

## Natural Weathering and Photostability of Wood Modified by Fatty Acid Esters

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### ABSTRACT

Polyunsaturated fatty acid vinyl ester was synthesized *via* a transition-metal catalyzed transvinylation reaction between vinyl acetate and fatty acids from Tung oil. The ensuing fatty acid vinyl ester (vinyl  $\alpha$ -eleostearate) was characterized by FTIR and NMR spectral analyses and used as reactive reagent for modification of wood veneers. The covalent grafting of polyunsaturated fatty acid moieties onto the wood was achieved through transesterification reaction between wood hydroxyl groups and fatty acid vinyl ester. The transesterification reaction was confirmed by FTIR, <sup>13</sup>C CP MAS NMR spectroscopy and the level of modification was estimated by determining the weight percentage gain (WPG). The photostability of modified wood veneers was evaluated by exposing wood veneers to natural weathering in Uppsala (Sweden) during April-May 2018. Upon 5 weeks of exposure to natural weathering, unmodified wood showed quick color changes and degradation of lignin, while modification of wood vinyl  $\alpha$ -eleostearate was very effective in suppressing light-induced color changes at wood surfaces.

### INTRODUCTION

Wood is a UV sensitive material. Exposed outdoors, wood undergoes rapid color change and breakdown of wood polymers in the surface (Derbyshire and Miller 1981; Evans *et al.* 1996; Evans *et al.* 2002; Jebrane *et al.* 2009). Because of its aromatic nature, lignin strongly absorbs UV light (Kalnins 1966), which leads to radical-induced depolymerisation of lignin and cellulose. Depolymerization of lignin generates unsaturated aromatic compounds, which are yellow in color. Hence, wood exposed outdoors yellows initially and becomes grey when blue-black staining fungi (Salla *et al.* 2012) colonize the white, cellulose-rich surface. To protect wood from photodegradation, a variety of different approaches has been investigated (Evans 2008) including using additives (UV absorbers) (Rabek 1990), chemical treatments (Evans *et al.* 2002, Jebrane *et al.* 2009). However, most of these approaches present many drawbacks, such as involving toxic chemicals, energy inefficiency, and expensive. In recent years, public concern about the environment has led to the creation of regulatory programs to reduce air pollution, increasing the pressure on wood manufacturers to reduce harmful emissions derived from chemical treatments. In this context, huge scientific research on the biobased products in the world has focused on the environmental impacts of continuing using fossil-based materials in diverse industries. Indeed, public concerns related to fossil-based resources have led politicians and administrators at EU and national level to set targets for shifting to low carbon societies by 2050. For achieving this target, the use of materials

originating from renewable resources in diverse industries has been pointed out as important strategies to decrease the dependency on fossil-based products. Several attempts have been made for the use of bio-based chemicals to protect wood (Jebrane *et al.* 2014; Kose Demirel *et al.* 2018), but the approaches tested are either expensive or involving multiple steps. In this context, a new method using a bio-based precursor for chemical functionalization of wood has been developed.

In this study, thin Scots pine (*Pinus sylvestris* L.) veneers were chemically modified (esterified) with polyunsaturated fatty acid vinyl ester and the photostability of the modified wood was assessed. Tung oil was hydrolyzed and the obtained fatty acids were chemically functionalized with vinyl acetate and used to react with hydroxyl groups in wood. Preliminary experimentation had shown that the vinyl ester form of triply conjugated fatty acid (vinyl  $\alpha$ -eleostearate) reacted with wood veneers producing esterified wood. Furthermore, it was assumed that the introduction of naturally triply conjugated fatty acid moieties into the wood cell wall might act as a UV screen protecting lignin and cellulose from photodegradation.

## EXPERIMENTAL

### **Wood treatment**

Scots pine sapwood veneers of 1 mm  $\times$  10 mm  $\times$  100 mm (along the grain) were cut from the radial face of defect free wood blocks. Prior to modification, all veneers including unmodified controls were extracted in a Soxhlet apparatus with a mixture of toluene: ethanol (2:1/v:v) for 8 h, and then with water for an additional 6 h, to remove all extractives. Wood veneers were then oven-dried at 103°C for 16 h and cooled to ambient temperature in a desiccator. Dried veneers were treated with vinyl  $\alpha$ -eleostearate in a reaction tube using catalyst  $K_2CO_3$  and solvent N-methyl-pyrrolidone (NMP) at 100°C for different reaction durations. Vinyl  $\alpha$ -eleostearate was synthesized from Tung oil following alkaline hydrolysis and according to the procedure described by Jebrane *et al.* (2016, 2017). For each reaction, 10 replicates of veneers were reacted together for 3, 6 and 9 h in a solution containing the vinyl ester,  $K_2CO_3$  (catalyst) and NMP. After reaction, the esterified veneers were Soxhlet extracted with water for 2 h and then with acetone for an additional 8 h to remove non-bonded chemicals. The weight percentage gains (WPGs) of modified and extracted veneers were then calculated.

### **Evaluation of photostability of esterified veneers**

The photostability of modified and unmodified veneers was assessed using natural weathering. Five veneers from each 10 modified veneers for the three different WPGs (3, 6 and 9 h) were selected at random, placed against glass backing plate and clamped lightly at their ends. The glass plate containing 15 esterified veneers (three different WPGs) and 5 unmodified samples were exposed outdoors for 5 weeks in Uppsala during the April-May of 2018. The glass plate was oriented horizontally and facing south to maximize the total UV radiation received by veneers. The veneers were removed from the weathering at regular interval (one week), the color was measured at four different locations for each sample, and average values were calculated. After weathering, veneers were oven-dried as above and the chemical changes were measured.

### **Analytical techniques**

**ATR-FTIR** spectra of oil, fatty acid, fatty acid vinyl ester (vinyl  $\alpha$ -eleostearate) and wood samples were acquired in the range of 4000–450  $cm^{-1}$  (spectral resolution 4  $cm^{-1}$ , 16 scans) on a Perkin Elmer Spectrum One FT-IR Spectrometer equipped with a Universal Attenuated Total Reflectance Accessory (UATR).

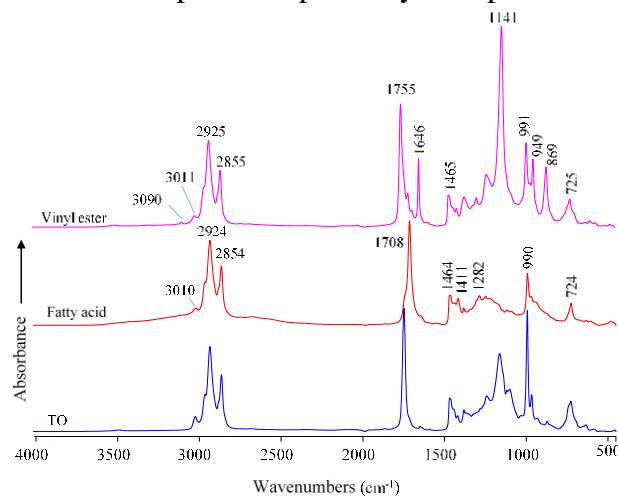
**Solid state  $^{13}\text{C}$  CP MAS NMR** spectra of modified and unmodified wood samples were obtained at room temperature on a Bruker Avance–II spectrometer operating at 150.9 MHz using a custom built MAS NMR probe. The samples were packed into 4 mm Zirconia rotors. Chemical shifts were relative to TMS used as an external standard. For each sample, a total of 20000 scans were accumulated.

**Colour measurements:** the colour change of modified and unmodified veneers exposed to natural weathering was monitored using Konica Minolta CM-2500d surface reflectance spectrophotometer. Co-ordinates CIELab color i.e. lightness (L), redness (a) and yellowness (b) were measured on each sample before and after irradiation and change in these parameters due to weathering  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  were calculated. The variables above were measured periodically and shown after 1, 2, 3, 4 and 5 weeks of exposure while spectral analyses of wood were carried out once after 5 weeks of exposure and compared to the control samples.

## RESULTS AND DISCUSSION

### *Chemical synthesis and spectroscopic characterization of wood reagent.*

For comparison with the classical acylation of wood with fatty acids by means of acyl chloride, the corresponding long chain vinyl ester was synthesized. Tung oil was hydrolyzed and the ensuing fatty acids were functionalized by transesterification with vinyl acetate in order to obtain vinyl  $\alpha$ -eleostearate according to the procedure described previously (Jebrane *et al.* 2018). The structure of the new bio-based long chain vinyl ester was confirmed by the combined spectroscopic analyses reported above.

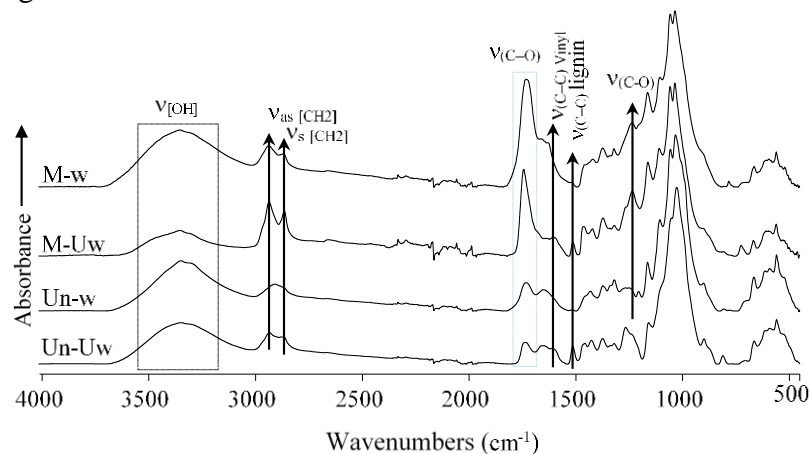


**Figure 1: FTIR absorbance spectra of Tung oil (TO),  $\alpha$ -eleostearic acid (fatty acid), and vinyl eleostearate (Vinyl ester)**

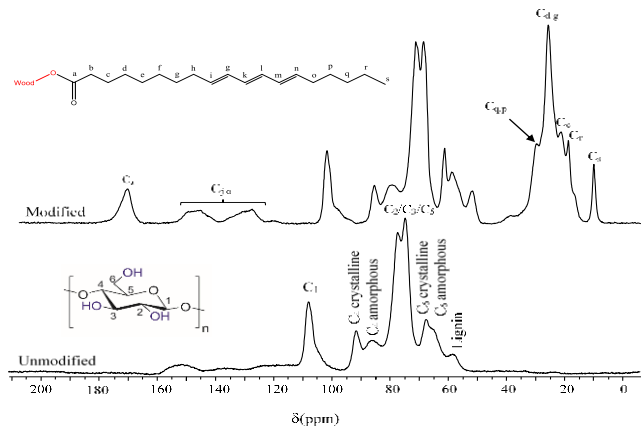
Compared with the FTIR spectra of the starting Tung oil (TO) and Tung oil's fatty acids (FA), the spectra of the synthesized fatty acid vinyl ester showed the emergence of new characteristic absorption bands (Fig. 1). These new absorption bands were observed around  $3090\text{ cm}^{-1}$  (vinyl C–H stretching),  $3011\text{ cm}^{-1}$  (chain unsaturation C–H stretching),  $1755\text{ cm}^{-1}$  (C=O stretching of vinyl ester),  $1141\text{ cm}^{-1}$  (ester C–O stretching),  $949\text{ cm}^{-1}$  (CH out of plane deformation of  $\text{CH}=\text{CH}_2$ ),  $869\text{ cm}^{-1}$  ( $\text{CH}_2$  out of plane deformation of  $-\text{CH}=\text{CH}_2$ ). In addition to the appearance of new characteristic bands, a disappearance of carboxyl groups at around  $2672\text{ cm}^{-1}$  (OH stretching) and at  $1708\text{ cm}^{-1}$  (C=O stretching) was observed, confirming the complete transformation of fatty acid into vinyl ester.

***Esterification of wood by fatty acid vinyl ester and spectroscopic characterization.***

A polyunsaturated fatty acid was investigated to verify whether this biobased precursor is effective for the photo-stabilization of wood polymers and offer improved mechanical properties and weathering performances owing to provide new biobased alternatives for wood protection. Polyunsaturated fatty acid vinyl ester was chosen as long acyl chain with a naturally triply conjugated fatty acid to increase the hydrophobicity and improve photostability of wood. Wood veneers were modified with the synthesized vinyl ester using a transesterification process. After 3, 6, and 9 h of reaction, WPG's of 6.7, 12.2 and 20.2% were obtained and the grafting of fatty acid moieties into wood was confirmed by FTIR and  $^{13}\text{C}$  CP-MAS NMR spectroscopy. Figure 2 depicts the FTIR spectra of unmodified and wood modified with fatty acid vinyl ester. In addition to the prominent carbonyl stretching vibration at  $1735\text{--}1743\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) and the C–O stretching vibrations at  $1157\text{--}1230\text{ cm}^{-1}$  ( $\nu_{\text{C-O}}$ ), some new characteristic vibrations of the grafted acyl chain moieties were identified namely, the strong skeletal bands of long chain moieties at  $2922$  and  $2853\text{ cm}^{-1}$  ( $\nu_{\text{C-H}}$ ),  $1370\text{ cm}^{-1}$  ( $\gamma_{\text{C-H}}$ ), and  $720\text{ cm}^{-1}$  ( $\text{CH}_2$  rocking).  $\alpha$ -eleostearate-modified wood samples were further characterized by  $^{13}\text{C}$  CP MAS NMR spectroscopy (Figure 3). In addition to the dominant pattern corresponding to the carbons of wood (cellulose, lignin), signals for carbons of the newly introduced long chain eleostearate moieties appeared clearly in the  $\alpha$ -eleostearate-modified wood spectra. These signals were assigned directly on the spectra of  $\alpha$ -eleostearate-modified wood according to the nomenclature given on the associated structure.



**Figure 2:** FTIR–ATR spectra of unmodified controls (Un-Uw) and veneers esterified (M) with vinyl eleostearate, before (Uw) and after (w) natural weathering.



**Figure 3:**  $^{13}\text{C}$  CP-MAS NMR spectra of unmodified controls and veneers esterified with vinyl eleostearate (Modified, WPG 20.3%)

### Photostability of modified veneers

Fig. 4 shows the effect of grafting triply conjugated fatty acid moieties onto the wood on colour changes of surfaces of scots pine veneers after five weeks of exposure to natural weathering. The colour of unmodified wood changed rapidly and darkened upon UV light irradiation. After modification, wood veneers become slightly yellower due to incorporation of additional chromophores (triply conjugated fatty acid). Contrary to unmodified wood, modified samples did not darken upon UV irradiation.

The observed colour changes were quantified by measuring CIELab parameters. The colour change observed in unmodified wood after exposure is demonstrated by the decreased value of lightness ( $\Delta L^*$ ) and the increased in the yellowness ( $\Delta b^*$ ) and redness ( $\Delta a^*$ ) (graph not shown). As expected, the yellowness of unmodified veneers increased progressively after weathering. In contrast, modified veneers became less yellow during weathering irrespective of weight gain due to the grafted fatty acid moieties. Similar results were reported in the literature (Evans *et al.* 2002; Jebrane *et al.* 2009; Sèbe *et al.* 2009; Nagarajappa and Pandey 2016). The increase in yellowness of veneers upon irradiation indicates photo yellowing of wood surfaces due to photodegradation of lignin ( $\Delta b^*$  values increased from  $22.7 \pm 0.5$  to  $37.2 \pm 0.8$  for unmodified wood, but decreased from  $38.3 \pm 0.3$  to  $26.5 \pm 0.7$  for modified wood). The high  $\Delta b^*$  value measured for modified wood before weathering is due to the incorporation of additional chromophores into the wood.

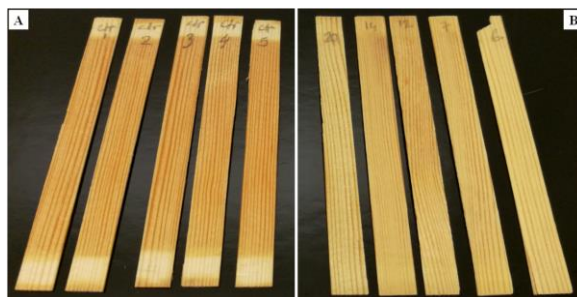


Figure 4: Photographs showing changes in colour of (A) unmodified and (B)  $\alpha$ -eleostearate-modified wood (different WPGs) after 5 weeks of exposure.

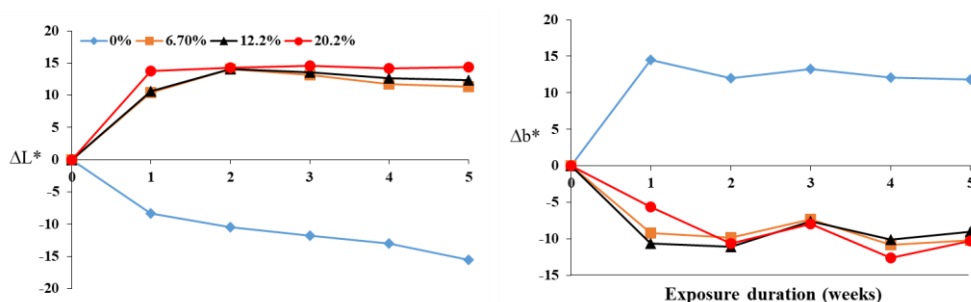


Figure 5: Changes in lightness ( $\Delta L^*$ ) and yellowness ( $\Delta b^*$ ) of unmodified (0%) and  $\alpha$ -eleostearate-modified wood (different WPGs) after 5 weeks of exposure.

The chemical changes occurring in unmodified and esterified wood veneers were examined by FTIR-ATR spectroscopy. Infrared spectra of unmodified wood before and after weathering are shown at the bottom of Fig. 2. The most obvious difference between the two spectra is the disappearance of the absorption band at  $1509 \text{ cm}^{-1}$  (benzene ring stretching in lignin), indicating delignification of weathered samples (Evans *et al.* 2002;

Jebrane *et al.* 2009; Nagarajappa and Pandey 2016) as expected. The IR spectra of modified veneers before and after weathering are shown at the top of Fig. 2. The characteristic vibrations of the grafted fatty acid moieties were easily identified in the FTIR spectra (Fig. 2) (Jebrane *et al.* 2017). After weathering, a decrease in the peak at  $1509\text{ cm}^{-1}$  was observed, indicating a delignification of modified veneers during weathering. An increase in the intensity and broadening as well as shifting of the peak at  $1735\text{ cm}^{-1}$  was observed after weathering and particularly in modified veneers, indicating a generation of moieties containing carbonyl groups. No significant changes were observed in other peaks, indicating less degradation of other wood polymers.

## CONCLUSIONS

A process of chemical modification of wood with polyunsaturated fatty acid vinyl ester (vinyl  $\alpha$ -eleostreate) has been developed. The process comprises a synthesis of vinyl ester of polyunsaturated fatty acid by the transvinilation of  $\alpha$ -eleostearic acid with vinyl acetate, followed by a covalent grafting of fatty acid moieties onto the wood via transesterification reaction between wood hydroxyl groups and the synthesized vinyl  $\alpha$ -eleostreate. Under studied conditions, WPGs ranging from 7 to 20 % was achieved, indicating that a significant amount of chemicals remained bonded in the wood. Weathering test indicates that the modification is very effective at protecting wood against photo yellowing and UV degradation of wood polymers.

## 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 Roh-Werkstoff*, 39:341–350.
- Evans, P.D. (2008) Weathering and photo-protection of wood. In: Schulz T, Militz H, Freeman MH, Goodell B, Nicholas DD, editors. Development of wood preservative systems. Washington, DC: ACS. p. 98.
- Evans, P.D., Owen, N.L., Schmid, J., Webster, R.D. (2002) Weathering and photostability of benzoylated wood. *Polymer degradation and stability*, 76(2):291–303.
- Evans, P.D., Thay, P.D., Schmalzl, K.J. (1996) Degradation of surfaces during natural weathering: Effects on lignin and cellulose and on the adhesion of acrylic latex primers. *Wood Science and Technology*, 30:411–422.
- Jebrane, M., Sèbe, G., Cullis, I., Evans, P.D. (2009) Photostabilisation of wood using aromatic vinyl esters. *Polymer degradation and stability*, 94:151–157.
- Jebrane, M., Fernández-Cano, V., Panov, D., Terziev, N., Daniel, G. (2014) Novel hydrophobization of wood by epoxidised linseed oil. Part 1. Process and anti-swelling efficiency of the treated wood. *Holzforschung*, 69(2):173–177.
- Jebrane, M., Terziev, N., Heinemaa, I. (2018) New bio-based alternative route to long chain esterified polysaccharides. *Biomacromolecules*, 18: 498–504.
- Kalnins, M.A. (1966) Surface characteristics of wood as they affect the durability of finishes. Part 2: photochemical degradation of wood. *US Forest Products Laboratory Report*, 57:23–60.
- Kose Demirel, G.; Temiz, A.; Demirel, S.; Jebrane, M.; Terziev, N.; Gezer, E.D. (2018) Microdistribution, water absorption and dimensional stability of wood treated with epoxidized plant oils. *BioResources*, 13(3), 5124–5138.
- Rabek, J.F. (1990) Photostabilisation of polymers: principles and application. London: Elsevier.
- Salla, J., Pandey, K. K., Prakash, G. K., Mahadevan, K.M. (2012) Photobleaching and dimensional stability of rubber wood esterified by fatty acid chlorides. *Journal of Wood Chemistry and Technology*, 32:121–136.