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Journal Article

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Abstract

The thin-veneer strip technique was applied to investigate the modifying effects of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) on the tensile strength of wood. Pinewood veneers treated with solutions of DMDHEU alone and in combination with magnesium chloride ($MgCl_2$) as a catalyst showed considerable strength losses of up to 50% in zero-span and up to 70% in finite-span testing modes. The higher strength losses in the latter case are due to hemicellulose degradation, which cannot be assessed in zero-span testing. Strength loss observed after treatment with DMDHEU and $MgCl_2$ was approximately as high as the sum of the strength losses determined after individual treatments with $MgCl_2$ or DMDHEU. Micrographs of veneers after finite-span testing revealed that catalysed DMDHEU treatment changed the predominant failure mode from interfibre fracture (in controls) to intrafibre fracture. The mechanism of strength loss resulting from treatment with DMDHEU is discussed.

Keywords: chemical modification; DMDHEU; scanning electron microscopy; tensile strength; wood degradation.

Introduction

Chemical modification changes the material properties of wood. Covalent bonds between chemicals and the hydroxyl groups of cell-wall polymers can be formed or compounds of high molecular mass can be deposited within the cell wall. Usually, the aim of chemical modification is to improve the dimensional stability and decay resistance and thereby prolong the service life. The treatment may, however, negatively affect mechanical properties, particularly dynamic strength such as impact bending. Strength losses are induced by the hydrolysis of cell-wall polysaccharides or the deposition of chemical agents within the cell wall. In the latter case, wood becomes brittle, since the deposits reduce the freedom of movement among the polysaccharides and impart a more rigid structure to the cell wall matrix (Rowell 1998).

According to the literature, conventional wood preservative treatment with aqueous solutions of metal compounds (chromium trioxide, ferric chloride and ferric nitrate) reduces the tensile strength of wood. Strength losses of up to 40% were observed as a result of the oxidative degradation of cellulose following treatment with ferric salt solutions (Evans and Schmalzl 1989).

In general, chemical modification processes include a curing step at temperatures up to 120°C. Elevated temperatures can lead to oxidative degradation or hydrolysis, particularly when the modification is catalysed by a Lewis acid (or protons) or base (hydroxyl ions, amines). When heat treatment is applied alone in thermal wood processes, the elasticity and tensile strength may be considerably reduced. In such processes, the dimensional stability and durability of wood increase; however, the strength properties generally decrease with increasing temperature and process duration (Militz 2002). The major causes of strength losses are hydrolytic and oxidative degradation of hemicellulose and lignin; the degradation of cellulose has only a minor effect (Tjeerdsma et al. 1998).

To date, acetylation of wood with acetic anhydride has been the most intensively studied chemical modification process. Only minor changes (positive or negative) in strength properties were observed. The modulus of elasticity (MOE) and modulus of rupture (MOR) did not change very much, in spite of severe chemical alteration of cell-wall constituents, resulting in significant cell-wall bulking (Dreher et al. 1964; Larsson and Simonson 1994; Bongers and Beckers 2003). The pH during acetylation is low and presumably partly hydrolyses the hemicelluloses. Modification with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) has been shown to improve the dimensional stability and decay resistance of wood (Nicholas and Williams 1987; Videlov 1989; Militz 1993; Yasuda and Minato 1994; Yalinkilic et al. 1999; Krause et al. 2003).

Treatment of thin veneer strips with DMDHEU enhanced the weathering resistance in an artificial weathering tester (QUV). Tensile strength losses (measured in the zero-span mode) of DMDHEU-treated veneers were lower after weathering than those of untreated veneers. DMDHEU treatment, however, had a deleterious effect on the tensile strength of the veneers, possibly associated with the presence of magnesium chloride catalyst in the treatment solution (Xie et al. 2005). In a very few other studies, the effect of DMDHEU treatment on the mechanical properties of wood is discussed, but the authors only refer to reduced bending strength without considering

possible reasons for this reduction in any detail (Nicholas and Williams 1987; Nurmi et al. 1999). The bending strength can be influenced by factors such as the strength of single fibres (tracheids in softwood) and of the adhesion between the fibres, and the compression strength of wood (Winandy and Rowell 2005). In contrast, the tensile strength of thin veneer strips measured in a zero-span mode is only determined by the strength of single fibres and, thus, by the degree of polymerisation of their cellulosic constituents (Derbyshire and Miller 1981).

Monitoring the loss in tensile strength of thin veneer strips has been reported as a means of evaluating the effectiveness of wood preservatives (Hartley 1958; Haider and Domsch 1969; Bravery and Grant 1971) and of studying the degradation of wood during weathering (Raczkowski 1980; Derbyshire and Miller 1981; Evans et al. 2000, 2002).

The main objective of this study was to establish the effect of DMDHEU modification and of the single constituents of the reaction system (catalyst and reactant) on the tensile strength of wood and, thus, on cellulose hydrolysis using thin veneer strips. The concentration of DMDHEU and the catalyst (magnesium chloride, $MgCl_2$), as well as the curing times, were varied to monitor the impact on tensile strength measured in zero- and finite-span modes.

Materials and methods

Wood veneers

Wood blocks measuring 100 mm$\times$50 mm$\times$15 mm (L$\times$T$\times$R) were cut from the sapwood of Scots pine (*Pinus sylvestris* L.) boards as previously described (Evans et al. 2000). The blocks were soaked in 10% aqueous ethanol under vacuum (100 mbar, 30 min) and kept in the solution for 14 days under ambient pressure. Veneers of approximately 100 μm in thickness were cut from the radial surface of each block using disposable microtome blades (Reichert-Jung, Nussloch, Germany) as previously described (Evans and Banks 1988; Turkulin 1996).

Chemicals

The modifying agent was a solution of 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) supplied by BASF AG (Ludwigshafen, Germany). Magnesium chloride hexahydrate ($MgCl_2\cdot6H_2O$) was used as catalyst. The pH of the final treatment solutions was measured at 21°C using a model 256 pH meter (Wissenschaftlich-Technische Werkstätten, Weilheim, Germany).

Treatment of veneers

Both the stock solution of DMDHEU and a typical treatment solution (30 wt.% DMDHEU, 1.5 wt.% $MgCl_2\cdot6H_2O$) displayed a pH of $\sim$5.2. Prior to treatment, the veneers were dried in a desiccator (approx. 20°C) for 3 days and then weighed. A total of 20 veneers per treatment were tested. Impregnation was performed under vacuum conditions (100 mbar, 30 min) and ambient pressure (10 min). After impregnation, excess treatment solution was blotted off the veneers with filter paper and the specimens were then cured at 120°C (240 min). The treatment solutions were as follows (all indications w/w; DMDHEU concentration related to the stock solution):

1. 0.5%, 1.5%, and 2.5% $MgCl_2\cdot6H_2O$ (pH $\sim$8.0)
2. 0%, 0.5%, 1.5%, 2.5%, and 3.5% $MgCl_2\cdot6H_2O$; adjusted to pH 5.2 (hydrochloric acid)
3. 30% DMDHEU with 0.5%, 1.5%, 2.5%, and 3.5% $MgCl_2\cdot6H_2O$, respectively (pH $\sim$5.2)
4. 10%, 30%, and 50% DMDHEU (pH $\sim$5.2)
5. 10% (0.5%), 30% (1.5%) and 50% (2.5%) DMDHEU ($MgCl_2\cdot6H_2O$), pH $\sim$5.2

To determine the influence of the curing time on strength loss, veneers were treated with a solution of 30% DMDHEU and 1.5% magnesium chloride and cured for 5, 30, 60, 120, 240, 360, and 480 min at 120°C.

After conditioning (20°C, 65% RH) for 24 h, all the treated specimens were first rinsed with running tap water (approx. 40°C) for 2 h to remove unreacted chemicals, then dried in a desiccator (3 days) and weighed. Untreated veneer strips served as control specimens. Prior to further tests, the veneers were conditioned in a climate chamber (20°C, 65% RH); their thickness was determined using a dial gauge micrometer (Mitutoyo, Mexico).

Zero-span tensile strength

Zero-span tensile strength loss of the veneers was determined with a Pulmac paper tester (Pulmac International Inc., Middlesex, USA) as previously described (Derbyshire et al. 1995; Evans and Schmalzl 1989). The rate of loading was set to 70 kPa s^{-1}. The initial clamping pressure was set to 0.52 MPa for untreated veneers and to 0.45 MPa for treated veneers. Tensile strength retention was compared to untreated veneers (controls). For each treatment, 20 veneers were used; each of them was cut into two parts, which were then measured separately.

Finite-span tensile strength

Finite-span tensile strength (25-mm distance between the clamps) was determined using a Zwick Z010 universal testing machine (Zwick, Ulm, Germany) at an elongation rate of 0.25 mm min^{-1}. Tensile strength retention was compared to untreated veneers (controls). For each treatment, 20 veneers were used; each veneer was cut into two parts, which were measured separately.

Morphological analysis

Veneers with typical failure modes after finite-span testing were scanned (CanoScan 3000, Canon Inc., Tokyo, Japan) for macroscopic inspection. The fractured veneer samples were trimmed and mounted on aluminium stubs and dried in a vacuum oven at 23°C for 24 h. The veneers were then sputter-coated with an approximately 10-nm layer of platinum and examined using a field-emission scanning electron microscope (FE-SEM; JSM-6300F, JEOL, Eching, Germany) operating at an accelerating voltage of 5 kV.

Results

Weight gain

The weight gain of treated veneers increased linearly with the concentration of DMDHEU in the treatment solution, irrespective of whether $MgCl_2$ was present. However, washing of the treated veneers showed that specimens treated in the presence of $MgCl_2$ had a significantly higher retention than those treated solely with DMDHEU (Figure 1a). At a fixed DMDHEU concentration of 30%, $MgCl_2$
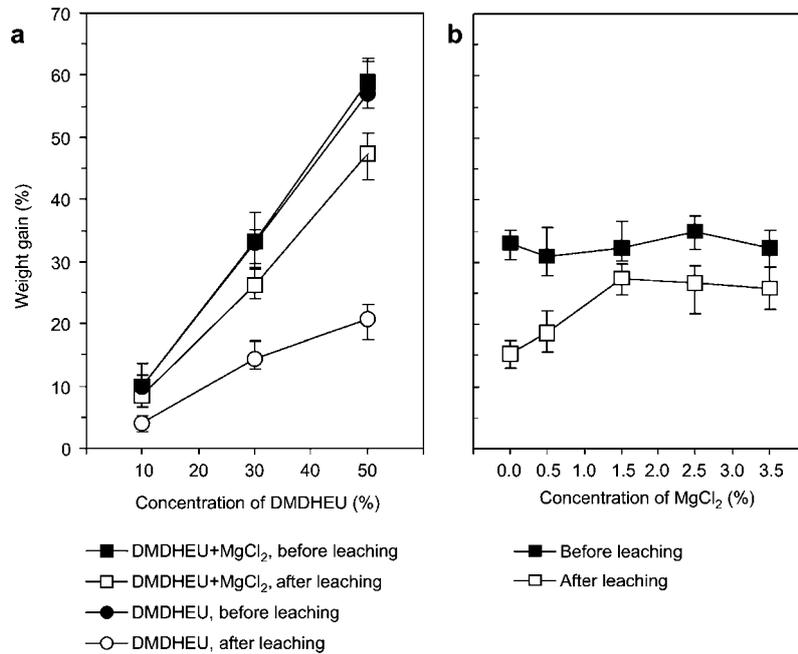
Figure 1 Weight percentage gain of veneers before and after washing: (a) treated with DMDHEU and MgCl₂ (5% related to the DMDHEU concentration) or DMDHEU alone; and (b) treated with 30% DMDHEU and different concentrations of MgCl₂. Error bars show the minimum and maximum values for a treatment.

concentration of at least 1.5% was required to reach maximum fixation of DMDHEU (Figure 1b).

Veneers that were only treated with acidic MgCl₂ (3.5%) had a weight loss of up to 3% after washing. Veneers treated only with water showed a weight loss of approximately 1%.

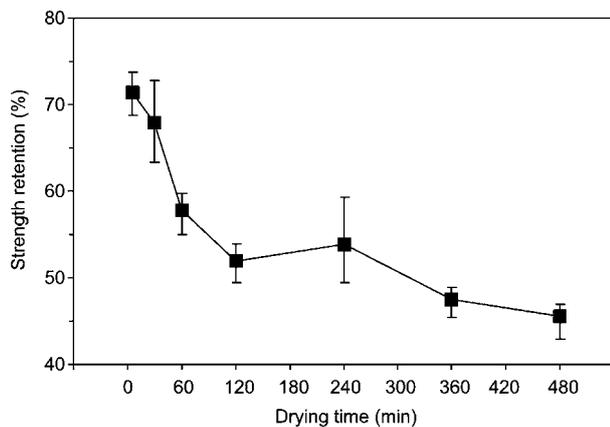**Tensile strength tested at zero-span (z-strength)**

Untreated veneers (controls) displayed a z-strength of 77.6 MPa. Treatment of veneers with a slightly acidic aqueous solution (pH 5.2) had a minor effect on z-strength (0% MgCl₂ in Figure 2a). The influence of MgCl₂ on z-strength clearly depends on the pH of the treatment solution. Under neutral conditions (pH 7–8), MgCl₂ treat-

ment did not change the z-strength, but under acidic conditions (pH 5.2) a severe decrease in z-strength occurred. Under these conditions, z-strength first began to decrease as the concentration of magnesium chloride was increased (Figure 2a). Veneers treated with 30% DMDHEU showed increasing z-strength losses with increasing MgCl₂ concentration and levelled off at 1.5% MgCl₂ and above (Figure 2a).

Treatment with aqueous DMDHEU alone reduced the z-strength by up to 20% and no significant concentration effect was observed (upper line in Figure 2b). In the DMDHEU/MgCl₂ systems, z-strength losses for veneers ranged between 30% and 45% (lower line in Figure 2b). The strength loss was not influenced by the DMDHEU concentration.
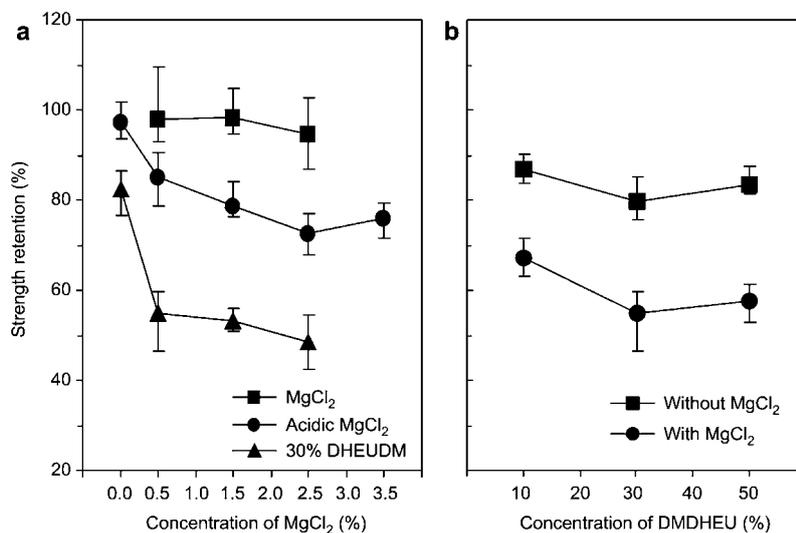
Figure 2 Retention of zero-span tensile strength in veneers: (a) treated with MgCl₂, acidic MgCl₂, or 30% DMDHEU and 1.5% MgCl₂; and (b) treated with DMDHEU alone, or with DMDHEU and 1.5% MgCl₂. Error bars show the minimum and maximum values.

Figure 3   Effect of drying time on the zero-span tensile strength of veneers treated with 30% DMDHEU and 1.5% MgCl$_2$. Error bars show the minimum and maximum values.

Drying time had a pronounced effect on the z-strength of veneers (Figure 3). While curing of water-treated veneers at 120°C for 240 min had a minor effect on strength loss, veneers treated with 30% DMDHEU and 1.5% MgCl$_2$ lost z-strength very rapidly (approx. 30% loss) within the first 5 min. A loss of almost 50% was observed during the first 120 min of curing at 120°C. After this initial stage, the z-strength levelled off and did not lose more than approximately 50% within the remaining 360 min.

Tensile strength tested at finite-span (f-strength)

Untreated veneers displayed an f-strength of 71.7 MPa. Since different instruments were used, the absolute values of z-strength and f-strength cannot be directly compared. As observed for z-strength, treatment of veneers with a slightly acidic solution (pH 5.2) had a minor effect on f-strength (0% MgCl$_2$ in Figure 4a). This indicates that degradation of cell-wall polymers hardly occurred at this pH level. The presence of MgCl$_2$ at the same pH, however, resulted in a 50% reduction in f-strength compared to untreated controls, even at a low concentration (0.5%). Higher catalyst concentrations did not lead to any further significant reductions in f-strength. Treatment with aqueous DMDHEU reduced f-strength by up to 30%, irrespective of the DMDHEU concentration used (Figure 4b). Veneers treated with DMDHEU and MgCl$_2$ only retained 30–40% of their initial f-strength, regardless of the concentration (Figure 4b).

Microscopic analysis

The failure modes of veneers after finite-span testing depended on the treatment applied (Figure 5). Untreated veneers fractured very irregularly, with a jagged breakage line (Figure 5a). Veneers treated with DMDHEU and MgCl$_2$ were the extreme opposite; they showed a straight breakage line almost perpendicular to the grain (Figure 5d). Veneers individually treated with acidic MgCl$_2$ (1.5%) or DMDHEU (30%) displayed a failure morphology between those for control veneers and those treated with DMDHEU and MgCl$_2$.

Micrographs of the breakage line after finite-span testing showed a dependence of the failure mode on the treatment (Figures 6 and 7). In the controls, fractures occurred both within a fibre (intracellular break) and between fibres (intercellular separation), with a high proportion of intercellular failures (Figure 6a,b). Fewer intercellular separations occurred in veneers treated with acidic MgCl$_2$ than in untreated controls (data not shown). Veneers treated with DMDHEU and MgCl$_2$ almost exclusively displayed intracellular failure, irrespective of the DMDHEU concentration (Figure 6c,d).

Cross-sections of fractured fibres in untreated early- and latewood showed an irregular, jagged surface (Figure 7a,b), while the cross-sectional surfaces of fibres in veneers treated with DMDHEU and MgCl$_2$ appeared very smooth in both early- and latewood (Figure 7e,f). The cross-sectional surface of fractured veneers treated with MgCl$_2$ alone displayed characteristics that could be categorised as being between those for untreated controls
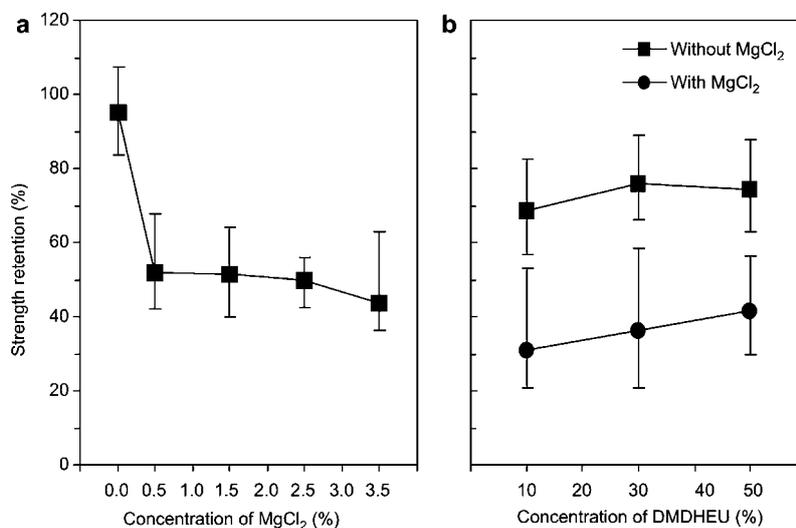
Figure 4   Retention of finite-span tensile strength in veneers: (a) treated with acidic MgCl$_2$ solutions; and (b) treated with only DMDHEU or with DMDHEU and MgCl$_2$ (5% related to the DMDHEU concentration). Error bars show the minimum and maximum values.
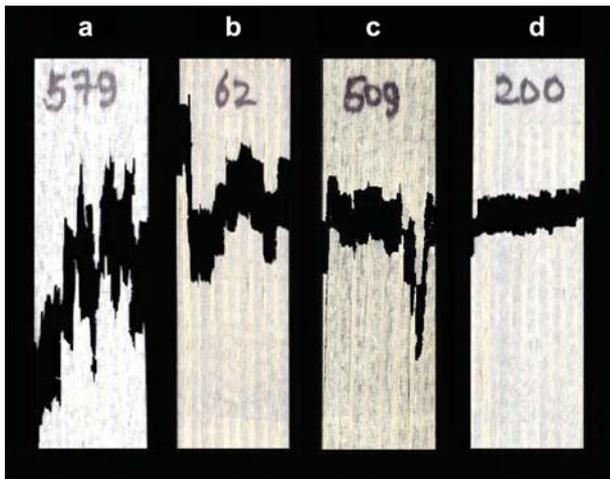
Figure 5 Typical fracture modes of wood veneers tested at finite span: (a) untreated controls; (b) treated with 1.5% acidic MgCl$_2$ (pH 5.2); (c) treated with 30% DMDHEU alone; and (d) treated with 30% DMDHEU and 1.5% MgCl$_2$.

and veneers treated with DMDHEU and magnesium chloride (Figure 7c,d).

Discussion

Effect of magnesium chloride on tensile strength

Hydrolytic degradation of polysaccharides occurs when wood is subjected to mineral acids such as HCl (Wangaard 1966). The rate of hydrolysis increases with increasing proton concentration and reaction temperature (Pisarnitsky et al. 2004).

In this study, the pH of a typical solution was 5.2. Veneers treated solely with water acidified to pH 5.2 showed only a minor reduction in tensile strength. Pinewood has a pH of approximately 5.1 due to acidic extractives (Sandermann and Rothkamm 1959). The extractives also act as a natural buffer (Fengel and Wegener 1984). This explains why additional protons at low concentration
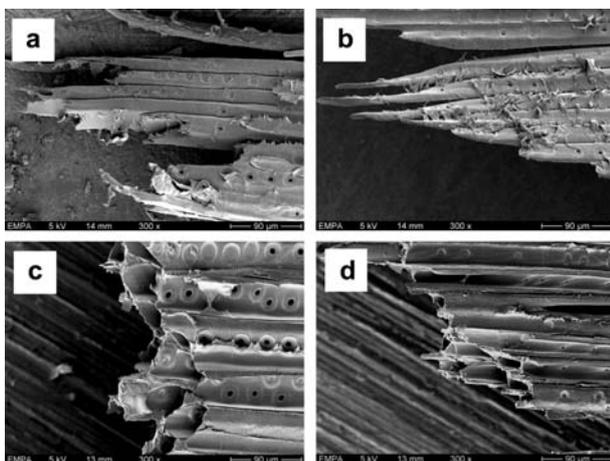
Figure 6 SEM photomicrograhs of typical failures of wood cells tested at finite span: (a,b) untreated early- and latewood; and (c,d) early- and latewood treated with 30% DMDHEU and 1.5% MgCl$_2$.
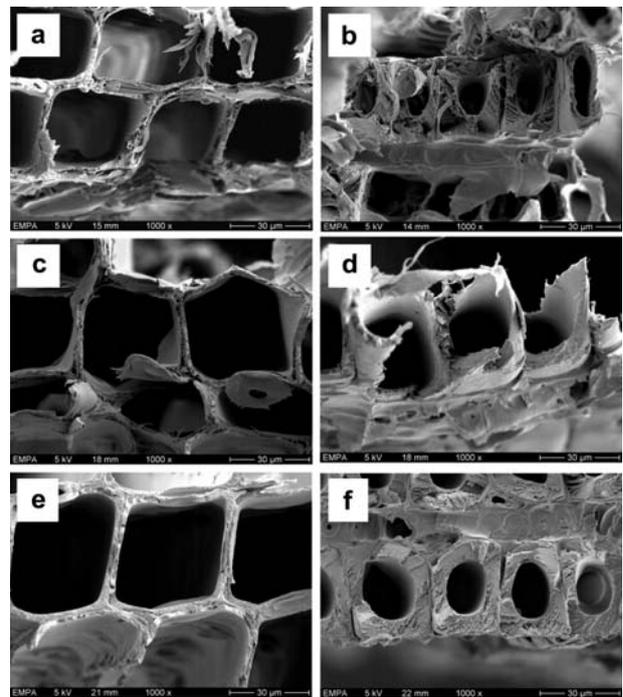
Figure 7 Typical characteristics of the cross-section of failed wood cells tested at finite span: (a,b) untreated early- and latewood; (c,d) early- and latewood treated with 1.5% acidic MgCl$_2$ (pH 5.2); and (e,f) early- and latewood treated with 30% DMDHEU and 1.5% MgCl$_2$.

(6.3 μM) have only a minor impact on the tensile strength of veneers.

Whereas a neutral solution of MgCl$_2$ (pH 7–8) did not influence the tensile strength of wood veneers, acidic MgCl$_2$ led to significant strength reductions. In contrast to HCl, MgCl$_2$ is a Lewis acid that does not provide protons via hydrolysis; however, it can form a Lewis acid adduct with the free electron pair of the oxygen atom in the glucosidic bonds of polysaccharides. Thus, it polarises the bond and makes it susceptible to hydrolytic attack by hydronium ions (H$_3$O$^+$).

The strong strength reduction observed in this study corresponds to results known from textile research. Cotton fabrics treated with MgCl$_2$ solutions (pH 5.5, curing at 160°C, 3 min) increasingly lost tensile strength with increasing MgCl$_2$ concentration (Meyer et al. 1976). Wood blocks treated with 10% DMDHEU and a two-component catalyst consisting of AlCl$_3$ (0.5%) and tartaric acid (0.5%) lost 38% of their bending strength (MOR); however, samples treated with the catalysts alone (both 0.5%) displayed the same loss in MOR (38%) (Nicholas and Williams 1987).

Strength losses of cotton fabrics, which initially increased with MgCl$_2$ concentration, levelled off at 50% strength loss (Yang et al. 2000). In this study the tensile strength loss of veneers showed similar behaviour for MgCl$_2$ concentrations greater than 0.5%. A possible explanation for this could be that the hydrolytic reaction is thermodynamically controlled and reaches a maximum during the relatively long curing time of 240 min. By definition, catalysts do not change the thermodynamic equilibrium, but do influence the velocity of a chemical reaction. To evaluate the influence of the catalyst con-

centration on the velocity, the reaction needs to be kinetically controlled and the time course of strength loss has to be monitored. This was not carried out in the present study.

The impact of treatment with acidic $MgCl_2$ was much greater for f-strength than for z-strength. In general, the absolute value for f-strength is much lower than for z-strength, since the forces required to separate fibres (f-strength) are much lower than those required to break the fibres themselves (z-strength). Thus, lower retention of f-strength can apparently be explained by the fact that $MgCl_2$ has a greater effect on lignin than on cellulose; however, $MgCl_2$ primarily catalyses the hydrolysis of polysaccharides. This salt does not have the oxidising potential required to disintegrate lignin. Micrograph observations imply that in finite-span testing the polysaccharides are weakened so much that intracellular fracture is the predominant failure mode (similar to z-strength testing). In the absence of lignin, z-strength appears to depend almost exclusively on cellulose, while f-strength is apparently determined by properties of both cellulose and hemicelluloses. Thus, treatment of kraft pulps with xylanase reduced the DP of xylans, but had no effect on the z-strength (Paice et al. 1992). In the wood matrix, hemicelluloses cover cellulose microfibrils and bind them together to form fibril aggregates (Fengel and Wegener 1984). Hydrolytic degradation of hemicelluloses should, therefore, further decrease the strength properties, since it enhances the possibility of separation of fibril aggregates. This model explains why hydrolysis due to acidic $MgCl_2$ has a greater influence on f-strength than on z-strength.

Effect of DMDHEU on tensile strength

The strength losses due to treatment with DMDHEU alone might be attributed to a hydrolytic effect of DMDHEU or/and to its physical incorporation into the cell wall. The deposition of DMDHEU could make the fibres less elastic and impede any slippage of single microfibrils as a result of cross-linking (Zeronian et al. 1989; Som and Mukherjee 1989). A study of cotton fabric showed that tensile strength reduced through DMDHEU and $MgCl_2$ treatment was partly restorable by the removal of DMDHEU by boiling it with sodium hydroxide (Lickfield et al. 1998). This demonstrates that the primary cause of strength loss is the deposition of DMDHEU in the cell wall rather than hydrolysis, even if the effect of polysaccharide hydrolysis is not considered.

In untreated veneers the compound middle lamella (CML), which mainly consists of lignin, is the weakest layer; therefore, whole fibres become separated during testing. Hydrolysis weakened the polysaccharides in the S2 layer to such an extent that it became weaker than the CML, and intracellular failures then predominated over intercellular failures.

Several studies have verified the initial reduction in tensile strength of cotton fibres with increasing DMDHEU concentration and levelling off at a certain concentration level (Weiss et al. 1970; de Boer and Borsten 1971; Zeronian et al. 1989; Yang et al. 2000). This is also true for cotton fabrics treated with 8% DMDHEU and different $MgCl_2$ concentrations (Lickfield et al. 1998). In this study,

tensile strength losses caused by catalysed DMDHEU treatment also reached a relatively constant level. The same type of saturation behaviour was observed when $MgCl_2$ and DMDHEU were applied alone. Strength losses measured both at zero- and finite-span appeared to be the sum of individual strength losses caused by $MgCl_2$ and DMDHEU alone. Thus, total strength loss is likely to be caused by the hydrolysis of polysaccharides catalysed by acidic $MgCl_2$ and through embrittlement of fibres as a result of DMDHEU deposition in the fibre cell wall.

Effect of curing time on tensile strength

Exposure of dry wood to temperatures of $\sim 120°C$ for more than 20 h caused a small loss of low-molecular-weight hemicelluloses (Kollmann and Fengel 1965). Dry wood blocks heated to 120°C for 1.5 h lost only 4% of their original bending strength (Nicholas and Williams 1987).

Veneers treated with DMDHEU and the catalyst displayed a maximum z-strength reduction of about 50%; longer curing time did not cause additional damage. A possible explanation for this levelling off might be that a maximum degree of cellulose hydrolysis catalysed by $MgCl_2$ was reached and that an additional loss occurred via the incorporation of reacted DMDHEU into the three-dimensional cellulose structure. Wood cellulose (chemical grade pulp) consists of approximately 70% crystalline regions (Hindeleh and Johnson 1972). Owing to the strict parallel alignment of the polyglucane chains and their tight packaging, the crystalline regions are hardly accessible for a solvent or chemical agent. Amorphous regions have larger pore sizes and a less compact structure that can be penetrated (Fengel and Wegener 1984). Therefore, the hydrolysis and deposition of DMDHEU occurs almost exclusively in the amorphous regions and contributes to z-strength losses. If these chemical alterations reach a maximum, retained z-strength stems primarily from the crystalline regions of cellulose.

Limited availability of water in the fibres is another possible explanation for the maximum z-strength loss. During the initial curing phase, water causes polysaccharide hydrolysis and evaporates from the veneers. In veneers treated with acidic $MgCl_2$, polysaccharide hydrolysis ceases when the water is fully evaporated and the temperature at the veneer surface increases. In the presence of DMDHEU, the condensation of N-methylol groups increases following water evaporation, thus giving rise to further water molecules. These might contribute to polysaccharide hydrolysis and, as a result, to z-strength loss until the condensation of DMDHEU is complete. It was previously reported that a hydrolytic reaction also proceeds in the dry state (Segal and Timpa 1973). It can be assumed that the water molecules that caused this hydrolysis were released during the condensation reaction of N-methylol groups in DMDHEU. Thus, z-strength loss, i.e., hydrolysis, reaches a maximum when the condensation is complete and no further water molecules are available.

Conclusions

A reduction in bending strength on treatment of wood with DMDHEU has been reported previously (Nicholas and Williams 1987; Nurmi et al. 1999). The bending strength is determined by several factors, such as the compression strength and tensile strength of a wood specimen. The influence of DMDHEU treatment on the compression strength has not been reported so far; however, the surface hardness was significantly increased through the treatment (unpublished results). A comparable increase in compression strength after DMDHEU treatment is likely. Specimens treated in a comparable way to that in this study displayed a minor reduction in bending strength (Bergemann 2003), because cellulose hydrolysis was obviously compensated by an increase in compression strength (or surface hardness). The change in tensile strength is thus a better indicator of cellulose hydrolysis through DMDHEU treatment than the change in bending strength.

Treatment of veneers with the N-methylol compound DMDHEU and $MgCl_2$ caused a marked reduction in both z- and f-strength. More than half of this reduction was attributed to the effect of acidic $MgCl_2$, which catalysed polysaccharide hydrolysis. The remaining proportion of strength loss was related to the application of DMDHEU. Its contribution to strength loss might be explained in terms of DMDHEU incorporation into fibre cell walls, resulting in embrittlement, and/or by a hydrolytic effect originating from the N-methylol groups in DMDHEU. Hydrolysis might be caused by direct cleavage of glucosidic bonds through the N-methylol groups or by the water produced during the condensation reaction of DMDHEU.

Our study demonstrates that new catalytic systems need to be found that cause minimum hydrolysis of wood polysaccharides but that show maximum effectiveness in catalysing the condensation of N-methylol groups in DMDHEU. In addition, water should be carefully removed by gentle pre-drying at low temperatures prior to final curing following the impregnation of wood with the DMDHEU solution. Strength loss due to hydrolysis could thus be minimised.

Acknowledgements

References

Bergemann, H. (2003) Untersuchung zur Veränderung der elasto-mechanischen Eigenschaften von Buchenholz nach Imprägnierung mit unterschiedlichen Textilchemikalien (in German). Master thesis. Faculty of Forestry and Forest Ecology, University of Göttingen.

Bongers, H.P.M., Beckers, E.P.J. (2003) Mechanical properties of acetylated solid wood treated on pilot plant scale. In: Proceedings of the 1st European Conference on Wood Modification, Ghent, Belgium, 3–4 April, 2003. Eds. Van Acker, J., Hill, C. pp. 341–350.

Bravery, A.F., Grant, C. (1971) Preliminary investigations into the use of a thin strip tensile strength test for the rapid evaluation of wood preservatives against Basidiomycete fungi. Int. Biodeter. Bull. 7:169–173.

de Boer, J.J., Borsten, H. (1971) The effect of improved hydrogen bonding on the properties of the cotton fibre before and after cross-linking. Text. Res. J. 41:368–369.

Derbyshire, H., Miller, E.R. (1981) The photodegradation of wood during solar irradiation. Part I: Effects on the structural integrity of thin wood strips. Holz Roh Werkst. 39:341–350.

Derbyshire, H., Miller, E.R., Turkulin, H. (1995) Investigations into the photodegradation of wood using microtensile testing. Part 1: The application of microtensile testing to measurement of photodegradation rates. Holz Roh Werkst. 53: 339–345.

Dreher, W.A., Goldstein, I.S., Cramer, G.R. (1964) Mechanical properties of acetylated wood. For. Prod. J. 14:66–68.

Evans, P.D., Banks, W.B. (1988) Degradation of wood surfaces by water. Changes in mechanical properties of thin wood strips. Holz Roh Werkst. 46:427–435.

Evans, P.D., Schmalzl, K.J. (1989) A quantitative weathering study of wood surfaces modified by chromium VI and iron III compounds. Part 1. Loss in zero-span tensile strength and weight of thin wood veneers. Holzforschung 43:289–292.

Evans, P.D., Owen, N.L., Schmid, S., Webster, R.D. (2002) Weathering and photostability of benzoylated wood. Polym. Degrad. Stabil. 76:291–303.

Evans, P.D., Wallis, A.F.A., Owen, N.L. (2000) Weathering of chemically modified wood surfaces. Natural weathering of Scots pine acetylated to different weight gains. Wood Sci. Technol. 34:151–165.

Fengel, D., Wegener, G. Wood: Chemistry, Ultrastructure, Reactions. De Gruyter, Berlin, 1984.

Haider, K., Domsch, K.H. (1969) Abbau und Umsetzung von lignifiziertem Pflanzenmaterial durch mikroskopische Bodenpilze. Arch. Mikrobiol. 64:338–348.

Hartley, C. (1958) Evaluation of wood decay in experimental work. Report No. 2119. Forest Products Laboratory, Madison, WI.

Hindeleh, A.M., Johnson, D.J. (1972) Crystallinity and crystallite size measurement in cellulose fibres: 1. Ramie and Fortisan. Polymer 13:423–430.

Kollmann, F., Fengel, D. (1965) Änderungen der chemischen Zusammensetzung von Holz durch thermische Behandlung. Holz Roh Werkst. 23:461–468.

Krause, A., Zee, M., Jones, D., Militz, H. (2003) Interlace treatment-wood modification with N-methylol compounds. In: Proceedings of the 1st European Conference on Wood Modification, Ghent, Belgium 3–4 April, 2003. Eds. Van Acker, J., Hill, C.A.S. pp. 319–324.

Larsson, P., Simonson, R. (1994) A study of strength, hardness and deformation of acetylated Scandinavian softwoods. Holz Roh Werkst. 52:83–86.

Lickfield, G., Yang, C.Q., Kang, I.S., Wei, W. (1998) Investigation of flexible crosslinking systems for the retention of mechanical strength and abrasion resistance in durable press cotton fabrics. Annual Report C97-C3. National Textile Center, USA.

Meyer, U., Müller, K., Zollinger, H. (1976) Comparison of textile mechanical properties of cotton in crosslinking with dimethylolethyleneurea and formaldehyde. Text. Res. J. 46:813–817.

Militz, H. (1993) Treatment of timber with water soluble dimethylol resins to improve their dimensional stability and durability. Wood Sci. Technol. 27:347–355.

Militz, H. (2002) Thermal treatment of wood: European processes and their background. Document No. IRG/WP 02-40241. International Research Group on Wood Protection, Stockholm, Sweden.

Nicholas, D.D., Williams, A.D. (1987) Dimensional stabilization of wood with dimethylol compounds. Document No. IRG/WP 87-3412. International Research Group on Wood Protection, Stockholm, Sweden.

Nurmi, A., Kokko, H., Peek R.D., Murphy, R.J., Stevens, M., Hill, C. (1999) European project report: Natural resins as a potential wood processing. Contract No. FAIR-CT95-0089. The Agriculture and Agro-Industry including Fisheries Program of Research and Technological Development (FAIR), Program: Forestry-Wood Chain. http://www.biomatnet.org/secure/Fair/F339.htm#summary.

Paice, M.G., Gurnagul, N., Page, D.H., Jurasek, L. (1992) Mechanism of hemicellulose-directed prebleaching of kraft pulps. Enzyme Microb. Technol. 14:272–276.

Pisarnitsky, A.F., Klimov, S.A., Brazhnikova, E.V. (2004) Effect of acid hydrolysis of oak wood on its aroma-forming complex. Appl. Biochem. Microbiol. 40:613–616.

Raczkowski, J. (1980) Seasonal effects on the atmospheric corrosion of spruce micro-sections. Holz Roh Werkst. 38:231–234.

Rowell, R.M. (1998) Property enhanced natural fibre composite materials based on chemical modification. In: Science and Technology of Polymers and Advanced Materials. Eds. Prasad, P.N., Mark, J.E., Kandil, S.H., Kafafi, Z.H. Plenum, New York. pp. 717–732.

Sandermann, W., Rothkamm, M. (1959) The determination of pH value of commercial woods and its practical importance. Holz Roh Werkst. 17:433–441.

Segal, L., Timpa, J.D. (1973) Strength losses and structural changes in cotton fabric crosslinked with dimethylolethyleneurea. Text. Res. J. 43:185–194.

Som, N.C., Mukherjee, A.K. (1989) Dimensional characteristics of jute and jute-rayon blended fabrics crosslinked with DMDHEU. Indian J. Fibre Text. 14:164–168.

Tjeerdsma, B.F., Boonstra, M., Militz, H. (1998) Thermal modification of non-durable wood species. 2. Improved wood properties of thermally treated wood. Document No. IRG/WP 98-40124. International Research Group on Wood Protection, Stockholm, Sweden.

Turkulin, H. (1996) Photodegradation of exterior timber building components. PhD thesis. Faculty of Forestry, Zagreb University, Zagreb, Croatia. pp. 48–71.

Videlov, C.L. (1989) Biological degradation resistance of pine wood treated with dimethylol compounds. Document No. IRG/WP 89-3528. International Research Group on Wood Protection, Stockholm, Sweden.

Wangaard, F.F. (1966) Resistance of wood to chemical degradation. For. Prod. J. 16:53–64.

Weiss, L.C., Grant, J.N., George, M. (1970) Recovery and strength of chemically modified single cotton fibres. Text. Res. J. 40:583–590.

Winandy, J.E., Rowell, R.M. (2005). Chemistry of wood strength. In: Handbook of Wood Chemistry and Wood Composites. Ed. Rowell, R.M. CRC Press, Boca Raton, FL pp. 303–347.

Xie, Y., Krause, A., Mai, C., Militz, H., Richter, K., Urban, K., Evans, P.D. (2005) Weathering of wood modified with the *N*-methylol compound 1,3-dimethylol-4,5-dihydroxyethyleneurea. Polym. Degrad. Stabil. 89:189–199.

Yalinkilic, M.K., Gezer, E.D., Takahashi, M., Demirci, Z. (1999) Boron addition to non- or low-formaldehyde cross-linking reagents to enhance biological resistance and dimensional stability of wood. Holz Roh Werkst. 57:351–357.

Yang, C.Q., Wei, W., Lickfield, G.C. (2000) Mechanical strength of durable press finishing cotton fabric. Part III: Change in cellulose molecular weight. Text. Res. J. 70:910–915.

Yasuda, R., Minato, K. (1994) Chemical modification of wood by non-formaldehyde cross-linking reagents. Part I. Improvement of dimensional stability and acoustic properties. Wood Sci. Technol. 28:101–110.

Zeronian, S.H., Bertoniere, N.R., Alger, K.W., Duffin, J.L., Kim, M.S., Dubuque, L.K., Collins, M.J., Xie, C. (1989) Effect of dimethyloldihydroxyethyleneurea on the properties of cellulosic fibres. Text. Res. J. 59:484–492.