

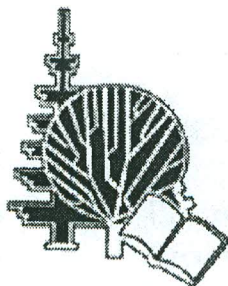
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DIMENSIONAL STABILITY AND DECAY RESISTANCE AGAINST *CONIOPHORA PUTEANA* OF SCOTS PINE SAPWOOD DUE TO REACTION WITH PROPIONIC ANHYDRIDE

G. A. Ntalos, A. N. Papadopoulos, S. P. Karastergiou, G. I. Mantanis, J. A. Kakaras

Technological Educational Institute of Karditsa, Department of Wood and Furniture

Abstract: The purpose of this paper is to show the effects of level of substitution with a linear chain anhydride (propionic anhydride) on dimensional stability and decay resistance of modified Scots pine sapwood. The work described herein has demonstrated that chemically modified Scots pine sapwood with propionic anhydride afforded substantial bioprotection against *Coniophora puteana*. It required a weight gain of approximately 16-18% following reaction to ensure complete protection. The dimensional stability of propionic anhydride modified wood was greatly improved.

Key words: Chemical modification, propionic anhydride, dimensional stability, decay resistance, *Coniophora puteana*, Scots pine

INTRODUCTION

Two goals of chemical modification of wood are to improve dimensional stability and decay resistance. Various chemical modification reactions have been studied for these purposes (Rowell, 1983). Acetylation is the most studied area of wood modification. For example, Stamm, Tarkow (1947), measured the equilibrium moisture content (e.m.c) of unreacted and vapour phase acetylated (30% acetyl content) Sitka spruce at various humidities and found a 67% reduction in water sorbed at 95% relative humidity. Peterson, Thomas (1978), acetylated loblolly pine, green ash and yellow poplar using acetic anhydride in xylene. The modified samples were tested against the brown rot fungus *G. trabeum* and the white rot fungus *Coriolus versicolor*. It was found that the white rot was generally easier to control than the brown rot, with levels of acetylation as low as 7% being able to provide protection.

Although of all the methods investigated, modification using acetic anhydride has received by far the most attention, there have been a number of papers published concerning modification of wood with other linear chain anhydrides (Rugevista, Embrehsha, 1988; Hill and Jones, 1996; Hill, Papadopoulos, 2002). Stamm, Tarkow (1947), reported that they propionylated and butyrylated whole wood and veneer, using pyridine as a catalyst, in the vapour or liquid phase using the corresponding anhydrides. It was reported that modified samples showed no sign of decay after three months exposure to *Poria versicolor*, whereas the unmodified samples showed weight losses of up to 50%. Suttie et al. (1999), modified Scots pine with acetic, propionic, butyric, or hexanoic anhydrides and determined decay resistance against the brown rot fungi *Coniophora puteana*, *Gloeophyllum trabeum*, *Poria placenta* and a white rot fungus (*Coriolus versicolor*) using European Standard method EN113 and a vermiculite overlay method. Resistance to soft rot attack

was also determined using a modified ENV 807 stake test in unsterile soil. The effect of different levels of reaction upon decay resistance was only tested with the soft rot experiment. In this, it was found that a threshold of *ca.* 23% was required to ensure protection, regardless of the anhydride used.

The purpose of this paper is to show the effects of level of substitution on dimensional stability and decay resistance of a linear chain anhydride (propionic anhydride) modified Scots pine sapwood. The reaction between wood and propionic anhydride is a single site reaction as depicted in figure 1 and yields the corresponding carboxylic acid (propionic acid) as a by-product of its reaction with wood.

MATERIALS AND METHODS

Chemical modification of wood samples

Scots pine (*Pinus sylvestris*) sapwood samples of dimension 20 mm x 20 mm x 5 mm (radial x tangential x longitudinal) were cut from freshly felled kiln dried logs. Samples were carefully sanded to remove loosely adhering fibres, then placed in a Soxhlet extractor for solvent extraction using toluene/methanol/acetone (4:1:1 by volume) for eight hours. Samples were dried in an oven for eight hours at 105°C. Prior to weighing (four figure balance), samples were transferred to a vacuum desiccator and allowed to cool to ambient temperature over silica gel. Weighed samples (W_1), were vacuum impregnated with pyridine for one hour then transferred to a flask containing pyridine set in an oil bath at 100°C. Pyridine swells the wood and acts as a catalyst for the modification reaction. Samples were allowed to equilibrate in the hot pyridine for one hour. Sets of hot samples (twenty eight replicates) were added to a flask containing a one molar solution of the propionic anhydride in pyridine set in an oil bath at 100°C for a specific length of time to achieve the desired level of modification. At the end of the reaction period, the flask was removed from the oil bath, the hot reagent decanted off and ice cold acetone added to quench the reaction. Samples were allowed to sit in the acetone for one hour before being transferred to the Soxhlet apparatus for solvent extraction as detailed previously. Samples were re-weighed (W_2) after oven drying as detailed previously. Samples were free of reagent, by-product and pyridine after this procedure.

The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of the sample before modification (W_1) and after modification (W_2) according to equation (Weight percent gain (WPG) = $(W_2 - W_1) / W_1 \times 100$).

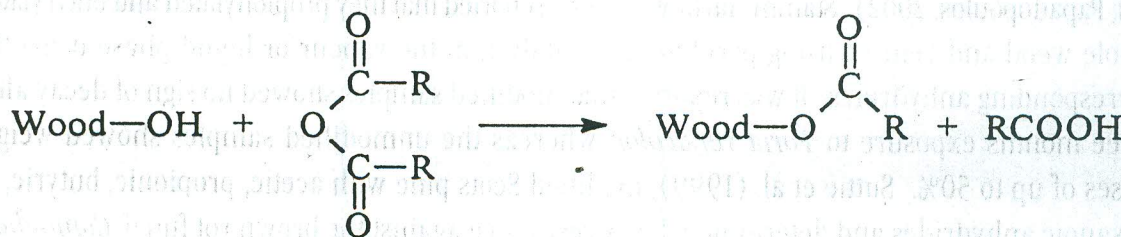


Fig. 1. Reaction of wood with propionic anhydride (R= C₂H₅, propionic anhydride)

Decay tests

Samples were packed in an argon atmosphere and sterilised by irradiation (2.5 mrad) prior to decay tests. Each set of 16 modified and unmodified control samples at each level of treatment were subdivided into four groups of four replicates. Laboratory pure strains of the brown rot fungi *Coniophora puteana* (No FPRL 11E) were used, grown on malt agar. Four unmodified control or modified wood samples were planted on sterile specimen supports placed on the cultures of the test fungus actively growing on 5% malt agar in 500ml capacity jars (EN 113, 1996; the only modification was the sample size, see 2.1). An additional set of sterile control samples were used to assess operational control losses. The closed jars were incubated for 16 weeks, at 22 +/- 1°C and 75 +/- 5% relative humidity to evaluate the efficacy of the treatments. After incubation, the samples were removed from the jars, cleaned, dried overnight at 105°C and weighed. Weight loss was expressed as a percentage of the initial oven dried weight of the sample. Weight losses from sterile controls were subtracted from the decay results to give corrected data.

Equilibrium moisture content

The method for controlling relative humidity as described by Stamm (1964), has been widely used and was selected for being simple, economical and reasonably precise. Test samples were kept above saturated solutions of various salts in containers stored in a controlled temperature room set at 20°C (variation +/- 1°C). Pure water results in the saturated vapour pressure corresponding to 100% relative humidity. The addition of a solute to water reduces its vapour pressure in proportion to its mole fraction in the case of diluted solutions. When a saturated solution at a controlled temperature is used, a constant relative humidity is maintained (Siau, 1996).

Six salts were chosen and these are listed in Table 1, along with the relative humidity of the atmosphere above each saturated solution at 20°C (according to Kaye, Laby, 1966). They were chosen on the basis of giving minimum relative humidity variation with changes in the temperature (Stamm, 1964). Excess salt was always present within each solution to ensure saturation was maintained. The solution and air in the container were agitated by bubbling air through the solution.

The oven dry wood samples (two replicates) were placed in the containers above saturated salt solutions. They were left to equilibrate for 4 weeks and then weighed once a week, using a four-place analytical balance until it became obvious that no significant weight change had occurred since the last weight was recorded (and e.m.c had been attained). Equilibrium moisture content (e.m.c) was reached within 6 weeks for all but the two highest humidities, which required longer exposure times.

RESULTS AND DISCUSSION

Decay resistance of modified wood

Chemical modification of wood with propionic anhydride afforded substantial bioprotection of Scots pine against *Coniophora puteana* (Table 2). The data were plotted and the fit shown by

Table 1
Saturated salt solutions used and their resultant relative humidities at 20 °C

Salt	Relative humidity (%)
Potassium nitrate (KNO ₃)	93
Sodium chloride (NaCl)	76
Sodium dichromate (Na ₂ Cr ₂ O ₇)	55
Potassium carbonate (K ₂ CO ₃)	44
Potassium acetate (CH ₃ COOK)	23
Lithium chloride (LiCl)	12

Table 2
Weight percent gain (WPG) and weight losses of Scots pine sapwood modified with propionic anhydride. (Standard deviation in parentheses)

Treatment	Reaction Time (min)	WPG (%)	Weight Loss (%)
Control	0	0	64.35 (2.5)
Propionic	45	5.6 (0.3)	41.08 (8.3)
	105	14.8 (0.2)	3.65 (2.3)
	300	20.5 (0.7)	1.52 (0.4)
	420	25.4 (0.4)	1.06 (0.3)

linear regression analysis indicates a positive relationship between extent of modification and decay resistance ($R^2 = 0.88$). Threshold value of protection of propionic anhydride was 17%; it is suggested therefore that a WPG of approximately 17% is required following reaction to ensure complete protection. Earlier soil block decay tests by Goldstein et al. (1961) and Peterson, Thomas (1978), showed adequate decay resistance against brown rot fungi in wood treated with acetic anhydride to 17%, whereas Forster (1998) reported a higher value (24%). Soft rot soil bed tests by Suttie et al. (1998), showed that a value of approximately 23% is required to ensure complete protection of wood treated with the series of anhydrides used in the present study against *C. puteana*.

Dimensional stability of modified wood

The e.m.cs at various levels of relative humidity for Scots pine sapwood modified with propionic anhydride are presented in Table 3. Table 3 indicates an obvious trend of reducing hygroscopicity with increasing WPG; this is true for the whole range of relative humidity. This is in agreement with the results reported earlier on various lignocellulosic fibres modified with acetic anhydride (Rowell and Rowell, 1989).

Table 3

Mean values for experimentally derived e.m.cs at various levels of relative humidity for Scots pine sapwood modified with propionic anhydride. (Standard deviation in parentheses)

Reagent	WPG(%)	EMC (%)					
		12	23	44	55	76	93
Control	0	2.33 (.05)	4.19 (.09)	7.02 (.02)	8.38 (.09)	12.68 (.19)	18.95 (.28)
Propionic	6.1	2.01 (.08)	3.45 (.08)	5.62 (.14)	6.88 (.05)	10.45 (.05)	15.62 (.24)
	10.9	1.81 (.08)	2.71 (.09)	5.19 (.05)	6.15 (.14)	9.33 (.14)	13.86 (.15)
	15.6	1.33 (.05)	2.1 (.12)	4.05 (.14)	5.01 (.15)	7.62 (.12)	12.01 (.18)
	19.7	1.19 (.09)	2.11 (.05)	3.32 (.09)	4.01 (.11)	6.55 (.08)	9.98 (.15)
	24.5	0.9 (.12)	1.62 (.05)	2.77 (.15)	3.65 (.05)	5.71 (.08)	9.42 (.12)

CONCLUSIONS

The work described herein has demonstrated that chemically modified Scots pine sapwood with propionic anhydride afforded substantial bioprotection against *Coniophora puteana*. It required a weight gain of approximately 16-18% following reaction to ensure complete protection. The dimensional stability of propionic anhydride modified wood was greatly improved.

REFERENCES

- EN 113 Wood Preservatives.1996. Determination of the toxic values against wood destroying Basidiomycetes cultured on an agar medium. British Standards Institution.
- Forster, S. 1998. Decay resistance of modified softwood. Ph.D thesis. University of Wales, Bangor.
- Goldstein, I.S., Jeroski, E.B., Lund, A.E., Nielson, J.F., Weaver, J.W. 1961. Acetylation of wood in lumber thickness. *Forest Products J.* 11(8), 363-370.
- Hill, C.A.S., Jones, D. 1996. The dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. *Holzforschung* 50(5), 457-462.
- Hill, C.A.S, Papadopoulos, A.N. 2002. The pyridine catalysed acylation of sapwood and phenolic model compounds with carboxylic acid anhydrides. Determination of activation energies and entropy of activation. *Holzforschung* 56(2), 150-156.
- Kaye, G.W.C., Laby, T.H. 1966. Tables of physical and chemicals constants and some mathematical functions. Longmans.
- Peterson, M.D., Thomas, R.J. 1978. Protection of wood from decay fungi by acetylation. An ultrastructural study. *Wood and Fiber* 10(3), 149-163.
- Rowell, R.M. 1983. Chemical modification of wood. *Forest Products Abstracts.* 6(12), 366-382.
- Rowell, R.M., Rowell, J.S. 1989. Moisture sorption properties of acetylated lignocellulosic fibres. In: *Proceedings of the 10th cellulose conference.* (C. Schuerch, ed.). John Wiley and Sons, New York, 343-355.
- Rugevista, A.A., Embreksha, A.E. 1988. Modification of wood with acylating agents and polyethylene glycol. *Trudy-Latviiskoi-Selskokhozyaistvennoi-Akad.* 253, 39-44.
- Siau, J.F. 1996. Wood: influence of moisture on physical properties. Department of Wood Science and Forest Products, Virginia Polytechnic Institute and State University.
- Stamm, A.J. 1964. *Wood and Cellulose Science.* New York: The Ronald Press.

Stamm, A.J., Tarkow, H. 1947. Dimensional stabilisation of wood. *J. of Colloid Chemistry* 51, 493-505.

Suttie, E.D., Hill, C.A.S, Jones, D., Orsler R.J. 1999. Chemically modified solid wood. I. Resistance to fungal attack. *Material und Organismen* 32(3), 159-182.

E-mail gntalos@teilar.gr