Modification of Wood with Glutaraldehyde

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ABSTRACT

Scots pine sapwood was treated with aqueous solutions (4, 12, 20, and 30wt%) of glutaraldehyde and magnesium chloride as a catalyst. The treatments caused a reduction of the reduced equilibrium moisture content (EMC_R) up to 30%. The anti-swelling efficiency (ASE) at water saturation reached up to 70% when wood was treated to a WPG of approx. 20%. Glutaraldehyde treatment reduced both maximum swelling and shrinking suggesting that bulking and cross-linking occurred within the wood cell walls. After 10 cycles of water saturation and oven drying the treated wood displayed minor reduction in WPG and ASE. Treatment of wood with glutaraldehyde did not change the modulus of rupture (MOR) compared to the controls; the impact bending strength and the work at maximum load in bending, however, were reduced by more than 55% and 65%, respectively.

INTRODUCTION

Glutaraldehyde (GA, pentane-1,5-dial) is a dialdehyde which can in principle react with four hydroxyl groups of cell wall polymers. Thus, glutaraldehyde may be used as a cross-linking agent to modify wood. An aldehyde function can react with one hydroxyl group to form a hemiacetal and with a second to acetals. While the former group is susceptible to hydrolysis, the latter is stable under neutral and acid conditions. Weaver and Nielson (1960) treated wood with glutaraldehyde using a series of catalysts such as magnesium chloride, zinc chloride, but did not find any swelling and cross-linking of the cell wall. In later studies, SO_2 gas was used to catalyse the reaction; this resulted in enhanced dimensional stability, acoustic properties and resistance towards decay fungi. Moduli of elasticity and of rupture were hardly changed through the treatment (Yasuda and Minato 1994, Yasuda *et al.* 1994). The aim of this study was to investigate the effects of treatment with glutaraldehyde and magnesium chloride as a catalyst with regard to moisture sorption and dimensional stability. In addition, dynamic and static strength properties were determined in order to evaluate the embrittlement of wood caused by the treatment.

MATERIALS AND METHODS

Wood samples and chemicals

Scots pine (*Pinus sylvestris* L.) sapwood specimens measuring $25 \times 25 \times 10$ mm^2 ($r \times t \times l$) were used to study dimensional stability and moisture sorption; specimens with a size of $10 \times 10 \times 180$ mm^2 ($r \times t \times l$) were used for strength tests. Glutaraldehyde (50% aqueous stock solution) was obtained from BASF AG (Germany). The catalyst used was magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$).

Treatment with glutaraldehyde

The wood specimens were impregnated with aqueous glutaraldehyde solutions (4, 12, 20, 30 wt%) and $MgCl_2$ under vacuum (100 mbar, 1 h) and pressure (10 bar, 2 h). Specimens used for dimensional testing were catalysed with 6.0% $MgCl_2$ related to GA (molar ratio); those for mechanical testing were treated with a constant $MgCl_2$ concentration of 1.5%, irrespective of GA concentration. The impregnated specimens were dried at ambient temperature (1 week), at 80°C (24 h) and at 120°C (48 h). The specimens used to determine EMC and ASE were leached 10 d in water and subsequently dried prior to the measurements. Weight percent gain (WPG), bulking coefficient (BC) and ASE after full water saturation were determined as previously described (Donath *et al*. 2004). The specimens were store subsequently at 30, 50, 65, 80, and 90% RH until a constant weight was reached. The reduced equilibrium moisture content (EMC_R) was calculated as follows (Hill 2006):

$$EMC_R\ (\%) = [(m_2 - m_1)/m_0] \qquad (1)$$

where m_0 is the dry weight of the specimens before treatment, m_1 is the dry weight after treatment and m_2 is the weight at a given RH. The specimens were subjected to 10 cycles of water submersion (48h) and drying (103°C, 48h) and WPG as well as ASE were determined after each cycle. Ten replicates were used per treatment.

Mechanical properties

Bending strength (modulus of rupture, MOR) and resulting work at maximum load in bending were determined according to DIN 52186 (1978) and impact bending strength according to DIN 52189 (1981). Thirty replicates were used per treatment.

RESULTS AND DICUSSION

EMC_R and dimensional stability

At all relative humidities tested, the reduced equilibrium moisture (EMC_R) decreased with increasing WPG of glutaraldehyde (Table 1). Reduction in moisture sorption can be explained by two reasons: 1) Glutaraldehyde deposition in the cell wall occupies space (cell wall bulking) which is usually occupied by sorped water; 2) glutaraldehyde cross-links the cell wall polymers by reacting with hydroxyl groups and, thus, reduces maximum swelling of the cell wall.

Table 1: Reduced equilibrium moisture content (EMC_R) of untreated and treated wood at varible RH

Concentration of GA [%]	WPG [%]	Relative humidity 30%	50%	65%	80%	90%
control	-	6.3	8.0	10.7	16.1	18.6
4	1.00	6.9	8.2	11.0	15.8	17.9
12	8.57	6.0	7.1	9.4	13.2	14.7
20	13.66	5.7	6.9	9.0	12.6	13.9
30	21.86	5.3	6.6	8.6	11.7	12.9

The bulking coefficient (BC) and the ASE increased with increasing WPG of GA and reached up to approx. 7% and 70%, respectively, at WPG above 20% (Figure 1A, B). Minor increase in BC and ASE occurred at higher WPG of GA. In contrast, maximum swelling in water decreased with increasing WPG (Figure 1C) indicating that the ASE was caused by both cell wall bulking and reduced maximum swelling due to cross-linking.

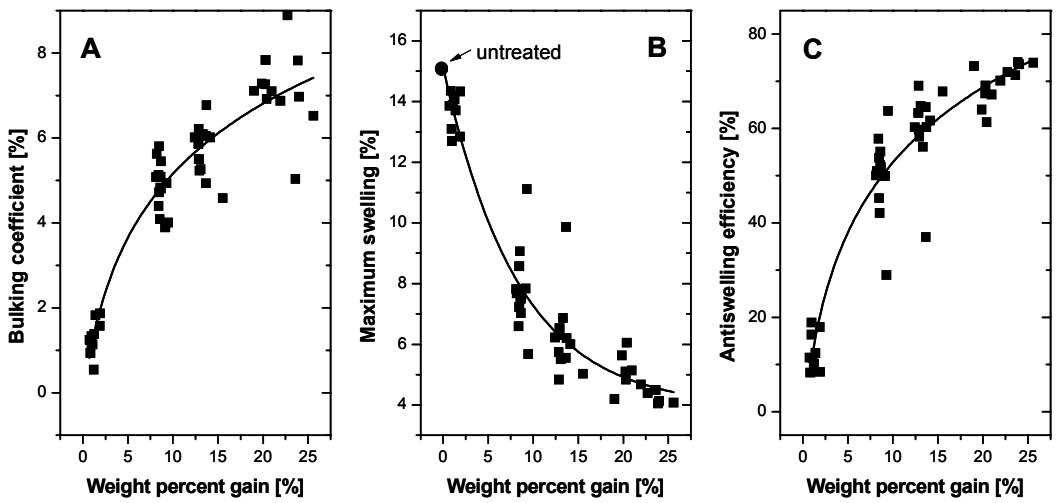

Figure 1: (A) Bulking coefficient, (B) maximum swelling, and (C) anti-swelling efficiency (ASE) at different weight percent gain (WPG) of glutaraldehyde.

Cyclic water saturation and oven-drying of the wood specimens caused a minor but steady loss in WPG and ASE over ten cycles (Figure 2). Both might be attributed to hydrolysis of hemiacetals and leaching of GA and wood constituents (extractives).

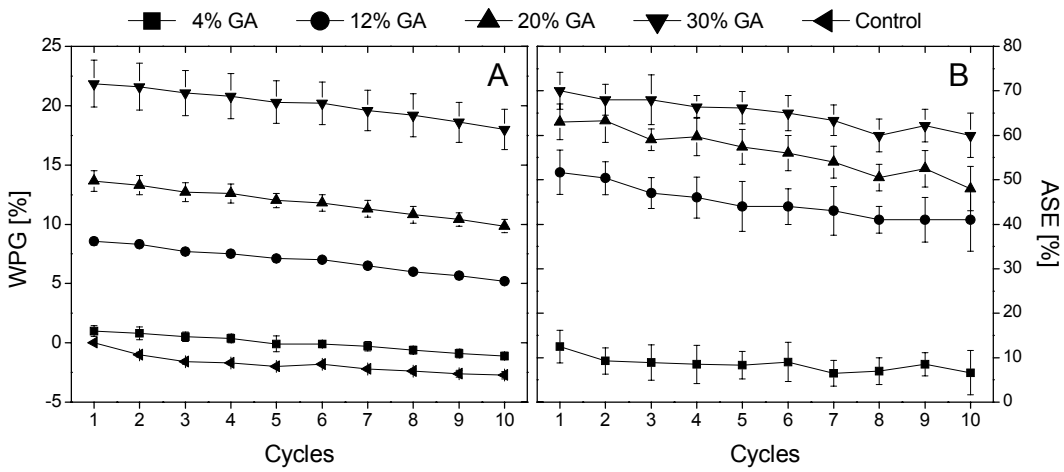

Figure 2: The change of WPG (A) and ASE of wood (B) during 10 cycles of water saturation and oven-drying.

Mechanical properties

Treatment with GA did not reduce the MOR of wood; however, the work at maximum load in bending and impact bending strength were reduced by up to 55% and 65%, respectively, due to GA treatment (Table 2). This indicates that GA treatment in presence of magnesium chloride catalyst makes wood brittle. The MOR is determined by several factors such as the compression strength and the tensile strength of a wood specimen. It was recently shown that GA treatment reduces the tensile strength of micro-veneers tested in zero-span mode (Mai *et al.* 2006). It is assumed that the MOR remained unchanged, because the compression strength was increased (data not shown) and compensated the tensile strength loss. The decrease in dynamic properties may be attributed to either cross-linking of cell wall polymers by GA or to a hydrolytic effect of the Lewis acid catalyst (magnesium chloride) on cellulose (Rowell 2005). Cross-linking might limit the flexibility and elasticity of the fiber compound.

Table 2: The MOR, work at maximum load in bending and impact bending strength of wood treated by glutaraldehyde. The concentration of $MgCl_2$ was 1.5% (w/w). The deviation is given in brackets.

Concentration of GA	MOR [N mm^{-2}]	Work to max. load in bending [N mm]	Impact bending strength [kJ m^{-2}]
control	104(±10)	1377(±250)	21.5(±4.3)
4%	99(±11)	760(±145)	11.4(±1.7)
12%	100(±20)	775(±169)	8.8(±2.7)
20%	105(±12)	792(±136)	7.7(±1.6)

CONCLUSIONS

Treatment of wood with GA reduced the EMC and increased the dimensional stability. Increase in ASE was shown to be due to cell wall bulking and cross-linking of polymers. WPG and ASE were slightly reduced during cyclic water saturation and subsequent drying indicating that a certain proportion of the formed groups were susceptible to hydrolysis and that GA leached out or evaporated. GA treatment resulted in unchanged MOR, but dynamic strength properties, *i.e.* work at maximum load in bending and impact bending strength were clearly reduced and indicated a severe embrittlement. Consequently, GA treated wood appears very suitable for application under conditions of outdoor weathering, but the severe reduction in impact strength may limit its utilization in areas where high dynamic strength is required.

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