

DIMENSIONAL STABILITY AND SORPTION CHARACTERISTICS OF WOOD TREATED WITH ALKYLENE OXIDE

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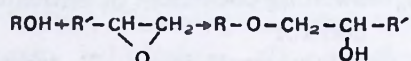
A high degree of dimensional stability was obtained by epoxy treatment of Corsican pine (*Pinus nigra*) wood. It was found that the degree of dimensional stability was strongly and positively correlated with the level of substitution obtained. The dimensional stability obtained was of permanent nature and was practically unaffected by quite severe simulated weathering. The introduced material was in the cell wall and probably covalently bonded to the same.

The wood specimens, chemically modified by propylene oxide under 10 bar N_2 pressure and 130°C temperature for 90 minutes, were tested for sorption at various relative humidities. Typical isotherms for normal pine wood were also found with controls, whereas, a noticeable change in the isotherms was observed with modified specimens. At low values of RH the treated specimens absorbed and retained less moisture than the controls. Above about 55% RH the modified wood started to absorb increasing quantities of moisture and in the 95–100% RH region the EMC of treated wood was slightly greater than that of controls.

Reduction in the degree of swelling of treated specimens compared to that of controls was reasonably constant throughout the sorption range. High moisture sorption at high levels of RH was not accompanied by a corresponding increase in dimensional change. Large water uptake was probably due to the rigid bulky propane chains retaining the cell walls in a swollen but relatively porous state. Treatment with propylene oxide, thus, led to significant improvement in dimensional stability throughout the hygroscopic range.

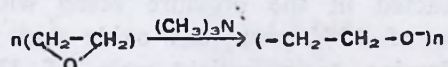
activation energy, needs more vigorous reaction conditions to achieve a rate of reaction comparable to that achieved with propylene oxide.

Epoxides react with wood hydroxyl groups in the presence of a basic catalyst to yield an ether bonded compound but leaving an additional primary or secondary alcoholic group in the ether bonded wood product :

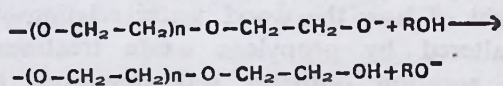


Wood Epoxide Ether bonded product

Ethylene oxide reacted with wood in the vapour phase with trimethylamine catalyst yields various polymerized products (McMillin 1963). The presence of abundant hydroxyl groups in wood is believed to give rise to chain transfer. The homopolymer chain formed by ethylene oxide probably proceeds thus :

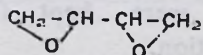


Theoretically, this chain may be very long. But the chain transfer process breaks the molecules to shorter chain products with the formation of alkoxide ions :



This process keeps the molecular weight of the reaction products low (Schuerch 1968).

By using a bifunctional epoxide, e. g. butadiene diepoxide,



in addition to the effects described, it is believed that cross-linking between adjacent polymer chains may be induced, giving rise to improved dimensional stability for a given weight gain (Schuerch 1968).

The hygroscopic nature of wood is mainly due to the presence of reactive hydroxyl groups in both the polysaccharide and lignin components of the cell wall. Shrinkage and swelling in wood resulting from this hygroscopic property can be drastically reduced by blocking these groups. Excellent dimensional stabilization has been obtained in wood specimens by reacting them with the first three members of the alkylene oxide series (McMillin 1963, Liu and McMillin 1965, Rowell and Gutzmer 1965).

Dimensional stability is believed to result from a combination of reduction in hydrophilic property due to elimination of hydroxyl groups and "bulking" effect. McMillin (1963) believed that the advantage of gas phase reaction over liquid phase impregnation was that the polymers were produced on and within cell walls without filling the lumen and vessels.

Treatment with epoxides has been shown to give anti-shrink efficiency (ASE) up to 82% depending on the weight gain brought about by the reactions (Liu and McMillin 1965, Barnes *et al.* 1969). The optimal weight gain seems to be about 33%. Above this level of treatment cell wall rupturing can occur allowing the wall to swell above the green volume, leading to a decrease in ASE (Rowell and Gutzmer 1975).

The stabilization achieved by epoxide reactions has been shown to be resistant to the effects of prolonged exposure to water (Rowell 1978). Furthermore, and importantly, it has been established that the strength properties of the treated wood are unimpaired (McMillin 1963).

MATERIALS AND METHODS

Transverse wafer specimens (2 x 2 x 0.6 cm) from Corsican pine sapwood were first dried at 105°C and then to constant weight over P₂O₅. Two different levels of treatment were achieved by varying the reaction conditions. In both experiments a mixture of 95% propylene oxide (PO) and 5% triethylamine (TEA) was used, the TEA acting as base-catalyst (McMillin 1963, Rowell 1975). In each experiment 20 wafer specimens were treated. The dry specimens were weighed, measured (with a micrometer) and placed in a steel high pressure reaction vessel along with the reaction mixture. The vessel was sealed, connected to a nitrogen gas cylinder and the pressure was raised to 9 bar. The gas in the vessel was then allowed to escape in order to sweep out the air originally present. This process was repeated twice more.

In the first experiment, pressure in the reaction vessel was increased to 10 bar and then the reaction vessel was placed in an oil bath at 125°C. The reaction was allowed to continue for 90 minutes. In the second experiment, a lower level epoxy treatment was effected by keeping the pressure at 8 bar and heating the reaction vessel at 125°C for 30 minutes. The specimens were then dried in a vacuum oven at 40°C and then over P₂O₅ in a desiccator. They were then re-weighed and measured to assess the effects achieved by the treatments.

As a further check of the degree of substitution achieved, the increase in dimension of dried treated specimens after 24 hours soak in water was determined. The results of these experiments were expressed as "Anti-Shrink Efficiency" (ASE) values as used by Stamm (1964) and Rowell and

Gutzmer (1975). The method of calculation is given below :

$$\text{Swelling coefficient, } S = \frac{V_2 - V_1}{V_1} \times 100$$

where V₂ = wet dimension

V₁ = dry dimension

$$\text{A.S.E.} = \frac{S_u - S_t}{S_u} \times 100$$

where S_u = swelling coefficient of untreated control

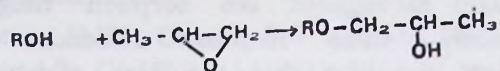
S_t = swelling coefficient of treated specimen

For simulated weathering the specimens were subjected to 5 and 15 soaking and drying cycles. Each cycle consisted of 24 hours immersion under 13 cm of mildly agitating water (25°C) followed by 24 hours drying at 35°C in a force draft oven.

A final batch of 8 wafer specimens was reacted in the pressure vessel with a mixture of 95% propylene oxide and 5% triethylamine to a weight gain of 33%. This set together with a set of 6 matched untreated control wafers was used to assess the change in sorption isotherm caused by such treatment. This was to provide an insight of how the wood water relationship is altered by propylene oxide treatment. The sorption isotherm was developed by exposing the wafer specimens to successively increased levels of relative humidity. To ensure that the specimens approached closely to equilibrium moisture contents they were kept for 72 hours at each condition.

RESULTS AND DISCUSSION

Reactions of epoxides with wood components form very stable ether bonds (Rowell and Gutzmer 1975).



Wood Epoxide Silylated wood
hydroxyl

The additional hydroxyl group formed in the reaction product, originating from the epoxide, is believed to participate in a polymerization reaction (Schuerch 1968). The presence of this polymer in the cell wall imparts dimensional stability. It is not known, however, to what extent the hydroxy substituted alkane chain may impart water repellency.

The ASE values achieved as a result of the propylene oxide treatments are given in Table 1.

From Table 1 it can be seen that the treatments carried out led to a very significant improvement in dimensional stability. It can further be seen that the level of improvement brought about appears to be strongly and positively correlated with the degree of chemical substitution/polymerization achieved.

An indication of the permanence of the modification is provided by the data relating to ASE values of the specimens treated at the higher level and then exposed to the simulated weathering procedure described above. These data are given in Table 2.

From the data in Table 2 it can be seen that the treatment imparts effective

Table 1. ASE values achieved on epoxy treatment

PO : TEA	Treatment level	Weight gain %	ASE		
			Tangential	Radial	Volumetric
95 : 5	Low (8 bar, 30 mins)	9.4	24.8(1.2)	36.3 (1.4)	32.0 (1.3)
95 : 5	High (10 bar, 90 mins)	43.4	55.9(2.3)	86.4 (3.1)	76.6 (2.8)

Figures in parenthesis represent Standard Deviation

Table 2. ASE values of weathered specimens

No. of weathering cycles	Antishrink efficiency %	
	Tangential	Volumetric
0	64.0(0.8)	81.7 (1.0)
5	62.5 (0.9)	79.9 (0.9)
15	60.9 (1.0)	83.3 (1.1)

Figures in parentheses represent Standard Deviation

resistance to swelling on exposure to quite severe simulated weathering.

The epoxy treatment causes significant increase in the dimension of the treated specimens as shown in Table 3.

constant throughout the sorption range. Certainly, there is no evidence to support the idea that the high moisture sorption exhibited at high levels of relative humidity is accompanied by a corresponding large increase in dimensional change. This

Table 3. Effect of treatment level on swelling of wood (mean of 20 wafers)

Treatment (PO : TEA)	Weight increase (gm)	Increase in dimension caused by treatment			
		Tangential	Radial	Longitudinal	Volumetric
95 : 5 (10 bar, 90 mins)	43.4	11.7 (1.0)	4.3 (0.7)	2.1 (0.4)	18.0 (1.4)
95 : 5 (8 bar, 30 mins)	9.4	3.0 (0.1)	2.0 (0.1)	0.3 (0.1)	5.4 (0.3)

Figures in parenthesis represent Standard Deviation

Here it is clear that the material introduced must be within the cell wall. The fact that it resists leaching due to simulated weathering (Table 2) suggests that this introduced material is strongly (probably covalently) bonded to the cell wall, as suggested by Rowell and Gutzmer (1975).

Figures in Table 4 suggest that reduction in the degree of swelling of treated specimens compared to controls is reasonably

large water uptake is probably due to the rigid bulky propane chains retaining the cell wall in a swollen but relatively porous state. This then allows some water to enter without bringing about a corresponding volumetric increase in specimen size rather like water entering a sponge. At a practical level, the data suggest that treatment with propylene oxide leads to significant improvement in dimensional stability throughout the hygroscopic range.

Table 4. Dimensional changes in control and epoxy treated specimens due to sorption under different RH conditions (Mean of 6 control and 8 treated specimens)

RH (%)	Control specimens		Epoxy-treated specimens	
	Wt increase (%)	Volumetric increase (%)	Wt. increase (%)	Volumetric increase (%)
9	2.6 (0.05)	00.9 (0.17)	0.9 (0.05)	0.2 (0.18)
33	6.3 (0.07)	2.8 (0.31)	2.8 (0.09)	0.9 (0.18)
55	9.0 (0.08)	4.7 (0.31)	4.7 (0.11)	1.5 (0.9)
81	15.5 (0.08)	8.4 (0.27)	11.5 (0.08)	2.0 (0.43)
93	24.8 (0.22)	13.6 (0.45)	27.6 (0.19)	2.5 (0.44)
100	26.5 (0.25)	15.8 (0.65)	30.7 (0.62)	4.1 (0.33)

Figures in parentheses represent Standard Deviation

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