Holz Roh Werkst (2008) 66: 249–252
DOI 10.1007/s00107-008-0252-6

ORIGINALARBEITEN · ORIGINALS

The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against the subterranean termites *Reticulitermes flavipes*

Antonios N. Papadopoulos · Dimitrios N. Avtzis · Nikolaos D. Avtzis

Published online: 19 June 2008

Abstract The work described in this paper has demonstrated that chemically modified Corsican pine sapwood with a homologous series of linear chain carboxylic acid anhydrides provided bioprotection against the subterranean termites *Reticulitermes flavipes*. By varying the reaction time, various levels of modifications were obtained. There was no significant reduction in feeding above 16% WPG (weight percent gain due to modification), suggesting that modification to WPGs greater than this did not offer additional protection. The type of anhydride employed has little influence on resistance against termites.

Biologische Wirksamkeit einer Behandlung von Holz mit unverzweigten Carbonsäureanhydriden gegen den Befall durch die Bodentermite *Reticulitermes flavipes*

Zusammenfassung In dieser Studie wird gezeigt, dass korsisches Kiefernsplintholz, das mit einer homologen Reihe unverzweigter Carbonsäureanhydride behandelt wurde, einen Schutz gegen die Bodentermite *Reticulitermes flavipes* bietet. Unterschiedliche Einwirkzeiten ergaben eine unterschiedliche Wirksamkeit der Behandlung. Ab einer Einbringmenge über 16% (Massezunahme, WPG) reduzierte sich der Befall nicht signifikant. Dies lässt darauf schließen, dass eine höhere Einbringmenge keinen erhöhten Schutz bietet. Die Art des verwendeten Anhydrids hat dabei keinen nennenswerten Einfluss auf die Termitenresistenz.

A. N. Papadopoulos (✉) · N. D. Avtzis
Technological Educational Institute of Kavala, Branch of Drama,
Department of Forestry and Management of Natural Environment,
Laboratory of Wood and Wood Products,
1o km Dramas – Mikrochriou,
TK 66100 Drama, Greece
e-mail: antonios1974@hotmail.com, antpap@teikav.edu.gr

D. N. Avtzis
Institute of Forest Entomology, Forest Pathology and Forest Protection, Department of Forest and Soil Sciences, BOKU,
University of Natural Resources and Applied Life Sciences,
Hasenauerstrasse 38,
1190 Vienna, Austria

1 Introduction

It is well established that the chemical modification of wood is able to provide protection against fungal attack (Rowell 1983, Hon 1996). A chemical modification reaction involves the formation of a chemical bond between a reagent and the cell wall polymers of wood. In almost all cases, this reaction occurs between some of the hydroxyl groups of these polymers and the reagent molecules. Such a reaction leads to a change in the chemical and physical properties of the substrate. For example, the acetylation of wood results in the substitution of hydrophilic hydroxyl groups with hydrophobic acetyl groups. Many studies have been performed and reviewed investigating the biological degradation resistance of acetylated wood to fungi and (Papadopoulos and Hill 2002). In this paper, the protection of Corsican pine sapwood modified to a range of WPGs with various linear chain anhydrides against attack by the subterranean termites *Reticulitermes flavipes* is described.

2 Experimental

2.1 Chemical modification of wood

The chemical modification of Corsican pine (*Pinus nigra* Schneid) sapwood samples with a homologous series of linear chain carboxylic acid anhydrides (acetic, propionic, butyric and valeric) has been fully described in previous publications (Papadopoulos and Hill 2002, Papadopoulos et al. 2008). The reaction time was varied (see Table 1) in order to achieve equivalent levels of modification (Papadopoulos 2001).

The extent of reaction was calculated as weight percent gain (WPG) determined by the differences between oven dry weight of the sample prior to modification (W_1) and after modification (W_2) according to the equation

$$[\text{Weight percent gain (WPG)} = (W_2 - W_1)/W_1 \times 100] .$$

The number of hydroxyl groups per gram of wood that are substituted when reacted with the corresponding anhydride can be calculated as follows:

$$\text{OH substd. (mmoles/gm)} = \frac{\text{Wmod.} - \text{Wunmod.}}{\text{Wunmod.} \times M_\text{w}} \times 1000$$

where:

Wmod. is the dry weight of modified wood

Wunmod. is the dry weight of unmodified wood

M_w is the molecular weight of the adduct -C(O)-R.

2.2 Termite test

Subterranean termites *Reticulitermes flavipes* were used for the termite bioassay. The modified samples of the dimension 2 cm × 2 cm × 0.5 cm (radial × tangential × longitudinal) were cut to the final dimension of 1 cm × 1 cm × 0.5 cm, prior to being subjected to a termite bioassay according to a no-choice test procedure (ASTM 1998). The only modification of the ASTM procedure was the sample thickness which was chosen to be 0.5 cm instead of 1 cm. Each wood sample was placed in a lidded test dish with 50 g sand, 8.5 mL deionised water and 1 g termites. The dishes were incubated at 27 °C and 80% relative humidity and examined after one and four weeks for evidence of tunnelling and termite mortality. After four weeks, the samples were removed from the dishes, cleaned, dried, conditioned and weighed to determine mass loss. A visual rating of the attack was recorded for each sample.

Table 1 Weight percent gain (WPG) of oven dried Corsican pine samples after reaction with a homologous series of linear chain carboxylic acid anhydrides (Standard deviation in parentheses)
Tabelle 1 Einbringmenge (Massezunahme, WPG) in darrtrockene korsische Kiefernproben in Abhängigkeit der Einwirkungsdauer einer homologen Reihe unverzweigter Carbonsäureanhydride (Standardabweichungen in Klammern)

Anhydride	Reaction Time (min)	WPG[a] (%)
Acetic	45	7.5 (0.3)
Acetic	140	16.6 (0.1)
Acetic	300	24.1 (0.4)
Acetic	420	31 (0.3)
Propionic	120	16.2 (0.2)
Butyric	130	15.8 (0.3)
Valeric	120	16.5 (0.3)

[a] Each value represents the mean of five replicates

3 Results and discussion

Figure1 depicts the mass loss (%) of the modified wood samples caused by *R. flavipes*. It can be observed that the highest mass loss was recorded for the untreated control samples (43.7%) and for samples modified with acetic anhydride (31.5%) at the lowest modification level (7.5%). The control samples were severely attacked, whereas the samples modified with acetic anhydride at the lowest modification level showed heavy attack. Wood samples modified at higher WPGs showed light attack.

Visual observation revealed that wood samples modified above 7.5% WPG showed slight decay, whereas the samples modified with acetic anhydride at 7.5% level of modification showed severe decay. On the other hand, the control samples showed mass loss.

As Fig. 1 depicts, chemical modification of wood with anhydrides resulted in improved termite resistance. Wood modified with acetic anhydride at 24.1% WPG showed the greatest resistance. As statistical analysis revealed, there was no significant reduction in mass loss above approxi-

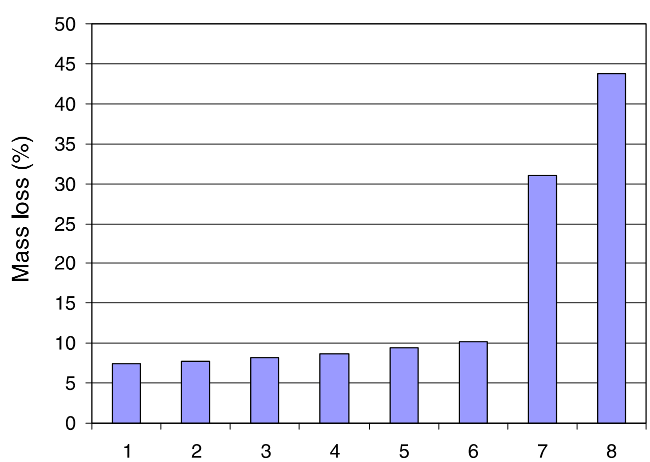

Fig. 1 Mass loss (%) by *Reticulitermes flavipes* of control and chemically modified wood (1: Acetic anhydride 24.1%, 2: Acetic anhydride: 31%, 3: Valeric anhydride 16.5%, 4: Propionic anhydride 16.2%, 5: Acetic anhydride 16.6%, 6: Butyric anhydride 15.8%, 7: Acetic anhydride 7.5%, 8: Unmodified wood)
Abb. 1 Masseverlust (%) chemisch behandelter Holzproben und einer Kontrollprobe infolge des Befalls durch die Bodentermite *Reticulitermes flavipes* (1: Essigsäureanhydrid 24,1 %, 2: Essigsäureanhydrid 31 %, 3: Valeriansäureanhydrid 16,5 %, 4: Propionsäureanhydrid 16,2 %, 5: Essigsäureanhydrid 16,6 %, 6: Buttersäureanhydrid 15,8 %, 7: Essigsäureanhydrid 7,5 %, 8: unbehandeltes Holz)

mately 16% suggesting that modification to WPGs greater than this did not provide additional protection.

The type of anhydride employed has little influence on feeding, since similar numbers of mass loss were recorded caused by *R. flavipes*. This is inline with the observation made earlier regarding the effect of the anhydride type on the decay resistance of modified softwood against brown and white rot fungi (Forster 1998, Papadopoulos and Hill 2002, Papadopoulos et al. 2002, Papadopoulos and Hill 2003) and the attack by the marine wood borer *Limnoria quadripunctata* Holthius (Papadopoulos et al. 2008).

This laboratory has extensively studied some key properties (sorption of water vapour, decay resistance against brown and white rot and resistance against wood borers) of wood modified with a series of linear chain carboxylic acid anhydrides. Wood samples were chemically modified with a series of anhydrides at equivalent levels of modification under identical conditions. An important target of this project was to determine the primary factor controlling these key properties. The following two options were offered: (i) the degree of cell wall bulking by the bonded adduct and (ii) the extent of hydroxyl substitution.

The results from this study indicate that the degree of cell wall bulking caused by the adduct, rather than the extent of hydroxyl substitution is the primary factor controlling the resistance against termites, since similar mass losses were found for wood modified with four different anhydrides at equivalent levels of modification (acetic 16.6%, propionic 16.2%, butyric 15.8% and valeric 16.5%). This was also the case for sorption of water vapour and resistance against decay and marine borers (Papadopoulos and Hill 2002, Papadopoulos and Hill 2003, Papadopoulos et al. 2008). This is illustrated more clearly in Table 2. It can been seen for example, that at a hypothetical 15% weight gain, 3.48 mmoles of OH groups per gram of wood are substituted when reacted with acetic anhydride, but only 1.76 mmoles of OH groups per gram when reacted with valeric anhydride (Papadopoulos 2001). Despite the large difference in the OH substitution level, reaction with different anhydrides results in the same level of protection against decay, marine borers and termites and in the same level of water vapour sorption. These observations suggest that the mechanism of protection is not of chemical/biochemical origin, but relates to the bulking of the cell wall by the reacted adduct.

Table 2 Molecular weight of the anhydrides used in this study
Tabelle 2 Molekulargewicht der verwendeten Anhydride

Anhydride	Molecular weight	WPG (%)	OH Groups Substd.
Acetic	43	15	3.48
Propionic	57	15	2.62
Butyric	71	15	2.11
Valeric	85	15	1.76

However, from the present data it cannot be clearly concluded whether protection against termites arising from a decrease in the moisture content of modified samples is due to the cell wall polymer OH groups being masked, or due to the cell wall being bulked by adduct, or finally is a combination of both these phenomena. Termites seek water and are attracted to conditions that might also be favourable for growth of decay and mould fungi. Evidence also suggests that they are attracted to wood decayed by certain brown rot fungi (Kartal et al. 2003). Once established, mould decay fungi and termites may independently increase the moisture in the infested area through water trapping or transporting or the conversion of cellulose to carbon dioxide and water. It is known that the enzymes associated with the degradation of the cell wall‘s main polymers components are too large to enter the cell wall of undegraded wood. For this reason, various low molecular weight diffusible agents were proposed to initiate degradation thereby allowing enzymes to penetrate in the wood cell wall (Eaton and Hale 1993, Green and Highley 1997). Any proposed mechanism by which chemical modification provides biological protection against termites should therefore take account of the presence of these low molecular weight diffusible agents.

4 Conclusion

The work described in this paper has demonstrated that chemically modified Corsican pine sapwood provided bio-protection against the subterranean termites *Reticulitermes flavipes*. Results from this and previous studies have shown that the improvement of key wood properties (sorption of water vapour, decay resistance and resistance against wood marine borers and termites) imparted by chemical modification is independent of the degree of substitution of the cell wall hydroxyl groups, but correlates with the degree of bulking of the cell wall.

References

American Society for Testing Materials (1998) Standard test method for laboratory evaluation of wood and other cellulosic materials for resistance to termites. Standard D 3345–74. Annual book of ASTM Standards, 4.10. pp 430–432

Eaton R, Hale MD (1993) Wood, decay, pests and protection. Chapman and Hall, London

Forster S (1998) Decay resistance of modified softwood. Ph.D thesis. University of Wales, Bangor

Green F, Highley T (1997) Mechanism of brown-rot decay: Paradox or paradigm. Int Biodeter Biodegr 39:113–124

Hon DNS (1996) Chemical modification of lignocellulosics. Marcel Dekker, New York

Kartal SN, Burdsall HH, Green IF (2003) Accident mold/termite testing of high density fiberboard treated with borates and N, N-Napthaloyhydroxylamine (NHA). International Research

Group on Wood Preservation, Stockholm, Sweeden, IRG/WP 03-10462
Papadopoulos AN (2001) Swelling, cell wall porosity and chemical modification of wood. Ph.D Thesis, University of Wales, Bangor
Papadopoulos AN, Hill CAS (2002) The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against *Coniophora puteana*. Holz Roh- Werkst 60: 329–332
Papadopoulos AN , Duquesnoy P, Cragg SM, Pitman AJ (2008) The resistance of wood modified with linear chain carboxylic acid anhydrides to attack by the marine wood borer *Limnoria quadripunctata* Hothius. Int Biodeter Biodegr 61: 199–202
Papadopoulos AN, Hale MD, Hill CAS (2002) Efficacy of linear chain carboxylic acid anhydrides as wood protecting chemicals. International Research Group on Wood Preservation, Document number IRG/WP 02-30295
Papadopoulos AN, Hill CAS (2003) The sorption of water vapour by anhydride modified softwood. Wood Sci Technol 37(3–4): 221–231
Rowell RM (1983) Chemical modification of wood. For Prod Abstr 6:366–382