

DIMENSIONAL STABILITY, UV RESISTANCE, AND STATIC MECHANICAL PROPERTIES OF SCOTS PINE CHEMICALLY MODIFIED WITH ALKYLENE EPOXIDES

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Unprotected wood exposed outdoors suffers from photodegradation due to absorption of UV light by lignin and dimensional changes because of moisture absorption or desorption by free hydroxyl groups in wood constituents. Chemical modification of cell wall polymers is one of the effective methods of inducing dimensional stability and UV resistance in wood. In this work, etherification of Scots pine (*Pinus sylvestris* L.) was carried out with alkylene epoxides. Extracted blocks of Scots pine were modified with propylene oxide (PO) and butylene oxide (BO) between 30 and 75 °C for different durations and under varying alkaline conditions. Different weight percent gains (WPG) were obtained. WPG increased with temperature, reaction time, and NaOH concentration. The dimensional stability, mechanical properties, and UV resistance of chemically modified wood were evaluated. Etherified wood exhibited an improvement in dimensional stability, but the efficacy dropped with successive water-soaking, oven-drying cycles, indicating a loss of modifying chemical. After four soak-dry cycles, both modifications retained positive anti-swelling efficiency (ASE) values; however, at WPG values >30%, the PO modified material exhibited a reduction in ASE, indicating cell wall degradation. Both PO and BO modified wood exhibited a loss in static mechanical properties measured as modulus of elasticity and modulus of rupture, with the reduction being dependent upon the level of modification. Modification of wood with PO provided partial photo stability to wood polymers, whereas BO was more promising in improving dimensional stability.

Keywords: Dimensional stability; Photodegradation; Weathering; Lignin; Chemical modification; Wood

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INTRODUCTION

In indoor applications, naturally light colored wood is darkened with time when exposed to light. In outdoor applications, unprotected wood surfaces change colour due to photodegradation of wood polymers, mainly lignin, and finally attain a characteristic grey color (Feist and Hon 1984). Bleached printing papers made of mechanical wood pulps are rapidly yellowed in sunlight. Wood exposed to outdoor conditions also undergoes dimensional changes resulting from moisture sorption because the cell wall polymers contain hydroxyl groups that attract moisture through hydrogen bonding.

The origin of light-induced discoloring of wood is reasonably well known. Lignin phenols are converted into quinones by the action of oxygen in the atmosphere (Hon 2001). The ultraviolet radiation of the sun or man-made light sources and the presence of carbonyl structures in lignin catalyze the oxidation. The increase in the hydrophilicity of lignin leads to its leaching by rain. The removal of lignin also enables the dissolution of hemicelluloses by water. The fragmentation of lignin weakens the native interfiber bonding because lignin acts as an adhesive in wood and holds the cellulose fibers together. This results in formation of microscale cracks on the wood surfaces (Evans et al. 2008).

Several treatments have been suggested to protect wood or wood fibers from the photo-discoloring phenomenon. The treatments include the reaction of lignin with chromic acid (Black and Mraz 1974; Evans et al. 1992), blocking of ultraviolet light with thin protecting films of UV absorbing materials, the use of organic radical scavengers, and the blocking of the free hydroxyl groups in the wood constituents with ether or ester groups (Feist and Hon 1984; Williams 2005; Plakett et al. 1996; Evans et al. 2000; 2002; Pandey and Chandrashekhara 2006; Chang and Chang 2001; 2006). Most of the treatments are unrealistically costly to apply industrially. Etherification of free phenolic groups in lignin has, nevertheless, been found to inhibit photodegradation in lignin-rich pulps (Singh 1966; Janson and Forsskahl 1989), whilst chemical modification of wood with propylene and butylene oxides has been found to improve dimensional stability and induces resistance to fungi and termites (Rowell et al. 1981; Feist and Rowell 1982; Rowell 1983; 1984; Rowell and Gutzmer 1975; Rowell et al. 1976; Kiguchi 1997; Matsuda 1996; Takahashi 1996; Rowell 2006; Hill 2006). The etherification of wood may have advantages because there is no by-product formed during modification; this is not so with esterification, which is generally associated with the formation of acids as byproducts; such acids need to be neutralized to avoid degradation of wood surfaces. Recently Evans (2009) has reviewed the weathering and photostability of chemically modified wood.

Rowell and coworkers (Rowell and Gutzmer 1975; Rowell et al. 1976; Rowell and Ellis 1984) have studied the properties of wood chemically modified with propylene and butylene oxides catalyzed with triethylamine. In their work, the reactions were carried out in a stainless steel reactor at 120°C and 150 lb/in² nitrogen pressure. Good dimensional stability and biological resistance to brown-rot fungi, white-rot fungi, and termites were reported by these workers; however, the modification was found to have no effect in improving the resistance to UV light in the weathering process (Rowell and Ellis 1984).

In an earlier work (Pandey and Vuorinen 2008a), the reaction between lignin model compounds (viz., phenol and guaiacol) and propylene oxide in aqueous media under alkaline conditions at moderate temperatures (temperature range 30-60 °C) has been demonstrated. The probability of an etherification reaction between phenolic compounds and alkylene epoxide occurring at neutral pH condition is negligible. The rate of reaction increases with an increase in temperature, the concentration of epoxides, and the initial pH of the solution. It is possible to interfere with the process of UV light absorption by wood by blocking free phenolic groups through etherification with alkylene epoxides and hence reduce the photodegradation of wood.

In this work, we have carried out chemical modification of solid wood blocks of Scots pine (*Pinus sylvestris* L.) with propylene oxide (PO) and butylene oxide (BO) at 30-75 °C for different durations and under varying alkaline conditions. The aim of our study was to evaluate the dimensional stability, UV resistance, and static mechanical properties of Scots pine modified with alkylene epoxides in aqueous media, under alkaline conditions and at moderate reaction temperatures, with a view of developing a simple and effective means of modifying wood.

EXPERIMENTAL

Wood Specimens

All specimens were of Scots pine sapwood having approximately 10 growth rings per centimeter. The specimens were machined from commercial kiln-dried boards. Specimens of Scots pine having the nominal dimensions 20 x 20 x 5 mm³ (radial, tangential, longitudinal) were prepared for the evaluation of dimensional stability and kinetic studies. Care was taken to ensure that the growth rings were oriented as nearly parallel to one side of the specimen as possible and that the specimens possessed the same number of growth rings. For evaluation of UV resistance and three-point bending tests, specimens of nominal dimensions 70 x 20 x 3.5 mm³ (length, width, thickness) were prepared such that the growth rings were oriented parallel to the thickness dimension. Specimens were extracted with a mixture of ethanol:benzene (1:2) for 6 h in a Soxhlet apparatus followed by washing with hot water (40-50 °C) for about 15 minutes. The specimens were oven-dried at 105 °C, following which the weight and volume of the specimens were determined. All modified and control specimens were subsequently conditioned at 65% RH and 20 °C for a minimum of 1 week prior to testing.

Etherification of Wood by Alkylene Oxides

The extracted wood blocks were modified with PO and BO at temperatures between 30 and 75 °C for different durations under different alkaline conditions. The wood specimens were submerged in an aqueous solution of sodium hydroxide (0.1 - 0.25 M) for up to 1 hour and then transferred to 500 ml reaction bottles containing the epoxide reagents. For dimensional stability measurements six replicates for each case were reacted with 30 ml of epoxide. For UV fastness tests and three-point bending tests, 10 replicates were reacted with 60 ml of epoxide. The desired amount of 10 M NaOH solution was then added to the solution to maintain the concentration of NaOH between 0.1 and 0.25 M. The reaction bottles were sealed and transferred to a water bath maintained at the desired reaction temperature. The bottles were stirred at regular time intervals and the reaction carried out for different durations up to 6 hours. The reaction was terminated by adding an equivalent amount of acetic acid relative to NaOH. The modified wood blocks were subsequently washed with running water and then extracted with ethanol and benzene (1:2) to remove the un-reacted PO/BO and oven dried to determine weight percent gain (WPG).

Estimation of Dimensional Stability of Modified Wood

The dimensional stability of the chemically modified wood was determined by estimating the volumetric swelling coefficient (S) and antishrink/antiswell efficiency (ASE) using the repeated water-soaking method described by Rowell and Ellis (1978). The external dimensions of the oven-dried specimens were measured to two decimal places using digital calipers and the weight recorded to three decimal places on a top-loading balance. The specimens were subsequently impregnated with distilled water under vacuum and submerged for at least 24 h at room temperature. Following removal from the water, the external dimensions were re-measured and the specimens again oven-dried at 105 °C for 24 h. This water-saturation oven drying process was repeated four times. The volumetric swelling coefficient (S) was determined using eqn. 1,

$$S (\%) = 100 (V_2 - V_1) / V_1 \quad (1)$$

where V_2 is the volume of the saturated sample and V_1 that of the oven dried sample. ASE was determined using eqn. 2,

$$ASE (\%) = 100 (S_u - S_m) / S_u \quad (2)$$

where S_u and S_m are the swelling coefficients of unmodified and modified wood, respectively.

Evaluation of Static Mechanical Properties

The static mechanical properties - modulus of elasticity (MOE) and modulus of rupture (MOR) - were measured in three-point flexure on a Zwick universal testing instrument equipped with a 100 kN load cell. The span was 50 mm, and the tests were performed under displacement control at a crosshead speed of 8 mm min⁻¹. Data were captured digitally, and MOE and MOR calculated automatically.

UV Fastness Experiments

The modified wood specimen along with unmodified control specimens were exposed to a xenon arc light source in an Atlas SUNTEST CPS+ system for up to 100h at a chamber temperature of 30 °C. The degradation of the aromatic structures in lignin was followed by UV resonance Raman (UVRR) spectroscopy and photoacoustic Fourier transform infrared (FTIR-PAS) spectroscopy.

Colour Measurements

Changes in the colour of wood surfaces due to modification and light irradiation were measured using a Minolta CM-2500d portable spectrophotometer using a 2° standard observer and standard illuminant D65. CIE L*, a*, b* colour coordinates were calculated from the measured spectra. Measurements were made at three different locations on each specimen and an average value was calculated.

Measurements of FTIR-PAS Spectra

FTIR spectra were measured directly from control (unirradiated) and irradiated wood surfaces using a Bio-Rad 6000 spectrometer equipped with an MTEX 300 photoacoustic (PA) detector. The PA cell was purged with helium gas before the measurements. The cross section of the beam inside the cell was $\sim 1 \text{ mm}^2$. The spectra were collected at an interferometer mirror speed of 5 kHz with a spectral resolution of 8 cm^{-1} .

Measurement of UV Resonance Raman Spectra (UVRRS)

UVRRS spectra were collected directly from the wood surfaces. The spectra were collected with a Renishaw 1000 UV Raman Spectrometer (Renishaw, Gloucestershire, UK) equipped with a Leica DMLM microscope (Leica Microsystem, Wetzlar, Germany). The light source was an Innova 90C FreDTM frequency-doubled Ar ion laser (Coherent Inc. California, USA) tuned to an excitation wavelength of 244 nm. This wavelength is appropriate for studying both guaiacyl (G) and syringyl (S) structures (Saariaho et al. 2003). The laser beam was focused on the sample with a 15X objective lens. The laser power was kept low ($\sim 1 \text{ mw}$), and samples were spun during measurements to avoid the effect of degradation due to laser irradiation. Average spectra were obtained from repeated measurements. The acquisition time was 45 s, consisting of 3 CCD readouts of 15 s. The spectral data were analyzed using GRAMS/32 software (Thermo Galactic, Woburn, MA, USA).

RESULTS AND DISCUSSION

Chemical Modification Reaction

The reaction scheme between alkylene oxides and wood is shown in Fig. 1.

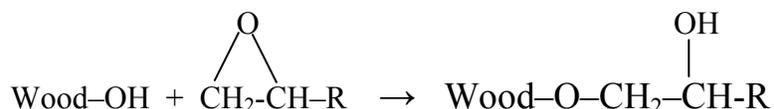


Fig. 1. Scheme for the reaction between alkylene oxide and wood (R = CH₃ for PO and R = C₂H₅ for BO)

The reaction of an alkylene epoxide reagent with wood results in the formation of an ether linkage with the hydroxyl groups of the cell wall polymers. This results in the formation of a new OH group that may react with another epoxide molecule, leading to formation of an oligomer attached to the original OH site (Hill 2006). There is also the possibility of the formation of epoxide oligomers that are merely entangled in the cell wall or settled in the free spaces in the cell lumen. A significant weight percent gain (WPG) due to etherification of wood polymers was obtained. The WPG depended upon reaction temperature and concentration of NaOH. The effects of reaction time, temperature, and NaOH concentration on the average WPG of wood modified with PO are shown in Fig. 2. The average WPG increased with increased reaction time and temperature. The high rate of reaction in the initial phase decreased as the reaction

progressed. The high rate of reaction during the initial phase can be explained on the basis of higher numbers of available OH groups in the wood macromolecules. Once the easily accessible OH groups on the surface layers are modified, the reactant has to diffuse into the cell wall. Modification of the outer layer of the wood surface also reduces the porosity and accessibility of the layers below. Consequently, the level of modification will be highest at the surfaces and will decrease as the penetration depth increases. The WPG values shown in Fig. 2 represent the overall weight gain. An increase in NaOH concentration results in a faster reaction, because of the conversion of lignin phenols into more reactive ionic form. However, at high NaOH concentration, cell wall degradation becomes more significant. Modification with BO follows similar behavior. Figure 3 shows the effect of NaOH concentration on the WPG of Scots pine modified with BO at 60 °C. However, reactivity of wood is much higher for PO than BO.

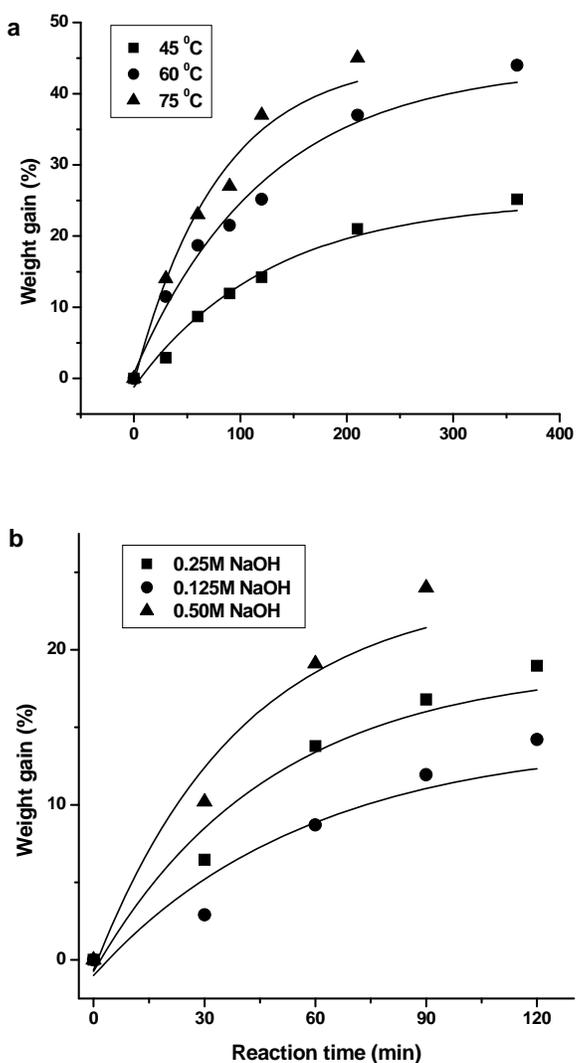


Fig. 2. (a) Effect of temperature on reaction of Scots pine with PO at 0.125 M NaOH; (b) Effect of NaOH concentration on reaction of Scots pine with PO at 45 °C.

FTIR-PAS spectroscopy was used to characterize chemical changes in the modified wood (Fig. 4). FTIR spectra of unmodified wood treated with NaOH showed a

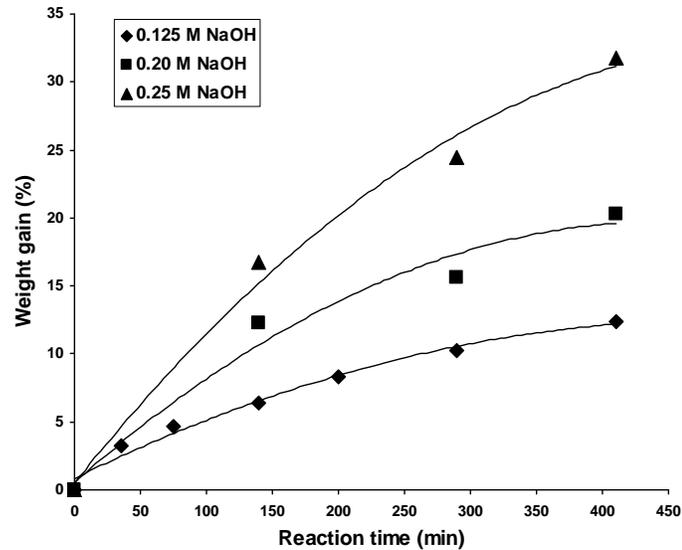


Fig. 3. Reaction of Scots pine with BO at 60 °C and different NaOH concentrations

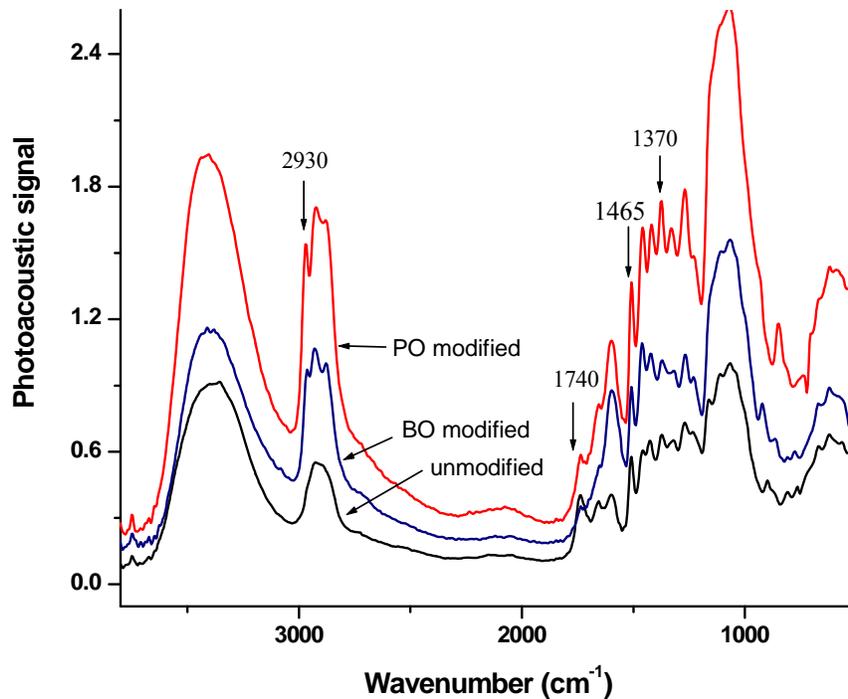


Fig. 4. FTIR spectra of unmodified and modified Scots pine wood.

significant reduction in the C=O absorbance at 1740 cm^{-1} , which indicates the deacetylation of hemicelluloses due to NaOH treatment. Significant changes in the FTIR spectra were obtained after modification. The increases in the intensity of bands at 1370 cm^{-1} (CH_3 bending) and 1465 cm^{-1} (CH_2 scissoring) are indicative of an increase in isopropyl and methylene groups as a result of modification. The absorption bands at 2930 cm^{-1} and 2859 cm^{-1} in modified wood are attributed to CH_3 and CH_2 vibration in alkylene oxides. No drastic change, as is usually observed in case of esterification reaction, was observed in the intensity of the OH stretching peak at 3400 cm^{-1} . This can be attributed to the formation of the new hydroxyl groups when wood reacted with alkylene oxides.

Dimensional Stability of Etherified Wood

In dimensional stability tests, Hill (2006) suggests that the first water-soak, oven-dry cycle should be discarded, since the results can be unrepresentative due to the leaching of non-bonded, but nevertheless bulking, chemical. For this reason, a series of four water-soaking, oven-drying cycles were performed in this work. Figure 5 shows ASE against initial WPG for PO and BO modified Scots pine reacted at $60\text{ }^\circ\text{C}$ in 0.125 M NaOH. ASE was calculated from the S_m and S_u values determined after the fourth water-soaking, oven-drying cycle. As may be observed, even after four soak-dry cycles, the specimens modified with butylene oxide retained an ASE value in excess of 25% at an initial WPG value of slightly greater than 10%. This contrasts with the propylene oxide modified material, which displayed an ASE value of less than 20% at an initial WPG value of around 25%. Above 30% WPG, the ASE value of PO modified wood dropped again. This finding is in accordance with that found by Rowell and coworkers (Rowell and Gutzmer 1975; Rowell et al. 1976; Rowell and Ellis 1984), who attributed a loss in ASE to the breaking up of the cell wall. Moreover, the relatively modest WPG values seen with the BO modified wood accords with the findings of these authors, who noted that the butylene oxide reaction system is slower than that of propylene oxide.

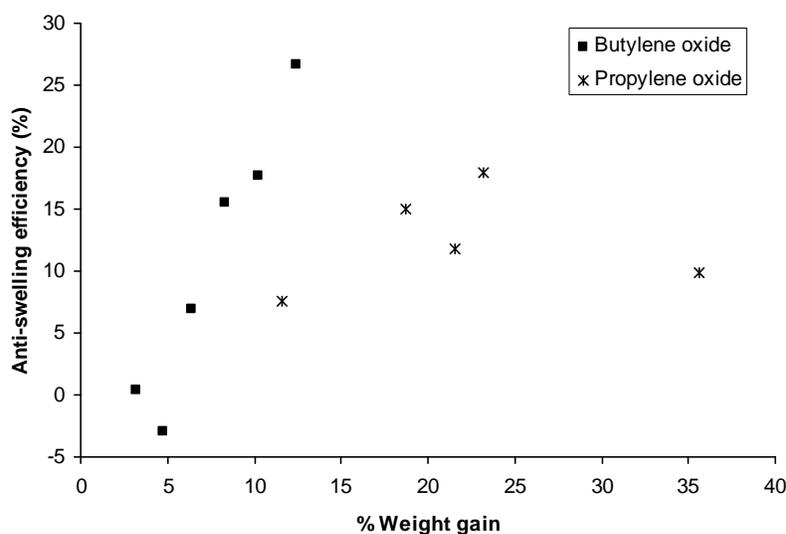


Fig. 5. Variation of ASE with WPG for BO and PO modified Scots pine reacted at $60\text{ }^\circ\text{C}$ in 0.125 M NaOH.

Figure 6 shows the effect of catalyst (NaOH) concentration on the dimensional stability of butylene and propylene oxide modified Scots pine. Figure 6 (a) shows ASE as a function of WPG for BO modified wood reacted at 60 °C with catalyst concentrations of 0.125, 0.2, and 0.25 M NaOH. As may be observed, a higher catalyst concentration resulted in greater WPG; however, as the concentration of NaOH increased, at equivalent WPG values, the ASE value diminished, indicating degradation of the cell wall. With the PO modified material reacted at 45 °C (Fig. 6b), the higher catalyst concentration was again shown to reduce dimensional stability at equivalent WPG values. Furthermore, weight gains in excess of 25% resulted in very low ASE values, suggesting cell wall degradation at the higher catalyst concentration.

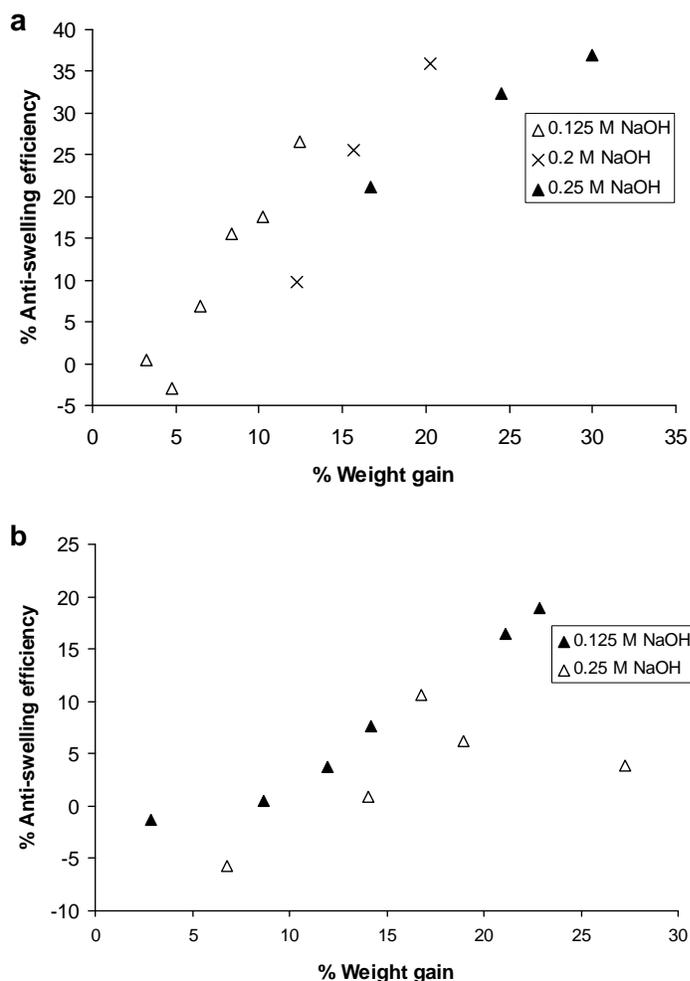


Fig. 6. Variation of ASE with WPG: (a) BO modified Scots pine reacted at 60 °C in 0.125, 0.2 and 0.25 M NaOH, (b) PO modified Scots pine reacted at 45 °C in 0.125 and 0.25 M NaOH.

A significant mass loss was observed during soaking-drying cycles. Figure 7 shows the mass loss of modified wood during soaking-drying cycles for comparable WPG values obtained at different NaOH concentration. Some mass loss was seen even with the control samples, with an average loss of 2.1% observed after cycle #1. The mass loss after cycle #1 for the modified samples ranged from 3.2% to 8.7%, all of which were

greater than the mass loss from the control samples, indicating the loss of some bulking chemical. The mass loss during repeated cycles of soaking and drying indicates formation of oligomers of epoxide, which are not permanently bonded to the cell wall polymers and may leach out during soaking drying cycles. The mass loss increased with increase in the NaOH concentration. The greatest mass loss after cycle #1 was observed in the PO and BO modified specimens reacted in 0.25 M NaOH, possibly the result of the removal of degraded cell wall polymers in addition to the removal of non-bonded epoxide. At the same reaction temperature, lower oven-dry mass losses were observed with the lower NaOH concentrations.

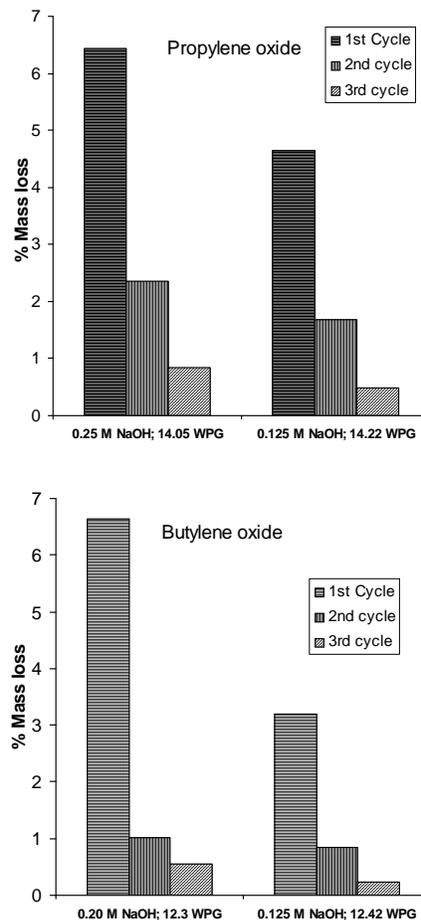


Fig. 7. Mass loss of modified wood during repeated soaking and drying cycles

Static Mechanical Properties of Modified Wood

The static mechanical properties of the etherified Scots pine samples are summarized in Table 1. The reaction conditions are also mentioned in Table 1. Although there was significant scatter in the results, indicated by the relatively high standard deviations, it may be observed that all samples modified with butylene and propylene oxides exhibited a reduction in both bending strength (MOR) and bending stiffness (MOE), following modification. At a WPG of 27.6%, for instance, the mean value of MOR of wood etherified with butylene oxide was approximately 40% lower than that of

unmodified wood, whilst the MOE was reduced by nearly 50%. Again, bearing in mind the scatter in the results, at lower WPG values of less than 10%, there did appear to be some loss in MOR of around 10-20% with the propylene and butylene oxide modified wood. MOE was also reduced by a comparable amount. Rowell and co-workers (1982) reported a reduction in static mechanical properties with propylene oxide modified sugar maple, however, the strength and stiffness reduction reported by these authors were less severe (9-17% at ~30% weight gain) than the reductions observed in this work. Although it is difficult to draw firm conclusions, it is probable that the greater reductions in strength and stiffness reported herein are in part due to degradation of the cell wall polymers by the NaOH used as catalyst. The base (NaOH) used in this study, being stronger than the triethylamine (TEA) used by Rowell and co-workers may, therefore, account for the higher strength losses. It can also be observed from Table 1 that loss in MOR and MOE at equivalent WPG values were more in the PO modified wood than in the BO modified specimens. Again, bearing in mind the scatter in the results, at ~ 14-15 WPG, MOR reduced from 99.5 N/mm² to 74.4 N/mm² and 80.9 N/mm² for PO and BO, respectively. Similarly MOE values were reduced from 10540 N/mm² to 7222 and 8317 N/mm² for PO and BO, respectively. This suggests that BO modified wood was less affected than PO modified wood, which is reflected in the more stable dimensional stability of BO modified wood.

Table 1. Summary of the Static Mechanical Properties (MOE and MOR) of PO and BO Modified Scots Pine Specimens at Different WPG.

Epoxide	N	Reaction conditions		Average WPG (%)	MOR (N/mm ²)	MOE (N/mm ²)
		Temperature (°C)	Reaction time (min)			
Control	9				99.5 (15.5)	10540 (1196)
PO	6	45	45	5.7 (0.7)	98.7 (7.2)	10612 (1283)
PO	6	45	90	8.8 (4.0)	91.9 (12.1)	9440 (1754)
PO	5	45	140	13.3 (4.6)	85.2 (10.9)	7559 (1152)
PO	5	45	220	15.5 (3.1)	74.4 (13.7)	7222 (1431)
BO	8	45	140	4.7 (0.4)	97.5 (7.9)	10030 (1164)
BO	7	45	220	9.3 (2.7)	85.8 (6.7)	8717 (847)
BO	5	76	135	8.9 (4.3)	71.7 (14.2)	7388 (993)
BO	8	76	210	9.7 (0.8)	85.6 (5.6)	8361 (1712)
BO	5	76	270	14.6 (0.1)	80.9 (12.7)	8317 (1354)
BO	7	76	335	27.6 (4.2)	60.9 (3.1)	5377 (834)

N is number of samples. Values in parentheses are standard deviations. Reaction was carried out at 45 °C and 76 °C for various times up to 335 minutes at 0.2 M NaOH. 10 replicates for each case were reacted in 60 ml of epoxide.

Photo-Stability of Modified Wood

Scots pine is a light colored wood ($L^* = 83.2$). The color of unmodified specimens darkened upon irradiation. The rapid color change due to irradiation in unmodified wood surfaces is indicated by a decreasing value of lightness (L^*). The reaction conditions for the photostability tests were similar to those mentioned in Table 1. Modification of wood with alkylene oxides resulted in some darkening (greenish yellow) of wood surfaces, which resulted in a decrease in L^* values. L^* values for PO modified wood were 75.6 and 74.7 for WPG of 11.9 and 16.1, respectively, whereas its value was 75.4 for BO modified wood (18.2 WPG). The color of modified specimens became lighter upon irradiation. While the value of L^* decreased upon irradiation in unmodified wood ($\Delta L^* = 6.19$), its value increased in modified wood. The values of ΔL^* for PO modified wood were -0.98 (corresponding to 12.9 WPG) and - 4.17 (corresponding to 18.2 WPG), whereas ΔL^* values for BO modified wood were - 2.60 (corresponding to 11.9 WPG) and - 4.91 (corresponding to 16.1 WPG). The darkening (yellowing) in the color of the surfaces in unmodified wood surfaces is due to the formation of unsaturated carbonyl structures as a result of lignin degradation (Hon 2001). The lightning in the color of irradiated modified wood may be attributed to photo-bleaching of modified wood surfaces, resulting in a reversal in the color of wood due to modification. The color changes due to irradiation in modified wood were less evident in specimens with low WPG. Among the two epoxides, less change in colour was observed for PO modified wood.

Figure 8 shows a comparison of the FTIR spectra of unmodified Scots pine wood surfaces before and after exposure to the xenon source. Irradiation of unmodified wood entailed a rapid and significant decrease of the aromatic absorption band at 1511 cm^{-1} and other lignin associated bands at 1465 cm^{-1} and 1270 cm^{-1} . The absorption bands assigned to polysaccharides at 1374 cm^{-1} (C-H deformation in carbohydrates), 1158 cm^{-1} (C-O-C vibration in cellulose and hemicellulose), and 898 cm^{-1} (C-H deformation in cellulose) were least affected by the irradiation, as would be expected. This is accompanied by a successive increase in carbonyl absorption at $\sim 1740\text{ cm}^{-1}$. This is the manifestation of the formation of *o*- and *p*- quinone type of carbonyl structures as a result of the degradation of the aromatic rings of lignin in a free radical triggered photoreaction (Hon 2001).

The FTIR spectra of modified Scots pine surfaces irradiated with the xenon source indicate that the modification with PO inhibits degradation of lignin to some extent in specimens with low WPG. The difference spectra (spectrum after aging - spectrum before aging) for the untreated and alkylene oxide treated samples are shown in Fig. 9. It can be seen that there was very little change in the intensity of 1511 cm^{-1} band in the FTIR spectra of PO modified wood surfaces, though there was a significant increase in the carbonyl absorption at $\sim 1730\text{ cm}^{-1}$. However, samples with higher WPG did not show any photostability. This is probably due to a breakdown in the cell wall structure resulting from modification. The origin of increased intensity at $\sim 1730\text{ cm}^{-1}$ in treated wood is not the same as in case of untreated wood since the color becomes lighter in modified wood. However, BO modified wood surfaces show comparatively less reduction in lignin degradation. Etherification with PO has been reported to inhibit photoyellowing in thermo mechanical pulp (Singh 1966). As noted previously, Rowell

and Ellis (1984) examined the weathering resistance of Southern pine sapwood modified with BO and found that BO modification was ineffective in improving UV resistance.

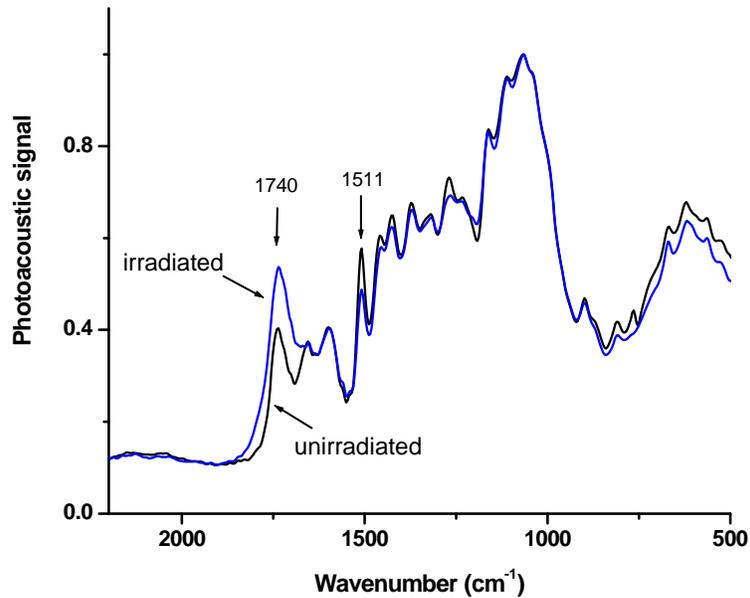


Fig. 8. FTIR spectra measured from of unmodified Scots pine un-irradiated and irradiated with xenon source for 100h

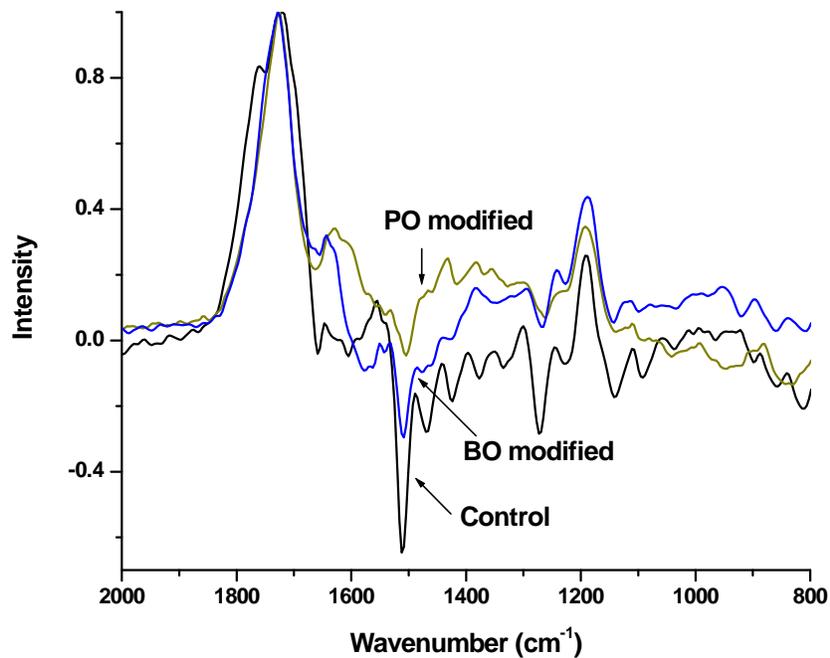


Fig. 9. The difference IR spectra (spectrum after irradiation – spectrum before irradiation) of unmodified and modified Scots pine irradiated for 100 h. WPG in PO and BO modified wood were 12.9 and 16.1, respectively.

The decrease in initial lightness resulting from modification with epoxides is likely the result of the formation of new chromophores due to the alkali treatment or alkaline conditions in the alkylene oxide treatment. The newly formed chromophores are probably the ones that are responsible for the observed photobleaching. The degradation products contain carbonyl/carboxyl groups that are detected in the FTIR spectra after the aging test. It can be seen from Fig. 9 that the origin of the carbonyl/carboxyl structures formed was different for untreated and treated wood. Untreated wood clearly shows two distinct peaks at ~ 1724 and 1760 cm^{-1} , whereas treated wood shows a single peak at $\sim 1730\text{ cm}^{-1}$. The increased intensity at $\sim 1730\text{ cm}^{-1}$ in treated wood is because of the photobleaching of chromophoric structures formed due to treatment. A comparatively smaller decrease in the lignin associated peak at 1511 cm^{-1} in treated wood provides the evidence of the photostabilisation of lignin due to treatment.

UVRR spectra of unmodified and modified Scots pine are shown in Fig. 10. In UVRR spectroscopy, the Raman signal of aromatic and conjugated lignin structures are intensively resonance enhanced, since UV is used for excitation, which is strongly absorbed by lignin. The contribution of cellulose and hemicellulose to the UVRR spectrum is only minor (Saariaho et al. 2003). The UVRR spectra of Scots pine shows the most prominent bands at ca. 1602 cm^{-1} (arising mainly from aromatic ring vibration), a shoulder at ca. 1650 cm^{-1} (mainly attributed to the C=O and C=C groups in the coniferaldehyde and coniferyl alcohol, respectively), 1370 cm^{-1} (phenolic OH bend in G-structure), 1270 cm^{-1} (aromatic ether in G structure), and 1150 cm^{-1} (Delta phenol mode of the G structure). The assignments of major peaks are well documented in the literature (Agarwal 1999; Saariaho et al. 2003). There was no noticeable change observed in the UVRR spectra of modified wood. The shape and relative intensities of all the lignin bands remained the same.

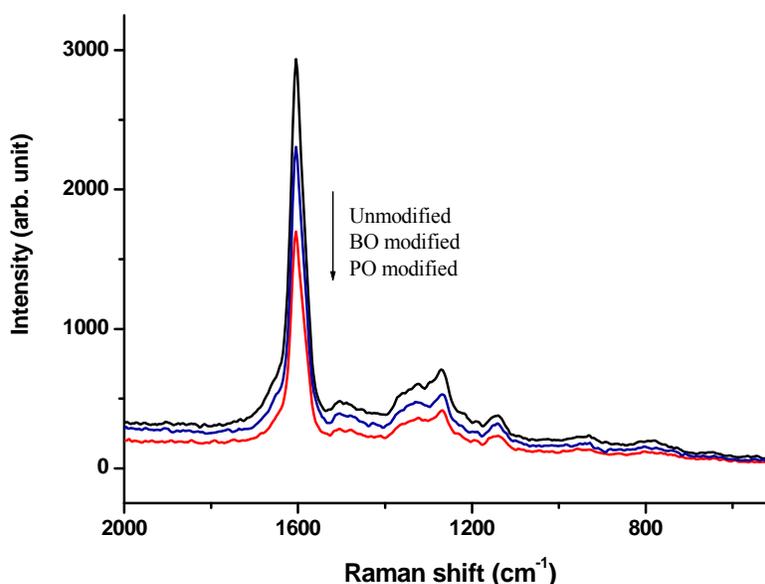


Fig. 10. UVRR spectra of Scots pine modified with PO (12.9 WPG) and BO (16.1 WPG)

The UVRR spectra measured from unmodified and modified wood surfaces exposed to the xenon source for 100h are compared in Fig. 11. The spectra were normalized at 1602 cm^{-1} . Irradiation had significant effect on the UVRR spectra of unmodified wood. The irradiation resulted in significant decrease in the intensity of prominent aromatic structures at 1602 cm^{-1} . There was also a significant band broadening and notable shift in the 1602 cm^{-1} band towards longer wavenumber due to increase in C=C or C=O structures in irradiated wood (Agarwal 1999; Jääskeläinen 2006; Pandey and Vuorinen 2008b). The intensity of all the peaks in the wavelength region below 1500 cm^{-1} decreased, accompanied by the development of a broad structure in $1500\text{-}1000\text{ cm}^{-1}$ region. The broad structure in the $1500\text{-}1000\text{ cm}^{-1}$ range is due to liberation of some unsaturated structures as a result of lignin degradation (Pandey and Vuorinen 2008b).

A significant band broadening and notable shift in the 1602 cm^{-1} band towards longer wavenumber due to irradiation can be seen in unmodified wood (curve 'd' in Fig. 11). The broadening was significantly suppressed in PO modified wood surfaces (curve 'b' in Fig. 11). Less broadening in the UVRR spectra of PO modified wood indicates that etherification with PO induced partial photo-stability in wood. However BO was not so effective. These results support the findings of FTIR spectroscopy (Fig. 9).

These findings are interesting and the systems need to be studied further to evaluate its industrial feasibility. The behavior of etherified wood at low NaOH concentrations, where cell wall degradation is less pronounced, needs to be investigated further. Treatment of wood at very high NaOH concentration makes it unsuitable due to significant loss in mechanical properties because of cell wall degradation.

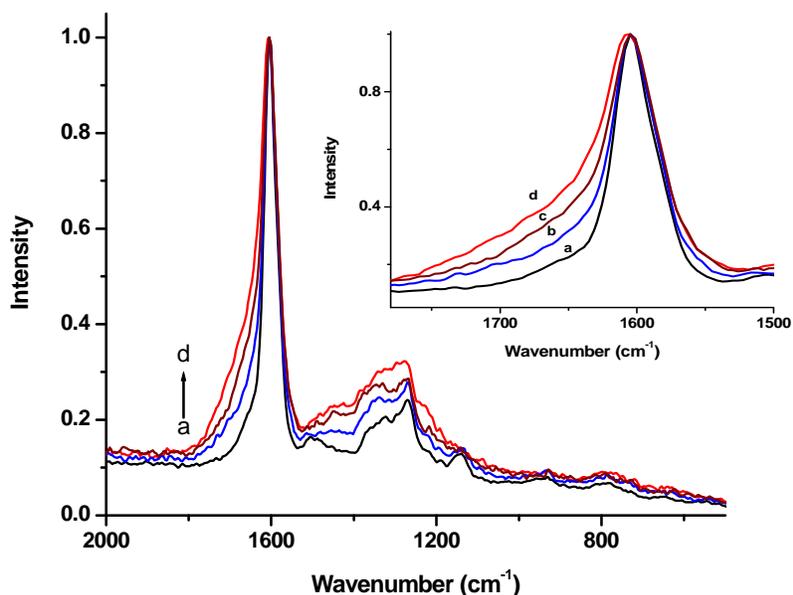


Fig. 11. Normalized UVRR spectra of unmodified and modified Scots pine irradiated with xenon source. (a) unmodified and un-irradiated, (b) modified with PO (12.9 WPG) and irradiated, (c) modified with BO (16.1 WPG) and irradiated, and (d) unmodified and irradiated. Spectra are normalized at 1602 cm^{-1} .

CONCLUSIONS

Chemical modification of Scots pine by alkylene oxides has been carried out. The degree of modification increases with NaOH concentration and temperature. Etherified wood showed improved dimensional stability, butylene oxide being more effective, although a loss in static mechanical properties was observed. BO-modified wood appeared to show more stable behavior, but nevertheless after the four soaking-oven drying cycles, the ASE value decreased, indicating significant leaching during repeated soaking tests. The use of NaOH appeared to lead to degradation of the cell wall polymers, influencing the dimensional stability and mechanical properties. UVRR and FTIR spectra showed that propylene oxide inhibited lignin degradation to some extent. However, the degree of photo-stability decreased rapidly at higher WPG. Modification with BO was less effective in restricting the photodegradation of lignin. In order to find practical applications for the findings, the behavior of etherified wood at low NaOH concentrations, where cell wall degradation is less pronounced, needs to be investigated further.

ACKNOWLEDGMENTS

This research was supported by Finnish Funding Agency for Technology and Innovation (TEKES) and from a group of industrial partners (Andritz, UPM-Kymmene, Kemira, Metso, and M-real). Krishna K. Pandey expresses his sincere thanks to the DG, ICFRE, Dehradun and the Director, IWST, Bangalore, India for their support and encouragement during his visit to Helsinki University of Technology. Thanks are also extended to Dmitri Šumigin for his assistance in carrying out the dimensional stability and mechanical property measurements.

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Article submitted: Dec. 23, 2009; Jan. 15, 2010; Revised version received and accepted: Feb. 9, 2010; Published: Feb. 10, 2010.