Decay Resistance of Acetic, Propionic, and Butyric Anhydrides Modified Rubberwood Against Brown Rot (*Coniophora puteana*)

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Rubber trees were cut to the dimensions 25 mm x 140 mm x 1000 mm (R x T x L) and kiln-dried (10% to 12% moisture content, MC). The specimens (20 mm x 20 mm x 5 mm) (R x T x L) were prepared, and a Soxhlet extraction with toluene/methanol/acetone (4:1:1 by volume) was performed for 8 h. The specimens were oven-dried (103 °C for 24 h) and cooled (gel silica). Then, vacuum impregnation was conducted, and reactions with acetic, propionic, and butyric anhydrides took place for 0.25 h, 1 h, 4 h, 8 h, 10 h, 15 h, 24 h, 30 h, 36 h, and 48 h at 120 °C. The chemical bonding was confirmed by Fourier transform infrared (FTIR) analysis. The specimens were leached in deionized water and exposed to brown rot (Coniophora puteana) in an incubation room at 22 °C for 16 weeks. The fastest reaction was with butyric anhydride, then propionic and acetic anhydrides. The lowest weight loss occurred with acetic anhydride after being decayed by C. puteana at 14.0% weight percent gain (WPG). All of the modified rubberwoods (acetic, propionic, and butyric anhydrides) at the maximum WPG were classified as durability class 1. The scanning electron microscopy (SEM) observation confirmed that the hyphae penetrated the cells in both the untreated and anhydride modified rubberwood.

Keywords: Rubberwood; Anhydrides; Decay resistance; Brown rot

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INTRODUCTION

Next to the tin industry, the rubber industry is the most important socio-economic sector in Malaysia in light of Malaysia's independence in 1957. To date, more than 80% of total rubber tree plantation areas in the world are in Asia. Malaysia, Indonesia, and Thailand contain almost 70% of the total rubber cultivation area in Asia. Malaysia was the largest producer of rubber in the world until the late 1980's. Indonesia then took over as the biggest rubber cultivator in the world, followed by Thailand. Malaysia is currently the third most important country in the world for rubber cultivation.

Rubberwood emerged as an alternative source of timber for the wood industry when restriction in logging activities was implemented by the Malaysian government. It is recognised as the most ecologically friendly lumber used in the furniture industry today. Generally, rubber trees (*Hevea brasiliensis*) are felled and replanted after 26 to 30 years of use for latex tapping. The wood is harvested for use as sawn timber, mouldings, furniture,

medium density fibreboard, chipboard, builders, joinery, carpentry, and wooden frames (Shigematsu *et al.* 2011). According to the Malaysian Furniture Promotion Council (MFPC) (2014), rubberwood sawn timber is the top raw material used in the furniture industry, and it constituted 85% of total wood furniture exports in Malaysia in 2013 (Merous *et al.* 2015).

The low dimensional stability and biodegradation problem are the main reasons why rubberwood has been less attractive for wood processing industries and has been mostly neglected in the past, despite the fact that it is abundant in supply and easily available. These problems also continue to hinder its expansion as a substitute for many tropical hardwood timber types, especially for building materials and in the construction industry. Rubberwood products are generally more susceptible to biodeterioration agents than solid wood, unless they are used in situations where exposure to moisture or risk of deterioration is unlikely (Zaidon *et al.* 2003).

Rubberwood appears to be the most susceptible to soft rot decay compared to other nondurable plants, such as punggai (*Coelostegia griffithii*), jelutong (*Dyera costulata*), and kayu arang (*Diospyros* spp.). However, against white rot (*Coriolus versicolor*), rubberwood was found to be more susceptible than non durable jelutong and ramin (*Gonystylus bancanus*) (Teoh *et al.* 2011).

Wood modification is getting attention in this new millenium because it offers a less or nontoxic solution to extend the service life of wood and it is an alternative to the toxic wood preservative copper chromium and aresenate (CCA). The preservative CCA was reported to be able to leach out from the wood into soils during the use of the wood. As a consequence, CCA-treated wood was banned from use in playgounds to prevent direct contact with skin (Hill 2006). Many wood modification treatments have different decay resistance perfromances and other overall properties (Li *et al.* 2000; Hill *et al.* 2005; Del Menezzi *et al.* 2008; Kartal *et al.* 2009; Unsal *et al.* 2009). Alternatively, chemical modification offers the best solution to improve the dimensional stability and decay resistance of wood, without altering important mechanical properties, especially the load bearing properties (Hisham and Hale 2012; Rowell 2014).

One of the best chemical modification treatments is acetylation (Rowell 2014). Despite its supreme decay resistance performance, the acetylation process is produced by a product of acetic acid that needs further separation processes to recycle the acetic anhydride (Hill 2006; Rowell 2014). Studies into using longer chain carboxylic acid anhydrides, such as propionic and butyric anhydrides, are needed to solve this issue.

The objective of this study was to investigate the decay resistance of rubberwood modified with acetic, propionic, and butyric anhydrides against basidiomycetes. The effectiveness of anhydride modified rubberwood was compared to Scots pine (*Pinus sylvestris*) sapwood and European beech (*Fagus sylvatica*). This study is vital to promote the use of modified rubber wood as substitution to the scarcity of tropical heavy hardwood from the natural forest. Unlike other studies using ready-made specimens from sawn timber factories, the specimens considered here were freshly harvested from a mature rubber tree plantation.

EXPERIMENTAL

Materials

Rubberwood, aged 30 years, was obtained from local plantations (Selangor Malaysia), and processed at the Forest Research Institute Malaysia (FRIM). The rubberwood was cut into 25 mm x 140 mm x 1000 mm (R x T x L) sized boards and kilndried to a 10% to 12% moisture content. Specimens sized 20 mm x 20 mm x 5 mm (R x T x L) were then cut using a small band saw.

Preparation of the specimens

The rubberwood specimens were carefully sanded to remove loosely adhering fibers, and they were then placed in a Soxhlet extractor for solvent extraction using toluene/methanol/acetone (4:1:1 by volume) for 8 h. The specimens were then oven-dried for 24 h at 104 °C, weighed to three decimal places, and its volume was measured using a Mitutoyo digimatic height gage (Mitutoyo Corporation, Kawasaki, Japan). The specimens were transferred to a vacuum desiccator and allowed to cool to ambient temperature over silica gel. The rubberwood specimens were arranged in a container by their reaction times (0.25 h, 1 h, 4 h, 8 h, 10 h, 15 h, 24 h, 30 h, 36 h, and 48 h), ballasted under metal wrapped with aluminum foil, and submerged in absolute acetic, butyric, and propionic anhydrides (Table 1).

Anhydride	Molecular Weight	Molecular Formula
Acetic anhydride	102.09 g/mol	(CH ₃ CO) ₂ O
Propionic anhydride	130.14 g/mol	(CH ₃ CH ₂ CO) ₂ O
Butyric anhydride	158.19 g/mol	(CH ₃ CH ₂ CH ₂ CO) ₂ O

Table 1. Molecular Weight of Carboxylic Acid Anhydrides

The containers were inserted at the bottom of a vacuum vessel, and the pressure was reduced to 0.7 kPa using a vacuum pump for 20 min. The stopcock to the vacuum pump was closed and then re-opened to allow the anhydrides to enter the glass container within the vacuum vessel until it completely covered the specimens. Air was slowly admitted to neutralize the vacuum vessel back to atmospheric pressure. The glass container was removed, covered, and left for 2 h. The ballast from a specimen was removed when the entire specimen had completely sunk under the anhydrides. The entire specimen was kept submerged under the anhydride for 3 days to maintain a wet and swollen state before reaction.

Modification of rubberwood

The impregnated specimens were transferred to a reactor, then heated with oil in a bath for 0.25 h, 1 h, 4 h, 8 h, 10 h, 15 h, 24 h, 30 h, 36 h, and 48 h at 120 °C. For the longest reaction time, the specimens were inserted at the beginning and other specimens with shorter reaction times were subsequently added as time passed. At the end of the reaction period, the reaction was quenched in ice until the liquid temperature reached 20 °C. The residue was drained off and replaced with acetone, and then the mixture was cooled in ice for 1 h. It was shaken a few times, discharged, and refilled with fresh acetone. This procedure was repeated twice. The modified rubberwood was finally Soxhlet-extracted with a toluene/methanol/acetone mixture (4:1:1) for 8 h and oven-dried at 103 °C for 24 h.

This procedure was sufficient to remove all unreacted acetic anhydride and by-product of acetic acid (Hill and Jones 1999). The dry specimens were cooled, weighed, and measured in the same manner as previously mentioned. The weight percent gain (WPG) was measured and, once the time for levelling-off the WPG was known, another set of specimens were reacted to obtain enough specimens for the decay test. The specimens were then air-dried to a constant weight in a conditioning room at 20 °C and 65% relative humidity. The WPG was calculated by the following formula,

$$WPG(\%) = [(W_m - W_{um}) / W_{um}] \times 100$$
(1)

where WPG is the weight percent gain (%), W_m is the mass of the modified wood (g), and W_{um} is the mass of the unmodified wood (g).

Methods

Fourier transform infrared (FTIR) analysis

The Fourier transform infrared (FTIR) analysis was performed using a Perkin Elmer Spectrum 100 FT-IR spectrometer (PerkinElmer, Shelton, USA). The main function of an FTIR analysis is to determine the chemical functional groups. In this study, an FTIR analysis was used to confirm the bonding of the wood and carboxylic anhydrides. The unmodified and modified wood specimens were shaved prior to the FTIR analysis. The individual specimens were tested consecutively. The infrared spectra of all of the specimens, which represented unmodified and modified with anhydrides, were obtained and evaluated *via* an FTIR analysis.

Decay test

The specimens that were selected for the decay test were the rubberwood that reacted with acetic, propionic, and butyric anhydrides for 0.25 h, 4 h, 10 h, and 24 h, which represented the lowest (5% to 7%), low (10%), medium (11% to 13%), and highest (14% to 16%) WPGs, respectively. Both the untreated and modified rubberwood were leached in water for 14 days according to EN 84 (1997), and then dried and weighed. They were γ irradiated and exposed to brown rot (Coniophora puteana) over 4% malt extract agar in vented 500-mL squat jars in accordance with the procedures in EN 113 (1996). For these purposes, 60 mL of 4% malt agar (40 g L21 Oxoid powdered malt extract, 20 g L21 Oxoid No. 3 agar, deionised water) was dispensed into 500-mL squat jars. These were sealed with vented lids that had non-absorbent cotton wool plugs, and the jars were autoclave sterilised. The C. puteana (FPRL 11E) was allowed to grow on the medium at 22 °C and 65% relative humidity for 2 weeks before exposure to the blocks. The blocks, one reacted and one untreated, were exposed over a sterilised polypropylene mesh in each jar. Twelve replicates were used for each reaction period and anhydride. In addition, similarly sized Scots pine (P. sylvestris) sapwood and European beech (F. sylvatica) blocks were exposed as reference specimens. There were six jars with two blocks in each for the reference specimens. All of the blocks were incubated for 16 weeks in the manner as stated above. At the end of the test, the excessive mycelium was removed, and the moisture content and mass loss due to decay and operational weight loss were determined. The durability classification was then determined by following the guidance given in EN 350-1 (1994), where a ratio, expressed as x, is determined in comparison to the reference species, such as Scots pine or beech, *i.e.* x is the ratio of the average mass loss of the test specimens to the average mass loss of the reference species. In this study, the x values using two different reference species were calculated. The durability classes were assigned according to EN

350-1 (1994), where class 1 (very durable) had an x value less than or equal to 0.15, class 2 (durable) had an x value greater than 0.15 and less than or equal to 0.30, class 3 (moderately durable) had an x value greater than 0.30 and less than or equal to 0.60, class 4 (slightly durable) had an x value greater than 0.60 and less than or equal to 0.90, and class 5 (not durable) had an x value greater than 0.90.

Scanning electron microscopy (SEM)

A thin surface layer from the decayed specimens was cut using a sharp razor-blade to obtain a smooth surface. The selected specimens were then separated into vials and fixed in 4% glutaraldehyde for 2 d at 4 °C. The specimens were then washed with 0.1 M sodium cacodylate buffer three times for 30 min each time, and post fixed in 1% osmium tetroxide for 2 h at 4 °C. The specimens were washed again with 0.1 M sodium cacodylate buffer three times for 30 min each time. The specimens were dehydrated three times with acetone at concentrations of 35%, 50%, 75%, and 95% for 30 min, and lastly at 100% concentration for 1 h. The specimens were critically dried with critical point drying for 30 min and coated with gold using a sputter coater. Scanning electron microscopy (SEM) was performed using a PHILIPS XL30 ESEM (Philips, IL, USA). A total of 34 clear images were selected for comparison purposes. All the results obtain in this study were analysed with analysis of variance (ANOVA), the Waller–Duncan (post hoc test) using SPSS (version 18) for statistical purposes.

RESULTS AND DISCUSSION



Fourier Transform Infrared (FTIR) Analysis

The FTIR spectra of the untreated and modified rubberwood are shown in Fig. 1.

Fig. 1. The FTIR spectra of unmodified and modified rubberwood

It was clear from the FTIR spectra that the unmodified rubberwood had a lower intensity of intermolecular bonded hydroxyl groups at 3339.9 cm⁻¹. The peak intensity of the bonded hydroxyl groups was highest in the butyrylated rubberwood at 3339.0 cm⁻¹,

followed by 3338.6 cm⁻¹ for the propionylated rubberwood and 3338.4 cm⁻¹ for the acetylated rubberwood.

A weak C-H stretching signal appeared at 2900 cm⁻¹ for all spectra. A sharp intensity ester carbonyl vibration appeared in the 1720 cm⁻¹ to 1730 cm⁻¹ region, which confirmed the formation of ester bonds, or esterification. The unmodified rubberwood spectrum had a lower intensity of 1729.7 cm⁻¹ in this region. An increase in the intensity of the C=O bonds occurred for all of the modified woods, with 1729.5 cm⁻¹ for butyrylated rubberwood, 1728.8 cm⁻¹ for acetylated rubberwood, and 1728.5 cm⁻¹ for propionylated rubberwood.

Weight Percent Gain

The WPG was significantly different for the different anhydrides and reaction times (Table 2).

Source	DF	F	Significance		
Anhydride	3	43.327	.000*		
Reaction	2	18.362	.000*		
Anhydride * Reaction	6	.652	.689 ^{NS}		
NS is not significant at P > 0.1, * significant at P < 0.01, DF is the degree of freedom, F is the F ratio					

Table 2. Summary of ANOVA of Weight Percent Gain of Modified Rubberwood

The WPG of the acetylated rubberwood was not significantly different within the 0.25 h to 1 h reaction time range, where it ranged from 7.0% to 7.3% (Fig. 2).



Fig. 2. The averaged WPG of acetylated rubberwood. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.

The WPG significantly increased in the 4 h to 15 h reaction time range, where it ranged from 10.1% to 11.5%. The maximum WPG was obtained for the 24 h reaction (14.0%), and then the WPG significantly decreased for the 30 h to 48 h reactions (11.9% to 12.4%). The same decrease trend for the WPG after prolonged reaction time also

occurred in the older acetylated rattan (*Calamus manan*) in a study done by Hisham and Hale (2012).

The low WPG after the 48 h reaction led to the interpretation that rubberwood was difficult to react with the anhydrides. This difficulty was also noted by Karim *et al.* (2006), in which the acetylated rubberwood obtained a 13% WPG after reaction for 27 h, and an extension of the reaction time for another 94 h and 144 h only increased the WPG to 15% and 16.6%, respectively.

Similarly, the WPG of the propionylated rubberwood was not significantly different within the 0.25 h to 1 h reaction time range, where it ranged from 7.2% to 8.4% (Fig. 3).



Fig. 3. The averaged WPG of propionylated rubberwood. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.

The WPG significantly increased after 4 h, where it ranged from 10.6% to 14.2%, and achieved a maximum value at 24 h. The WPG then significantly declined for the 30 h to 48 h reaction times (10.1% to 11.1%).

In contrast, the averaged WPGs of the butyrylated rubberwood significantly increased in the 0.25 h to 15 h reaction time range, where it ranged from 5.7% to 14.3% (Fig. 4).



Fig. 4. The averaged WPG of butyrylated rubberwood. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.

The maximum WPG was achieved at the 24 h reaction time (16.4%), before it significantly declined for the 30 h to 48 h reactions (12.0% to 13.4%).

It was seen that the reaction rate in terms of WPG was fastest with an increasing chain of anhydride in the ascending order of acetic, propionic, and butyric. The WPGs from 0.25 h to 1 h reaction times were 5.7% to 8.6% for the butyrylated rubberwood, 7.2% to 8.4% for the propionylated rubberwood, and 7.0% to 7.3% for the acetylated rubberwood. The WPGs from the 4 h to 10 h reaction times were 10.7% to 13.6% for the butyrylated rubberwood, 10.6% to 12.2% for propionylated rubberwood, and 10.1% to 11.3% for the acetylated rubberwood. The WPGs from the 15 h to 24 h reaction times were 14.3% to 16.4% for the butyrylated rubberwood, 13.2% to 14.2% for the propionylated rubberwood, and 11.5% to 14.0% for the acetylated rubberwood. This also indicated that the reaction kinetics of the rubberwood increased with a longer chain of anhydrides.

However, when the average of the reaction times was calculated, the reactivity of the rubberwood was not significantly different among the anhydrides. The WPGs were 10.5%, 10.6%, and 11.5% for acetic, propionic, and butyric anhydrides, respectively (Fig. 5).



Fig. 5. The averaged WPG of acetylated rubberwood, propionylated rubberwood, and butyrylated rubberwood. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.

The amount of chemical constituents in each wood species influenced the WPG. Among the structural chemical components, cellulose reacts the fastest with acetic anhydride, followed by hemicellulose and lignin (Rowell 1980, 1982, 1984). Stamm (1964) estimated that only 35% of the OH groups in the amorphous cellulose are accessible for reaction, and the remaining 65% is inaccessible crystalline cellulose. This indicated that the reactivity differs due to plants with monocotyledon or dicotyledon, reaction temperature, time, and procedure. The acetylation of pine wood using a microwave (460 W) gave a maximum WPG of 20% after a 200 min reaction (Larsson and Simonson 1994). The modification of hinoki wood with acetic, propionic, butyric, isobutyric, and hexanoic anhydrides using a conventional heating method had a maximum WPG that ranged from 20% to 40% after reacting at a temperature of 140 °C for 24 h (Li *et al.* 2000). The WPGs of acetylated rattan aged 10 years and 13 years were 14% to 15% after a 24 h reaction (Hisham and Hale 2012). This was probably due to the lower hemicellulose (13% to 14.5%) and lignin (17.3% to 19.4%) contents in rattan compared to wood. In contrast, the rubberwood had 40% of cellulose, 30% of hemicellulose and 22 to 29% of lignin (Thong

and Choh 1994). The mature pine wood that reacted with acetic anhydride had a maximum WPG of 25% after a 7.5 h reaction, while the juvenile pine wood only had 10% WPG after the same reaction time. These studies indicated that the WPG was influenced by the amount of structural chemical components in the wood.

Regardless of the anhydrides, the time for levelling-off the WPG of rubberwood (24 h) was the slowest compared to Sitka spruce (uncatalysed, 2.5 h), which reacted at 120 °C (Minato and Ogura 2003). This can be explained by the kinetic perspective that resulted from the different modification procedures. The kinetics of the reaction depends on the access of the reagent to the reaction site and the real chemical reaction (Minato and Ogura 2003). The maximum WPG of acetylated rattan was 13.4% after a 10 h reaction (Hisham and Hale 2012).

Decay Resistance Against Coniophora puteana

The weight loss of the untreated and modified rubberwood decayed by *C. puteana* is shown in Figs. 6 through 8.



Fig. 6. The figure shows the averaged weight losses of untreated rubberwood and acetylated rubberwood decayed by *C. puteana*. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.



Fig. 7. The figure shows the averaged weight losses of untreated rubberwood and propionylated rubberwood decayed by *C. puteana*. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.



Fig. 8. The figure shows the averaged weight losses of untreated rubberwood and butyrylated rubberwood decayed by *C. puteana*. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.

The weight loss of the untreated rubberwood decayed by *C. puteana* was not much different when exposed with each set of the acetylated rubberwood (26.5% to 41.7%), propionylated rubberwood (21.4% to 23.6%), and butyrylated rubberwood (29.8% to 43.2%).

The weight loss gradually declined with increased reaction time, regardless of the type of anhydride. The weight losses were 19.5% to 2.4%, 20.4% to 6.1%, and 13.1% to 4.5% for acetylated rubberwood, propionylated rubberwood, and butyrylated rubberwood, respectively. In all cases, the acetylated rubberwood had the lowest weight loss after being decayed by *C. puteana* (2.39%).

The reduction of weight loss with increased WPG also occurred for the Corsican pine modified with acetic, propionic, and butyric anhydrides that were decayed by *C*. *puteana* and soft rot in the studies by Papadopoulus and Hill (2002) and Papadopoulos *et al.* (2010), and for the acetylated rattan decayed by *Tinea versicolor*, *C. puteana*, and soft rot in the studies by Hisham and Hale (2012) and Hisham and Hale (2013).

Moisture Content of Modified Rubberwood Decayed by Coniophora puteana

The moisture contents of the untreated rubberwood and rubberwood modified with acetic, propionic, and butyric anhydrides are shown in Figs. 9 through 11.

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Fig. 9. The figure shows the averaged final moisture contents of untreated rubberwood and acetylated rubberwood decayed by *C. puteana*. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.



Fig. 10. The figure shows the averaged final moisture contents of untreated rubberwood and propionylated rubberwood decayed by *C. puteana*. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.



Fig. 11. The averaged final moisture contents of untreated rubberwood and butyrylated rubberwood decayed by *C. puteana*. Figures in the parentheses are standard deviations. Mean values followed by the same letter (s) in the same bar are not significantly different at the 0.05 probability level according to the Duncan test.

The untreated rubberwood took up more moisture than the rubberwood modified with anhydrides. Generally, the moisture uptake ranged from 126.0% to 181.9%, 36.6% to 111.8%, and 89.2% to 174.3% for the acetylated rubberwood, propionylated rubberwood, and butyrylated rubberwood, respectively.

The moisture content ranged from 17.7% to 77.5%, 19.9% to 105.3%, and 27.2% to 47.6% for acetylated rubberwood, propionylated rubberwood, and butyrylated rubberwood, respectively. The low moisture content that followed decay was consistent with the weight loss. The modification with anhydrides retarded the moisture absorption of rubberwood, which increased the decay resistance. The moisture contents at the decay protection threshold against *C. puteana* were 10.7% and 10.1% for acetylated rattan aged 10 years and 13 years, respectively (Hisham and Hale 2012).

Correlation between the Basic Properties and Percent Weight Loss of Decayed Untreated and Modified Rubberwood

The correlation between the basic properties and percent weight loss of the modified rubberwood following decay is shown in Table 3.

	Basic Properties	Weight Loss			
		Coniophora puteana			
Acetylated Rubberwood	Weight percent gain	-0.62**			
	Final moisture content	0.74**			
Propionylated Rubberwood	Weight percent gain	-0.28			
	Final moisture content	0.72**			
Butyrylated Rubberwood	Weigh percent gain	0.00			
	Final moisture content	0.77**			
* Significant at P < 0.01, ** significant at P < 0.001					

Table 3. Summary of the Correlation between the Basic Properties and Percent

 Weight Loss of Decayed Modified Rubberwood

The final moisture content following decay was the only parameter that positively correlated with the percent weight loss. Overall, the strongest correlation was obtained for the butyrylated rubberwood (P = 0.77), followed by acetylated rubberwood (P = 0.74) and propionylated rubberwood (P = 0.72). This correlation trend was consistent with acetylated rattan decayed by C. puteana (Hisham and Hale 2012). Hill et al. (2005) concluded that acetylation reduces decay by reducing the cell wall moisture content. In contrast, Papadopoulus and Hill (2002) and Papodopoulus et al. (2010) proposed that the mechanism for decay protection was due to the blocking of the cell wall microcapillaries, which prevented access of the low molecular weight degradative agents produced by the fungus. In a very detailed discussion by Ringman et al. (2014a) on the mode of action of brown rot decay resistance, it was suggested that moisture exclusion caused by reductions in the wood cell wall void volume was the most essential parameter that delayed the onset of wood decay. Other mechanisms, such as non-recognition of the enzyme, micro pore blocking, and reduced number of free OH-groups, also possibly affect the degradation speed after water uptake is initiated. This was shown in this study because a minor weight loss still occurred in all of the modified rubberwood at low moisture contents after the decaying process, which indicated that the enzymes still recognised the structural chemical organic content, such as hemicellulose and cellulose. Ringman *et al.* (2014b) experimentally established that brown rot enzyme cellulases were able to degrade acetylated wood at a WPG of 22%.

Durability Classes of Untreated Rubberwood and Modified Rubberwood

When Scots pine was used as the reference specimen, almost all of the untreated rubberwood was classified as not durable, moderately durable, or slightly durable against *C. puteana*, except for the propionylated rubberwood and the untreated rubberwood exposed alongside the sample (Table 4).

		Pine		Beech					
		Untre	ated	Modified		Untreated		Modified	
Anhydrides	Reaction	Х	Class	Х	Class	Х	Class	Х	Class
	(h)								
Acetic	0.25	0.45	4	0.26	3	0.61	4	0.35	3
	4	0.56	3	0.13	1	0.76	4	0.18	2
	10	0.43	3	0.08	1	0.57	3	0.11	1
	24	0.30	3	0.04	1	0.41	3	0.06	1
	Average	0.44	3	0.13	1	0.59	3	0.18	2
Propionic	0.25	0.22	2	0.31	3	0.3	3	0.42	3
	4	0.29	2	0.2	2	0.4	3	0.27	2
	10	0.25	2	0.10	1	0.34	3	0.13	1
	24	0.30	2	0.09	1	0.4	3	0.12	1
	Average	0.27	2	0.18	2	0.36	3	0.24	2
Butyric	0.25	1.04	5	0.17	2	0.64	4	0.23	2
	4	0.35	3	0.22	2	0.48	3	0.3	2
	10	0.37	3	0.08	1	0.5	3	0.12	1
	24	0.67	4	0.06	1	0.9	4	0.08	1
	Average	0.61	4	0.13	1	0.63	4	0.18	2
* X values and durability classes of untreated and modified rubberwood using Scots pine and									
beech wood as reference specimens									

Table 4. X Values and Durability Classes of Untreated and Modified Rubberwoods Using Scots Pine and Beech Wood as Reference Specimens

Generally, the acetylated rubberwood, propionylated rubberwood, and butyrylated rubberwood that reacted for 10 h or more was classified as very durable (class 1) against *C. puteana*. When beech wood was used as the reference specimen, all of the untreated rubberwood was classified either as moderately durable or slightly durable against *C. puteana*. For the Scots pine, the acetylated rubberwood, butyrylated rubberwood, and propionylated rubberwood that reacted for 10 h or more was also classified as very durable (class 1) against *C. puteana*. This was achieved at the leveled-off WPG of 14%. The maximum WPG of rubberwood was higher than acetylated rattan, which was 13.5% and 10.3% WPG against *C. puteana* for 10-year-old and 13-year-old rattan, respectively

(Hisham and Hale 2012). The maximum WPG of the rubberwood modified with any anhydride against *C. puteana* was lower than acetylated *Pinus nigra*, *Pinus koraiensis*, and *Larix kaempferi* (18% to 24% WPG), as shown in Table 5.

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Fungus	Wood Species	Threshold [WPG (%)]	References
Coniophora	Corsican pine (<i>Pinus nigra</i>)	24	Forster et al. (1997)
puteana	Corsican pine (<i>Pinus nigra</i>)	18	Hill <i>et al</i> . (2003)
	Korean pine (<i>Pinus koraiensis</i>)	20	Hill <i>et al</i> . (2009)
	Japanese larch (Larix kaempferi)	20	Hill <i>et al</i> . (2009)

Microstructure of Decayed Untreated Rubberwood and Modified Rubberwood

The microstructures of the untreated rubberwood, acetylated rubberwood, propionylated rubberwood, and butyrylated rubberwood decayed by *C. puteana* are shown in Figs. 12 through 14.





Fig. 12. The microstructure of untreated rubberwood and acetylated rubberwood decayed by *C. puteana* (a: transverse, b: longitudinal)



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Fig. 13. The microstructure of untreated rubberwood and propionylated rubberwood decayed by *C. puteana* (a: transverse, b: longitudinal)



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Fig. 14. The microstructure of untreated rubberwood and butyrylated rubberwood decayed by *C. puteana* (a: transverse, b: longitudinal)

In almost all cases, the hyphae penetration was more prominent in the longitudinal direction than in the transverse direction. All of the untreated and modified rubberwood specimens were penetrated by hyphae, even at the highest WPG. This indicated that the fungi hyphae were able to penetrate the wood cells, but access was limited due to the lower moisture content. A lower weight loss recorded even at the highest WPG proved that the fungus enzymes still recognized the structural chemical organic content. These SEM images supported the theory that the decaying process was slowed by lower moisture content. In the DNA and genes expression study by Alfredsen *et al.* (2014), brown rot DNA was present inside the modified wood for up to 36 weeks without any mass loss being recorded, which was also consistent with the SEM images. This study strongly suggested that the low moisture content was the mechanism that slowed the decay process in the modified rubberwood.

CONCLUSIONS

- 1. The rubberwood modified with acetic anhydride had the lowest weight loss after being decayed by *C. puteana*, which was achieved at 14.0% WPG.
- 2. All of the rubberwood modified with acetic, propionic, and butyric anhydrides at the maximum WPG were classified as durability class 1.
- 3. The final moisture content had a positive correlation with the weight loss following decay.
- 4. The SEM observation confirmed that the hyphae penetrated the cells in both the untreated and anhydride modified rubberwood, even at the highest WPG.
- 5. Based on the correlation test and SEM images, this study suggested that the lower moisture content was a mechanism that slowed the decay process in modified rubberwood.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Education, Malaysia for providing the Fundamental Research Grant Scheme.

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Article submitted: January 19, 2017; Peer review completed: March 26, 2017; Revisions accepted: April 20, 2017; Published: May 3, 2017. DOI: 10.15376/biores.12.3.4527-4546