Using a Water-Soluble Melamine-Formaldehyde Resin to Improve the Hardness of Norway Spruce Wood

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ABSTRACT: Samples of Norway spruce wood were impregnated with a water-soluble melamine formaldehyde resin by using short-term vacuum treatment and long-term immersion, respectively. By means of Fourier transform infrared (FTIR) spectroscopy and UV microspectrophotometry, it was shown that only diffusion during long-term immersion leads to sufficient penetration of melamine resin into the wood structure, the flow of liquids in Norway spruce wood during vacuum treatment being greatly hindered by aspirated pits. After an immersion in aqueous melamine resin solution for 3 days, the resin had penetrated to a depth > 4 mm, which, after polymerization of the resin, resulted in an improvement of hardness comparable to the hardwood beech. A finite element model describing the effect of increasing depth of modification on hardness demonstrated that under the test conditions chosen for this study, a minimum impregnation depth of 2 mm is necessary to achieve an optimum increase in hardness. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1900–1907, 2004

Key words: hardness; diffusion; mechanical properties; melamine-formaldehyde; wood

INTRODUCTION

Wood is a hierarchically structured cellular solid consisting of different cell types, which are oriented in longitudinal direction (i.e., parallel to the stem axis of the tree, tracheids in softwood, and libriform fibers and vessels in hardwood) or in radial direction from pith to bark (ray cells). In general, wood fibers are 1 to 4 mm long, but only 20 to 40 μm wide. The cell walls of wood fibers are built up by largely crystalline cellulose and other noncrystalline carbohydrate polymers subsumed under the term hemicellulose, as well as the amorphous aromatic polymer lignin.[1] Because of its cellular structure, wood is characterized by a high degree of anisotropy regarding its physical properties. Although the mechanical strength in the longitudinal direction is excellent, considering the comparably low density of wood,[2] transverse mechanical properties are far from satisfactory for certain applications. This is particularly true for wood flooring using solid softwood. In the northern hemisphere, softwoods are more abundant and available at much lower price than dense hardwoods (e.g., beech, oak, and maple), which are commonly used for flooring. Because the hardness of softwoods is often insufficient for flooring, an improvement of the transverse hardness to a level comparable to hardwoods is desirable. Such improvements may be achieved by using densification by pressure treatment,[3] or by filling the cell cavities with polymer resins such as styrene or phenol–formaldehyde.[4–7]

A different approach of improving wood properties is the modification of the cell wall itself with polymers. The cell wall is theoretically free of pores in dry condition, but the estimated pore volume of the cell wall in fully swollen state may be as high as 38%.[8] For a successful modification of wood cell walls with polymer resins, it is thus necessary that the resin may swell the wood cell wall. In a review of the swelling of wood in different organic and inorganic solvents, Mantanis et al.[9–10] found that swelling is promoted by low molecular volume and the ability to form hydrogen bonds. Because melamine–formaldehyde resins are well capable of forming hydrogen bonds and display a number of advantageous properties (e.g., high hardness and stiffness and low flammability),[11] they ap-

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pear to be very well suited to modify the mechanical properties of softwood.

It was shown that water-saturated wood immersed into an aqueous solution of melamine–formaldehyde resin with a content of solids of 20–30% takes up resin by diffusion.[12–13] While the cell walls incorporate up to 30% melamine resin, which improves their mechanical strength,[14] the wood remains porous because the resin does not entirely fill up the interior cavities of wood cells at the chosen content of solids.

The present study examines the effect of melamine–formaldehyde treatment on the hardness of Norway spruce wood and evaluates the efficiency of different impregnation procedures.

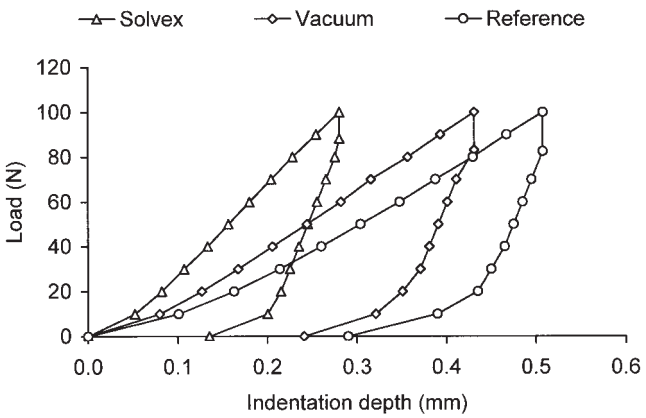

Figure 1 Typical load-depth curves from hardness tests.

EXPERIMENTAL

Sample preparation

The material properties of Norway spruce wood (*Picea abies*) are subject to effects of variable ring width, because the proportion of high-density latewood (the wood formed in summer) with respect to low-density earlywood (the wood formed in spring) varies with the width of an annual growth ring. To ensure homogeneous material properties, spruce wood with similar growth-ring width was selected for all tests. Spruce wood slats with a cross section of 40 × 10 mm were prepared on a rotary planing machine. Specimens with a length of 80 mm were cut from the slats on a circular saw and stored in a chamber with a constant ambient moisture content of 65% and a temperature of 20°C. A liquid, water-soluble melamine–formaldehyde resin (abbreviated in the text to melamine resin or MF, respectively) was diluted to a content of solids of 30% by adding distilled water. Two different procedures were applied to treat the spruce wood blocks with the resin. One group of specimens was immersed into the resin and evacuated to 20 mbar. The reestablishing air pressure after breaking the vacuum forced the resin into the cavities of the wood structure. The procedure of evacuating and breaking the vacuum was repeated three times for a total duration of 10 min. The second group of specimens was subjected to a solvent exchange treatment. The wood blocks were first immersed in distilled water for at least 1 week, until they had taken up so much water that they sunk, and were subsequently placed in MF resin for 70 h to allow for resin diffusion into the wood.

After the impregnation treatment, all specimens were air-dried for 3 days. Thereafter, the melamine resin was polymerized for 10 min at a temperature of 150°C in a hot-press. The press, equipped with polished stainless steel platens, was closed tightly to provide a smooth surface, but no additional pressure was applied. The specimens were postcured in an oven for 24 h at a temperature of 100°C. Reference specimens not modified with melamine resin were subjected to the same heat treatment in the press and postcuring in the oven. The weight percent gain was calculated by relating the increase in mass because of melamine treatment to the dry mass prior to treatment.

Furthermore, non-melamine-treated spruce samples were coated with a high-quality polyurethane (PU) flooring lacquer (Durlin DD313; Murexin, Graz, Austria). Durlin DD313 is based on 2,4-diisocyanate-toluene, mixed with its 2,6-isomer. The PU coating was applied by immersing the specimens for 1 min and subsequent air-drying for 3 days. A coating thickness of 200 μm was achieved.

Finally, specimens were also prepared from the hardwood beech (*Fagus sylvatica*) for reference purposes. These samples were neither treated with melamine resin nor coated.

Hardness testing

Hardness is the resistance of a material against indentation. The mean pressure between the surface of the indenter body and the material is equal to the ratio of the load to the projected area of the indentation. By using a ball indenter, the hardness H is calculated according to

$$H = P(\pi\delta(D - \delta))^{-1}$$

where P is the load, δ is the depth of the indentation, and D is the diameter of the indenter. For the present study, a 5-mm-diameter steel ball indenter was loaded to a peak load of 100N. After peak load, the indenter was held at constant depth for 20 s and then unloaded. All tests were done on an Instron universal testing machine equipped with a 10-kN load cell. Figure 1 shows typical load-depth curves from hardness tests.

One day after hardness testing, digital images of the residual indents left by the 5-mm ball were captured by means of a video camera attached to an incident

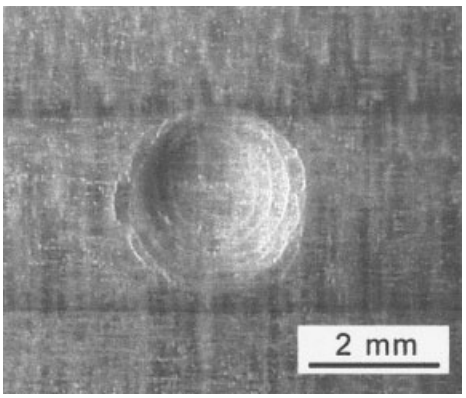

Figure 2 Micrograph of an indent in melamine-treated wood after hardness testing.

light microscope (Fig. 2). The largest and the smallest diameter of each indent was measured by using Scion Image beta 3b software (http://www.scioncorp.com) and averaged. Assuming indents in the shape of spherical cups, the residual indentation depth δ_r was calculated according to

$$\delta_r \frac{1}{2}(D - (D^2 - d^2)^{1/2})$$

where d is the mean diameter of the spherical imprint on the wood surface. By inserting δ_r for δ in eq. (1), the hardness only accounting for residual plastic deformation after unloading was calculated.

FTIR spectroscopy

Melamine resin provides a characteristic spectrum in the mid-IR region. A conspicuous IR active triazine ring sextant out-of-plane vibration is observed at 822–809 cm^{-1}.[15] To evaluate the penetration of melamine into the wood specimens after different treatments, two vacuum-treated and two solvent-exchange-treated samples were selected. From their original dimensions of 80 × 40 × 10 mm, the samples were cut to the size of 60 × 20 × 10 mm, removing 10 mm of material from the TL and TR planes at both ends. A layer of 1 mm thickness was chipped from both LR surfaces by means of a razor blade. The chips from both opposing surfaces were mixed and milled with a Retsch Ultra Centrifugal Mill ZM 1000 with a fixed ring sieve with 80 μm hole width. Special care was taken to avoid heating of the wood during the milling process. The remaining 8-mm cores and an untreated reference were also milled. FTIR spectra of the untreated and treated samples were acquired with a Bruker FTIR spectrometer (Equinox 55) equipped with a deuterated L-alanine triglycine sulfate (DLATGS) detector. Two milligrams of wood powder was diluted with 200 mg KBr (Aldrich; 22,186-4; FTIR grade) and 13 mm KBr pellets were prepared under vacuum in a standard device applying a pressure of 75 kN cm^{-2} for 3 min. Thirty-two scans per sample were collected at a spectral resolution of 4 cm^{-1}, and the collected spectra were rationed against air.[16]

Postspectroscopic manipulation was kept to a minimum. The spectra were only shifted parallel to the wavenumber axis so that the minimum between 2000 and 800 cm^{-1} was equal to zero, as suggested by Zavarin et al.,[17] and normalized to the highest band, as suggested by Fengel and Ludwig.[18]

UV microspectrophotometry

To study the distribution of melamine resin across the sample thickness at higher spatial resolution than possible by FTIR, UV microspectrophotometry was performed on the samples previously analyzed with FTIR. Wood specimens were embedded in epoxy resin[19] and sectioned on a Reichert Ultracut ultramicrotome by using a Diatome Histo diamond knife. The 1-μm-thick sections were transferred to quartz glass slides and transmitted light spectra at wavelengths between 235 and 350 nm were recorded in a Zeiss MPM-800 UV microscope. UV microspectrophotometry makes use of the UV absorbance of melamine. A detailed description of the UV microspectrophotometric method for the determination of melamine content in wood cell walls is given in Gindl et al.[13,20] In brief, melamine shows a broad band of absorbance around 240 nm, whereas it shows negligibly small absorbance at 280 nm, where lignin has a characteristic maximum. Thus, the ratio of the absorbance at 240 nm and the absorbance at 280 nm can be used as a relative measure for melamine concentration in the wood cell wall, provided that the variability of lignin content in the cell wall is much smaller that melamine content variability. This prerequisite is fulfilled for normal softwood.[21] In melamine-free cell walls, the ratio 240/280 is typically 1.8–2.[13,20] Because the measuring spot in the MPM 800 UV microscope is 1 μm in diameter, it was possible to perform accurate measurements of absorbance spectra in the wood cell walls.

Finite element modeling

It is reasonable to assume that an increase in the depth of penetration of melamine–formaldehyde resin into the wood structure will result in a concurrent increase of hardness. By using material properties of unmodified and melamine-modified Norway spruce wood acquired in uniaxial compression tests transverse to the grain,[22–23] 2D plane strain finite element analysis of hardness testing at different modification depths was carried out by using MSC.Marc software. The 2D model for the wood cross section, a rectangle measuring 50 × 10 mm, consisted of 2000 plane strain quad-

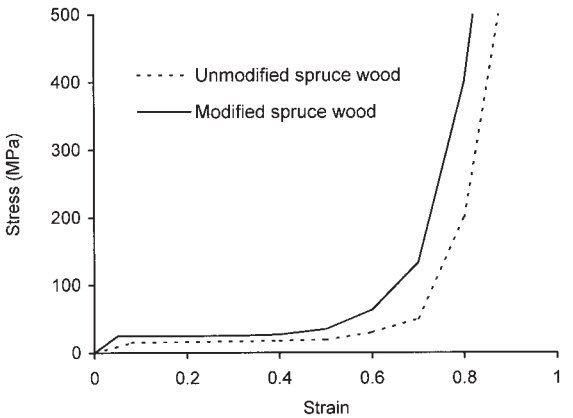

Figure 3 Stress–strain curves for transverse compression used to describe the material properties of unmodified and modified spruce wood in finite element analysis. The stress–strain curves represent an average of tangential and radial properties.

rilateral elements (MSC.Marc element type 11) with a height and width of 0.5 mm. Piecewise linear plastic material properties as shown in Figure 3 were assigned to elements simulating unmodified and modified Norway spruce wood, assuming a Young's modulus of 250 and 580 MPa, respectively, for the initial elastic phase. The steel ball used for hardness testing was modeled by using a rigid circle with a diameter of 5 mm.

In the first modeling run, the rigid indenter body was set to move into the deformable body (i.e., the wood sample) up to an indentation depth of 0.5 mm, which is equivalent to the maximum depth obtained in hardness tests performed on unmodified spruce wood using a 5-mm steel ball (Fig. 1) as described above. In the subsequent runs, the material properties of a 0.5-mm-thick layer of elements, starting at the surface, were changed from unmodified wood to modified wood, thus simulating increasing depth of modification by melamine resin in steps of 0.5 mm. Each run on modified wood was halted as soon as the load at the rigid indenter body reached the previously recorded load required to produce a 0.5-mm-deep indent in unmodified wood. The calculated load-depth curves of the rigid indenter body as well as the residual indentation depth after unloading were recorded.

RESULTS

An average weight percent gain of 25.1% was obtained by solvent exchange treatment of spruce wood samples, whereas vacuum treatment resulted in a weight percent gain of 6.5%. Results from FTIR spectroscopy confirm differences in melamine uptake caused by the respective impregnation procedure. Figure 4 shows an overview of IR spectra obtained from MF-treated and untreated wood. It can be seen that the spectra show clear differences in the fingerprint region. The band at 813 cm^{-1}, characteristic for the triazine ring, is shown in more detail in Figure 5. The 1-mm surface layer of the sample treated by solvent exchange (Solvex) is most thoroughly impregnated, as it exhibits the highest absorbance. The melamine con-

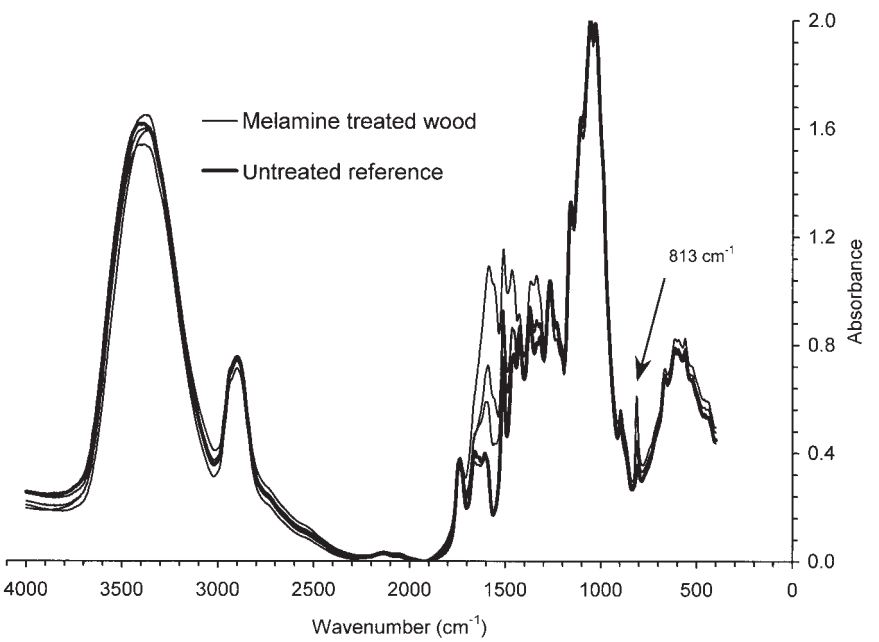

Figure 4 Overview of infrared spectra averaged from two replications of untreated and differently melamine-treated spruce wood.

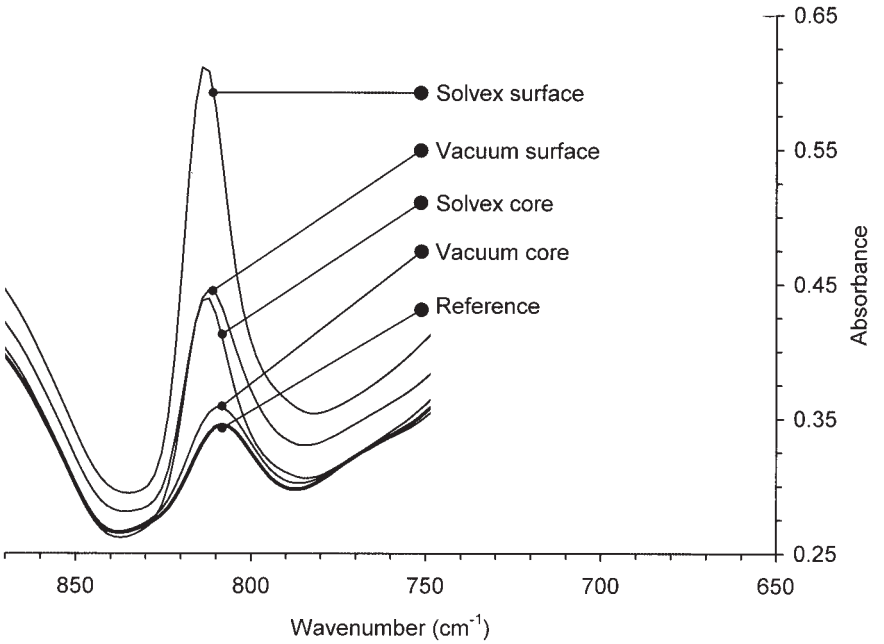

Figure 5 Detail of infrared spectra showing the band at 813 cm^{-1} caused by the triazine ring in melamine.

centration in the core region of this sample is in the same order as the melamine concentration in the surface layer of the vacuum-treated sample. The core region of the vacuum-treated sample, however, shows hardly any significant melamine content.

These results are confirmed by UV microspectrophotometry (Fig. 6). In the vacuum-impregnated sample, high melamine content is observed near the surface, where also the inner cavities (lumina) of a few rows of cells were filled with MF. The concentration decreases rapidly and reaches zero level (absorbance ratio 240/280 $\leq$ 2) at a depth of approximately 0.8 mm. By contrast, melamine content decreases less rapidly in the solvent-exchange impregnated sample. Even at a depth of 4.5 mm, melamine is found in cell walls, as indicated by an absorbance ratio 240/280 of 2.8–3. The lumina of a few rows of cells at the surface are filled with MF also in the solvent-exchange impregnated sample, whereas no MF is visible in lumina deeper in the sample.

The results of hardness measurements performed with a 5-mm steel ball are displayed in Figure 7. Figure 7(a) shows the hardness calculated from the indentation depth at peak load. These hardness values

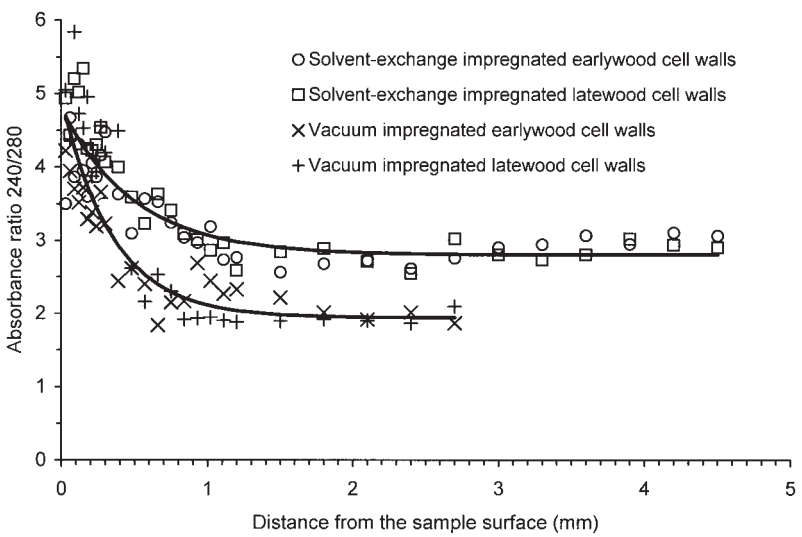

Figure 6 Absorbance ratio indicating melamine concentration plotted against distance from the sample surface (thick lines represent an exponential function fitted to measured values of solvent-exchange and vacuum-treated samples, respectively).

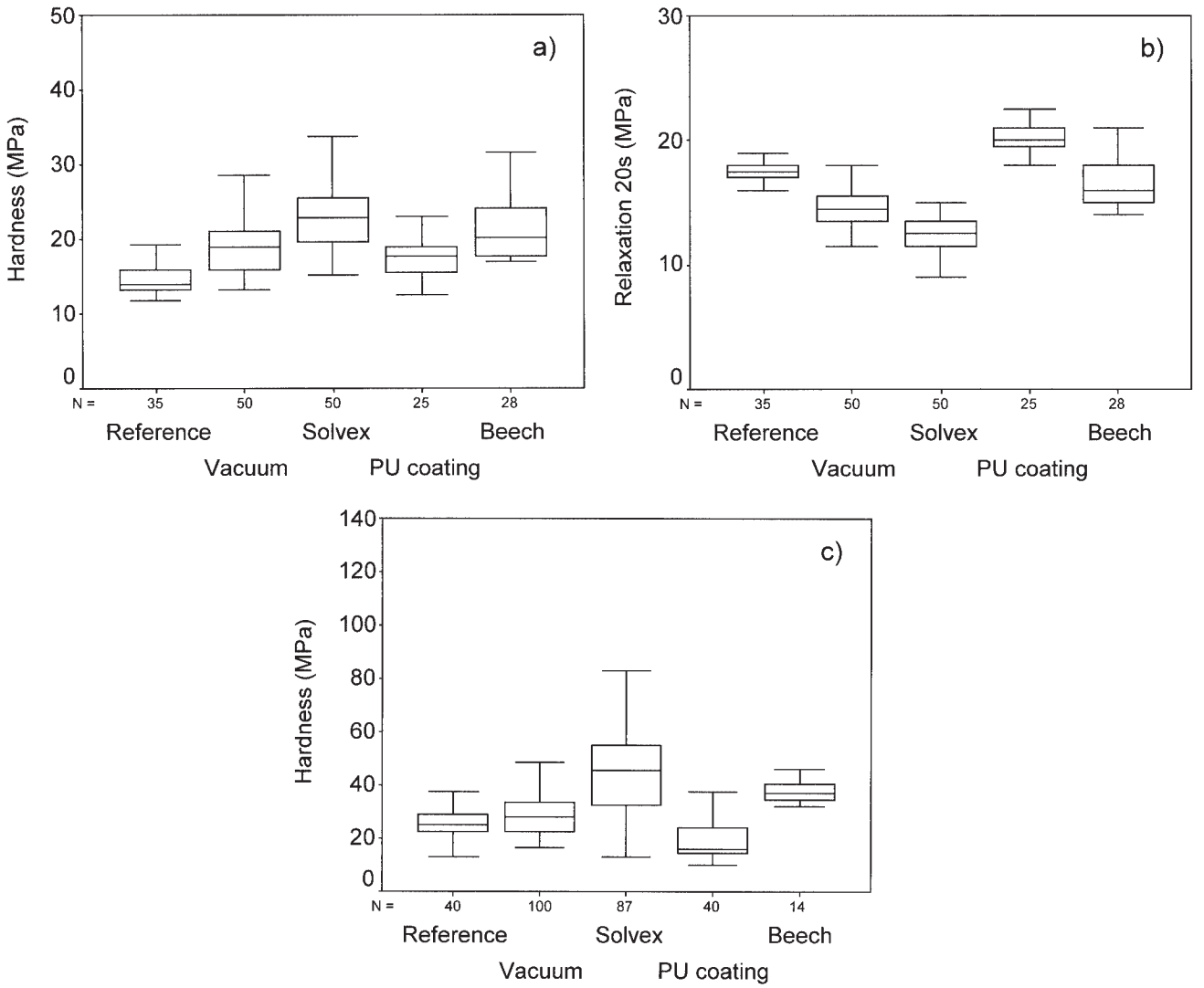

Figure 7 Results of hardness tests: (a) hardness calculated from the indentation depth at a load of 100*N*, (b) load drop during 20 s at constant depth, (c) hardness calculated from the diameter of residual imprints after unloading.

thus account for both plastic and elastic deformation. An analysis of variance (ANOVA, $P < 0.5$) indicates that both melamine treatments (Vacuum and Solvex) resulted in a statistically significant increase of hardness. Although the increase of hardness was smaller for vacuum-treated samples, the hardness of solvent-exchange impregnated samples was comparable to beech wood. By contrast, the PU coating used for reference purposes had no significant effect on hardness. In addition to the hardness at peak load, the load-drop (i.e., stress relaxation) after holding the indentation depth constant for 20 s was also evaluated [Fig. 7(b)]. Compared to untreated spruce wood specimens, stress relaxation was similar in hardwood and slightly more pronounced for the PU-coated spruce wood. The melamine-treated specimens showed a reduction of stress relaxation. This reduction was more distinctive for the solvent-exchange-treated group compared to the vacuum-treated group.

After unloading, indents remained in the material due to plastic deformation. By measuring the diameter of the indents, only the hardness accounting for plastic deformation was calculated [Fig. 7(c)]. The variability of this type of hardness according to different treatments is similar to the hardness calculated at peak load [Fig. 7(a)], with solvent-exchange-treated specimens being hardest (i.e., equally hard or even harder than the hardwood beech). Both vacuum treatment with melamine resin and PU coating by immersion showed no significant effect on hardness. Figure 7(c) suggests that the hardness of PU-coated samples is even lower than the untreated reference.

Although the hardness calculated from the indentation depth at peak load [Fig. 7(a)] accounts for both plastic and elastic deformation, the hardness calculated from residual indents after unloading accounts only for plastic deformation. The difference of these two hardness values (Fig. 8) is indicative of the de-

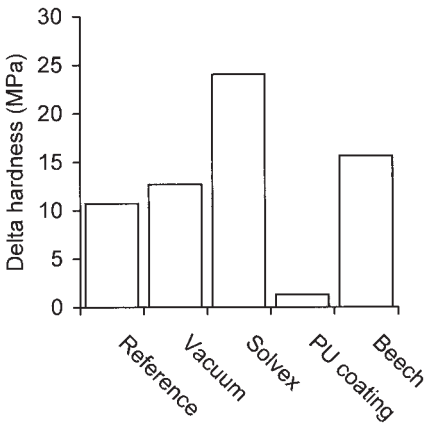

Figure 8 The difference in hardness (ΔH) obtained when the hardness calculated from the indentation depth δ at peak load ($100N$) is subtracted from the hardness obtained using the residual indentation depth δ_r after unloading.

crease in resistance to indentation due to elastic deformation of the material. The difference is largest for the solvent-exchange-treated samples, indicating that a significant amount of deformation is recovered elastically after unloading. By contrast, the deformation of the PU-coated surface is almost entirely plastic.

Results of the 2D finite element analysis are shown in Figure 9. When the reduction of indentation depth, which is indicative of the improvement of hardness, is plotted against the depth of modification, an S-shaped curve is obtained. At the chosen settings, a modification depth of 2 mm is most efficient. Modification to a smaller impregnation depth does not provide the desired increase in hardness, whereas modification to an impregnation depth larger than 2 mm only results in a small additional improvement of hardness calculated from the maximum indentation depth at a given load recorded during testing. The hardness calculated from residual plastic indents is not improved by impregnation depths larger than 2 mm. Experimental results for hardness calculated at maximum indentation depth agree well with the simulation. A good but less clear agreement was also found for the hardness calculated from residual plastic indents.

DISCUSSION

The water-soluble melamine–formaldehyde resin proved to diffuse well into the wood structure as already demonstrated in an earlier study.[13] In excellent agreement, both FTIR spectroscopy and UV microspectrophotometry indicate that the type of treatment [i.e., vacuum impregnation (flow) or solvent exchange (diffusion)] exerts a strong influence on the achievable depth of penetration of MF into Norway spruce samples. As shown in Figures 4–6 and also by the differences in weight percent gain (25.1% for Solvex and 6.5% for Vacuum, respectively), a significant impregnation depth in spruce wood can only be achieved by diffusion, because the flow of liquids from cell to cell in softwoods is greatly hindered by the closure of pits occurring during drying of wood and during heartwood formation.[24–26] Therefore, the efficiency of vacuum impregnation of Norway spruce wood is poor, and liquids may only penetrate deeper into the wood by way of diffusion through the cell wall. Because diffusion through the cell wall is the main path of transport, MF is deposited in the cell wall, whereas the lumina of cells remain largely free of MF. MF-filled lumina were only occasionally observed in deeper regions of the sample, particularly, in the vicinity of ray tissue, which is a preferred path for the flow of liquids in softwood.[27]

Hardness tests of melamine-modified spruce samples revealed a considerable improvement for solvent-exchange impregnated specimens, comparable to the reference hardwood beech. The improvement of hardness was even more remarkable compared with conventionally PU-coated spruce wood samples. The PU coating used in the present study exhibited high plasticity, resulting in the plastic component of deformation during the hardness test being larger than the elastic component (Fig. 8). Therefore, similar to a number of other wood coatings,[28] the PU coating does not improve hardness but acts mainly as a protective layer against dust and moisture. Although melamine modification shows a clear potential to improve the hardness of softwood, there remains the drawback of a certain embrittlement of the material.[22–23,29] The long-term stability and resistance to cracking of melamine-modified wood under variable ambient moisture conditions needs therefore to be investigated.

As shown in Figure 9, a reasonably good agreement between the finite element model of the effect of in-

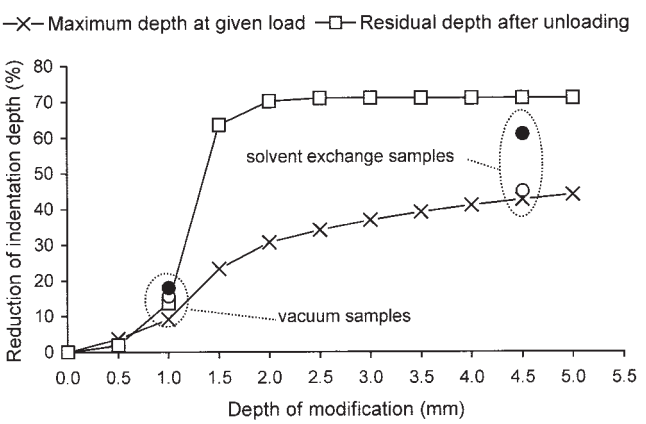

Figure 9 Finite element modeling of the reduction of indentation depth at a given load plotted against the depth of modification (○, experimental data for indentation depth a given load; ●, experimental data for residual indentation depth after unloading).

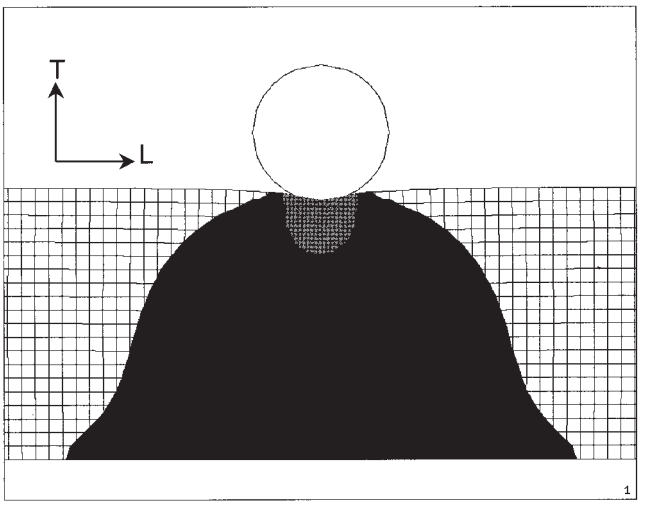

Figure 10 Elastic (black) and plastic (gray) strain field in a hardness test on wood (depth of indent = 0.5 mm, diameter of steel ball = 5 mm, thickness of wood = 10 mm). L denotes the longitudinal sample direction, whereas T stands for the tangential direction. The radial direction R is normal to the T and L direction.

creasing impregnation depth on the reduction of indentation depth on the one hand and experimental data on hardness and impregnation depth on the other hand was achieved. It appears justified therefore to use only a 2D finite element representation. Because only transverse mechanical properties are significantly affected by melamine modification,[22] axial wood properties were not considered. Both the indentation depth calculated at maximum load and the residual indentation depth measured after unloading show an S-shaped relationship with modification depth. The indentation depth calculated at maximum load decreases continuously with increasing modification depth, because the elastic strain field under the indenter body extends across the entire specimen thickness (Fig. 10). By contrast, the plastic strain field extends to a maximum of 2 mm below the surface under the chosen load settings (5 mm ball, maximum indentation depth 0.5 mm). Therefore, modification depths larger than 2 mm achieve no further reduction of the residual indentation depth after unloading.

To conclude, the results presented in this study show that melamine–formaldehyde modification is a viable technique to improve the hardness of softwood to a level comparable to hardwood. However, a certain minimum modification depth is necessary, as shown by hardness tests and confirmed by finite element modeling. This depth of modification can be achieved by choosing a comparably slow solvent exchange impregnation procedure.

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