DECAY RESISTANCE OF ESTERIFIED AND OLIGO-ESTERIFIED RUBBERWOOD (*HEVEA BRASILIENSIS*)

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NAGAVENI, H. C., VIJAYALAKSHMI, G. & CHAUHAN, S. S. 2005. **Decay resistance of esterified and oligoesterified rubberwood (*Hevea brasiliensis*)**. Rubberwood samples were chemically modified using a two-step reaction. The wood was esterified with two different dicarboxylic acid anhydrides, namely, maleic anhydride and phthalic anhydride and subsequently treated with epichlorohydrin to obtain oligoesterified wood. The treated wooden blocks were assessed for bio-resistance against white and brown rot fungi. Maleic anhydride alone treated samples showed resistance only for the brown rot attack but failed to protect against the white rot fungi. Except for the maleic anhydride treatment, other treatments showed a weight loss of less than 10%. All these treatments can be taken as effective treatments for rubberwood. However, the best effect was shown in the combination of phthalic anhydride and epichlorohydrin. This technique was found to be promising as an environmental-friendly method to protect rubberwood against decay fungi and to provide dimensional stability required for better uses of timber. This treatment helps to promote the use of low quality timber such as rubberwood, which is a cheaper alternative to primary timber.

Key words: Maleic anhydride – phthalic anhydride – epichlorohydrin – brown rot – white rot

NAGAVENI, H. C., VIJAYALAKSHMI, G. & CHAUHAN, S. S. 2005. **Ketahanan pereputan bagi kayu getah (*Hevea brasiliensis*) yang melalui proses ester dan oligoester.** Sampel kayu getah telah diubah suai secara kimia menggunakan tindak balas dua peringkat. Kayu getah melalui proses ester menggunakan dua asid dikarboksilik anhidrida iaitu maleik anhidrid dan ftalik anhidrid. Kayu ini kemudiannya melalui proses oligoester menggunakan epiklorohidrin. Bongkah kayu yang dirawat dinilai ketahanan biologinya terhadap kulat-kulat reput putih dan perang. Sampel yang dirawat dengan maleik anhidrid sahaja tahan kepada serangan kulat reput perang tetapi tidak kepada serangan kulat reput putih. Semua rawatan menunjukkan kehilangan berat kurang daripada 10% kecuali rawatan dengan maleik anhidrid. Semua rawatan ini boleh dikatakan berkesan untuk melindungi kayu getah. Kesan yang paling baik ditunjukkan oleh rawatan dengan ftalik anhidrid dan epiklorohidrin. Rawatan ini mempunyai harapan menjadi kaedah mesra alam yang dapat melindungi kayu getah daripada kulat reput. Di samping itu, rawatan ini juga dapat menyediakan kestabilan dimensi yang diperlukan untuk penggunaan kayu yang lebih berkesan. Rawatan ini membantu mempromosi penggunaan kayu bermutu rendah seperti kayu getah, suatu pilihan yang lebih murah berbanding kayu utama yang lain.

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Introduction

Chemical modification of wood is one of the well-known methods for protecting the wood against degrading organisms as well as to improve dimensional stability (Eaton & Hale 1993). It involves the reaction of a chemical reagent with hydroxyl groups, the most abundant reactive chemical sites in the wood cell wall polymer, forming a covalent bond between the components. By altering chemical configurations of wood components, enzymes are disabled from degrading the modified holocellulose and lignin, thus leaving physical properties of the material more or less unchanged. The chemical used for modification need not be toxic to the organism because their action renders the substrate unrecognizable as a food source to support microbial growth (Rowell 1984).

Extensive research has been carried out on chemical modification of wood using organic chemicals such as anhydrides, epoxides and isocyanates. However, the research has been carried out on relatively few wood species, mostly softwoods from temperate region.

In the present study, rubberwood (*Hevea brasiliensis*) was used to study effects of chemical modification on its resistance to biodegrading organisms. Plantation-grown rubberwood is assuming importance as a low cost timber for a wide variety of end-uses, substituting primary timbers from natural forests. Rubberwood has a number of advantages over some of the timbers for its favourable woodworking qualities and these timber properties make it suitable for wide applications (Sekhar 1989). However, its potential use has been hampered due to its high susceptibility to fungi and insects.

With the attention focused on the environmental impact of wood preservatives as well as their performance, wood modification is a particularly interesting area of investigation since comparatively less toxic residues are left in the wood after treatment. Chemical modification technique is considered to be a promising environmental-friendly method to protect wood against most of the bio-deteriorating agents (Rowell 1983).

In the present study, rubberwood was modified using a two-step reaction. Firstly, wood was esterified with two different dicarboxylic acid anhydrides, namely, maleic anhydride and phthalic anhydride. These esterified samples were subsequently treated with epichlorohydrin to obtain oligoesterified wood. The modified wood samples, both esterified and oligoesterified, were evaluated for their efficacy against wood decay fungi.

Materials and methods

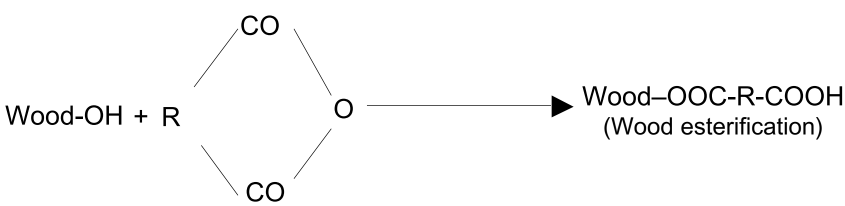
Sample preparation

Rubberwood specimens of size 20 × 20 × 20 mm were prepared from defect-free air-dried wood. Sapwood and heartwood are indistinguishable in rubberwood (Sekhar 1989). Therefore, wood samples were prepared leaving 1.27 cm margin towards both pith and periphery as suggested by Bakshi (1967). Samples were extracted for six hours in toluene:ethanol:acetone mixture (4:1:1 v/v) by Soxhlet extraction to remove extractives present in wood. The extractive-free wood samples were oven dried at 105 °C and the oven-dried weight was measured.

Reaction process

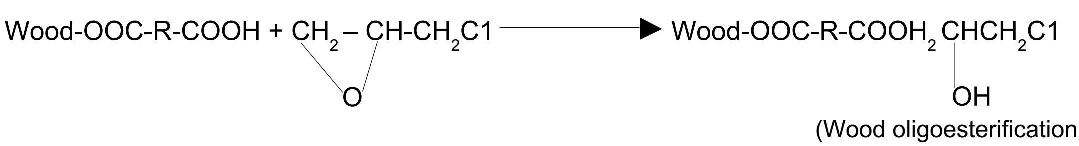
Esterification

Two dicarboxylic acid anhydrides, namely, maleic anhydride and phthalic anhydride were used for esterification. Prior to esterificaton reaction, specimens were soaked in di-methyl formamide (DMF) for half an hour, which has a high swelling ability for wood. The esterification reaction was carried out in a reaction vessel in the presence of DMF as a solvent at 120 °C for four hours. The reaction vessel was equipped with a stirrer, thermometer and condenser. Thirty specimens were treated with each maleic anhydride and phthalic anhydride separately. After the reaction period, test blocks were soaked in acetone to quench the reaction and extracted for six hours in toluene:ethanol:acetone (4:1:1 v/v) to remove unreacted chemicals. Extracted specimens were oven dried at 105 °C and then weighed to calculate the loading of chemical. The reaction resulted in the esterified wood bearing carboxyl groups as shown below.



Oligoesterification

Maleic anhydride and phthalic anhydride treated blocks (fifteen blocks from each treatment) were further reacted with epichlorohydrin (double the volume of wood) for two hours in a reaction vessel at 120 °C separately to obtain oligoesterified wood as shown below.



After the reaction period, blocks were soaked in acetone to quench the reaction and extracted for six hours in toluene:ethanol:acetone (4:1:1 v/v) to remove unreacted chemicals. Extracted specimens were oven dried and then weighed to obtain the loading of chemicals.

The weight percentage gain (WPG) for wood blocks were calculated after each treatment.

In total, there were four treatment combinations as follows:

1. Treatment with maleic anhydride only (MA)
2. Treatment with phthalic anhydride only (PA)
3. Treatment with MA + Epichlorohydrin (MA + EpCl)
4. Treatment with PA + Epichlorohydrin (PA + EpCl)

Fungal resistance test

The fungal resistance of treated blocks was tested as per Indian test standard IS 4873 (Anonymous 1968) using *Coriolus versicolor* (white rot fungi) and *Polyporous meliae* (brown rot fungi) in culture bottles. Six matched replicates were taken from each treatment and for each fungus. Untreated blocks were taken as controls. Treated and control test blocks were kept for conditioning in incubators at 70% relative humidity and 24 °C to attain constant weight (W1) and then these blocks were subjected to accelerated laboratory test using the malt agar method (Anonymous 1968).

After 16 weeks, the test blocks were withdrawn from the culture bottles. Fungal mats were carefully brushed off and individual blocks were weighed (W2) to find out the moisture content and dried using hot air blower and again conditioned and weighed to obtain constant weight (W3). After recording W3, the exposed samples were oven dried at 105 °C and weighed (W4) to obtain the moisture content in the samples after exposure. Weight loss and moisture content in samples after fungal exposure was calculated as follows:

$$\text{Weight loss (\%)} = \frac{W3 - W1}{W1} \times 100$$

$$\text{Moisture content (\%)} = \frac{W2 - W4}{W4} \times 100$$

Statistical analysis

One-way ANOVA was performed on weight loss data to determine significant differences between treatments within the individual fungus ($p = 0.05$).

Results and discussion

Esterification and oligoesterification reactions

Treatment with anhydrides resulted in average WPG of 16–18% (Table 1). Further reaction of the esterified treated blocks with epichlorohydrin resulted in addition of 15% weight gain with maleic anhydride treated samples and about 7% weight gain with phthalic anhydride treated samples. Since unreacted chemicals from treated blocks were extracted after treatment, the increase in weight of samples after treatment indicated the evidence of chemical reactions. The chemical reactions of maleic anhydride and phthalic anhydride with rubberwood were also demonstrated and characterized by FTIR spectroscopy (Chauhan *et al.* 1998).

Decay resistance

White rot is generally more virulent than brown rot fungi in hardwood species (Eaton & Hale 1993) and their relative virulence in rubberwood is not exceptional. In untreated blocks (Table 2), weight loss of up to 70% was observed in samples exposed to white rot (*C. versicolor*) as compared with 40% in samples exposed to brown rot fungus (*P. meliae*).

Among the esterified wood, MA treatment had given significant protection against brown rot with weight loss of about 7%. However, MA treatment failed to protect wood against the white rotter with average weight loss of 36%. In comparison, esterification by phthalic anhydride offered acceptable protection against both brown and white rotters with weight losses of less than 8%.

It has been reported that when rubberwood is reacted with dicarboxylic acid anhydrides, hydrophilic hydroxyl groups associated with cell wall polymers, mainly cellulose and hemicellulose, are replaced by the hydrophobic ester bonds (Chauhan *et al.* 2001). These ester bonds result in considerable reduction in the hygroscopicity of wood. The fibre saturation point in the modified rubberwood

Table 1 Weight percentage gain in esterified and oligoesterified rubberwood

Treatment	% Weight gain[a]	Standard deviation
Maleic anhydride	16.07	2.16
Phthalic anhydride	18.09	1.98
Maleic anhydride + Epichlorohydrin	31.58	3.24
Phthalic anhydride + Epichlorohydrin	25.55	3.23

[a]Average of 15 replications

Table 2 Weight loss (%) in esterified and oligoesterified rubberwood against wood decay

Treatment	*Coriolus versicolor*	Standard deviation	*Polyporous meliae*	Standard deviation
Maleic anhydride	36.04 b	3.58	7.09 b	0.84
Phthalic anhydride	8.27 a	0.7	8.34 b	2.44
Maleic anhydride + Epichlorohydrin	7.61 a	1.19	7.01 b	2.02
Phthalic anhydride + Epichlorohydrin	7.52 a	1.88	5.15 a	2.89
Control	70.88 c	10.53	40.69c	2.78

Values in the same column followed by the same letter are not significantly different ($p < 0.05$).

was reported to be about 30% less as compared with that of untreated wood (Chauhan *et al.* 1998). The extent of modification was further demonstrated by Chauhan *et al.* 2001 using FTIR spectroscopy where reduction in the intensity of O-H stretching vibration accompanied by enhancement in intensity of C=O and C-O band, provides the evidence for chemical reaction between anhydride and hydroxyl groups associated with wood cell polymers. The efficiency of chemical reaction of rubberwood by both maleic and phthalic anhydrides was reported to be in the similar range (Chauhan *et al.* 2001). Since brown rot fungi destroys mainly cellulose and hemicellulose fractions without excessively depleting lignin, with chemical modification of the cell wall constituents, mainly cellulose and hemicellulose, and reduction in hygroscopicity would have inhibited the decay process by brown rot fungi in the case of maleic and phthalic anhydrides.

However, white rotter degrades lignin together with holocellulose simultaneously. During the decay process, fungi utilize wood as a carbon source and produce carbon dioxide and water as by-products. In the case of wood modified with dicarboxylic acid anhydrides, with the increase in water in wood, partial de-esterification takes place due to hydrolysis of the monoesters attached to polysaccharides and thus results in the cleavage of ester linkages. Among the two anhydrides, hydrophobicity of phthalic anhydride treatment is superior to the maleic anhydride treatment, as indicated by the water-adsorption and absorption studies (Matsuda 1987, Chauhan *et al.* 1998). In the case of maleic anhydride treatment, the ester bonds are not very stable and de-esterification takes place when exposed to high humidity or moisture. The de-esterification creates new moisture adsorption sites and also releases corresponding dicarboxylic acids which contribute to the hygroscopicity of wood. As a result of de-esterification, increase of moisture content in the maleic anhydride treated wood could be noted (Table 3), resulting in decay and further weight loss of wood samples. The differences in

Table 3 Moisture content (%) of esterified and oligoesterified rubberwood samples after exposure to decay fungus

Treatments	*Coriolus versicolor*	Standard deviation	*Polyporous meliae*	Standard deviation
Maleic anhydride	33.13	2.32	19.2	1.34
Phthalic anhydride	14.46	0.77	15.62	0.28
Maleic anhydride + Epichlorohydrin	15.97	0.9	15.42	2.55
Phthalic anhydride + Epichlorohydrin	13.38	0.66	14.21	2.41
Control	51.03	3.1	43.4	1.02

molecular geometry, i.e. the aromatic nature of phthalic anhydride and the aliphatic nature of maleic anhydride, could also have resulted in differences in the decay activity by white rot.

In the case of oligoesterified blocks, the virulence of both fungi reduced drastically to less than 10% irrespective of initial esterification reagents (Table 2). The effect of combined treatment of anhydrides and epichlorohydrin has resulted in discernibly high protection against wood rotters. Matsuda *et al.* (1988) had demonstrated that the dimensional stability markedly improves by adding epichlorohydrin to the carboxyl groups bearing esterified wood. The use of epichlorohydrin in addition to anhydrides (oligoesterification) has resulted in the blocking effect by replacing carboxyl group with more stable hydrophobic ester linkage and also in the bulking effect of epichlorohydrin.

Treated wood blocks, which showed less than 10% of weight loss can be considered as an effective treatment and this treated wood can be grouped under high resistance class (Bakshi 1967). This classification of resistance is only for comparison with the natural resistance of durable species as per ASTM (Anonymous 1981) and Bakshi (1967). Except for the maleic anhydride treatment, other treatments had shown weight losses of less than 10%. All these treatments could be taken as effective treatments for rubberwood. The effect of combined treatment of anhydrides and epichlorohydrin had resulted in providing good resistance against both wood rotters. The best effect was shown with the combination of phthalic anhydride and epichlorohydrin.

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References

Anonymous. 1968. *IS 4873. Methods for Laboratory Testing of Wood Preservatives Against Fungi.* Bureau of Indian Standards, New Delhi.

Anonymous. 1981. *D 2017-81. Standard Method of Accelerated Laboratory Test of Natural Decay Resistance of Woods.* American Society for Testing and Material, Philadelphia.

Bakshi, B. K. 1967. *Accelerated Laboratory Investigation on Durability of Wood.* Final technical report. FRI & Colleges, Dehradun.

Chauhan, S. S., Ajay Karmakar & Pandey, K. K. 1998. Dimensional stabilisation of rubber wood by chemical modification. Pp. 164–168 in *Proceedings of the National Seminar on Processing and Utilisation of Plantation Timbers and Bamboo.* 23–24 July 1998. Bangalore.

Chauhan, S. S., Aggarwal, P., Karmakar, A. & Pandey, K. K. 2001. Moisture adsorption behaviour of esterified rubber wood (*Hevea brasiliensis*). *Holz als Roh- und werkstoff* 59: 250–253.

Eaton, R. A. & Hale, M. D. C. 1993. *Wood Decay, Pests and Protection.* Chapman & Hall, London.

Matsuda, H. 1987. Preparation and utilisation of esterified wood bearing carboxyl groups. *Wood Science and Technology* 21: 75–88.

Matsuda, H., Ueda, M. & Murakami, K.1988. Oligoesterified woods based on anhydride and epoxide 1. Preparation and dimensional stability of oligoesterified woods by stepwise addition reaction. *Mokuzai Gakkaishi* 34(2): 140–148.

Rowell, R. M. 1983. Chemical modification of wood. *Forest Products Abstracts* 6(12): 363–382.

Rowell, R. M. 1984. Penetration and reactivity of cell wall components. Pp. 177 in Rowell, R. M. (Ed.) *The Chemistry of Solid Wood.* American Chemical Society, Washington DC.

Sekhar, A. C. 1989. *Rubber Wood Production and Utilization.* Rubber Research Institute of India, Kottayam.