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Physico-mechanical and Decay Resistance Properties of Chemically Modified Tropical Wood Material

Md. Saiful Islam,[1] Sinin Hamdan,[1] Mahbub Hasan,[2] Mohamad Rusop,[3] Md. Rezaur Rahman,[1] M. A. M. Mohd Idrus[1]

[1]Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

[2]Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

[3]Faculty of Electrical Engineering, Universiti Technology MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia

Correspondence to: M. S. Islam (E-mail: msaifuli2007@gmail.com)

ABSTRACT: In this present research, several kinds of selected tropical light hardwoods were chemically modified with benzene diazonium salt to improve their physico-mechanical and decay resistance properties. Benzene diazonium salt underwent a coupling reaction with wood which was confirmed through fourier transform infrared spectroscopic analysis. The compressive modulus of the treated wood increased, whereas modulus of rupture was shown to decrease on treatment. Water absorption was also found to decrease considerably after modification. The modified wood samples had higher hardness (Shore D) value compared to that of the control ones. The wood was exposed to two types of fungi; white-rot (*Polyporus versicolor*) and brown-rot (*Postia placenta*), for 12 weeks and then decay was assessed through weight loss percentage (%). A significant improvement was found in the modified wood compared to the control wood. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: modification; FTIR; modulus; hardness

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INTRODUCTION

Wood is a natural complex polymeric material, constituted mainly of cellulose, hemicellulose, and lignin with a minor proportion of extractives that is subjected to biodegradation. Growing environmental awareness and new regulations are forcing the industry to seek more ecological friendly additives materials for their products.[1] To extend the life time of wood proper protection required, and a board range of chemicals may be used. Recent environmental concerns about the toxicity and persistence of some preservative products have stimulated researcher to find alternatives.[2] Modifying wood using nontoxic chemical/resin and environmental friendly thermal treatments shows potential to improve performance characteristics.[3,4] Chemically modified wood typically have low moisture absorption and high resistance to decay, insects, and ultra violet ray damage. Over the years, wood has been treated with a variety of chemicals to change its physical, mechanical, and biological properties. Such modified wood is not only more resistive against decay but also has much improved mechanical properties, in particular strength.[5] Wood has been modified with a variety of chemicals such as acidic anhydride, isocyantaes, vinyl or acrylic monomers, and so on.[5,6] When wood is subjected to fungal and termite attacks most of the fungi penetrates, the material through checks associated with incisions in the wood. It has been shown that 43.6% of wood crossties were removed from track owing to decay and this has serious economic applications.[7] Recently, more efforts have been made to improve the decay resistance of wood with zinc borate and other chemicals.[8,9] Little research work, however, has been devoted to Malaysian tropical light hardwood species and their chemical treatment with benzene diazonium salt.

In present research, five species of selected Malaysian tropical light hardwood namely, Jelutong (*Dyera costulata*), Terbulan (*Endospermum diadenum*), Batai (*Paraserianthes moluccana*), Rubberwood (*Hevea brasiliensis*), and Pulai (*Alstonia pneumatophora*) were evaluated. The major drawback of using these species is their high moisture uptake, biodegradation, physical, and mechanical properties change with environmental variations, which limit their use. By reducing the moisture content of wood, fungal growth can be inhibited.[10,11] The physical, mechanical, and biological properties changes of wood can be minimized by suitable chemical treatment, which is a promising way to improve wood properties.[12,13] To tackle this problem, all

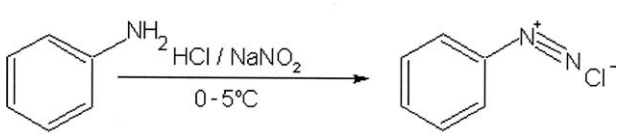

Figure 1. The reaction scheme for the synthesis of benzene diazonium salt.

wood species were chemically treated with benzene diazonium salt. Therefore, the main objectives of the present research are (i) to develop the coupling reaction with tropical light hardwood species and evaluate their physicomechanical properties and (ii) to compare the rate of decay of raw and modified wood against the brown-rot and white-rot decay fungi.

MATERIALS AND METHODS

Materials

In the present research, five kinds of tropical light hard woods species namely Jelutong (*D. costulata*), Terbulan (*E. diadenum*), Batai (*P. moluccana*), Rubberwood (*H. brasiliensis*), and Pulai (*A. pneumatophora*) were collected from the local forest of Sarawak, Malaysia. Chemicals used for the 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 of analytical reagent grade products of Merck, Germany.

Synthesis of Benzene Diazonium Salt

Benzene diazonium salt was synthesized in the laboratory with aniline and sodium nitrite in the presence of a mineral acid at 0–5°C using the standard diazotization method.[14] The solution of phenylamine (aniline) in hydrochloric acid (phenylammonium chloride solution) is usually stood in a beaker of ice. The sodium nitrite solution is also cooled in the ice. The solution of the nitrite is then added very slowly to the phenylammonium chloride solution, so that the temperature never goes above 5°C. The reaction scheme for the synthesis of benzene diazonium salt is shown in Figure 1. The solution containing diazonium salt was used very quickly in the coupling reaction with the wood species.

Sample Preparation

The sapwood portions of plant were cut into three bolts of 1.2 m length. Each bolt was quarter sawn to produce planks of 4 cm thickness and subsequently conditioned to air-dry in a room with relative humidity of 60% and ambient temperature of 25°C for 6 months prior to testing. For physical and mechanical properties measurement, 10 samples were used for each test.

Density Determination

All samples were kept in the oven at 103°C for 72 h before density determination. Oven-dry density of each sample was then determined by using the Water Immersion Method.[15]

Chemical Treatment of Wood Specimens

The reaction of benzene diazonium salt with cellulose or cellulose derivatives is known as the coupling reaction.[16] All oven-dried raw wood specimens were submersed in a benzene diazonium salt solution (kept at 5°C) containing 5 L of 5% NaOH solution in a reaction vessel for 30 min at ambient pressure. Samples 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 oven dried at 105°C for 24 h. The weight percentage gains (WPG) of the samples were measured.

Fourier Transform Infrared Spectroscopic Analysis

The infrared spectra of the untreated and treated grounded powder wood samples were recorded on a Shimadzu 81001 Fourier transform infrared spectrometer (FTIR) in the transmittance mode.

Mechanical Tests

To characterize various wood samples, bending and compression tests were carried out according to ASTM D-143 (1996) using a Shimadzu Universal Testing Machine having a loading capacity of 300 kN.[17] The crosshead speed used was 2 mm/min and span of 180 mm. According to ASTM D 143 (1996), the clear, defect-free planks were ripped and sized to 300 mm (L) × 20 mm (T) × 20 mm (R) for three-point bending test and 30 mm (L) × 20 mm (T) × 20 mm (R) for compression parallel to grain test. Compressive modulus was measured using the uniaxial compression test. The modulus of elasticity (MOE) and modulus of rupture (MOR) were measured using the three-point bending method. The hardness of the wood samples was determined and expressed as Durometer Hardness (Shore-D) according to the ASTM D 2240 method. The samples were sized to 60 mm (L) × 20 mm (T) × 20 mm (R) for surface hardness measurement.

Laboratory Fungal 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).[18] For this test, samples were sized to 9 mm (L) × 25 mm (T) × 25 mm (R). The samples were air dried and after conditioning to constant weight, those were weighed accurately in the laboratory and transferred into a large totally dark container maintained at 20 ± 1°C and a relative humidity of 65 ± 4%. Two types of fungus, white-rot (*Polyporus versicolor* L.ex. Fr.) ATCC No. 12679 and brown-rot (*Postia placenta*) (Fr). Cke. ATCC No. 11538, were used to study the resistance of WPC against the 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 samples were air dried and again conditioned to constant weight. The weight was recorded for each sample to determine % weight loss.

Water Absorption Test

To determine the water uptake, the water absorption test of the control and modified wood samples was carried out according to ASTM-1037, 1999.[19] The samples were dried in an oven at 105°C, cooled in a dessicator containing silica gel and immediately weighed. The dried samples were immersed in distilled water for 7 days at ambient temperature. The samples were then removed from the water and dried with a cotton cloth. The final weight of the samples was then taken. The increase in the weight of the samples was calculated.

Statistical Analysis

The significant difference between control and treated wood samples was evaluated by a computerized statistical program

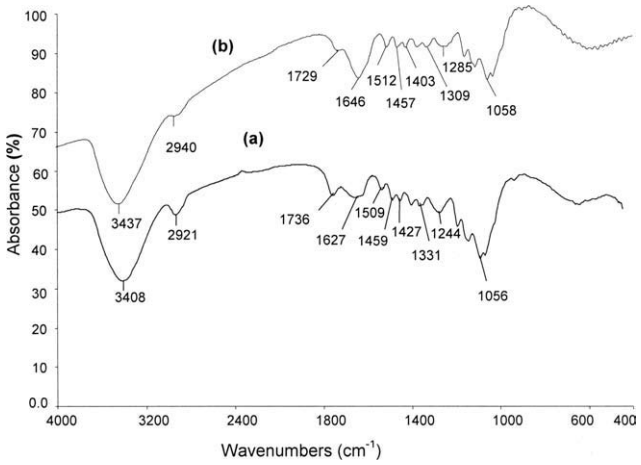

Figure 2. Typical FTIR spectrum of (a) control Jelutong wood and (b) modified Jelutong wood.

(SPSS-14.0) composed of analysis of variance (one-way ANOVA) and following Tukey tests at the 95% confidence level. Statistical evaluations were made on homogeneity groups of which different letters reflected statistical significance.

RESULTS AND DISCUSSION

The average WPGs of diazonium salt treated Jelutong, Terbulan, Batai, Rubberwood, and Pulai wood samples were 6, 4.5, 5.5, 4, and 5.3, respectively. It was found that the WPGs of wood samples were dependent on the density of wood species. The densities of Batai, Jelutong, Pulai, Terbulan, and Rubberwood found were 380, 450, 455, 480, and 650 kg/m^3, respectively.

Fourier Transform Infrared Spectroscopy (FTIR)

The formation of wood-azo derivative by the coupling reaction with diazonium salt and wood was indicated by the FTIR analysis of the control and modified wood as shown in Figure 2(a). The FTIR spectrum of the control wood sample [Figure 2(a)] clearly shows the absorption bands in the region of 3408, 2921, and 1736 cm^{-1} owing to O—H stretching vibration, C—H stretching vibration, and C=O stretching vibration, respectively. These absorption bands are owing to the hydroxyl group in cellulose, carbonyl group of acetyl ester in hemicellulose, and carbonyl aldehyde in lignin.[20] On the other hand, FTIR spectra of treated wood in Figure 2(b) clearly show the presence of the characteristic band of NO group in the region of 1512 and 1646 cm^{-1}. The peaks at 1403 and 1457 cm^{-1} are owing to the —N=N— moiety of the azo compound, and the absorption band at 1309 cm^{-1} may be attributed to the symmetric deformations of NO_2 presence in the wood azo compound.[21] The absorption band of O—H group also shifted toward higher wave number (3408–3437 cm^{-1}) with narrowed band intensity, which gives further evidence of the reaction of wood-based hydroxyl groups with diazonium salt.[22]

The formation of wood-azo derivative can be explained as being owing to the presence of three hydroxyl groups in wood. One is the primary hydroxyl group at C_6 and the other two are secondary hydroxyl groups at C_2 and C_3. The primary hydroxyl group is more reactive than the secondary groups, and the coupling reaction with carbon 2 and carbon 6 resulted in the formation of wood-azo derivative.[23]

Bend Test Analysis

The MOE and MOR of control and modified wood samples are summarized in Table I. The effects of coupling reaction on the MOE and MOR of the selected woods were investigated. No statistical difference was observed for MOE of the all modified wood samples relative to the controls.[21,24] In the wood samples, coupling reagent reacts with OH groups of wood fiber and yielded a wood-azo derivative, but did not enhance the MOE of wood significantly.

As summarized in Table I, the MOR decreased after chemical modification. The MOR of Rubberwood showed highest decrement (63%) on modification, followed by Pulai (51%), Jelutong (40%), Terbulan (8), and Batai (7%), respectively. The lower MOR of modified samples compared to the controls is possibly owing to the azo substitution of cellulose in the wood. The Batai wood had the lowest decrement between treated and its modified and control samples. This indicates that MOR also depends on the wood properties.[25]

Table I. MOE and MOR of Control and Modified Wood[a]

Wood species	Sample particulars	MOE (GPa)	Std.	HG	MOR (MPa)	Std.	HG
Jelutong	Control	5.31	0.45	a	46.58	0.47	a
	Modified	5.45	0.52	a	28.17	0.65	b
Terbulan	Control	7.39	1.10	b	60.19	0.56	c
	Modified	7.75	0.75	b	55.27	1.10	d
Batai	Control	6.51	0.45	c	55.35	0.76	e
	Modified	7.55	1.13	c	51.55	0.77	f
Rubberwood	Control	11.62	1.30	d	105.94	0.74	g
	Modified	11.75	0.65	d	39.00	0.54	h
Pulai	Control	4.12	1.43	e	37.83	1.30	k
	Modified	4.15	0.65	e	18.60	0.65	i

[a]Std.: standard deviation, HG: homogeneity group; Mean value is the average of 10 specimens. The same letters are not significantly different at α = 5%. Comparisons were carried out within the each wood species group.

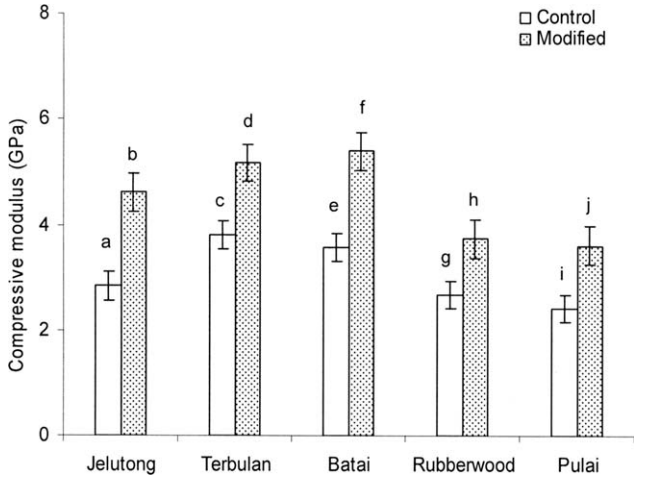

Figure 3. Compressive modulus of control and modified wood (different letters reflecting statistical significance).

Compression Test Analysis

Figure 3 shows the compressive modulus parallel to the grain for treated and control wood samples. Figure 3 shows that there was a significant increase (35–62%) of compressive modulus for all modified wood samples. The highest increment of compressive modulus was observed in Jelutong, followed by Batai, Pulai, Terbulan, and Rubberwood, respectively. Control wood samples failed in compression because of the buckling of relatively thin cell walls owing to a long column type of instability. The wood modification coats the cell walls, thus greatly increasing their lateral stability.[26] It is also expected because benzene diazonium salt has the ability to react with the wood fiber, thus forming azo compound with improved compressive strength. The increase of compressive modulus in modified wood compared to raw wood was also reported by the previous researchers.[27]

Surface Hardness Results

The hardness (Shore D) values of control and modified wood samples are shown in Figure 4. Figure 4 shows that all the modified wood samples had higher hardness compared to their corresponding control wood. The best increment of hardness was obtained in Pulai wood followed by Jelutong, Terbulan, Batai, and Rubberwood, respectively. The improvement of wood hardness can be explained earlier owing to the substitution onto the wood fiber.[21,28]

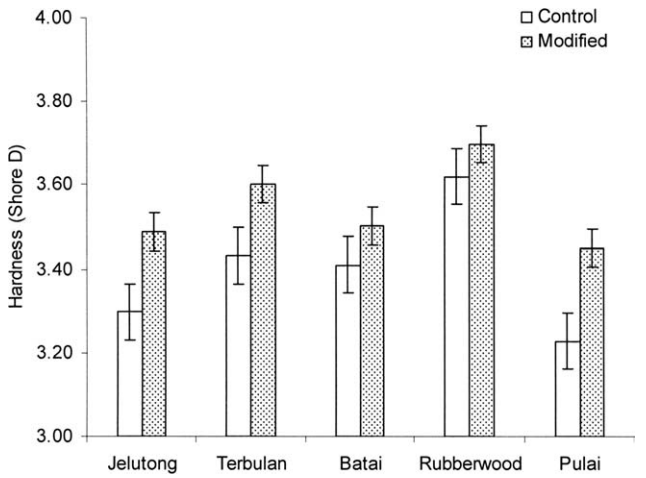

Figure 4. Surface hardness of control and modified wood samples.

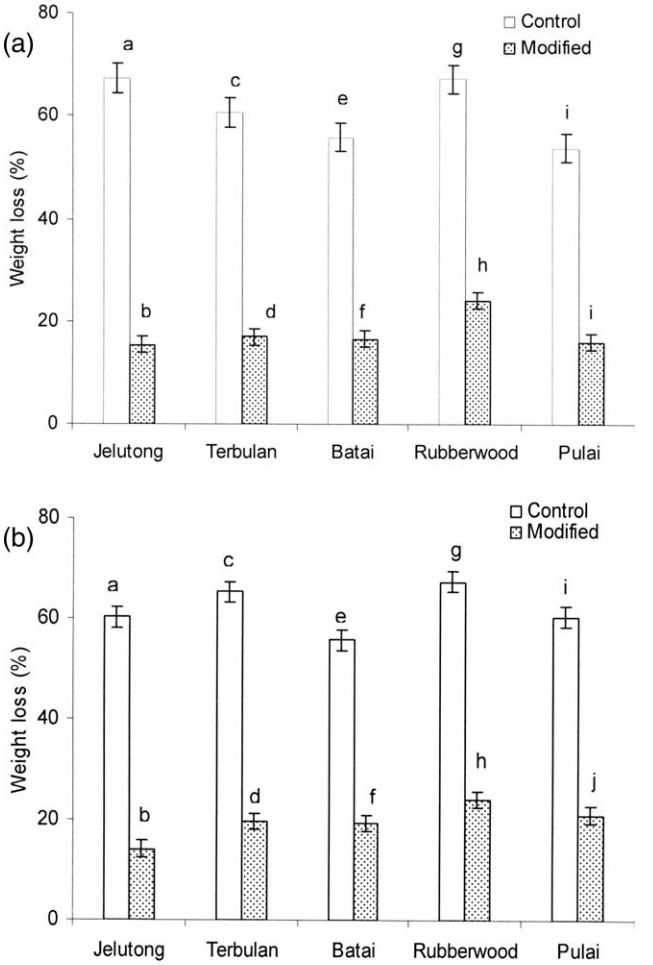

Figure 5. (a) Weight losses of control and modified wood samples after exposure to the decay fungus (white-rot fungus) for 12 weeks (different letters reflected statistical significance). (b) Weight losses of control and modified wood samples after exposure to the decay fungus (brown-rot fungus) for 12 weeks (different letters reflected statistical significance).

Fungal Decay Resistance Test Analysis

Weight loss owing to fungal attack for control and treated wood samples is shown in Figure 5(a,b). The results showed that both the control and the modified wood were affected by the exposure to the decay fungi *P. versicolor* and *P. placenta*, respectively. Modified wood showed considerable resistance to both the decay fungus, representing brown and white rot fungi compared to control wood species. The modified Jelutong wood gave the best results compared to Terbulan, Batai, Pulai, and Rubberwood, respectively. The results also showed that generally all raw wood species were nonresistant to decay exposure. However, coupling reaction enhanced the decay resistance and

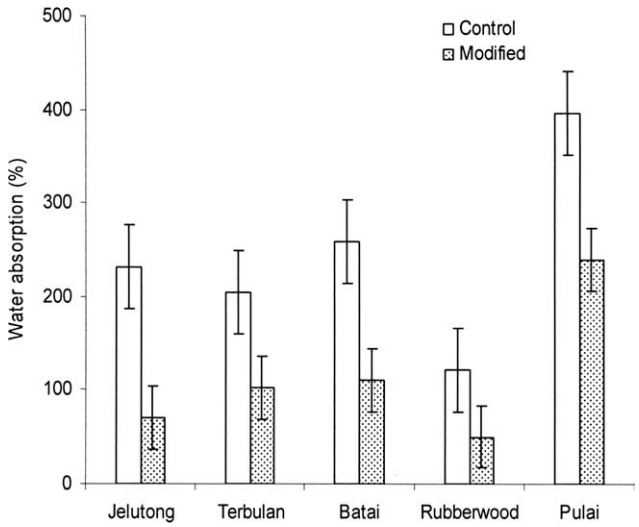

Figure 6. Variation of water absorption for control and modified wood samples.

decreased the weight losses owing to both fungi for all wood species. According to the results, the modified Jelutong wood samples were highly resistant to white-rot fungi decay exposure followed by Terbulan, Batai, Pulai, and Rubberwood, respectively. On the other hand, the modified Jelutong, Terbulan, Batai, Pulai, and Rubberwood were moderately resistant to brown-rot fungi decay exposure. The remarkably good decay resistance of modified wood can be explained by its high-moisture exclusion efficiency and inhibition of mycelial spread.[29] Therefore, it can be concluded that chemical modification was highly effective in improving decay resistance, as found by the previous researchers.[30]

Water Absorption Test Analysis

Figure 6 shows the result of water absorption properties of control wood and modified wood. All control wood samples exhibited higher percentage of water absorption compared to the chemically modified wood. It is expected because cell wall of hydrophilic hydroxyl groups absorbs water to its surface through the formation of hydrogen bonding.[31,32] Modified Pulai wood had the least water absorption, followed by Batai, Rubberwood, Terbulan, and Jelutong, respectively. However, suitable chemical modification blocked accessible hydroxyl groups in wood samples and reduced the water absorption.[33,34]

CONCLUSIONS

From the present research, it can be concluded that optimistic improvement in compressive modulus and decay resistance properties was obtained for all selected woods which were modified by benzene diazonium salt formulation. In addition, the surface hardness of modified wood samples exhibited higher values compared to their control ones. The decay exposure of modified woods was higher compared to those of control wood. Furthermore, modified wood showed lower water absorption compared to the control ones. The authors propose that all tropical light hardwoods used in the present research are suitable for coupling reaction with increased physico-mechanical and decay resistances. However, benzene diazonium salt modification is not suitable for commercialization owing to upscaling issues from laboratory conditions, costliness, and decrease in the MOR of wood.

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