	-	260.35
	MMA/WPC	151.75	-	262.11
	MMA/HMDIC/WPC	135.92	256.11	265.23

N, *N*-Dimethylacetamid treated WPC.[27] It can also be ascertained that the crystallization enthalpy ($-\Delta H$) of MMA/HMDIC impregnated samples were higher compared to untreated and MMA impregnated samples. From the earlier report on XRD analysis by our preceding investigation, it is clear that the crystallinity of MMA/HMDIC/WPC samples increases significantly than raw and MMA-treated samples.[12] This result provides further evidence of the improvement of thermal stability on combined MMA/HMDIC treatment. The main reason of the increment of $-\Delta H$ values for MMA/HMDIC-treated samples can be attributed as was before to the presence of HMDIC crosslinker which penetrated into the wood cells and provided better interaction between the MMA and the wood. As the interaction between wood fibers and polymer in wood interfered with crystallization, it is assumed that the increase of $-\Delta H$ was closely related to the increase of crystal size of the wood fiber itself.

Decay Resistance Test

To determine resistance to biodegradation of the wood samples, fungi decay resistance test was performed. Weight loss due to white-rot (*polyporous versicolor*) and brown-rot (*postia placenta*) fungi attacks on untreated wood and treated WPC samples is shown in Figures 3 and 4. The results showed that the raw wood was severely attacked by both decay fungi with large weight loss. Meanwhile, WPC samples impregnated with MMA and MMA/HMDIC showed considerable resistance toward both

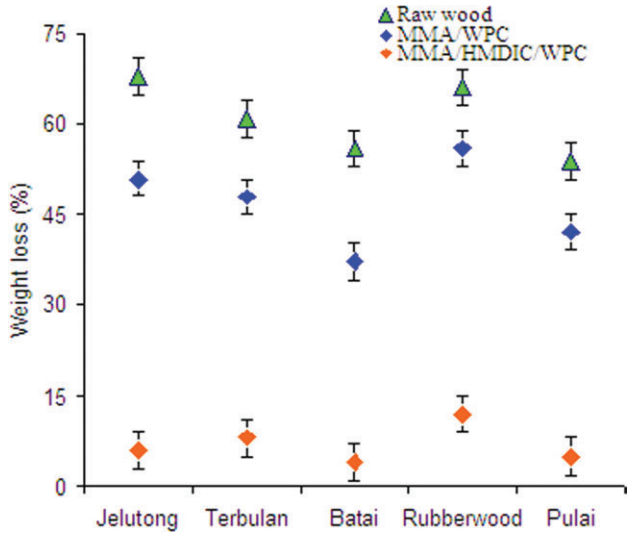

Figure 3. Weight loss of raw wood, MMA, and MMA/HMDIC-treated WPC samples due to white rot fungi exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

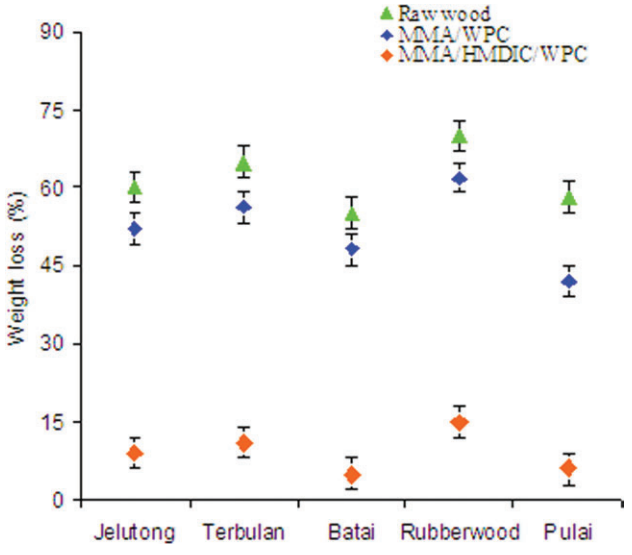

Figure 4. Weight loss of raw wood, MMA, and MMA/HMDIC-treated WPC samples due to brown rot fungi exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decay fungi. Nevertheless, combined MMA/HMDIC impregnated was shown to produce the best result in terms of decay resistance for all species. The extremely superior decay resistance resulting from MMA/HMDIC impregnated can be explained by its high water exclusion efficiency and inhibition of mycelial spread.[28,29] This result has been expected and the reason of this trend could be explained by the dual nature of HMDIC (i.e., reaction capability with wood fibers —OH groups and crosslinking character) which significantly decreased the water-uptake capacity of the treated wood. The same result was reflected both in moisture content and DSC results.[13] The results also indicated that generally, all raw wood species were nonresistant to decay exposure. However, HMDIC as a crosslinker enhanced the decay resistance and decreased the weight loss caused by both fungi for all wood species. Hence, it can be concluded that HMDIC as a crosslinker reagent was highly effective in improving decay resistance, a result which was in accordance with previous researchers.[8,30,31]

CONCLUSIONS

From this study, it can be concluded that thermal and biodegradation resistance properties of all selected tropical wood species studied were significantly increased by MMA/HMDIC treatment. The thermal analysis in terms of TGA and DSC indicated that the MMA/HMDIC led to significant improvements in thermal stability over certain temperature range. In addition, the resistance toward fungi decay exposure of MMA/HMDIC/WPC samples was higher compared to the MMA/WPC and raw wood samples. This research therefore, contends that HMDIC as a crosslinker enhances the interaction between wood, MMA, and HMDIC, which significantly increases the thermal and biodegradation resistance properties of all selected tropical light hardwoods used in this study.

Due to the shortage of high quality hardwood, there is an increased demand in the global market. However, tropical light wood could be the substitute of good quality wood though the quality is questionable due to thermal and decay resistance properties which can be resolved by treatment with MMA/HMDIC. In this regard, it is recommended that tropical light wood treated with MMA/HMDIC could be good replacement of high quality woods.

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