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Changes in Cell Wall Dimensions during the Different Stages of Furfuryl Alcohol Modification

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Furfuryl alcohol modification of wood is a well-known process for wood property enhancement. The present project focuses on veneer molding for high-value applications using the plasticizing effect of furfuryl alcohol. Adding maleic anhydride to furfuryl alcohol leads to an acid-catalyzed polymerization of furfuryl alcohol at elevated temperatures, fixing the shape of the veneer. In contrast to water or water vapor treatment, furfuryl alcohol-modified cell walls face a lower degree of shrinkage due to the polymer formation and possibly experience less drying-induced cracks. Earlier studies show a distinct influence of maleic anhydride on the curing of furfuryl alcohol. To determine the impact of different maleic anhydride contents on the polymer formation and the corresponding shrinkage of wood cell walls, microscopic studies were carried out on various maple microtome sections (*Acer* sp.), *i.e.*, when dry, water-impregnated, after furfuryl alcohol impregnation, and after curing at elevated temperatures. At each state, the cell walls of 30 appointed early wood cells were determined by cell wall area measurements. The lowest shrinkage of impregnated samples was realized by using 10 wt% maleic anhydride in the impregnation solution and after 48 h soaking. Here, cell wall shrinkage could be reduced by approx. 42.6% compared to water-impregnation.

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INTRODUCTION

In the automobile and yacht interior industries, valuable wood veneer is of great interest for decorative purposes. However, veneer application on surfaces is limited to simple shapes due to mechanical restrictions. During the molding process, various stresses are applied to the veneer. Resulting cracks cause significant damage to the veneer (Wagenführ *et al.* 2005). In the past several decades, various attempts have been made to improve the molding behavior of wood and wood veneer. However, all approaches (*e.g.* anhydrous ammonia for impregnation (Schuerch 1966), angle grinded veneer bond to fleece (Leimeister 2008), enzymatic (Goswami *et al.* 2007), and hygrothermal treatments of wood and wood veneer) have one or more disadvantages. For this reason, many modern manufacturers working with veneer bending or molding use water or water vapor for veneer plasticization, although they have to accept the disadvantage of set-recovery of the molded veneers and material failure due to drying-induced shrinkage.

The present project focuses on furfuryl alcohol modification of wood veneer to improve the veneers' molding ability. Furfuryl alcohol modification of wood is a well-known process for wood property enhancement (Epmeier *et al.* 2004; Lande *et al.* 2004;

Esteves *et al.* 2011). In addition to the known benefits, furfuryl alcohol treatment plasticizes wood similar to water usage and enhances the molding behavior of veneers (Herold and Pfriem 2013). Adding maleic anhydride to furfuryl alcohol leads to an acid-catalyzed polymerization of furfuryl alcohol at elevated temperatures resulting in a dark-brown polymer (*e.g.*, Barr and Wallon 1971; Choura *et al.* 1996; Guigo *et al.* 2007). The complex polymer residing primarily inside the cell wall significantly reduces the set-recovery of modified veneer samples compared to water treated samples (Herold and Pfriem 2014).

For the present work, microscopic studies were performed on maple microtome sections (*Acer* sp.) to evaluate the swelling and shrinkage due to furfuryl alcohol impregnation and polymerization. Microscopic studies on furfuryl alcohol penetration into wood cell walls were done earlier by Buchelt *et al.* (2012). Results exhibit a retarded penetration of furfuryl alcohol into the cell wall, which induces swelling. For purposes of process development of furfuryl alcohol-modified veneer for improved molding, it is of interest to gain further knowledge about the degree of swelling due to furfuryl alcohol impregnation compared to the use of water and about the effect of modification on wood cell walls after the curing step. Earlier studies show that the maleic anhydride content in the furfuryl alcohol solution significantly influences the furfuryl alcohol polymerization (Herold *et al.* 2013). Lower maleic anhydride content leads to lower weight percentage gains (WPG) corresponding with higher furfuryl alcohol evaporation from the cell wall. To determine the influence of maleic anhydride content on the polymer formation inside the cell wall, samples were impregnated with furfuryl alcohol containing 0, 5, and 10 wt% maleic anhydride. Results from furfuryl alcohol impregnation are compared to cell wall swelling and shrinkage due to water impregnation.

EXPERIMENTAL

Sample Preparation

For this study, cross-section microtome samples (thickness 20 μm) were cut from a single piece of European maple wood (*Acer* sp.). For each microtome section, 30 early wood cells were defined to be surveyed. Each cell was measured under four conditions: dry, water-impregnated, furfuryl alcohol-impregnated, and cured states. At first, the microtome sections were impregnated with water at low pressure (80 mbar) for 15 min. After the microscopic photographs were taken and saved for subsequent measurements of the cell wall, the microtome sections were dried at 80 °C in a conventional laboratory kiln for 30 min. Again, microscopic photographs were taken before dry samples were impregnated at a low pressure (80 mbar) for 15 min with furfuryl alcohol solutions containing 0, 5, or 10 wt% maleic anhydride. Furfuryl alcohol was provided by International Furan Chemical B.V., Rotterdam, The Netherlands, and maleic anhydride (p.A.) was obtained from Merck KGaA, Darmstadt, Germany. For each charge, microscopic photographs were taken directly after impregnation for one half of the samples. The remaining samples were left in their respective furfuryl alcohol solutions to soak for 48 h before being microscopically evaluated, as increased swelling has been reported for samples soaked for longer periods of time (Buchelt *et al.* 2012; Hermescec *et al.* 2002). Immediately after photographing the impregnated state (with and without soaking), samples were cured at 120 °C for 15 min in a conventional laboratory kiln. To avoid sticking to the microscope slide, a plastic film (Exact-Film 210 from Exact Plastics)

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was placed between the microtome section and the microscope slide. Final microscopic images were taken after curing.

Microscopic Studies

The microscope used for this study was an Olympus BX41, equipped with a digital CCD camera and an additional reflected fluorescence system using a mercury lamp. For this study, a FITC filter was used as the excitation filter. The TSO-Software NewVidmess was used for all measurements.

The cell walls were measured for all conditions described above using a 500-fold magnification. For each condition and cell, three measurements were done for the lumen and cell area (Fig. 1).
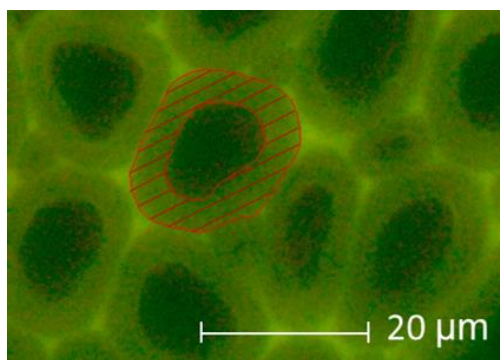
Fig. 1. Cell wall measurement.

Subsequently, the cell wall areas were calculated from the mean of the total cell area and lumen and area swelling coefficients were determined according to Buchelt *et al.* (2012). However, for the present study the dry cell wall areas were used as the basis to calculate the area swelling coefficient as given in Eq. 1,

$$S\,[\%] = \frac{A_{a,b,c} - A_0}{A_0} * 100 \tag{1}$$

where S is the Area swelling coefficient [%], $A_{a,b,c}$ is the cell wall area when water-impregnated, furfuryl alcohol- impregnated and cured, and A_0 is the cell wall area under dry condition.

RESULTS AND DISCUSSION

In general, area swelling coefficients at chosen conditions vary strongly between the individual cells, explaining the high variety of values in Figs. 2 to 4. Buchelt *et al.* (2012) explained this high variation by size and available space. Furthermore, the microfibril angle, especially of the S2-layer, influences the swelling and shrinking behavior of the wood cells (Cave 1972; Boyd 1977; Pang 2002; Burgert *et al.* 2007) as well as the cellulose volume ratio (Cave 1972), thickness of the S2-layer relative to the S1-layer of the cell wall, and the degree of lignification (Boyd 1977). Pang (2002) concludes shrinkage to be a combined effect of cell wall shrinkage and lumen shape change influenced by other

tissues. All of these parameters vary with each cell and possibly lead to the wide range of values measured.

Results for water-induced cell wall swelling are given in Figs. 2 to 4. Means of water impregnated area swelling coefficients ranged from 39 to 45%. The impregnation of the maple microtome sections with neat furfuryl alcohol and without soaking increased the cell wall area by approximately 35% (Fig. 2). Furfuryl alcohol impregnation with additional soaking time promoted the penetration of furfuryl alcohol into the cell wall, resulting in higher cell wall swelling (approximately 42%, Fig. 2). These results are in good accordance with the findings of Buchelt *et al.* (2012). Furthermore, furfuryl alcohol impregnated samples with extended soaking time exhibited similar cell wall swelling to that of water-soaked cell walls. This finding supports the earlier assumption from the cupping test with samples prepared in a similar manner to this study (Herold and Pfriem 2013). Hereby, furfuryl alcohol and water-impregnated samples gave similar results regarding the shaping path. The shaping path has been used for indicating the molding capability and plasticization.

Finally, the heat treatment (120 °C) of the samples displayed in Fig. 2 led to full furfuryl alcohol evaporation due to a missing initiator for furfuryl alcohol polymerization. Consequently, no noticeable change can be noticed between cured and dry cell walls.
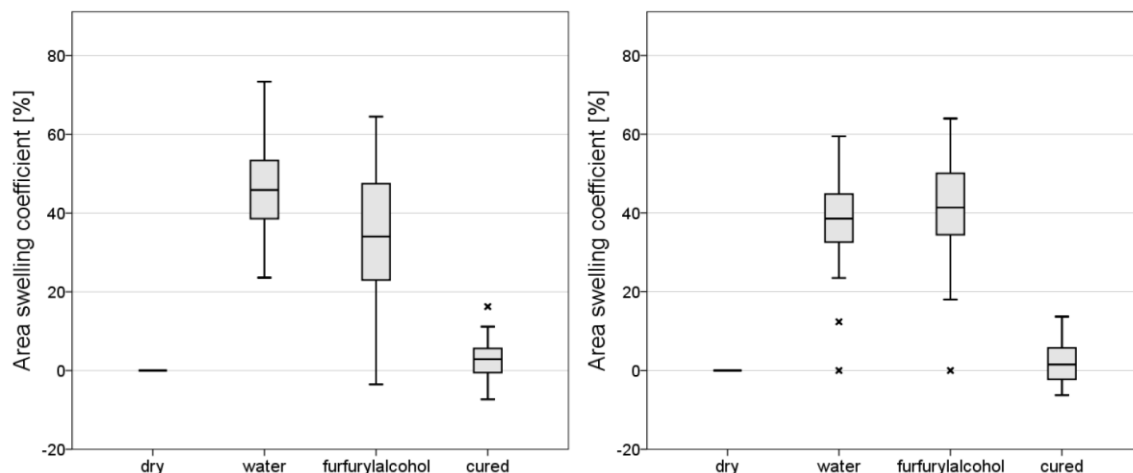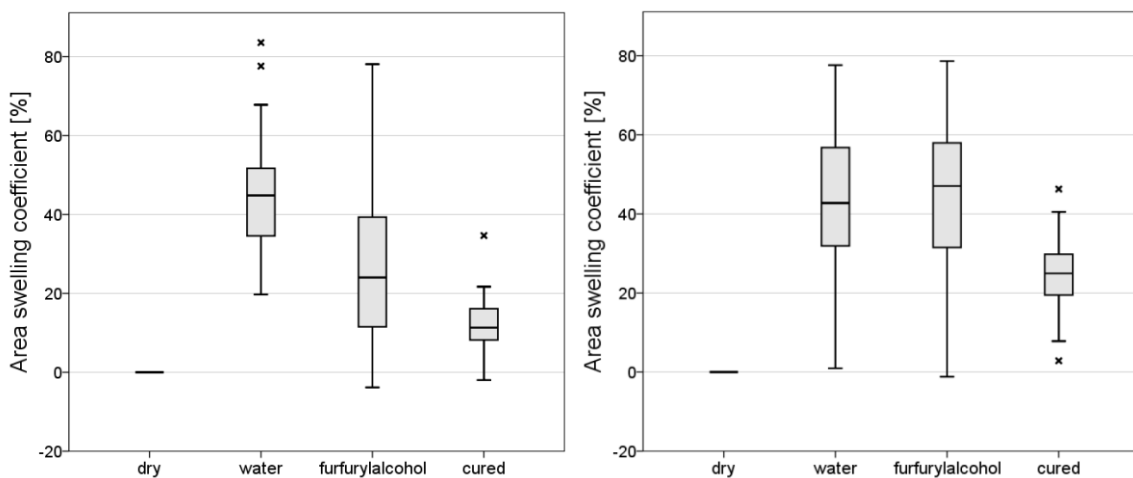

Fig. 2. Cell wall changes of samples impregnated with neat furfuryl alcohol. Left: Without soaking. Right: After soaking. Box plots depict minimum, 1st quartile, median, 3rd quartile, and maximum; outliers are plotted as individual points.

Samples impregnated with furfuryl alcohol solutions containing 5 and 10 wt% maleic anhydride were prepared to determine the impact of maleic anhydride and soaking on the cell wall after curing. Results are demonstrated in Fig. 3 and 4 for samples impregnated with furfuryl alcohol solution containing 5 *resp.* 10 wt% maleic anhydride. Similar to the results from neat furfuryl alcohol impregnation, cell wall swelling was higher after soaking compared to that immediately after furfuryl alcohol impregnation. Furthermore, results from cell wall measurements after curing showed the effect of soaking on the polymer formation inside the cell wall. Without soaking, the cell wall area was increased by 6.2% *resp.* 12.2% compared to dry conditions. Samples left in furfuryl alcohol for soaking exhibited higher permanent cell wall swelling at the cured state (18.4% *resp.* 24.8%).
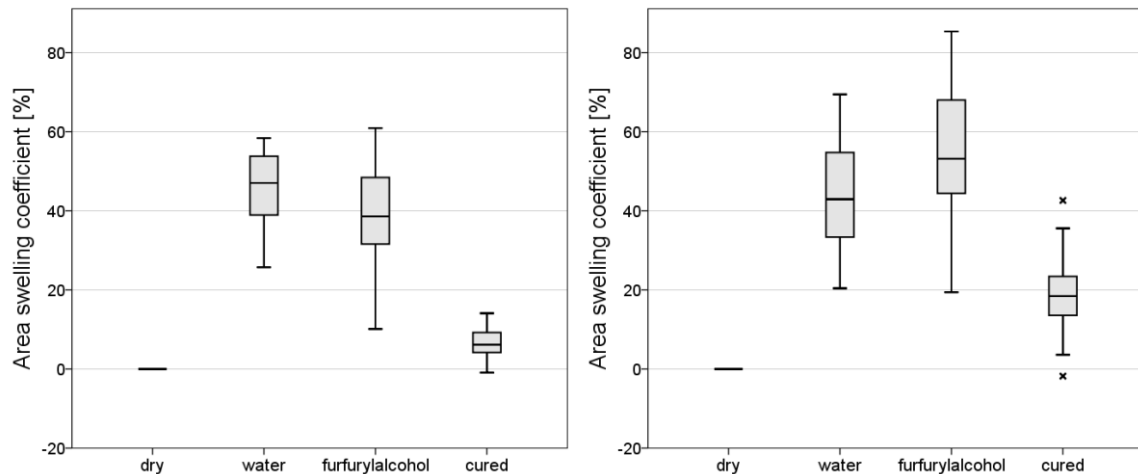
Fig. 3. Cell wall changes of samples impregnated with furfuryl alcohol containing 5 wt% maleic anhydride. Left: Without soaking. Right: After soaking. Box plots depict minimum, 1st quartile, median, 3rd quartile, and maximum; outliers are plotted as individual points.


Fig. 4. Cell wall changes of samples impregnated with furfuryl alcohol containing 10 wt% maleic anhydride. Left: Without soaking. Right: After soaking. Box plots depict minimum, 1st quartile, median, 3rd quartile, and maximum; outliers are plotted as individual points.

The impact of maleic anhydride content and soaking on the furfuryl alcohol polymer formation in the cell wall can be visualized in Fig. 5. Generally, higher curing-induced shrinkage was observed for samples impregnated with furfuryl alcohol solutions containing lower maleic anhydride contents and for samples prepared without soaking. No noticeable change in the cell wall dimensions was detected for samples impregnated with neat furfuryl alcohol. For these samples, soaking had no influence on the cured cell wall.

As shown before in detail, for the samples impregnated with furfuryl containing 5 and 10 wt% maleic anhydride, soaking significantly influenced the cell wall swelling as well as the cell wall area after curing. Samples impregnated with furfuryl alcohol containing 5 wt% maleic anhydride had a mean cell wall area swelling coefficient of 6.2% when cured immediately after impregnation. On the other hand, samples prepared with additional soaking time exhibit higher cell wall area swelling (18.4%) after curing at 120

°C. In comparison to these samples, less cell wall shrinkage was found for cured samples impregnated with furfuryl alcohol solutions containing 10 wt% maleic anhydride. Without soaking, cell walls exhibited an increase in area of approximately 12.2%. In comparison, additional soaking doubled the cell wall area increase (24.8%). Inversely concluded, samples impregnated with furfuryl alcohol containing 10 wt% maleic anhydride and with additional soaking time displayed the lowest cell wall shrinkage due to curing among all samples.
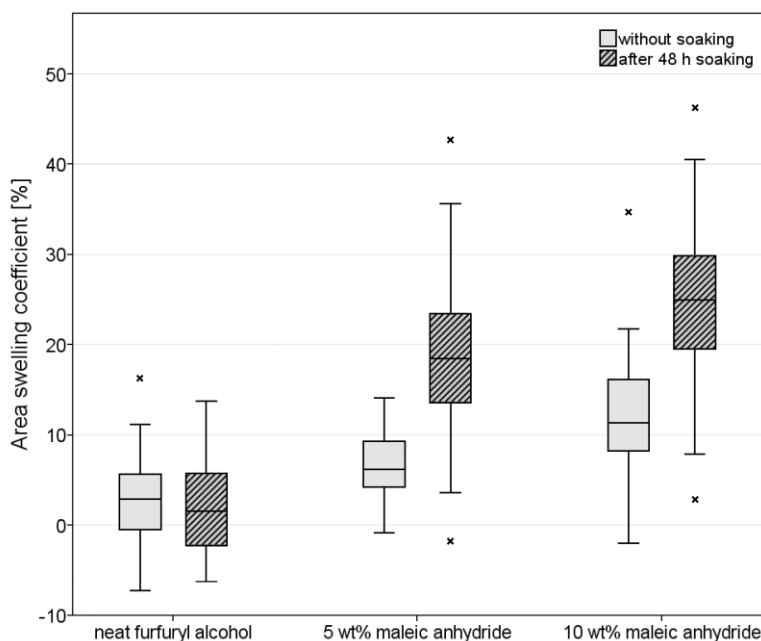
Fig. 5. Changes in cell wall area due to furfuryl alcohol modification after curing using 0, 5, and 10 wt% maleic anhydride

These results are in compliance with results from earlier studies. Those studies suggest a significant influence of the maleic anhydride content on the furfuryl alcohol polymerization and polymer formation. Lower maleic anhydride contents has been found to result in lower degrees of polymerization and lower weight percentage gains (WPG) compared to higher maleic anhydride contents (Herold *et al.* 2013).

Results of the present study negate the feasibility of a permanently and fully swollen wood cell wall by furfurylation to avoid unfavorable shrinkage and resulting cracks. However, shrinkage can be noticeably reduced by furfurylation compared to water-impregnation with similar wood cell wall swelling, indicating a similar degree of plasticization.

Conclusions from this study are only applicable to furfuryl alcohol modification of maple microtome sections (*Acer* sp.). Such samples are characterized by a higher ratio of surface area to cell wall volume compared to veneer samples used in an industrial process. Thus, furfuryl alcohol evaporation might be less intense for veneer modification, resulting in higher furfuryl alcohol polymer gains inside the cell walls.

CONCLUSIONS

1. On a microscopic level, furfuryl alcohol impregnation of European maple microtome sections (*Acer* sp.) followed by 48 h of soaking in furfuryl alcohol leads to similar cell wall swelling as that found for water-impregnation.

2. During the curing process, European maple microtome sections (*Acer* sp.) impregnated with furfuryl alcohol solutions containing 0, 5, or 10 wt% maleic anhydride to initiate furfuryl alcohol polymerization shrink due to furfuryl alcohol evaporation and loss of water from condensation reactions. Treatment solutions using lower maleic anhydride contents cause noticeably higher shrinkage.

3. Compared to the use of water for wood cell wall plasticization and the subsequent drying-induced cell wall shrinkage, this shrinkage can be reduced by furfuryl alcohol modification.

ACKNOWLEDGMENTS

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