DIMENSIONAL STABILITY AND WATER REPELLENT EFFICIENCY MEASUREMENT OF CHEMICALLY MODIFIED TROPICAL LIGHT HARDWOOD

Md. Saiful Islam,[a,]* Sinin Hamdan,[a] Mohamad Rusop,[b] Md. Rezaur Rahman,[a] Abu Saleh Ahmed,[a] and M. A. M. Mohd Idrus [a]

Chemical modification is an often-followed route to improve physical and mechanical properties of solid wood materials. In this study five kinds of tropical light hardwoods species, namely jelutong (*Dyera costulata),* terbulan *(Endospermum diadenum*), batai (*Paraserianthes moluccana),* rubberwood (*Hevea brasiliensis)*, and pulai (*Alstonia pneumatophora*), were chemically modified with benzene diazonium salt to improve their dimensional stability and water repellent efficiency. The dimensional stability of treated samples in terms of volumetric swelling coefficient (S) and anti-swelling-efficiency (ASE) were found to improve with treatment. The water repellent efficiency (WRE) values also seemed to improve considerably with treatment of wood samples. Furthermore, treated wood samples had lower water and moisture absorption compared to that of untreated ones.

Keywords: Chemical modification; Moisture content; Dimensional stability; Water repellent efficiency

Contact information: a: Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia; b: Faculty of Electrical Engineering, Universiti Technology Mara (UiTM), Shah Alam, Selangor, Malaysia.

INTRODUCTION

Wood is a natural polymeric composite material, made up mainly of cellulose, hemicellulose, and lignin, and it possesses unique structural and chemical characteristics that render it desirable for a wide variety of end uses. Structural wood, despite its many valuable properties, also displays some disadvantages, such as a poor dimensional stability and a high moisture absorption, which results in rapid deterioration by rotting (Devi et al. 2003; Kumar 1994; Galperin et al. 1995). These effects are especially pronounced in tropical areas where wood suffers from exposure to sunlight and to a high humidity. The presence of hydrophilic hydroxyl groups (-OH) in the three major wood polymeric components (cellulose, hemicellulose, and lignin) is the main factor responsible for the unfavourable attributes. The hydroxyl group of wood attracts water molecules through hydrogen bonding from the surrounding environment, causing swelling, and making it dimensionally unstable.

The dimensional changes of wood due to atmospheric moisture can be minimized by appropriate chemical treatment, which is a promising way to improve wood properties (Schneider and Brebner 1985; Hartely and Schender 1993; Rowell 1983; Pandey et al. 2009). Chemically modified woods, which are environmental friendly, have high dimensional stability, low moisture absorption, and resistance to decay, insects, and ultraviolet ray damage (Rowell 2005; Hill 2006). They have become one of the fastest-growing materials in the wood industry (Cai et al. 2007). However, some properties (i.e. mechanical, thermal, and thermo-mechanical) of wood have been found to lack significant improvement upon chemical treatment (Larsson and Simonson 1994).

Over the years, wood has been treated with a variety of chemicals to improve its physical and mechanical properties (Gregorova et al. 2009; Hill 2011; Islam et al. 2010 2011b) The chemical modification of wood with various reagents including anhydrides (such as acidic, phthalic, succinic, maleic, propionic, and butyric anhydride, acid chlorides, ketene carboxylic acids), many different types of isocyanates, several types of monomers, such as vinyl or acrylic monomers, and so on have been the subject of research for many decades (Rowell 2005; Hill 2006). However, very few of them have been shown to be effective in improving the desired properties of wood. In addition, some modification chemicals do not react with cell wall polymers in a so-called substitution reaction (Elvy et al. 1995). Many polymers, even though formed in situ, only fill the empty lumens in the wood, which leads to a mixture of two materials rather than a real interaction. Benzene diazonium salt has been widely used to reduce hydrophilicity of raw fibers in composites manufacturing (Haque et al. 2009; Rahman et al. 2009).

The synthesis of benzene diazonium salt is very simple, and the synthesized product is abundantly available in the commercial market with low price. It has also been established that benzene diazonium salt yields a di-azo cellulose compound by the coupling reaction with –OH groups of cellulose fiber (Islam et al. 2011a). This reaction can also create new structures in materials that can influence morphology, crystallization, mechanical, thermal, biological, and other properties of wood. However, in the literature, most of the coupling reaction studies have been performed on raw fiber such as jute, coir, abaca, etc., while there were few studies carried out on solid wood modification using diazonium salt. Also, little work has been devoted to Malaysian tropical wood species and their chemical modification (Yap et al. 1990). A number of studies have been carried out on dimensional stability of various woods and their chemical modification, but so far no work has been devoted to Malaysian tropical light hardwoods and their chemical modification with benzene diazonium salt. In our earlier work, we reported on dynamic Young's modulus, morphological, and thermal stability of five tropical light hardwoods modified by benzene diazonium salt treatment (Islam et al. 2011a). Investigational results indicated that significant improvement in wood properties such as mechanical, morphological, and thermal stability were achieved by the benzene diazonium salt treatment. In this paper, we have studied the dimensional stability and water repellent efficiency of diazonium salt-treated tropical wood species.

Five species of selected tropical light hardwood, namely jelutong (*Dyera costulata),* terbulan *(Endospermum diadenum*), batai (*Paraserianthes moluccana*), rubberwood (*Hevea brasiliensis),* and pulai (*Alstonia pneumatophora*) were utilized as starting materials, since they are abundantly available in the tropical region. In addition, the stock volume of these kinds of wood species is very high. The main drawback of using these species is their high moisture intake, biodegradation, and physical properties changes with environmental variations, which limit their use (Hamdan et al. 2010). In order to protect dimensional changes and improve water repellent efficiency, all wood species were chemically treated with benzene diazonium salt. This study thus aims to investigate the dimensional stability and water repellent efficiency of tropical light hardwoods species modified with benzene diazonium salt treatment.

MATERIALS AND METHODS

Materials

Five kinds of tropical light hardwoods species, namely jelutong (*Dyera costulata)*, terbulan *(Endospermum diadenum*), batai (*Paraserianthes moluccana)*, rubberwood (*Hevea brasiliensis)*, and pulai (*Alstonia pneumatophora*) were collected from the local forest of Sarawak, Malaysia. Chemicals used for synthesis of benzene diazonium salt were aniline, sodium nitrite, and hydrochloric acid. Treatment of wood species was performed using a benzene diazonium salt solution containing sodium hydroxide. All chemicals were analytical reagent grade products of Merck, Germany.

Synthesis of Benzenediazonium Salt

Benzene diazonium salt was synthesized in the laboratory with aniline and sodium nitrite in the presence of a mineral acid at 0°C to 5°C using the standard diazotization method (Ismail et al. 2002). In our earlier work, the preparation procedure of benzene diazonium salt was described in detail (Islam et al. 2011a).

Specimen Preparation

Three trees per wood species and sapwood portions of plant were cut into three bolts of 1.2 m length. Each part was quarter-sawn to produce planks of 4 cm thickness. Then they were subsequently conditioned to air-dry in a room with a relative humidity of 60% and an ambient temperature of 25^{o}C for six month prior to testing. The clear, defect-free planks were ripped and sized to 60 mm (L) x 20 mm (T) x 20 mm (R) samples for moisture absorption, water absorption, and dimensional stability testing. Ten samples were used per test.

Density Determination

All specimens were kept in the oven at 103°C for 72 hours before density determination. Oven-dry density of each sample was then determined by using the water immersion method (Bowyer et al. 2007).

Chemical Treatment of Wood Specimens

The reaction of benzene diazonium salt with cellulose, or cellulose derivatives, is known as the coupling reaction (Islam et al. 2011a). All oven-dried raw wood specimens were submersed in a benzene diazonium salt solution (kept 5^{o}C) containing 5 L of NaOH 5% solution in an impregnation vacuum-chamber, and a maximum vacuum (10 kPa) was drawn on the wood for 30 minutes. The samples were then soaked in benzene diazonium salt solution for 3 hours at ambient temperature and atmospheric pressure to obtain further impregnation. Specimens were then removed and soaked in cold acetone to quench the reaction. Chemically modified wood species were subsequently extracted with acetone:toluene (1:1) to remove unreacted reagents, and the specimens were oven dried at 105^{o}C for 24 hours. The weight percentage gains (WPG) of the samples were then measured using the Eq. 1,

$$WPG(\%) = [(Wi-Wo)/Wo] \times 100 \quad (1)$$

where *Wo* and *Wi* are oven-dried weight of untreated and treated wood samples, respectively.

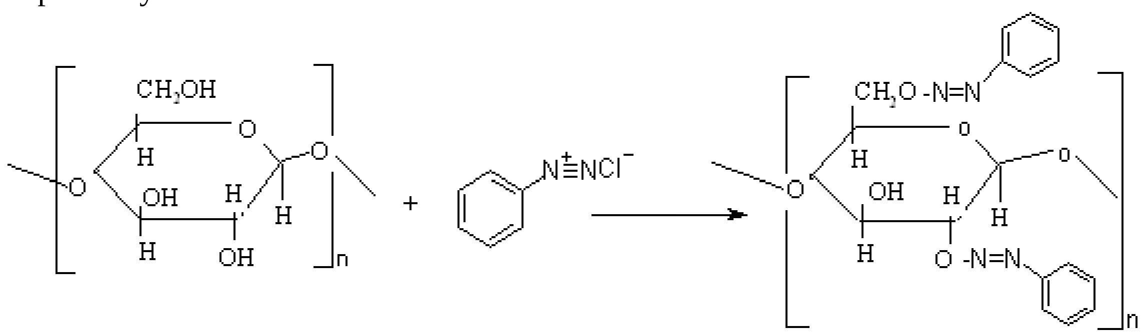

Fig. 1. The coupling reaction scheme of benzene diazonium chloride with cellulose unit

Determination of Moisture Absorption

The untreated and treated wood samples were oven-dried at 50^{o}C for 24 h. They were then placed in a conditioning chamber at a temperature of 22^{o}C and a relative humidity of 65% for approximately 6 weeks. After stabilization, the weight of each sample was measured. The moisture content (MC) at equilibrium (Eq.) was calculated as follows,

$$EMC(\%) = (M_2 - M_1)/ M_1 \times 100 \quad (2)$$

where M_2 is the weight of the raw wood at moisture absorption equilibrium, and M_1 is the oven-dried weight of the untreated or treated wood sample.

Estimation of Dimensional Stability

Water repellent efficiency (WRE) and dimensional stability for both the modified and the untreated wood samples were measured according to ASTM-1037 (1999). The weight gain and dimensional changes of each sample were determined by soaking the oven-dried specimens in a water bath at a temperature of 20 ± 1 ^{o}C for 24 hours for each type of sample for 7 days. The weight and dimension of the specimens were measured before and after soaking.

The water repellent efficiency (WRE) and anti-swelling efficiency (ASE) were calculated as follows,

$$WRE(\%) = (W_r - W_t)/ W_r \times 100 \quad (3)$$

where W_r is the water absorption of untreated wood sample, and W_t is the water absorption of treated wood sample, which was calculated by Eq. (4),

$$Water\ absorption\ (\%) = (W_a - W_b)/ W_b \times 100 \tag{4}$$

where W_b is the initial weight of an oven-dried sample before water soaking, and W_a is the weight after water soaking for 7 days,

$$Anti\text{-}swelling\text{-}efficiency,\ ASE\ (\%) = (S_r - S_t)/S_t \times 100 \tag{5}$$

where S_r is the volumetric swelling coefficient of the untreated samples, and S_t is the volumetric swelling coefficient of the treated samples. The volumetric swelling coefficients were calculated according to the formula,

$$S\ (\%) = (V_2 - V_1)/ V_1 \times 100 \tag{6}$$

where V_2 is the volume of wood after soaking and V_1 is the volume of wood before soaking.

Statistical Analysis

The significance of differences between untreated and treated wood samples was evaluated by a computerized statistical program (SPSS) composed of analysis of variance (one way ANOVA) and following Tukey tests at the 95% confidence level. Statistical evaluations were made on homogeneity groups (HG), of which different letters reflected statistical significance.

RESULTS AND DISCUSSION

Weight Percentage Gain (WPG)

Figure 2 shows the relationship between density of wood species and weight percentage gain (WPG) of treated wood samples. The average WPG of diazonium salt treated wood samples of jelutong, terbulan, batai, rubberwood, and pulai were 5.5, 4.5, 6, 4, and 5.3, respectively. It was found that the WPG values of wood samples were dependent on the density of wood species. The densities of these tropical wood species were 380, 450, 455, 480, and 650 kg/m^3 for batai, jelutong, pulai, terbulan, and rubberwood, respectively. And the amounts of diazonium salt penetration in wood were 1.3, 1.07, 1.4, 2.00, and 0.92 mg for jelutong, terbulan, batai, rubberwood, and pulai respectively.

From Fig. 2, a correlation was obtained between density and WPG of wood species. These results also indicate that the amount of chemicals that can be introduced into the wood is dependent on the density of wood species. This is expected, because lower density wood species gain higher amounts of chemical and vice-versa (Yap et al. 1990).

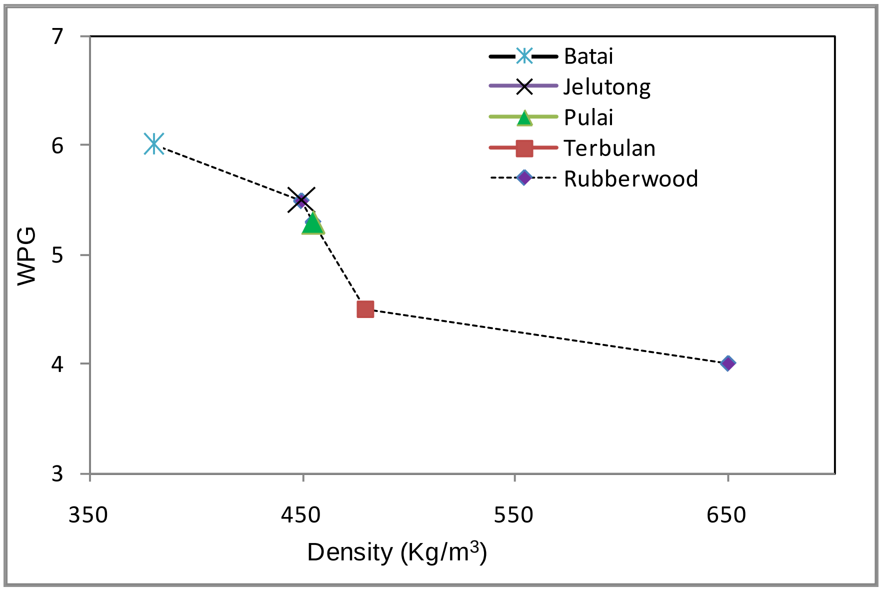

Fig. 2. Relationship between wood density and WPG

Moisture Absorption

The moisture absorption of untreated and treated wood samples was measured, and results are shown in Fig. 3. All untreated wood samples displayed a higher percentage of moisture absorption than the treated wood samples. This was expected based on the mechanism that hydrophilic hydroxyl groups will absorb moisture to their surfaces through the formation of hydrogen bonds (Rozman et al. 1998).

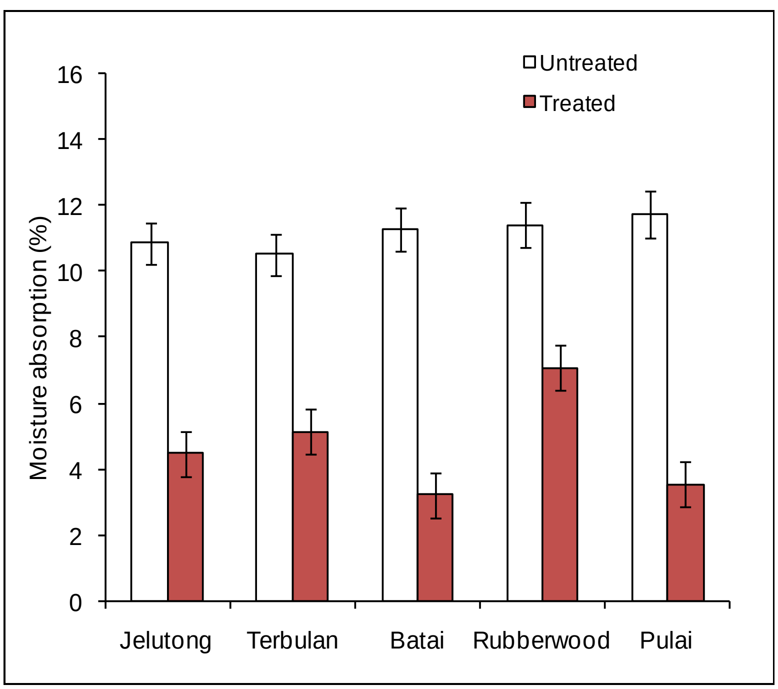

Fig. 3. Moisture absorption of untreated and treated wood samples

From the figure it can be seen that benzene diazonium salt treated wood samples had much lower moisture absorption than raw wood samples. Among the wood species used, the highest decrement of moisture absorption was observed in pulai, followed by batai, jelutong, terbulan, and rubberwood for the benzene diazonium salt treatment. The reduction in moisture absorption for the treated wood samples could be attributed to the coupling reaction and the formation of a 2,6-diazo cellulose compound, as stated earlier, which may reduce and block some sorption sites (i.e. hydroxyl groups) in the interior of wood cell lumens and the cell wall (Gindl and Gupta 2002). It has been established that the number of hydroxyl groups in the raw wood increases the moisture absorption (Haque et al. 2009). Results are consistent with a reaction of diazonium salt with OH groups of wood through its azo functional group (-N=N-), yielding an azo-cellulose compound, which significantly reduces moisture absorption. Such a chemical treatment has been reported to exhibit reduced water absorption compared to the untreated material (Haque et al. 2009).

Water Repellent Efficiency (WRE)

Table 1 gives the water repellent efficiencies (WREs) and absorption properties of untreated and treated wood samples. The WREs of treated wood samples were signify-cantly higher than those of untreated samples. The highest increment of WRE was observed in pulai, followed by jelutong, batai, terbulan, and rubberwood. The improvement in WRE for treatment provides evidence of the role of diazonium salt reaction with hydroxyl groups of the wood components. As with the WPG and coupling reaction, fewer water absorption sites remain, and this effect also contributes to the reduction in water uptake (Gindl and Gupta 2002; Williams and Hale 2003). Furthermore, all untreated wood specimens exhibited higher percentage of water absorption compared to the chemically treated wood. Again, treated pulai had the least water absorption, followed by batai, rubberwood, terbulan and jelutong, respectively.

Table 1. Water Repellent Efficiency and Water Absorption of Untreated and Treated Wood Samples

Wood species and sample particulars		Water absorption (%)	Homogeneity group(HG)	Water Repellent Efficiency (WRE)
Jelutong	Untreated	332±12.15	A	-
	Treated	70±5.22	B	70±2.37
Terbulan	Untreated	205±10.44	C	-
	Treated	102±6.27	D	50±1.84
Batai	Untreated	259±11.12	E	-
	Treated	110±5.27	F	58±2.05
Rubberwood	Untreated	112±8.70	G	-
	Treated	50±3.25	H	59±12.33
Pulai	Untreated	396±13.25	I	-
	Treated	240±7.35	J	39±1.14

Each value is the average of 10 specimens.
The same letters are not significantly different at α =5%. Comparison were done within each wood species group.

The results suggest that the coupling reagent has the ability to form cross-links by coupling adjacent surfaces of cellulosic fiber together, which strongly inhibit swelling and uptake of water. This is consistent with the ability of diazonium salt to react with cellulose hydroxyl groups of the wood.

Dimensional Stability

Volumetric swelling coefficient (S %) and Anti-Swelling-Efficiency (ASE %)

The results of dimensional stability in terms of volumetric swelling coefficient (S) and anti-swelling-efficiency (ASE) of untreated and treated wood samples are given in Table 2. From the table it is clear that all the untreated wood samples exhibited higher swelling coefficient values compared to the treated wood samples. Benzene diazonium salt treatments significantly decreased the volumetric swelling coefficient in all five wood species.

The reduction of S in treated samples corresponded to the moisture excluding capacity of the treatment (Rashmi et al. 2003). As is also observed from Table 2, wood samples treated with diazonium salt demonstrated significant improvement in ASE compared to their corresponding untreated wood samples. This result is evidently because diazonium salt has not only reacted with the hydroxyl group of wood component but also blocked water molecule movement pathways inside the wood cell wall (Baysal et al. 2004). This predisposition of diazonium salt and aforesaid azo-cellulose product significantly improved the ASE of all treated wood species. The highest increment of ASE was observed in pulai, followed by jelutong, batai, terbulan, and rubberwood. The particular interaction between wood and chemical is considered to effectively improve ASE (Baysal et al. 2004; Deka et al. 2002). The treatments improved ASE significantly compared to the untreated one, which means that better dimensional stability could be obtained using benzene diazonium salt treated wood samples.

Table 2. Volumetric Swelling Coefficient and Anti-Swelling-Efficiency of Untreated and Treated Wood Samples.

Wood species and sample particulars		Volumetric swelling coefficient (S %)	Homogeneity group(HG)	Anti-swelling efficiency (ASE%)
Jelutong	Untreated	7.28±0.13	A	-
	Treated	4.15±0.10	B	43±1.2
Terbulan	Untreated	8.17±0.09	C	-
	Treated	5.10±0.06	D	38±1.3
Batai	Untreated	9.31±0.08	E	-
	Treated	4.10±0.07	F	56±1.5
Rubber	Untreated	9.13±0.10	G	-
	Treated	5.70±0.08	H	38±1.35
Pulai	Untreated	5.44±0.05	I	-
	Treated	2.13±0.02	J	61±1.40

Each value is the average of 10 specimens.
The same letters are not significantly different at α =5%. Comparison were done within each wood species group.

CONCLUSIONS

1. Significant improvements in dimensional stability and water repellent efficiency of treated wood samples were obtained for all selected woods that had been treated with benzene diazonium salt formulation.
2. The volumetric swelling coefficient of treated wood sample decreased by 40 to 55% and the anti-swelling-efficiency increased by 38 to 61%.
3. The treated woods had increased water repellent efficiency (WRE) and decreased moisture content by 39 to 70% and 38 to 71%, respectively, compared to their untreated counterparts.

   Since there is a shortage of high quality hardwood, many types of tropical low quality light hardwood can be chemically modified and utilized for indoor and outdoor applications.

REFERENCES CITED

ASTM D-1037. (1999). "Standard test methods for evaluating properties of wood-base fiber and particle panel materials," American Society for Testing and Materials, West Conshohocken, PA.

Bowyer, J. L., Shmulsky, R., and Haygreen, J. G. (2007). *Forest Products and Wood Science –An Introduction*, Blackwell Publishing Ltd., 201-221.

Baysal, E., Ozaki, S. K., and Yalinkilic, M. K. (2004). "Dimensional stabilization of wood treated with furfuryl alcohol catalyst by borates," *Wood Sci. Technol.* 38, 405-415.

Cai, X., Riedl, B., Zhang, S. Y., and Wan, H. (2007a). "Effects of nanofillers on water resistance and dimensional stability of solid wood modified by melamine-urea-formaldehyde resin," *Wood Fib. Sci.* 39(2), 307-318.

Cai, X., Riedl, B., Zhang, S.Y., and Wan, H. (2007b). "Formation and properties of nanocomposites made up from solid aspen wood, melamine-urea-formaldehyde, and clay," *Holzforschung* 61, 148-154.

Deka, M., Saikia, C. N., and Baruah, K. K.(2002). "Studies on thermal degradation and termit resistant properties of chemically modified wood," *Bioresource Technol.* 84, 151-157.

Devi, R. R., Ali, I., and Maji, T. K. (2003). "Chemical modification of rubber wood with styrene in combination with a crosslinker: Effect on dimensional stability and strength property," *Bioresource Technol.* 88,185-188.

Elvy, S. B., Dennis, G. R., and Loo-teck, N.G. (1995). "Effect of coupling agent on the physical properties of wood-polymer composites," *J. Mat. Proc. Techonol.* 48, 365-372.

Galpperin, A. S., Kuleshov, G. G., Tarashkevich, V. I., and Smtov, G. M. (1995). "Manufacturing and properties of modified wood: A review of 25 years work," *Holzforschung* 49, 45- 50.

Gregorova, A., Wimmer. R., Hrabalova, M., Koller, M., and Ters, T (2009). "Effect of surface modification of beech wood flour on mechanical and thermal properties of poly(3-hydroxybutyrate)/wood flour composites," *Holzforschung* 63, 565-570.

Gindl, W., and Gupta, H. S. (2002). "Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation," *Compos. Part A*, 33, 1141-1145.

Hartley, I. D., and Schxeider, M. H. (1993). "Water vapour diffusion and absorption characteristics of sugar maple (*Acer saccharum*, Marsh.), wood polymer composites," *Wood Sci.Technol.* 27, 421-427.

Hill, C. A. S. (2006). "Chemical modification of wood," In: *Wood Modification: Chemical, Thermal and Other Processes,* John Wiley & Sons Ltd, 45-99.

Hill, C. A. S. (2011). "Wood modification: An update," *BioResources* 6(2), 918-919.

Haque, M. M., Hasan, M., Islam, M. S., and Ali, M. E. (2009). "Physico-mechanical properties of chemically treated palm and coir fiber reinforced polypropylene composites," *Bio Tec.* 100, 4903-4906.

Hamdan, S., Talib, Z. A. Rahman, M. R., Ahmed, A. S., and Islam, M.S. (2010). "Dynamic Young's modulus measurement of treated and post-treated tropical wood polymer composites (WPC)," *BioResources* 5(1), 324-342.

Islam, M. S., Hamdan, S., Rahman, M. R., Jusoh, I., and Ibrahim, N. F. (2010). "Dynamic Young's modulus and dimensional stability of Batai tropical wood impregnated with polyvinyl alcohol," *J. Sci. Res.* 2(2), 227-236.

Islam, M. S., Hamdan, S., Rahman, M. R., Jusoh, I., Saleh, A. A., and Idrus, M. (2011a). "Dynamic Young's modulus, morphological, and thermal stability of 5 tropical light hardwoods modified by benzene diazonium salt treatment," *BioResources* 6(1), 737-750.

Ismail, H., Edyhan, M., and Wirjosentono, B. (2002). "Bamboo fiber filled natural rubber composites: The effects of filler loading and bonding agent," *Polymer Testing* 21(2), 139-144.

Islam, M. S., Hamdan, S., Jusoh, I., Rahman, M. R., and Talib, Z. A. (2011b). "Dimensional stability and dynamic young's modulus of tropical light hardwood chemically treated with methyl methacrylate in combination with hexamethylene diisocyanate cross-linker," *Indus. Eng. & Chem. Res.* 50, 3900-3906.

Kumar, S. (1994). "Chemical modification of wood," *Wood Fib. Sci.* 26(2), 270-280.

Larsson, P, Simonson, R. (1994). "A study of strength, hardness and deformation of cetylated Scandinavian softwood," *Holz Roh Werkst.* 52, 83-86.

Pandey, K. K., Jayashree, and Nagaveni, H. C. (2009). "Study of dimensional stability, decay resistance and light stability of phenylisothiocyanate modified rubberwood. *BioResources* 4(1), 257-267.

Rahman, M. R., Haque, M. M., Islam, M. N., and Hasan, M. (2009). "Mechanical properties of polypropylene composites reinforced with chemically treated abaca," *Compos Part A* 40, 511-517.

Rashmi, R., Devi, A., Ali, I., and Maji, T. K. (2003). "Chemical modification of rubber wood with styrene in combination with a crosslinker: Effect on dimensional stability and strength property," *Bio Tech.* 88, 185-188.

Rashmi, R., Devi, A., Maji, T. K., and Banerjee, A. N. (2004). "Studies on dimensional stability and thermal properties of rubber wood chemically modified with styrene and glycidyl methacrylate," *J. App. Polym. Sci.* 93, 1938-1945.

Rowell, R. M. (1983). "Chemical modification of wood," *Forest Prod. Abst.* 6(12), 363-382.

Rowell, R. M. (2005). "Chemical modification of wood," In: *Handbook of Wood Chemistry and Wood Composite*, Rowell, R. M. (ed.), Taylor and Francis, CRC, 381-420.

Rozman, H. D., Kumar, R. N., Abusamah, A., and Saad, M. J. (1998). "Rubberwood-polymer composites based on glycidyl methacrylate and diallyl phthalate," *J. App. Polym. Sci.* 67, 1221-1226.

Schneider, M. H., and Brebner, K. I. (1985). "Wood-polymer combinations: The chemical modificaiton of wood by alkoxysilane coupling agents," *Wood Sci. Technol.* 19, 67-73.

Yap, M. G. S., Chia, L.H. L., and Teoh, S. H. (1990). "Wood polymer composites from some tropical hardwood," *J. Wood Chem. Technol.* 10(1), 1-19.

Article submitted: October 2, 2011; Peer review completed: November 27, 2011; Revised version received: January 10, 2012; Accepted: January 21, 2012; Published: January 24, 2012.