Shape Retention of Furfurylated and Moulded Wood Veneer

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High-value wood veneer is used in the furniture and automobile interior industries for decorative purposes. Due to mechanical restrictions, veneer application on surfaces is limited to simple shapes. In the last century, many approaches were developed to improve the moulding behaviour of veneer. However, all of these processes face several difficulties. Currently, water is primarily used for veneer plasticization, with the disadvantages of shrinkage and cracks due to drying. Furthermore, products often fail during material climate testing due to set recovery. Thus, a veneer modification process was considered combining plasticization, moulding, and shape fixation of veneer with reduced set recovery. To accomplish this, veneers were impregnated with furfuryl alcohol/maleic anhydride solutions to improve plasticization and moulding properties. Subsequently, veneers were moulded, and the realized shapes were fixed by temperature-induced acid-catalyzed polymerization. Due to the polymer in the cell wall, set recovery of all modified samples was noticeably reduced compared to reference samples plasticized with water prior to moulding. The degree of set recovery reduction due to modification varied with the modification intensity. Samples with higher weight percentage gain (WPG = 126.4%) were more stable in the presence of moisture than samples with lower polymer yields (WPG = 107.4%).

Keywords: Furfuryl alcohol; Moulded wood veneer; Set recovery; Shape retention

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INTRODUCTION

The application of valuable wood veneer for decorative purposes is of high interest for many industries, especially for the automobile and yacht interior industries. However, veneer application on surfaces is limited to rather simply shaped elements due to mechanical restrictions. The main restriction is cracks that occur during moulding, caused by various stresses applied to the veneer during the process (Wagenführ and Buchelt 2005). Minor failures can be concealed, though this effort is time-consuming and costly. To extend the range of application, various approaches have been developed to improve the moulding behaviour, including several chemical, *e.g.*, anhydrous ammonia (Schuerch 1963); mechanical, *e.g.*, angle-grinded veneer bond to fleece (Leimeister 2008); enzymatic (Goswami *et al*. 2007); and hygrothermal treatments of wood and wood veneer (Navi and Sandberg 2011). However, all processes face several disadvantages. Today, many manufacturers use water or water vapor for veneer plasticization, with the disadvantage of material failure due to shrinkage and set recovery of the moulded veneers.

Thus, the main objective of the current project is the development of a veneer modification process combining plasticization, moulding, and shape fixation of veneer. To accomplish this, veneers were impregnated with furfuryl alcohol solutions containing maleic anhydride as an initiator. In general, wood modification using furfuryl alcohol solutions with different initiators for impregnation is a well-known method for wood preservation affecting several wood properties (Schneider 2002; Westin 2004; Epmeier *et al.* 2004). After impregnation, furfuryl alcohol was polymerized at an elevated temperature, forming a complex polymer residing mainly in the cell wall (Barr and Wallon 1971; Choura *et al.* 1996; Lande *et al.* 2004; Guigo *et al.* 2007; Barsberg and Thygesen 2009; Thygesen *et al.* 2010a).

Previous results from mechanical testing of veneer demonstrate a similar degree of plasticization realized with furfuryl alcohol impregnation compared to the usage of water (Herold and Pfriem 2013). Studies on furfurylated and compressed solid wood have demonstrated a reduced spring-back effect due to the modification (Buchelt *et al.* 2012). Thus, it is assumed that the polymer formed during heat-induced acid-catalyzed polymerization likewise affects the fixation of the furfurylated and shaped veneer. To verify this assumption, veneer stripes were impregnated, shaped, and cured at elevated temperatures. After curing, samples were exposed to three different climate conditions to evaluate the impact of different modification intensities and climate conditions on the shape retention of the samples.

EXPERIMENTAL

Sample Preparation

For this study, all samples were taken from a single veneer sheet of European maple (*Acer* sp.) produced as rift veneer. Samples were cut in a rectangular shape (20 mm x 100 mm) with the long edge being aligned parallel to the fiber orientation. Annual rings were chosen to be narrow and comparable in width. The thickness of unmodified veneer was 0.53 to 0.57 mm. Samples were dried at 80 °C to constant weight. Afterwards, dry samples were evacuated under low pressure (60 mbar) for 30 min, followed by impregnation at 60 mbar for 3 h, allowing a maximum uptake. For impregnation, three solutions of varying furfuryl alcohol and maleic anhydride contents (2, 5, and 10 wt% maleic anhydride) were prepared to provide different modification intensities, expressed by different WPGs (Herold *et al.* 2013). Furfuryl alcohol (> 98 vol%) was provided by International Furan Chemical B.V., Rotterdam, The Netherlands, and maleic anhydride (p.A.) was obtained from Merck KGaA, Darmstadt, Germany. After impregnation, samples were left in aluminum foil to soak for 24 h. Likewise, reference samples were prepared using deionized water for plasticization.

For this study, two rectangular brackets from premium steel sheets were used to accomplish the moulding. After the steel brackets were heated to 120 °C, the veneer samples were bent gently transversely to the grain around one of the steel brackets, covered with the second steel bracket, and fixed in between. To keep the veneer sample from sticking to the steel brackets, a plastic film (Exact-Film 210 from Exact Plastics) was wrapped around the samples. Additionally, cellulosic sheets were used to absorb leaking impregnation solution separated from the veneer with perforated film (P1 from R&G Faserverbundwerkstoffe GmbH).

The prepared samples were kept at 120 °C in a heating chamber to start the polymerization. After 1.5 h, foils and cellulosic sheets were removed and samples were cured further for 30 min at 120 °C fixed between the steel brackets. Water-impregnated reference samples were treated in a similar fashion.

Modification Intensity

Generally, the intensity of wood modification processes has a strong influence on the physical properties. To determine the impact of the modification intensity on the shape retention of moulded samples, samples were impregnated with three different furfuryl alcohol/maleic anhydride solutions to realize different treatment intensities. Increased maleic anhydride content leads to higher weight percentage gains (WPGs) (Herold *et al.* 2013). The treatment intensity is in accordance with the WPG of samples.

To determine the WPG, the samples were weighed in dry conditions, after soaking, and finally after curing. From these weights, the mass uptake was determined as WPG using Eq. (1),

$$WPG = \frac{W_t - W_u}{W_u} * 100 \tag{1}$$

where WPG is the weight percentage gain of the sample after curing [%], W_t is the weight of the sample after curing [g], and W_u is the weight of the absolutely dry sample [g].

Shape Retention

There have been few reports concerning the set recovery or shape retention of moulded wood veneer. Fang *et al.* (2011) used a cyclic recovery test to determine the set recovery of compressed wood veneer. Similar to known recovery tests of solid compressed wood (*e.g.*, Navi and Girardet 2000; Rautkari *et al.* 2009; Kutnar and Kamke 2011; Laine *et al.* 2012; Buchelt *et al.* 2013), the compressed veneer was saturated with water followed by oven drying five times. Afterwards, samples were boiled in water for 30 min. For the present study, the impact of treatment intensity on the shape retention at various climatic conditions was evaluated. Each charge was exposed to three different climates (room temperature: approximately 25 °C/50% RH; climate chamber: 25 °C/90% RH; and water at 25 °C) for 24 h to survey the climate- and time-dependent shape retention. After 24 h at the chosen climate, all samples were placed in water (95 °C) for one hour.

For this study, shape retention is defined by the change of angle. After moulding, samples ideally have an angle of 90°, which is also considered the reference angle for full shape retention (= 100%). Changes of angle due to set recovery were measured in defined intervals over 24 h. Additionally, photos of each sample were taken at every measurement point.

RESULTS AND DISCUSSION

The distinct effects of different climates on the shape retention of native wood veneer are shown in Fig. 1. The reference sample placed at *ca.* 25 °C and 50% RH exhibited the highest shape retention after 24 h (92.4%). Increasing the humidity to 90% RH resulted in shape retention of 72.8%. As expected, water exposure led to the set recovery of the reference sample. After 15 min, the sample’s shape retention was about 38.7%, reaching 17.6% after 24 h. After one hour in heated water (95 °C), all reference samples displayed a shape retention of 7.9 to 10.4%. The retained shape is therefore a result of plastic deformation of the veneer.

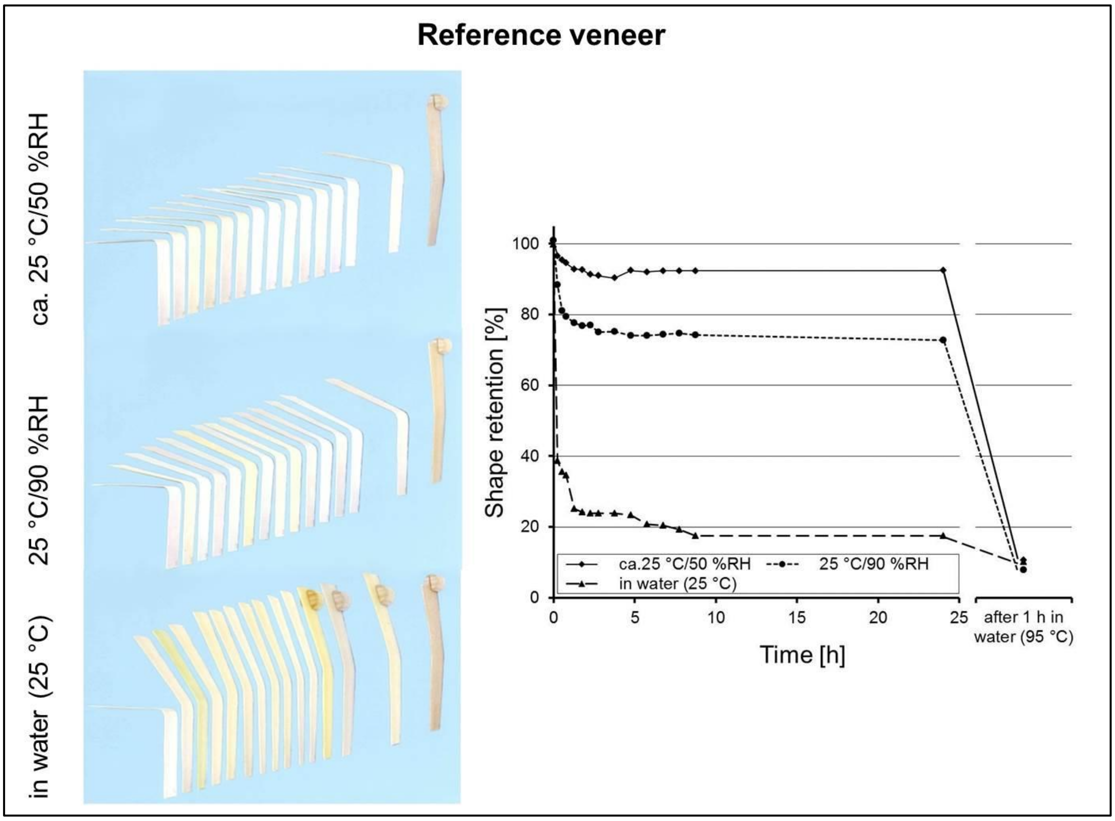

Fig. 1. Shape retention of reference samples under different climate conditions

Generally, each furfuryl alcohol-modified sample had a reduced memory effect and increased shape retention compared to the corresponding reference sample (Figs. 1 to 4). Increasing maleic anhydride content correlated with increasing shape retention. However, findings from earlier studies (Herold *et al*. 2013) concerning the linear relation of maleic anhydride content and WPG could not be confirmed for the curing of samples using additional films and cellulosic sheets. The WPGs determined in this work were generally higher because the films seemed to restrain evaporation of furfuryl alcohol. As a result, 2 wt% maleic anhydride led to an average WPG of 107.4%; average WPGs of 123.3% and 126.4% were recorded with 5 wt% and 10 wt% maleic anhydride, respectively.

The impact of modification intensity on the shape retention of modified samples is shown in Figs. 2 through 4. As expected, climate conditions strongly influenced the shape retention of the samples. While room climate led to little change, higher humidity/water contents promoted the memory effect of the veneer samples. However, the differences in climate affected shape retentions less distinctively for higher modification intensities compared to lower modification intensities.

Figure 2 depicts results from samples modified with a furfuryl alcohol/maleic anhydride solution containing 2 wt% maleic anhydride. After curing, all samples showed a spring-back effect. After 24 h, small changes were observed for the sample exposed to room climate (shape-retention: 93.7%). In contrast, the sample in the climate chamber experienced greater changes in shape, approaching a shape retention of 78.2% after 24 h. Predictably, the most distinct change was observed for the water-stored sample with a shape retention of 67.7%. After being exposed to hot water (95 °C) for one hour, samples exhibited a distinct reduction in shape retention (38 to 43%).

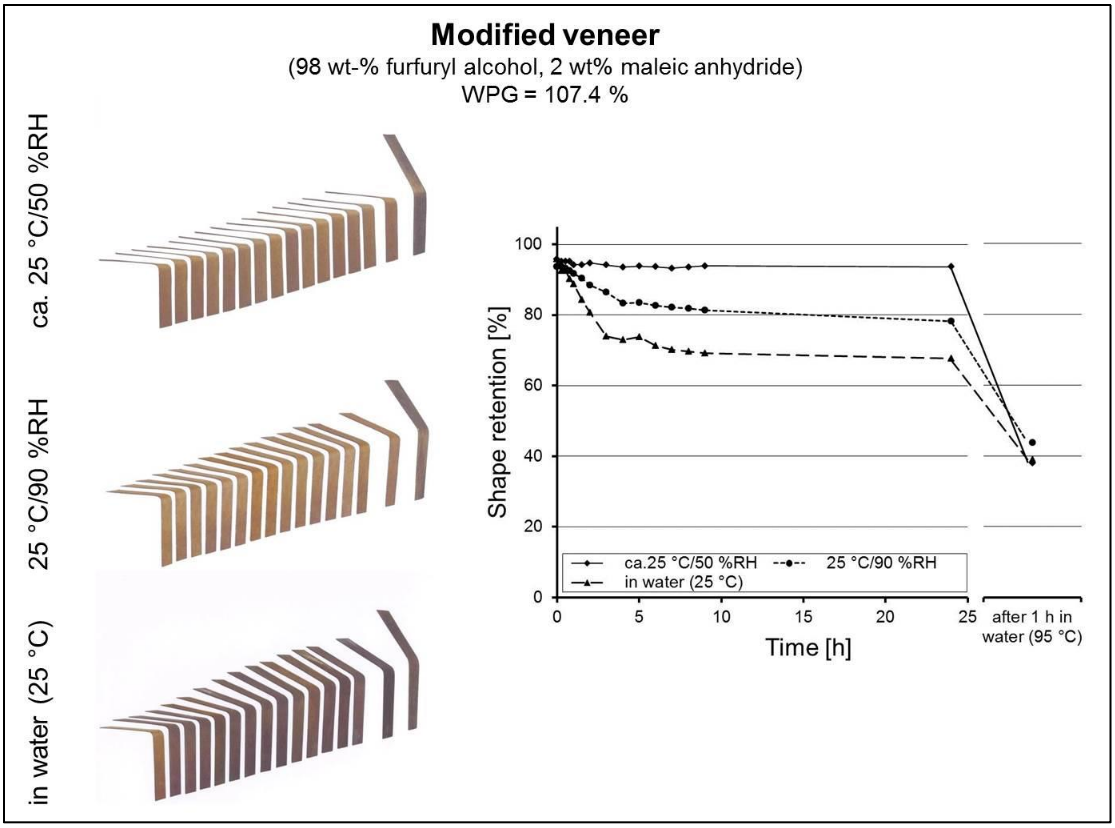

Fig. 2. Shape retention of modified samples (2 wt% maleic anhydride, WPG = 107.4% (2.06)) under different climate conditions

Compared to results from less intensely modified samples (2 wt% maleic anhydride), higher shape retentions were generally recorded for samples modified with furfuryl alcohol solution containing 5 wt% maleic anhydride (Fig. 3). Almost no spring-back was observed when samples were removed from moulds after curing. The effect of different climate conditions could still be observed, but to a significantly lower extent. After 24 h at room climate, a shape retention of 98.2% was documented. Increasing the humidity to 90% RH led to a shape retention of 90.9%. Water storage for the same duration led to a further decreased shape retention (86.6%). After being placed in hot water (95 °C) for one hour, samples still demonstrated a shape retention of about 65%.

Further reductions of the memory effect could be realized using 10 wt% maleic anhydride in the furfuryl alcohol solution, leading to a WPG of 126.4% (Fig. 4). However, a negative spring-back effect was noticed when samples were removed from brackets after curing. Samples had an initial angle of 87 to 89°. After 24 h in the different climates, all samples retained their shape by at least 94.7%. Hot water storage (95 °C) decreased the shape-retention to no less than 78.6%.

Overall, these findings indicate improved shape retentions for all modified samples compared to the reference samples. However, a strong difference in shape retention is evident for the different modification intensities. Figure 5 displays samples from each charge, which were soaked in water (25 °C) for 24 h. The unmodified reference sample exhibited the lowest shape retention (17.4%). The sample with the lowest modification intensity (WPG = 107.4%) exhibited a shape retention of 67.7%. With increasing modification intensity, shape retention was noticeably improved. A WPG of 123.3% led to a shape retention of 86.6%; a WPG of 126.4% achieved nearly full shape retention (94.7%).

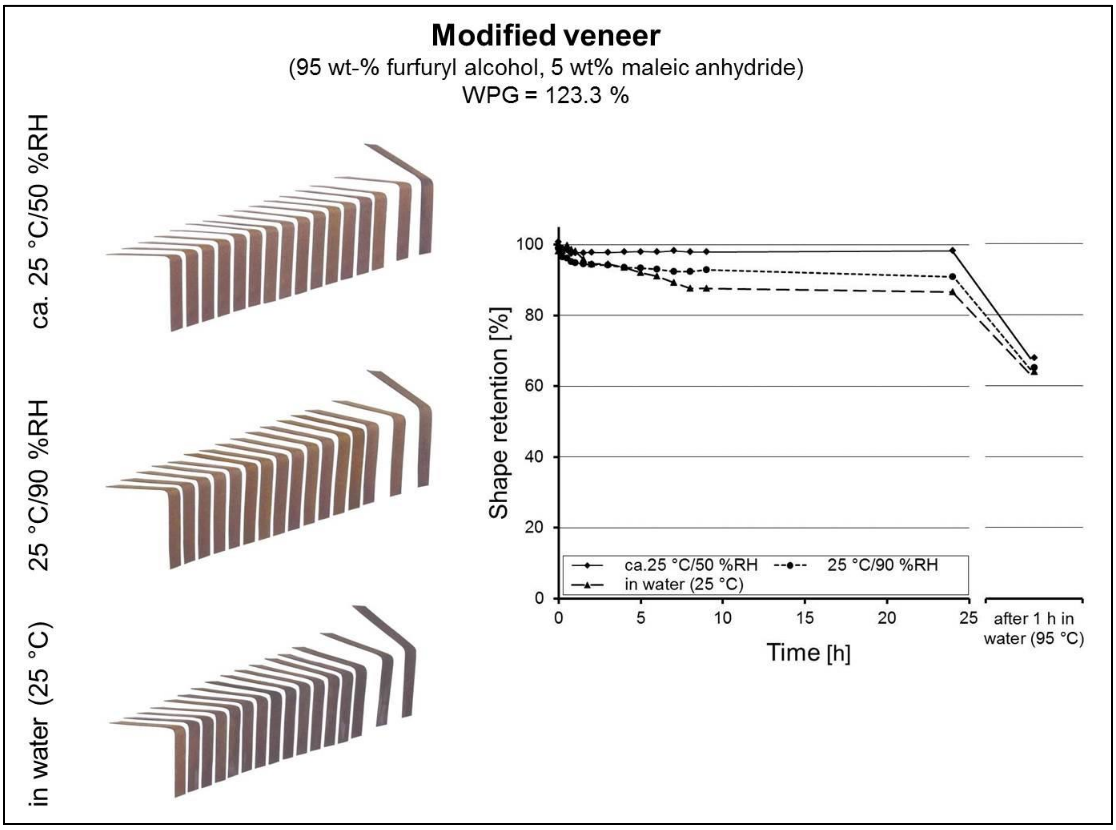

Fig. 3. Shape retention of modified samples (5 wt% maleic anhydride, WPG = 123.3% (1.75)) under different climate conditions

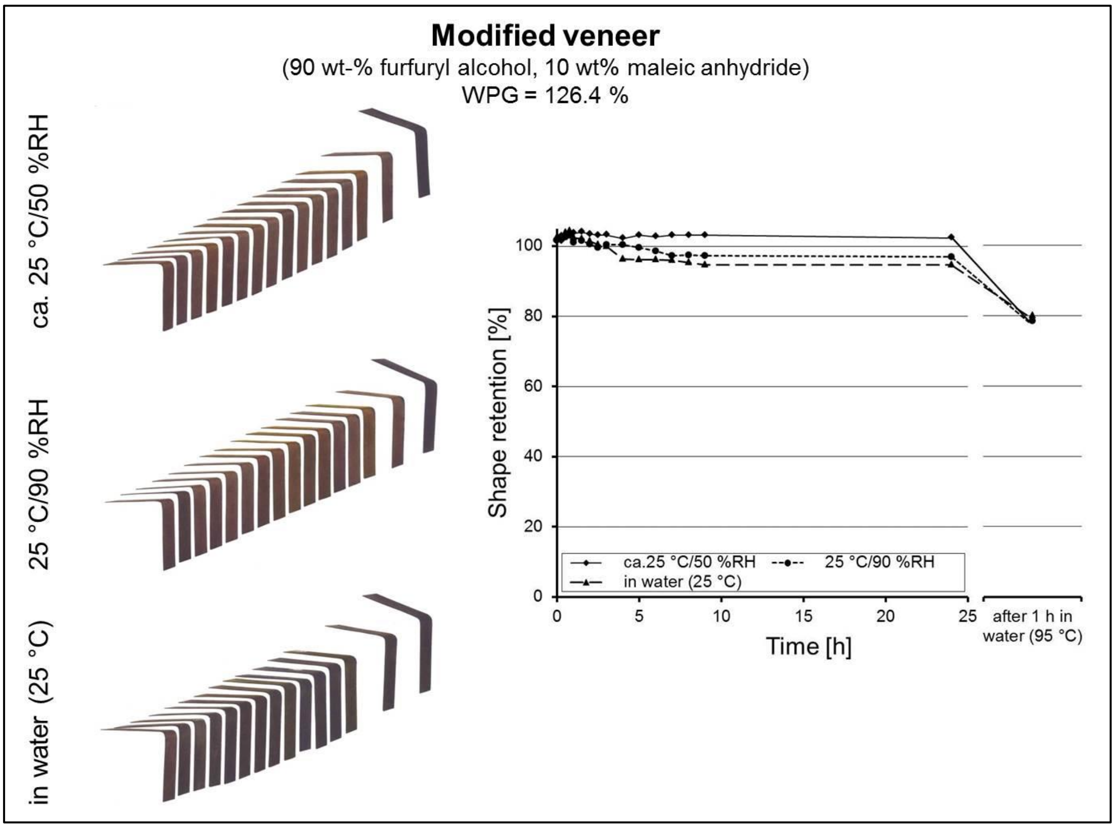

Fig. 4. Shape retention of modified samples (10 wt% maleic anhydride, WPG = 126.4% (1.25)) under different climate conditions

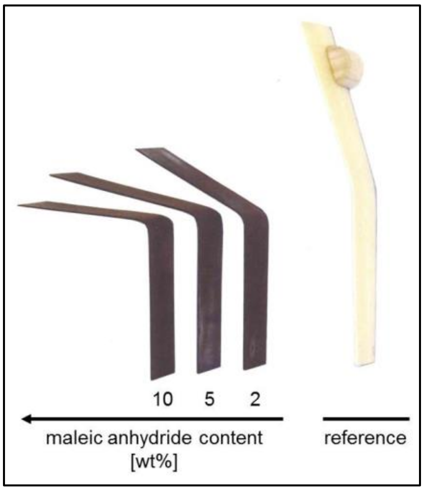

Fig. 5. Shape retention of veneers after 24 h in water (25 °C)

Most likely, the observed increased shape retention of the modified and shaped veneers resulted from a combination of effects. Thygesen *et al.* (2010b) studied the sorption behavior of differently modified wood including furfurylated wood (WPG=63%). Compared to native wood, furfurylated wood showed a small reduction of sorption below 96% RH moisture content and even increased wood water content above 96% RH. These results suggest that water sorption is not remarkably reduced by furfuryl alcohol modification or by the hydrophobic furfuryl alcohol polymer itself. Thus, water sorption cannot sufficiently explain the effect of furfuryl alcohol modification on the increased shape retention of the shaped veneers. Yet, WPGs were much higher in this study and water sorption sites might be more strongly affected. Another hypothesis for the increased shape retention is the impact of the polymers' structure on the mobility of the cell wall components and the woods' plasticization. Possibly, the polymer in the cell wall may build a dimensionally stable compound that hinders noticeable movement of the wood components. Hereby, results indicate that WPG might not be the most important parameter to influence the shape retention, as the WPGs of all modified samples were nearly similar. Samples impregnated with 5 and 10 wt% maleic anhydride content in furfuryl alcohol solution exhibited a difference of 3.1% in WPG with a total WPG of no less than 123%. Yet, the shape retention of both modifications showed noticeable differences. Possibly, different amounts of maleic anhydride lead to different polymer structures and/or compositions. This suggestion is consistent with earlier findings from Thygesen *et al.* (2010a). Furthermore, samples modified with less intensity (WPG = 107.4%, 2 wt% maleic anhydride) showed a change in appearance after one hour in hot water (95 °C): small polymeric accumulations were formed on the veneers' surface, possibly indicating a retarded or incomplete polymerization of furfuryl alcohol. This suggestion correlates with earlier findings from DSC studies (Herold *et al.* 2013).

CONCLUSIONS

1. Furfuryl alcohol-modified samples exhibited improved shape retention compared to the corresponding reference samples.
2. Shape retention increased with modification intensity. The highest shape retention was observed for the highest modification intensity (WPG = 126.4%, 10 wt% maleic anhydride).

3. The maleic anhydride content affects the treatment intensity, the resulting chemical composition and structure of the furfuryl alcohol polymer in the cell wall, and the shape retention.

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