

Weathering and Photostability of Wood Modified by Aromatic Vinyl Esters

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ABSTRACT

Thin wood veneers were esterified to different weight gains with three different aromatic vinyl esters, vinyl benzoate, vinyl cinnamate and vinyl 4-ter-butylbenzoate and the photostability of the modified wood was examined. There was a linear relationship between the level of esterification of wood with vinyl-benzoate and the photostability of the modified veneers exposed to natural weathering. Vinyl-benzoate protected lignin and cellulose in wood from photodegradation at high weight gains (>30%) whereas modification of wood with vinyl-4-T-butylbenzoate provided no such protection and vinyl cinnamate increased the photodegradation of wood. We provide an explanation for why these effects occurred and discuss the implications of our findings for the development of weather-resistant wood materials.

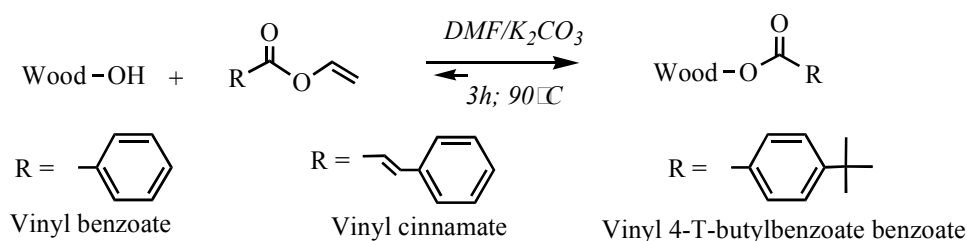
INTRODUCTION

The photostability and weathering resistance of wood can be improved by esterification with acid chlorides or anhydrides (Rowell 1983, Hill 2006). In particular, it has been shown that esterification with benzoyl chloride can photostabilize lignin in wood, and provide high levels of UV protection (Evans *et al.* 2002, Pandey and Chandrashekar 2006). Benzoyl chloride introduces large numbers of aromatic groups into wood, which may protect lignin and cellulose from photodegradation by absorbing UV radiation (Evans *et al.* 2002). Modification of wood with benzoyl chloride, however, generates hydrochloric acid as a by-product, and this can depolymerize cellulose or cause corrosion of metal fasteners (Rowell 1983, Hill 2006). This problem can be overcome by modifying wood using a novel method based on the transesterification of vinyl esters (Jebrane and Sèbe 2007, Jebrane and Sèbe 2008). The by-product of this reaction is acetaldehyde, which is not acidic and can be easily removed from wood after esterification because of its low boiling point (b.p. [760 mm Hg] = 21 °C). Accordingly, in this work we esterified thin wood veneers to different weight gains with three different aromatic vinyl esters, vinyl benzoate, vinyl cinnamate and vinyl 4-ter-butylbenzoate and examined the photostability of the modified wood. We hypothesize that the introduction of aromatic groups into wood as a result of modification of wood with these vinyl esters will protect the wood from photodegradation.

EXPERIMENTAL

Chemical modification of wood veneers

One hundred wood veneers approximately 85 μm thick were cut from the radial face of each of five different water-saturated yellow cedar (*Chamaecyparis nootkatensis* (D. Don) Spach) blocks, as described previously (Evans and Schmalzl 1989). All veneers were soxhlet-extracted with toluene/ethanol (2:1 v:v) for 8 h, then with water for an additional 8 h, and were oven-dried at 105°C for 16h. For each treatment 10 veneers were treated together in a solution containing the vinyl ester, 0.15 g of K_2CO_3 (catalyst) and 20 mL of DMF. The concentration of vinyl esters in solution was varied to obtain different weight gains and percentages of substituted OH groups in reacted veneers (Table 1). All reactions were performed at 90 °C for 3 hours. The esterification reaction proceeds as follows, releasing acetaldehyde as a by-product:



After reaction the esterified veneers were soxhlet extracted with water for 2 h, then with toluene/ethanol/acetone (4:1:1 v:v:v) for an additional 8 h. The percentage weight gains (WPG) of treated and extracted veneers was then calculated. The number of OH groups substituted in wood after treatment was calculated from the WPG and the molecular weight of the adduct, assuming a 1:1 molar reaction between the vinyl esters and wood hydroxyl groups.

Photostability of esterified veneers

Five veneers from each batch of 10 treated veneers were selected at random, placed against glass backing plates and clamped lightly at their ends. The remaining five veneers for each treatment were placed in a conditioning room at $20 \pm 1^\circ\text{C}$ and $65 \pm 5\%$ relative humidity for the duration of the exposure trial. The esterified and untreated veneers were then exposed outdoors for 25 days in Vancouver during the summer of 2007. After weathering, veneers were oven dried as above and the mass of each individual veneer was recorded. Tensile strength tests were carried out on conditioned veneers at zero-span using a Pulmac paper tester as described previously (Evans and Schmalzl 1989).

Analytical techniques

Infrared spectra of weathered veneers and controls were obtained using an Omnic spectrometer. Weathered and unexposed veneers were placed under the silicon crystal of an attenuated total reflectance (ATR) accessory of the spectrometer. Spectra were collected over 4000 to 650 cm^{-1} , with a resolution of 8 (SSP 3.857 cm^{-1}) and 64 scans per sample. Three spectra were collected for each strip and averaged. The spectral data were imported into software (CAMO, v. 9.6), normalized and averaged.

Figure 1 plots the average percentage weight losses of batches of five veneers during weathering against their average percentage weight gain due to esterification. There is an inverse linear relationship between weight gain of veneers due to esterification and weight losses of veneers during weathering. Modification with the different vinyl esters slightly increased the tensile strength of veneers (Table 1), whereas there were significant losses in tensile strength of modified veneers exposed to natural weathering (Figure 1b).

Table 1: Solution concentrations, weight gains, degree of substitution and tensile strength gains of veneers modified with vinyl benzoate, vinyl cinnamate and vinyl 4-T-butylbenzoate

Vinyl ester	Vinyl benzoate			Vinyl cinnamate			Vinyl 4-T-butylbenzoate		
Solution concentration (mol/L)	0.12	0.78	1.52	0.07	0.18	0.9	0.32	0.88	1.13
Average WPG (%)	14.8	24.1	29.8	10.1	17.6	29.1	11.4	16.1	15.9
OH substitution (mmol/g dry wood)	1.42	2.32	2.87	0.78	1.35	2.24	0.71	1.01	0.99
Strength gain (%)	7.2	8.1	4.5	5.0	5.8	2.8	2.8	4.1	9.6

Strength losses during weathering of veneers modified to high weight gains (>30%) with vinyl benzoate were lower than untreated veneers and those modified with vinyl cinnamate, vinyl 4-T-butylbenzoate or vinyl benzoate to lower weight gains (Figure 1b). Regression analysis indicated that there was a moderate inverse linear relationship between weight gain of veneers due to esterification with vinyl benzoate and tensile strength losses of veneers during weathering. There was no relationship between weight gain of veneers as a result of esterification with vinyl cinnamate or vinyl 4-T-butylbenzoate and tensile strength losses of veneers during weathering.

Colour measurements

Figure 2 shows the yellowness (b^*) of esterified veneers and controls before and after natural weathering. Each point in the graph represents the mean of individual colour measurements made on five different veneers and the y-axes of both graphs are drawn to the same scale.

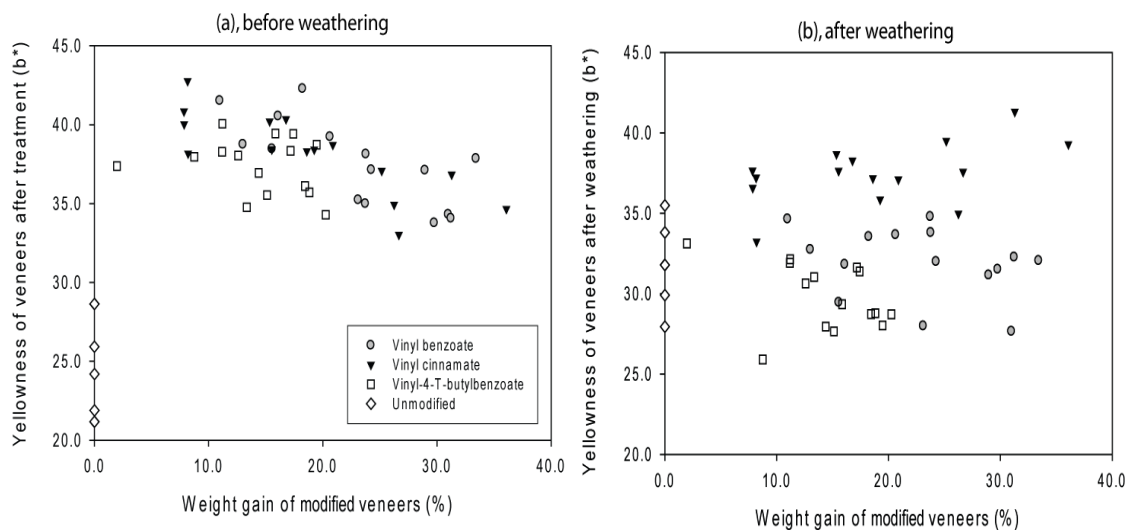


Figure 2: Relationship between weight gain of esterified veneers and their yellow colour (b^*) before (a) and after (b) exposure to natural weathering for 25 days

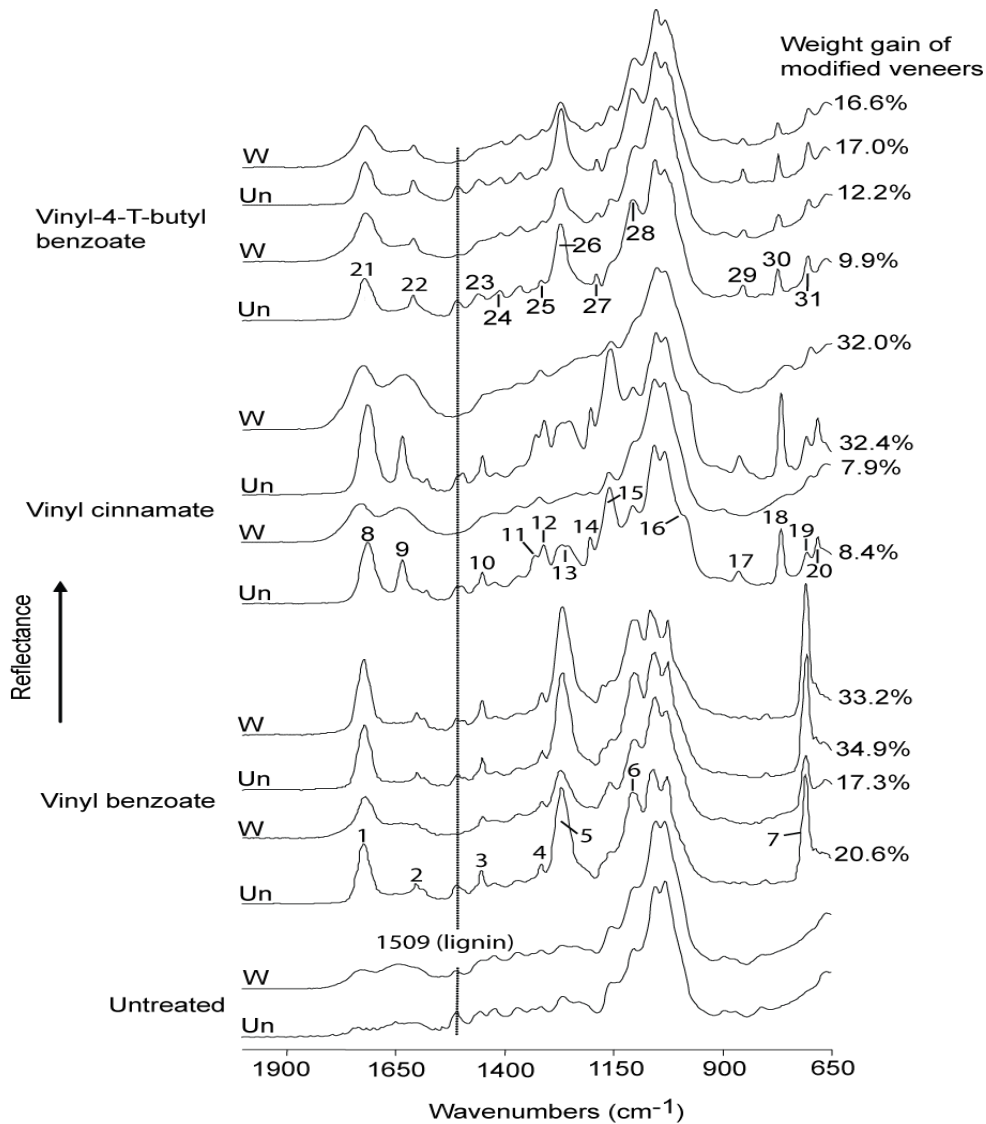
Esterification made veneers yellower particularly modification with vinyl cinnamate to low weight gains (Figure 2a). The yellowness of unmodified veneers increased during weathering as expected (Figure 2b). In contrast, veneers modified with vinyl benzoate or vinyl 4-T-butylbenzoate became less yellow during weathering, irrespective of weight gain due to esterification. The changes in yellowness of veneers modified with vinyl cinnamate, however, appeared to depend on their weight gain due to treatment. The yellowness of veneers modified to low weight gains with vinyl cinnamate decreased during weathering whereas the opposite occurred for veneers modified to higher weight gains.

FTIR spectroscopy

The chemical changes occurring in untreated and esterified wood veneers were examined by Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy (Figure 3). The weakening of the absorption band at 1509 cm^{-1} (benzene ring stretching in lignin) after weathering of untreated wood indicates delignification of weathered samples, as expected. The characteristic vibrations of the grafted acyl groups in the spectra of esterified veneers were identified by numbers on the different spectra. There was no significant change in the spectrum of veneers modified to high weight gain with vinyl benzoate (WPG 33.2%) after weathering, indicating that this treatment was able to photostabilize wood. The spectra of veneers subjected to all of the other treatments including modification with vinyl benzoate to lower weight gains showed a decrease in the peak at 1509 cm^{-1} indicating delignification of veneers during weathering. This delignification was associated with decreases in the intensity of the vibrations associated with grafted acyl groups, suggesting that esterified wood was lost during weathering, or that partial hydrolysis of these groups occurred. An unexpected broadening of absorption bands occurred in spectra of veneers treated with vinyl cinnamate after weathering. This phenomenon has not been clarified, but it may be associated with the inherent photo-reactivity of cinnamate groups. Upon irradiation in the ultraviolet-B region, vinylene C=C conjugated with the aromatic rings, can undergo a trans/cis isomerization and/or a photodimerization through cycloaddition reactions (Hu *et al.* 2002, Gupta *et al.* 2004). Some other radical additions between cinnamate groups and lignin cannot be excluded, either.

DISCUSSION

After treatment with vinyl benzoate, there was a positive linear relationship between weight gain of veneers due to treatment and restrictions in losses of weight and tensile strength of modified veneers during weathering and, accordingly, at high weight gains, vinyl benzoate was able to protect wood from photodegradation. In contrast, the majority of our results suggested the opposite for veneers modified with vinyl cinnamate. This treatment did not restrict yellowing nor delignification of veneers during weathering. However, there was a linear relationship between weight gain due to treatment and the ability of vinyl cinnamate to restrict weight losses of veneers exposed to the weather. The lower weight loss is probably due to the ability of this treatment to increase the hydrophobicity and restrict leaching of photodegraded lignin fragments from wood surfaces. The accumulation of such lignin fragments in wood is responsible for the yellowing of wood during weathering (Evans 2008). This could explain why veneers modified to high weight gains with vinyl cinnamate became yellower when they were exposed to the weather than similarly exposed untreated wood veneers.



Assignments of the bands:

ν [C=O]: 1, 8, 21	δ [=C-H]: 4, 11, 12, 25	Not assigned: 13, 14,
ν [C=C]: 2, 3, 9, 10, 22, 24	ν [C-O]: 5, 6, 15, 26, 28	17, 18, 27, 30, 31
δ_{as} [CH ₃]: 23	γ [=C-H]: 7, 16, 19, 20, 29	

ν : stretching vibration; δ : in-plane bending; γ : out-of-plane bending as: asymmetrical

Figure 3: FTIR-ATR spectra of untreated controls and veneers esterified with vinyl benzoate, vinyl cinnamate and vinyl 4-T-butylbenzoate, before and after natural weathering (Un = unweathered; W = weathered)

Modification of wood with vinyl 4-T-butylbenzoate provided little protection against photodegradation, but weight gains of veneers with this treatment were much lower than those of veneers modified with vinyl benzoate or vinyl cinnamate. The presence of a bulky side chain on vinyl 4-T-butylbenzoate has probably reduced its diffusion into wood cell walls and the numbers of hydroxyl groups on lignin, cellulose and hemicelluloses that are esterified. The number of OH groups substituted by vinyl 4-T-butylbenzoate at 15.9% weight gain was 0.99 mmol OH/g dry wood compared with a figure of 1.42 for veneers modified with vinyl benzoate to 14.8% weight gain (Table 1). Therefore wood modified with vinyl 4-T-butylbenzoate contained lower quantities of

aromatic groups to absorb UV radiation and block photodegradation. In contrast, the degree of substitution of hydroxyl groups with vinyl cinnamate is much closer to that of vinyl benzoate (Table 1). Hence, the inability of vinyl cinnamate to photostabilize wood probably cannot be wholly explained by lower levels of aromatic groups in wood cell walls. An alternative explanation is that cinnamate side chains acted as a photosensitizer as has been shown for other natural polymers, and this increased the susceptibility of the wood to photodegradation (Haque *et al.* 1986).

Esterification of wood with vinyl benzoate had no adverse effects on the tensile strength properties of wood and it was able to protect lignin from photodegradation. Tensile strength losses of wood veneers during natural weathering occur due to photo-induced depolymerization of cellulose (Derbyshire and Miller, 1981). Hence, the ability of vinyl benzoate to reduce losses in tensile strength of wood veneers during weathering suggests that it was also able to photostabilize cellulose to some extent. In contrast, chemical modification of wood with benzoyl chloride, which can photostabilize wood, causes losses in the tensile strength of wood (Evans *et al.* 2002). Thus the finding that esterification of wood with vinyl benzoate to high weight gains can photostabilize lignin and cellulose in wood without adversely affecting the tensile strength of wood is noteworthy and certainly justifies further research to examine whether it can improve the durability of clear coatings, as has been demonstrated for other treatments that can protect wood from photodegradation (Kiguchi *et al.*, 2001).

CONCLUSION

In conclusion we have found that esterification with aromatic vinyl esters can protect wood from photodegradation, but the degree of protection depends on the type of ester and the level of modification of the wood. Vinyl benzoate was more effective than vinyl cinnamate and vinyl 4-T-butylbenzoate at protecting wood from photodegradation, and this treatment showed a linear relationship between the level of modification (weight gain) and the photostability of the modified wood. Vinyl benzoate only protected lignin and cellulose in wood from photodegradation, however, at weight gains of 30% or more. Such weight gains due to esterification are much higher than those that are normally required to significantly reduce the swelling and shrinkage of wood and protect it from fungal decay. Therefore, we conclude that more complete chemical modification of wood's molecular constituents is needed to protect it from photodegradation compared to the level of modification required to dimensionally stabilize wood and prevent its biological deterioration. Modification of wood with vinyl 4-T-butylbenzoate or vinyl cinnamate was ineffective at photostabilizing wood, because the side chains attached to their benzene ring made it more difficult, to modify wood to high weight gains (vinyl 4-T-butylbenzoate) or increased photodegradation of the wood (vinyl cinnamate). Hence, we conclude that chemical modification to improve the photostability of wood should use simple (unbranched) low molecular weight aromatic compounds that can easily react with wood's molecular constituents to achieve a high degree of substitution of available hydroxyl groups. Vinyl benzoate fulfils this criterion and furthermore it has no adverse effects on the tensile strength properties of wood, unlike benzoyl chloride, which can also modify and protect wood from photodegradation. We conclude that modification of wood with vinyl benzoate shows promise as a way of improving the photostability of wood and it may find a niche for the treatment of higher value products used outdoors that need to be able to resist weathering and maintain their appearance.

REFERENCES

- Derbyshire, H., Miller, E.R. (1981). The photodegradation of wood during solar irradiation. Part 1: Effects on the structural integrity of thin wood strips. *Holz als Roh- und Werkstoff*, **39**, 341-350.
- Evans, P.D., Schmalzl, K.J. (1989). A quantitative weathering study of wood surfaces modified by chromium VI and iron III compounds. Part I. Loss in zero-span tensile strength and weight of thin wood veneers. *Holzforschung*, **43**(5), 289-293.
- Evans, P.D., Owen, N.L., Schmid, S., Webster, R.D. (2002). Weathering and photostability of benzoylated wood. *Polym. Deg. & Stability*, **76**, 291-303.
- Evans, P.D. (2008). Weathering and photo-protection of wood. In: *Development of Wood Preservative Systems*. Schulz, T., Militz, H., Freeman, M.H., Goodell, B., Nicholas, D.D. (Eds). ACS, Washington DC, USA, p. 98.
- Gupta, P., Trenor, S.R., Long, T.E., Wilkes, G.L. (2004). In situ photo-cross-linking of cinnamate functionalized poly(methylmethacrylate-co-2-hydroxyethyl acrylate) fibers during electrospinning. *Macromolecules*, **37**, 9211-9218.
- Haque, S.A., Kuruda, Y., Hatanaka, K., Uryu, T. (1986). Synthesis of novel photosensitive polymers with photosensitive group. *J. Polymer Materials*, **3**(2), 87-99.
- Hill, C.A.S. (2006). Wood modification: Chemical, thermal and other processes.: John Wiley and Sons, Chichester, UK.
- Hu, Y., Gamble, V., Painter, P.C., Coleman, M.M. (2002). Functional group accessibility in hydrogen-bonded polymer blends. 4. Cross-linking effects. *Macromolecules*, **35**, 1289-1298.
- Jebrane, M., Sèbe, G. (2007). A novel simple route to wood acetylation by transesterification with vinyl acetate. *Holzforschung*, **61**, 143-147.
- Jebrane, M., Sèbe, G. (2008). A new process for the esterification of wood by reaction with vinyl esters. *Carbohydrate Polymers*, **72**, 657-663.
- Kiguchi, M., Evans, P.D., Ekstedt, J., Williams, R.S., Kataoka, Y. (2001). Improvement of the durability of clear coatings by grafting of UV-absorbers on to wood. *Surface Coatings International Part B: Coatings Transactions*, **84**, 243-336.
- Pandey, K.K., Chandrashekar, N. (2006). Photostability of wood surfaces esterified by benzoyl chloride. *J. Appl Polym Sci.*, **99**, 2367-2374.
- Rowell, R.M. (1983). Chemical modification of wood. *For Prod Abstracts*, **6**, 363-382.