TRANSVERSE COMPRESSION STRENGTH AND FRACTURE OF SPRUCE WOOD MODIFIED BY MELAMINE-FORMALDEHYDE IMPREGNATION OF CELL WALLS

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ABSTRACT

In comparison with mechanical properties in longitudinal direction, the transverse mechanical properties of wood are far from satisfying. In an attempt to modify wood for improved transverse compression strength and stiffness, spruce wood samples were impregnated with an aqueous solution of melamine-formaldehyde resin. After polymerization, the tangential compression strength of treated samples was 82% higher compared to the untreated reference, and radial compression strength had increased by 290%. The average resin concentration in the cell walls of treated samples amounted to 0.125 g g^{-1}, as measured with the UV-microscope. In contrast, less than 2% of the cell cavities (lumina), were found to be filled with resin. Thus the improvement of strength and stiffness obtained is attributed to modification of the cell wall and not to filing of tracheid lumina. Yielding-behavior under excessive compression load changed from plastic buckling in the reference samples to brittle fracture of cell walls in the treated samples. Even though a certain increase of brittleness has to be tolerated, it is demonstrated that melamine-formaldehyde reinforcement of cell walls has a distinctly improving effect on the properties of spruce in transverse compression.

Keywords: Impregnation, melamine-formaldehyde resin, spruce wood, transverse compression, UV-microscopy.

INTRODUCTION

The modification of wood with the aim of improving certain properties has received considerable attention in the past decades. Attempts to improve dimensional stability and decay resistance by chemical (e.g., Lutomski and Lawniczak 1977; Meyer 1981; Ellis and Rowell 1984; Militz 1991; Galperin et al. 1995; Larsson-Brelid et al. 2000) or thermal modification (e.g., Buro 1954; Kollmann and Schneider 1963; Burmester 1973) have been highly successful, but mechanical properties are significantly impaired by most of these treatments (Schneider 1971; Larsson and Simonson 1994; Rowell 1996). When the objec-

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tive of wood modification lies in the improvement of mechanical properties, two approaches may be followed. Firstly, the cell cavities can be filled with a resin, e.g., styrene or phenol-formaldehyde, by vacuum-pressure treatment. After impregnation the resin is cured, which results in increased compression strength, but gives the wood a plastic-like appearance (e.g., Lutomski and Lawniczak 1977; Meyer 1981; Galperin et al. 1995). Secondly, only the cell wall can be impregnated with a polymerizable resin, without leaving filled cell cavities after curing. This type of modification preserves the porous character of wood. By impregnating wood with methoxymethyl melamine, which is not capable of reacting with itself, but can react with hydroxy groups in wood, an increase of Brinell hardness was achieved (Miroy et al. 1995). Aqueous melamine-formaldehyde (MF) resins can penetrate into the wood cell wall (Rapp et al. 1999; Gindl et al. 2002) and the amorphous region of cellulose fibrils (Hua et al. 1987a, b). Evidence for covalent bonding between MF resins and both the lignin and cellulose components of wood has been reported (Troughton and Chow 1968; Troughton 1969). Melamine is added to urea-formaldehyde resins in the wood composite industry, to enhance the resistance of glue bonds to hydrolysis, i.e., improve the resistance of products to humidity, water, and weather (Dunky 1998). Melamine-based adhesives are colorless and therefore preferred to brownish phenolic resins in the production of glue-laminated timber beams, when customers do not wish visible glue-lines. Melamine-impregnated papers mimicking the optical appearance of wood are used for the production of highly wear-resistant laminate floorings. Finally, melamine resins are characterized by a number of advantageous properties, such as hardness, scratch resistance, low inflammability, and UV-resistance (Hagstrand 1999). Therefore, MF resin is an interesting material for modifying wood cell walls.

Wood is a valued building material because of a favorable strength/weight ratio (Dinwoodie 1975), but this holds true only for the lon-

gitudinal axis defined by the orientation of wood fibers. Due to its anatomical structure, which results in high anisotropy, wood is much less strong in the transverse than in the longitudinal direction. For softwood, the ratio of longitudinal to transverse properties is roughly 10:1 for Young's modulus, 50:1 for tensile strength, and 5:1 for compression strength (Dinwoodie 1975). Motivated by reported positive effects of methoxymethyl melamine treatment on hardness (Miroy et al. 1995), this study examines the influence of melamine-formaldehyde impregnation on the strength and stiffness of spruce in transverse compression.

MATERIALS AND METHODS

Eighty pieces of dry spruce wood (*Picea abies*) with a length of 15 mm were sawn off to a strip with a cross section of 15×15 mm. The specimens were numbered consecutively according to their position in the strip. Even numbered specimens served as reference samples; odd numbered pieces were treated. A commercially available MF resin (Hilamin M562, Dynea) was diluted with distilled water to obtain a content of solids of 25%. The wood specimens were impregnated with distilled water and placed in the MF resin for four days. Subsequently the treated samples were oven-dried at 103°C together with the reference samples. No catalyst was added to the resin.

Tangential and radial compression tests, respectively, on the series of 20 treated and untreated oven-dry samples each, were performed on a Schenk-Trebel UPM 20 universal testing machine. The load was applied at a constant displacement rate of 0.5 mm/min. Since no strain gauges were attached to the samples because of their small size, the displacement of the crosshead was recorded and used for the calculation of strain. Thus, the absolute strain values are not entirely correct, but still useful for a comparison of treated and untreated specimens. All samples were loaded
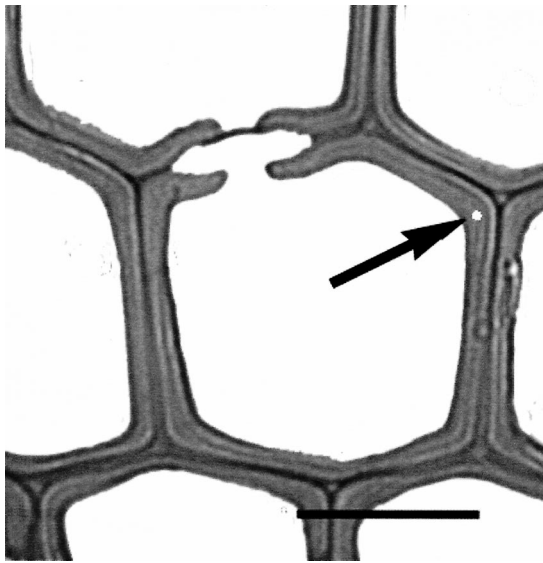
FIG. 1. Cross section of a spruce sample in the UV-microscope with a 1-μm measuring spot displayed in the secondary cell wall (arrow). Scale bar = 10 μm.

FIG. 2. Typical stress strain graphs for melamine-treated and reference samples in tangential and radial compression.

to failure, indicated by the first local maximum in the load displacement graph.

After testing, the cross section of the spruce blocks loaded to failure was sanded to identify zones where failure had occurred. From these zones, small sticks with a cross section of approximately 1 mm^2 were dissected with a razor blade. The sticks were dehydrated in a graded ethanol-acetone series and embedded in Spurr's resin (Spurr 1969). Cross sections with a thickness of 1 μm were cut from the embedded wood sticks by means of an ultra-microtome (Reichert) equipped with a diamond knife (Histo, Diatome). The sections were transferred to quartz glass slides and examined in the UV-microscope (MPM 800, Zeiss) to detect melamine in the cell wall (Gindl et al. 2002), using a measuring spot diameter of 1 μm (Fig. 1). With this small measuring spot, measurements of absorbance could be performed directly in the 3–5-μm-thick cell walls. Absorbance spectra of untreated cell walls, pure cured melamine formaldehyde resin, and melamine impregnated cell walls were recorded.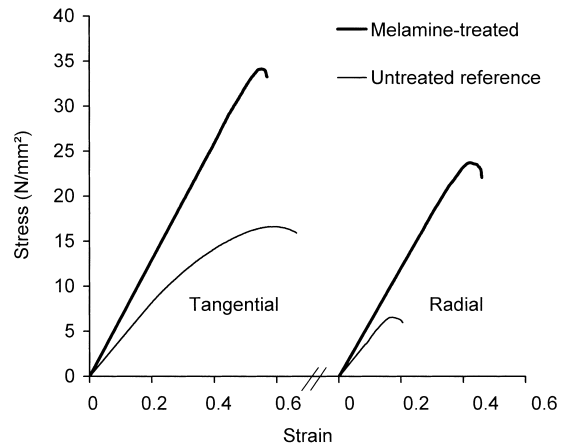 Following UV-microscopy, the sections were stained with gentian violet (Chroma) to observe fracture morphology in transmitted light mode. Images were captured with a CCD camera attached to the light microscope.

RESULTS

After oven-drying, the density of the reference specimens was 0.440 g/cm^3. The density of the melamine-treated specimens had increased to 0.605 g/cm^3. Typical stress-strain graphs under tangential and radial loading for melamine-treated and reference samples are displayed in Fig. 2. All curves show an initially linear increase of stress with strain. The slope of the curves (i.e., stiffness) is distinctly steeper for the melamine-treated samples compared to the untreated reference. After a distinct maximum stress point, failure of individual cells sets in. While the transition from the initial linear increase of stress to failure was gradual in untreated samples, the stress in treated samples dropped more abruptly after reaching maximum strength.

Values of radial and tangential compression strength obtained from the mechanical tests are given in Fig. 3. Tangential compression strength increased to 33.2 N/mm^2 (reference = 18.2 N/mm^2) and radial compression strength increased to 25.6 N/mm^2 (reference
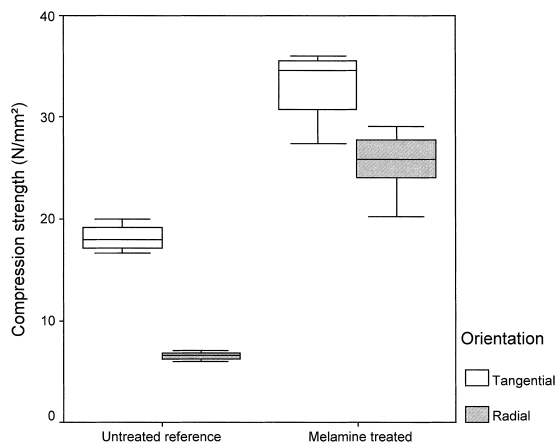
F‍IG. 3.   Box and whisker plot displaying the results of compression testing of melamine-treated and untreated samples in radial and tangential compression (n = 20 each). The box and whisker plot shows the median (horizontal line in the box), the 50% interquartile range (box), and the maximum and minimum value (whiskers).

= 6.5 N/mm^2). The ratio of radial to tangential strength increased from 0.36 in untreated wood to 0.77 in melamine-treated samples. Thus, a reduction of anisotropy is observed.

Microphotographs of cross sections from regions of failure showed clear differences in the mode of failure between the reference and the treated specimens (Fig. 4a–d). In untreated spruce wood, plastic buckling of the cell wall was observed. Frequently, the tension-loaded wall of a buckling compound double cell wall had fractured. The compression-loaded part of the buckling double cell wall did not exhibit any damage, as far as this was detectable in the light microscope. In the melamine-treated samples, brittle fracture of cell walls was dominating instead of plastic buckling. Both individual cell walls of the compound double cell wall were visibly damaged in fractured cells. Only images from tangential tests are displayed, since the fracture mechanism is basically the same in radial direction, with the limitation that the failure in the latter loading case occurred only in earlywood.

In addition to differences in fracture morphology, the cross sections also revealed clear differences in uptake of gentian violet stain by the cell walls. In comparison with the reference samples, which stained in a bright violet, the treated cell walls remained almost unaffected by the stain (Fig. 4a–d). Few cell cavities (less than 2%) in the treated samples were filled with melamine, which was easily distinguished from the embedding medium by its wavy-rippled appearance (Fig. 4b). Spectra taken from the cell walls of tested specimens clearly confirmed that significant amounts of melamine had diffused into the cell wall (Fig. 5). While the spectral characteristics of the reference and treated samples did not differ significantly at wavelengths above 260 nm, a clearly altered pattern of absorbance was seen in the deeper UV. In this region, the absorbance of melamine-treated samples was constantly higher than the reference, and a peak at 240 nm, which was absent in the reference, was observed. Since the pure MF resin shows high absorbance at this wavelength, the change in the spectra of MF-treated cell walls is due to melamine.

DISCUSSION

The results presented above clearly show that the impregnation of cell walls with MF resin has a strong effect on the compressive mechanical properties of wood and on the pattern of fracture in transverse compression. Probing the wood cell wall directly using nano-indentation technique, Gindl and Gupta (2002) demonstrated that melamine treatment results in a significant increase of the cell wall modulus of elasticity and hardness. In the present study, a positive effect of MF treatment on macro-scale compression samples is proven.

Figure 2 gives typical stress strain curves for tangential and radial compression. The stiffness derived from the initial slope of the graphs is twice as high in melamine-treated samples compared to the reference. On average, cell cavities representing less than 2% of the entire sample cross section were found to be filled with MF in the microscopic analysis of microsections. Thus, if melamine in the cell
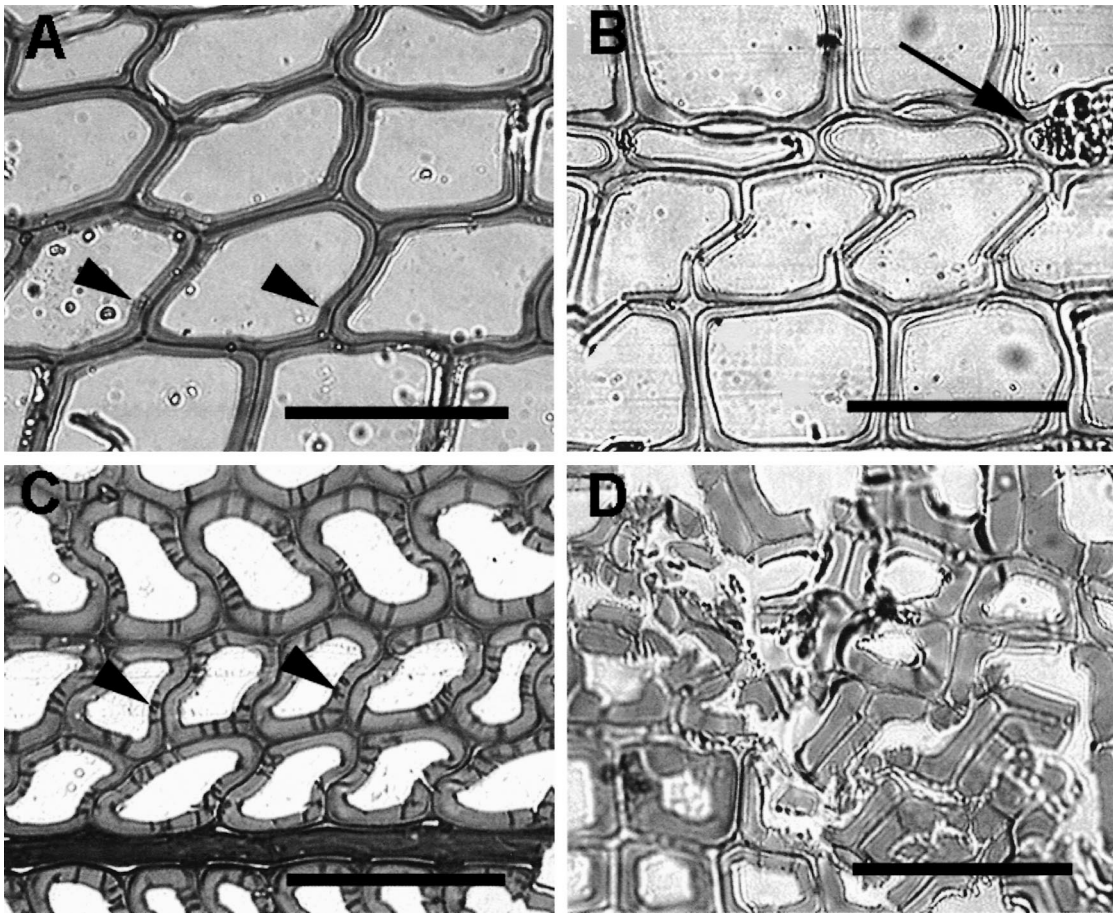
FIG. 4A–D.   Cross sections from untreated (A—earlywood, C—latewood) and melamine-treated (B—earlywood, D—latewood) spruce wood samples subjected to compression in tangential direction (i.e., vertical axis of the image). Arrowheads (A) indicate microscopically visible damage in tension-loaded parts of buckling compound double cell walls. The arrow (B) points to a cell cavity filled with melamine resin. Scale bars = 30 μm.

walls is not considered, a volume fraction of 0.02 may be assumed for MF, and a volume fraction of 0.98 is assigned to wood. Assuming a tangential modulus of elasticity of 700 N/mm^2 for untreated spruce wood (Keylwerth 1951) MF resin, with 9,000 N/mm^2, is much stiffer (Landolt 1950). Applying the rules of mixture assuming an isostress state (Daniel and Ishai 1994) to these data, a rough estimate of the composite modulus of melamine-treated wood may be performed using Eq. (1):

$$\frac{1}{E_{comp}} = \frac{v_{wood}}{E_{wood}} + \frac{v_{mel}}{E_{mel}} \qquad (1)$$

where E_{comp} is the composite modulus, $v_{wood(mel)}$ is the volume fraction of wood(melamine), and $E_{wood(mel)}$ is the modulus of elasticity of wood(melamine). An E_{comp} of 713 N/mm^2 results from this estimate, which is by far not sufficient to explain the observed doubling of the modulus of elasticity after melamine treatment. Similar observations are valid for the radial direction, where a theoretical E_{comp} of 408 N/mm^2 is calculated assuming a radial modulus of 400 N/mm^2 for untreated radial compression samples (Keylwerth 1951). It is therefore clear that not the filling of a few tracheid lumina (i.e., 2%) is responsible for the obtained effects on mechanical properties, but
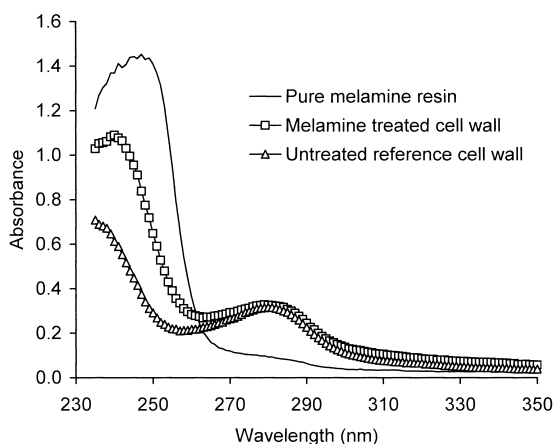
FIG. 5. Absorbance spectra of pure melamine resin in cell cavities, cell walls from melamine-treated specimens, and cell walls from the untreated reference.

rather a modification of the cell-wall material itself.

Repeatedly, evidence for modified cell-wall material properties of treated samples was found in the microscopic analyses performed in this study. First, a reduced uptake of gentian violet stain as seen in Fig. 4 points to an altered cell-wall chemistry. A similar effect is observed when wood modified with melamine resin is stained with the dye basic violet 16 (Rapp and Behrmann 1998).

Furthermore, UV-microscopy reveals the presence of melamine in the cell wall. It is evident from Fig. 5 that melamine contributes to the absorbance spectrum of MF-treated specimens. Beer Lambert's law, as used in UV microscopy (Scott et al. 1969), states that absorbance is proportional to the concentration of the absorbing substance multiplied by a coefficient of extinction and the thickness of the microsection. An estimate based on the absorbance at 240 nm yields a concentration of 0.125 gram MF resin per gram of melamine-treated cell wall (a more detailed description on how this estimate is performed is given in Gindl et al. (2002)). After MF treatment, the density of the specimens had increased from 0.440 g/cm^3 to 0.605 g/cm^3. If possible changes in volume due to melamine uptake are neglected, the 0.125 g/g of MF estimated to be present in the cell walls using UV-microscopy can be added to the initial density of 0.440 g/cm^3, resulting in 0.565 g/cm^3. Also, the MF in the 2% filled cell cavities can be added, giving 0.595 g/cm^3 at a density of 1.5 g/cm^3 for MF resin (Landolt 1950). The remaining difference of 0.01 g/cm^3 may be due to scatter and possibly due to MF adhering to the cell-wall surface in a thin film.

Finally, the difference in fracture morphology between reference and treated samples provides additional evidence for a modification of the cell walls. Maiti et al. (1984) classified cellular solids according to their mode of yielding under load. Among the three types of cellular solids defined, i.e., flexible, plastic, and brittle, the behavior of the reference samples as described in Figs. 2, 4a and 4c matches that of a plastic cellular solid best. This type of material is characterized by plastic buckling of the cell walls. Plastic buckling has also been identified as primary mode of yielding of softwood under transverse compression by a number of earlier studies (e.g., Tabarsa and Chui 2000, 2001). As can be seen from the stress strain graph (Fig. 2) and, more clearly, from the micrographs (Fig. 4b, d), the behavior of MF-treated samples no longer equals that of a purely plastic cellular solid according to Maiti et al. (1984), but its character has shifted to a more brittle response. Brittle cellular materials are characterized by a brittle fracture of the cell walls under excessive load, which is the case in MF-treated samples. Brittle fracture has also been observed in flax fiber reinforced melamine composites (Hagstrand and Oksman 2001), and it appears to be one of the major disadvantages when melamine is used in composite engineering (Hagstrand 1999).

In conclusion, it can be stated that MF resin impregnation of the cell walls is capable of considerably raising the strength and stiffness of spruce wood in transverse compression. This increase is, however, accompanied by the development of a certain brittleness of the cell walls. Notwithstanding this drawback, an application of MF resin treatment in the modi-

fication of wood for improved mechanical properties in transverse compression seems highly promising.

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