

Wood Chemical Modification with Alkenyl Succinic Anhydrides Bearing an Ester Group

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ABSTRACT

A new family of vegetable oil derivatives was obtained by reaction of alkyl esters of rapeseed and sunflower oils with maleic anhydride. Alkenyl succinic anhydrides bearing a terminal ester group (ASA-R) were thus prepared and assessed for the chemical modification of wood and the subsequent protection against softrot microorganisms. Utilized characterization techniques were: determination of the grafting yield by the saponification method of extracted samples, FTIR spectroscopy, and accelerated tests for biological protection of poplar inspired by the ENV807 standard. Other parameters were investigated as well: the swelling due to the treatment, the potential leaching of non-extracted samples, the anti-swelling efficiency, and the water absorption after water soaking. Correlations of these properties were established with the structure of the ASA-R and with the loading extent of ASA-R of Scots pine samples.

INTRODUCTION

The microbiological degradation of lignocellulosics limits timber use by reducing its density, strength and aesthetic properties. Chemical modification is an innovative strategy for the eco-compatible protection of wood. When the appropriate reagents are used, the major wood macromolecules are modified without leaving toxic residues within the wood. Anhydrides have a high reactivity to hydroxyl groups and the grafting of the substituent molecule has been shown to occur using relatively simple reaction systems (Goldstein *et al.* 1961, Rowell *et al.* 1988, Hill and Jones 1996, Ramsden *et al.* 1997). The most common anhydride still used today is acetic anhydride, which improves the technical properties of Scots pine sapwood as the resistance to brown and white rot fungi, as well as the resistance to insects (Imamura and Nishimoto 1986, Rowell *et al.* 1988, Hill and Jones 1996, Larsson-Brelind *et al.* 1997). A new anhydride recently synthesized (Quesada *et al.* 2003): Methyl Alkenoate Succinic Anhydride (ASAMe) was prepared by reaction of rapeseed oil methyl esters (RME) with maleic anhydride (MAH). This compound was reported to protect wood efficiently against insects and white and brown decay fungi but the protection against softrot was quite limited (Morard *et al.* 2007). Our main objective in this work was to evaluate, with a portfolio of tests, the impact of changing the alkyl moiety in the oil esters (raw material for the ASAMe), from methyl to hexyl.

EXPERIMENTAL

Alkenyl Succinic Anhydrides

The reactive treating agents were prepared in two steps. First a transesterification reaction of RME with ethanol, propanol, butanol, pentanol and hexanol was conducted. All of the alcohols were of reagent grade from Sigma-Aldrich. Reactions were carried out with standard protocol reactions under acidic catalyst as described in organic chemistry textbooks. The reaction was stopped at 92% yield of the desired alkyl rapeseed ester (oleic acid was used as reference for monitoring). Second, the alkyl rapeseed ester was purified from residual alcohol and catalyst, and then it was reacted with maleic anhydride as described by Stefanoiu *et al.* (2008). Different isomers were obtained for the main oleic molecule as shown in Figure 1. They were not separated. The adducts were directly used after reaction and shown the following average composition: 47% oleic ASA-R, 30% linoleic ASA-R, 2% residual MAH, 1% secondary products and the rest (about 20%) was constituted by the unreacted alkyl rapeseed esters. The viscosity of the liquid ASA-R was comparable to that of rapeseed oil.

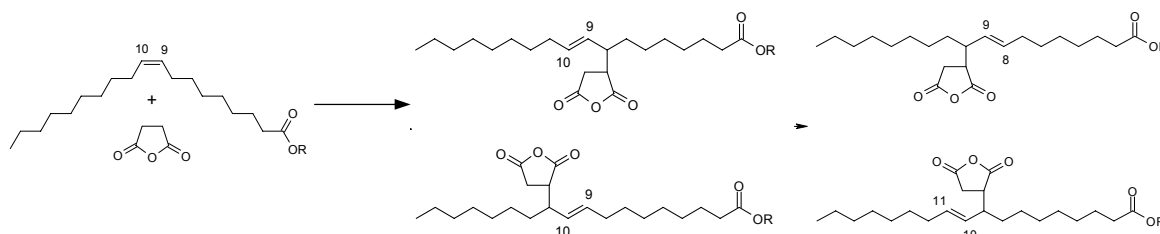


Figure 1: Main molecules present in ASA-R from maleic anhydride-grafted rapeseed alkyl esters

Wood treatment

Wood pieces of small dimensions (which depended on the test) were vacuum-impregnated in ASA-R at room temperature for 30 min. The impregnated pieces were then immersed in ASA-R at 140 °C for 2 h. The treated wood pieces were then taken out of the liquid, wiped, and let cool down in a condition chamber at 25 °C and 60%RH for at least one week prior to testing.

Special treatments

For comparison testing, some treated samples were acetone-extracted with a Soxhlet apparatus for 12 h. They were then dried in a vacuum oven at 60 °C until constant weight, then let stand to equilibrium in the same condition chamber as above. In the case of biological testing, impregnation was done at room temperature with solutions of ASA-R in acetone so that after evaporation of the solvent the retention level of ASA-R was around 140 kg/m³. After evaporation of the solvent, the impregnated wood pieces were put in an oven at 140 °C for 2 h.

RESULTS AND DISCUSSION

Bulk characteristics of treated wood

Treated Scots pine pieces of dimensions 20x20x5 mm (RxTxL) demonstrated that when no acetone was used for diluting the ASA-R, the retention level was as high as 275-550 kg/m³. Despite of this high quantity of introduced oleochemical, the volume swelling of the wood was in all cases maintained below 0.5%. In the other cases, the swelling was not significant either. This opens the possibility of treating machined pieces. The obtained colour was amber and the surface was “oil”-free.

Evaluation of the chemical modification

Cellulose fibres were treated with ASA-R in the same way as wood pieces. The treated fibres were acetone-extracted to remove the free molecules of ASA-R. By a widely known saponification method with ethanolic solution of NaOH, the amount of grafted ASA-R molecules was determined (Figure 2). When the ester moiety contains 1 to 3 carbon atoms, the extent of grafting is similar. When the alkyl chains are longer than 4 carbon atoms the number of molecules reacted with cellulose at 140 °C decrease significantly. The highest level of grafting corresponds to 820 mmol/kg in the case of the ASA from rapeseed propyl esters.

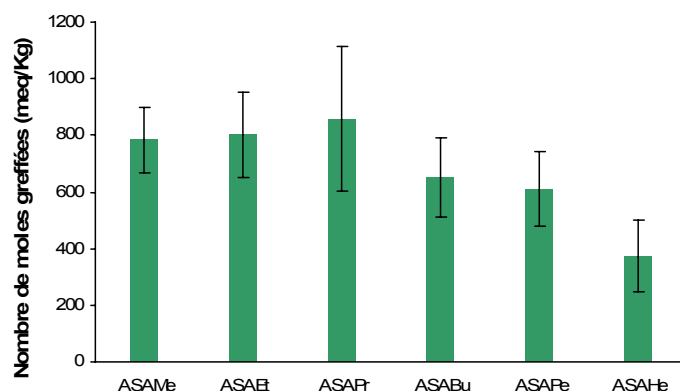


Figure 2: Amount of grafting of different alkyl ASA

Absorption of water during soaking

Treated Scots pine samples (non-extracted) were immersed in distilled water and the weight of the samples was monitored (Figure 3). After 24 hours, the absorption has not reached the equilibrium but these data were useful to determine the best ASA-R in terms of water repellency. The butyl and pentyl derivatives were the most efficient, less than 20% uptake. In these experiments, a comparative set of samples was treated under the same conditions with rapeseed methyl esters, which is the hydrophobic chemical accompanying ASA-Me but cannot be covalently grafted to wood. The higher water uptake for RME (+10% compared to ASA-Me with the same retention content) demonstrates that it is not enough to introduce a fatty compound in wood voids, but the blocking of hydroxyl groups by covalent bonding is important to decrease water affinity. Moreover, no significant leaching was observed.

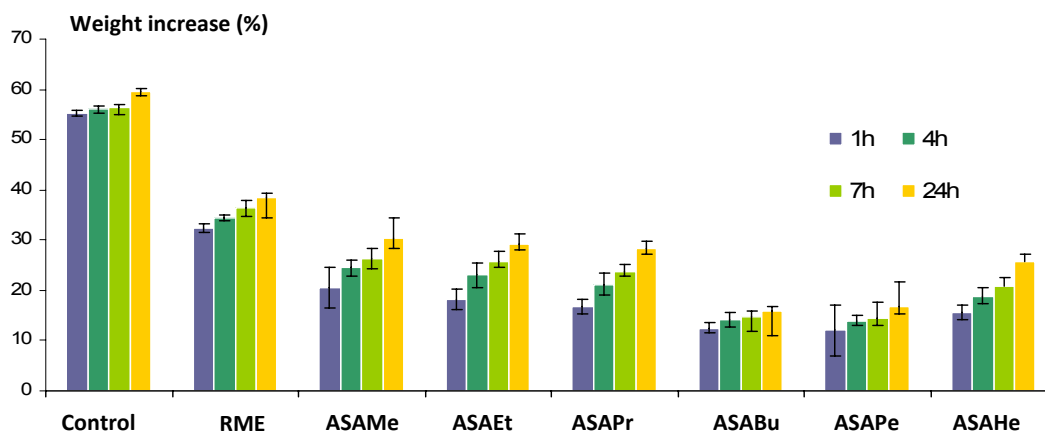


Figure 3: Water uptake after soaking treated Scots pine with different ASA-R. Average and standard deviation values from 10 samples.

Anti-swelling efficiency

Other samples (lots of 10) of the same dimensions were soaked for 48 h then dried at 70 °C for 24 h and at 103 °C for 12 h. This soaking-drying cycle was repeated 5 times. At the end, the dimensions of the samples were measured. The swelling and ASE values are reported in Table 1.

Table 1: Swelling of ASA-R treated Scots pine after soaking and Anti-Swelling Efficiency

	Retention [kg/m ³]	Tangential [%]	Radial [%]	ASE [%]
ASAMe	275 ± 84	6.88 ± 0.23	4.90 ± 1.35	22
ASAEt	311 ± 33	6.39 ± 0.29	5.12 ± 0.33	23
ASAPr	332 ± 29	6.69 ± 0.71	4.83 ± 0.40	27
ASABu	541 ± 34	6.29 ± 0.39	4.68 ± 0.35	27
ASAPe	551 ± 97	6.48 ± 0.33	5.08 ± 0.21	25
ASAHe	361 ± 29	6.38 ± 0.25	4.68 ± 1.52	26

Hill and Jones (1996) have demonstrated that ASE depended on the weight gain of the samples (directly related to the grafting extent). In our case we cannot establish directly this correlation because the samples were not solvent-extracted before. The grafting extent showed in Figure 2 was evaluated on cellulose fibres. It is expected that the same tendency is obtained in the case of wood. The decreasing trend when increasing the length of the alkyl chain is not found here, as the ASE remains practically constant, especially in the case of ASA-R with alkyl groups higher than ethyl. The value of 26% is not high, as acetylation can provide up to 70% ASE. However, the comparison is difficult because when the reaction between ASA-R and the hydroxyl groups in wood occurs, a carboxyl acid group is formed. It has a strong hydrophobic character that counterbalances the hydrophobicity given by the fatty compound and the reduction of hydroxyl groups. Moreover, this kind of molecules were not designed with the aim of reducing the swelling of wood, but improving the resistance against biological predators.

Softrot accelerated test

An accelerated test based on the European standard ENV807 was designed by CIDEMCO to quickly evaluate the comparative global performance of wood treatments. It uses the same activated soil but the samples used are small poplar pieces. The corrected mass loss is calculated at 5 and 12 weeks. The results for 12 weeks of exposition to decay are presented in Figure 4. Let us remind that the retention level of ASA-R is 150 kg/m³ for all the samples.

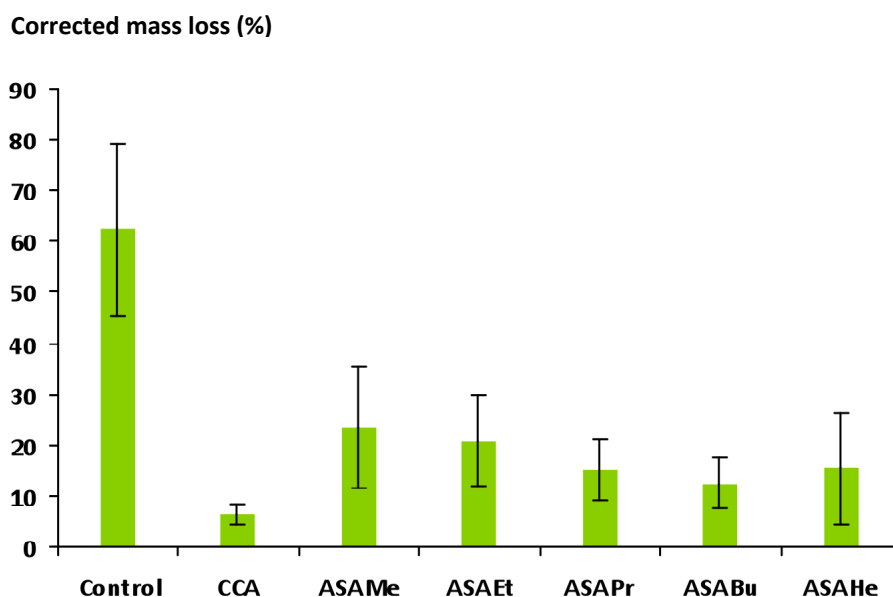


Figure 4: Corrected mass loss in an accelerated (12 weeks) ENV807-type softrot decay test on ASA-R treated samples of poplar. Retention of ASA-R: 150 kg/m³. CCA standard treatment for comparison.

A comparison control treated with a standard CCA formulation was also treated in the same conditions. From Figure 4 it is clear that the ASA-R treatments improve the resistance of wood against softrot. The ASA-R molecules with propyl, butyl and hexyl moieties are significantly more efficient than the methyl ASA that was tested by Morard *et al.* (2007). In those tests, an improvement of only 10% was observed compared to untreated control samples. None of the ASA-R molecules is as efficient as the CCA treatment at the retention levels tested. Further investigation with standard ENV807 tests are being carried out to determine the critical concentration level of ASABu, which shows the best promising performance.

CONCLUSIONS

ASA molecules from rapeseed alkyl esters are a good alternative for treating machined pieces of wood to improve some of their properties. In particular, the higher alkyl derivatives (propyl to hexyl) are significantly more interesting than the methyl derivative studied in 2007 by Morard *et al.* Further testing will allow to determine if the butyl derivative is capable of reaching the use class 4 requirements as demanded by the EN599-1 European standard.

REFERENCES

Goldstein, J.S., Jerosky, E.B., Lund, A.E., Nielson, F.J. and Weaver, J.W. (1961). Acetylation of wood in lumber thickness. *Forest Product Journal*, **11**, 363-370.

Hill, C.A.S and Jones, D.J. (1996). The dimensional stabilization of Corsican pine sapwood by reaction with carboxylic acid anhydrides. *Holzforschung*, **50**, 457-462.

Imamura, Y. and Nishimoto, K. (1986). Resistance of acetylated wood to attack by subterranean termites. *Wood Research*, **72**, 37-44.

Larsson-Brelind, P., Simonson, R. and Risman, P.O. (1997). Acetylation of solid wood to biological degradation. Evaluation field test. International research Group on Wood Preservation IRG/WP/30139.

Quesada, J., Morard, M., Vaca-Garcia, C. and Borredon M.E. (2003). Preparation of alkenyl succinic anhydrides from vegetable oil fame. *Journal of the American Oil Chemists' Society*, **80**, 281-286.

Ramsdam, M.J., Blake, F.S.R. and Fey, N.J. (1997). The effects of acetylation on mechanical properties, hydrophobicity and dimensional stability of *Pinus sylvestris*. *Wood Science and Technology*, **31**, 45-50.

Rowell, R.M., Youngquist, J.A. and Montrey, H.M. (1988). Chemical modification: adding value trough new FPL composite processing technology. *Forest Product Journal*, **38**, 67-70.

Morard, M., Vaca-Garcia, C., Stevens, M., Van Acker, J., Pignolet, O. and Borredon, E. (2007). Durability improvement of wood by treatment with Methyl Alkenoate Succinic Anhydrides (M-ASA) of vegetable origin. *International Biodeterioration and Biodegradation*, **59**, 103-110.

Stefanoiu, F., Candy, L., Vaca-Garcia, C. and Borredon, E. (2008). Kinetics and mechanism of the reaction between maleic anhydride and fatty acid esters. *European Journal of Lipid Science and Technology*, **110**, 441-447.