

Wood Physics/Mechanical Properties

Christoph Hötte*, Martin Nopens and Holger Militz

Esterification of wood with citric acid and sorbitol: effect of the copolymer on the properties of the modified wood. Part 2: swelling and shrinking, sorption behaviour and liquid water uptake

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Abstract: Formaldehyde-free, bio-based wood modification processes are gaining importance. One well-developed method is modification with citric acid and sorbitol as a copolymer (SorCA). However, some studies report that citric acid (CA) alone can be used for modification. In our previous paper, we showed that although the addition of sorbitol leads to a higher weight percent gain (WPG), the cell wall bulking (CWB), chemical fixation and impact bending strength were only marginally different compared to modification with pure citric acid. This study compares water-related properties, namely (1) dimensional stability and (2) swelling and shrinking behaviour, (3) water vapour uptake, (4) liquid water absorption and release and (5) capillary water uptake (CWU). Modification with pure citric acid resulted in higher dimensional stability compared to modification with SorCA. Dynamic vapour sorption (DVS) measurements showed that the modification with CA leads to a higher reduction in water vapour uptake. Liquid water uptake and release tests on the other hand revealed that, after leaching, SorCA-modified samples exhibited significantly lower water absorption. In summary, this study identified that while the addition of a copolymer has little effect on dimensional stability and water vapour sorption, it exerts a clear positive influence on liquid water absorption.

1 Introduction

Although modified wood products are by definition non-toxic and non-biocidal in their mode of action (Hill 2006), many established processes nevertheless pose sustainability concerns, since they are based on non-renewable petroleum-derived chemicals such as phenolic or melamine resins. Recently, the research field of wood modification has increasingly focused on harmless, sustainable and bio-based chemicals. These processes include the esterification of wood with polycarboxylic acids, a technology originally used in textile finishing to cross-link cotton fibres (Yang et al. 1997). Favourable reaction conditions are achieved when the acid used bears at least three carboxyl groups (Lee et al. 2020). For this reason, citric acid, a tricarboxylic acid that occurs naturally in citrus fruits and is produced commercially by biotechnological fermentation, particularly of residues from the agricultural industry, has proved to be well suited (Doll et al. 2006; Larnøy et al. 2018; Kurkowiak et al. 2022). As a citric acid molecule has three carboxy groups and one hydroxyl group, citric acid can in principle react with itself to form a polymer but can also cross-link the hydroxyl groups of the cell walls (Lee et al. 2020; Yu et al. 2018). Wood modified with citric acid does principally show increased dimensional stability and improved durability against wood-degrading fungi and blue stain pathogens (Despot et al. 2008; Hodžić and Hasan 2013; Katović et al. 2004; Samani et al. 2020; Vukusic et al. 2006).

Citric acid can also be used to cross-link other chemicals in the wood to form a copolymer. On this basis, many processes have been developed in recent years in which citric acid is used in combination with glycerin or glucose, for example (Berube et al. 2018; He et al. 2016). By far the most

*Corresponding author: **Christoph Hötte**, Department of Wood Biology and Wood Products, Faculty of Forest Sciences and Forest Ecology, University of Goettingen, Buesgenweg 4, D-37077 Goettingen, Germany, E-mail: christoph.hoette@uni-goettingen.de

Martin Nopens, Thuenen Institute of Wood Research, Leuschnerstrasse 91C, 21031 Hamburg, Germany. <https://orcid.org/0000-0002-4751-7459>

Holger Militz, Department of Wood Biology and Wood Products, Faculty of Forest Sciences and Forest Ecology, University of Goettingen, Buesgenweg 4, D-37077 Goettingen, Germany

frequently used and best-studied process is the combination of citric acid and sorbitol (SorCA), a hexavalent sugar alcohol (Doll et al. 2006; Kurkowiak et al. 2021; Larnøy et al. 2018). Modification with SorCA increases the dimensional stability and durability of the wood against rot and blue stain pathogens (Beck 2020; Kurkowiak 2023; Kurkowiak et al. 2021; Larnøy et al. 2018; Mubarak et al. 2020; Treu et al. 2020).

Previous studies have shown that SorCA-treated wood exhibits different sorption behaviour compared to wood treated through other modification processes. For example, while acetylated wood or wood treated with phenolic resins shows lower water vapour sorption (Himmel and Mai 2016; Lang et al. 2023), the sorption rate of SorCA-treated wood is hardly changed or even increases compared to untreated wood (Kurkowiak et al. 2021). Beck (2020) found that SorCA-treated wood exhibits an increased non-freezing water content – representing the proportion of water within the cell walls – as a result of the modification process. This result is unexpected, as it can be generally assumed that modification with SorCA would lead to a reduction in the amount of water sorption sites due to several mechanisms: Firstly, the modification causes a bulking effect, whereby water molecules are spatially excluded from the cell wall; secondly, it can be assumed that citric acid reacts with the cell wall polymers, eliminating possible binding sites accessible for water molecules and also creating fewer new binding sites by cross-linking reactions. The reduced water vapour sorption is thought to be balanced by the hygroscopic properties of the SorCA polyester, which contributes to overall moisture uptake (Kurkowiak et al. 2021). This hygroscopicity is due to the fact that only two of the six hydroxyl groups of the sorbitol molecule are highly reactive and can react with the carboxyl groups of citric acid to form a polyester. The remaining four hydroxyl groups, on the other hand, presumably remain free and are able to attract water (Kurkowiak et al. 2021). This also manifests itself macroscopically: when water-swollen, wood treated with SorCA takes on larger dimensions than untreated wood. This phenomenon is referred to as super-swelling and is attributed by Beck (2020) to the swelling of the wood by the acidic impregnating solution and the subsequent hardening of the polyester in this state.

To the best of our knowledge, the direct influence of adding sorbitol as a copolymer on the water-related properties of wood modified with citric acid has not been investigated to date. In this study we compared the dimensional stability, swelling and shrinkage behaviour, water vapour sorption, liquid water absorption and capillary water absorption of wood treated with pure citric acid (CA) and wood treated with sorbitol and citric acid (SorCA).

2 Materials and methods

2.1 Modification

Defect-free samples made of Scots pine sapwood (*Pinus sylvestris* L.) measuring 25 mm × 25 mm × 10 mm (axial) were treated with an aqueous solution of citric acid and a solution of sorbitol and citric acid (molar ratio 1:3). The citric acid was supplied in hydrated form (citric acid monohydrate, approx. 97 % purity) by BÜFA Chemikalien GmbH & Co. KG (Oldenburg, Germany) and the technical sorbitol (approx. 98 % purity) from Ecogreen Oleochemicals GmbH (Dessau-Roßlau, Germany).

Prior to modification, all samples were dried at 103 (±2) °C and the mass and dimensions were determined in the oven-dry state (MC = 0 %). Samples were impregnated with CA and SorCA in an air-conditioned state (20 °C/65 % RH) using a vacuum-pressure process (50 mbar/60 min, 10 bar/120 min) in solution concentrations of 5, 10, 15 and 30 %.

Following impregnation, the samples were re-dried for one week under room climate conditions and then cured at 140 °C for 24 h in a heating cabinet equipped with forced air ventilation to allow continuous exchange of moist exhaust air and dry fresh air ('dry curing'). The weight per cent gain (WPG) was calculated based on the oven-dry mass before ($m_{\text{untreated}}$) and after modification (m_{modified}) as follows:

$$\text{WPG (\%)} = (m_{\text{modified}} - m_{\text{untreated}}) / m_{\text{untreated}} \times 100 \quad (1)$$

Cell wall bulking (CWB), also referred to as chemical swelling, describes the permanent increase in sample dimensions due to modification. It was calculated based on the oven-dry dimensions in the radial and tangential directions before modification ($A_{\text{untreated}}$) and after modification (A_{modified}) according to Equation (2):

$$\text{CWB (\%)} = (A_{\text{modified}} - A_{\text{untreated}}) / A_{\text{untreated}} \times 100 \quad (2)$$

2.2 Cold water leaching (EN 84)

The modified samples, together with untreated samples and samples thermally treated at 140 °C (curing temperature) as references, were subjected to cold water leaching in accordance with EN 84 (2020). The mass loss of the samples was calculated based on the oven-dry mass before (m_{cured}) and after the leaching procedure (m_{leached}) as follows:

$$\text{mass loss}_{\text{total}} (\%) = (m_{\text{cured}} - m_{\text{leached}}) / m_{\text{cured}} \times 100 \quad (3)$$

2.3 Anti-shrink efficiency

The anti-shrink efficiency or anti-swell efficiency (ASE) was calculated from the swelling coefficients of the modified samples and the untreated reference samples according to Equation (4). The swelling coefficients (Equation (5)) describe the percentage increase in cross-sectional area (radial \times tangential) of the samples from the oven-dry ($A_{\text{oven-dry}}$) to the water-saturated state ($A_{\text{saturated}}$).

$$\text{ASE} = (S_{\text{untreated}} - S_{\text{modified}}) / S_{\text{untreated}} \times 100 \quad (4)$$

with

$$S = (A_{\text{saturated}} - A_{\text{oven-dry}}) / A_{\text{oven-dry}} \times 100 \quad (5)$$

In addition to the ASE, the ASE' was calculated as follows

$$\begin{aligned} \text{ASE}' &= (S(\text{untreated})) - S'(\text{modified}) / S(\text{untreated}) \\ &\times 100 \end{aligned} \quad (6)$$

with

$$\begin{aligned} S'_{\text{modified}} &= (A_{\text{treated, saturated}} - A_{\text{untreated, oven-dry}}) / A_{\text{treated, oven-dry}} \\ &\times 100 \end{aligned} \quad (7)$$

2.4 Relative dimensions

The relative dimensions (radial \times tangential) were used to display the swelling and shrinkage behaviour of the samples over the course of the experiment. For the modified samples, the dimensions after leaching and the respective water saturation cycles were related to the dimensions after modification in the oven-dry state (A_{cured}). In the case of the untreated reference samples, the dimensions refer to the oven-dry dimensions ($A_{\text{untreated}}$) before leaching.

2.5 Dynamic vapour sorption

Dynamic water vapour sorption (DVS) measurements were carried out on small wood shavings in a sorption balance (ProUmid GmbH Ulm, Germany). At the beginning of each measurement cycle, the samples were dried at 0 % air humidity. The absorption isotherms were measured at a constant temperature of 20 °C in the humidity intervals 0.2, 5, 10, 20, 30, 40, 50, 60, 70, 80 and 90 %, followed by the scanning desorption isotherms in the opposite direction. Each humidity condition was held until the change in mass was <0.01 % per minute over a period of 100 min. The equilib-

rium moisture content (EMC) after each RH step was calculated as follows:

$$\text{EMC} (\%) = (m_{\text{equilibrium}} - m_{\text{dry}}) / m_{\text{dry}} \times 100 \quad (8)$$

In order to exclude the influence of the additional weight of the chemicals introduced during modification on the EMC, the reduced EMC (EMC_R) was calculated according to Popescu et al. (2014). This corrects the EMC by the mass of the chemicals introduced:

$$\text{EMC}_R (\%) = \text{EMC} \times (1 + \text{WPG} / 100) \quad (9)$$

The EMC_R ratio was calculated as the ratio of the EMC_R of the modified samples to the EMC of the untreated references:

$$\text{EMC}_R \text{ ratio} = \text{EMC}_{R, \text{modified}} / \text{EMC}_{\text{untreated}} \quad (10)$$

The hysteresis describes the difference between the equilibrium humidity of the absorption and desorption process for each given RH step.

$$\text{hysteresis} (\%) = \text{EMC}_{R, \text{Absorption}} - \text{EMC}_{R, \text{Desorption}} \quad (11)$$

2.6 Liquid vapour absorption and release

The liquid water absorption was tested based on DIN CEN/TS 16818 (2018) with slight modifications to the test setup. For this purpose, samples measuring 50 mm \times 25 mm \times 50 mm (axial) were modified with CA and SorCA and sealed on all four narrow sides to control water ingress pathways. Before the test, the samples were conditioned at 20 °C and 65 % humidity and their mass were determined. Deviating from the standard, the samples were placed on a sponge placed on the bottom of a plastic container. The container was then filled with water up to the top edge of the sponge, and the filling level was kept constant during the test by regular refilling. In this way, one 50 \times 50 mm² surface of the samples had constant contact with the moistened sponge. After 1 h, the samples were removed from the water, lightly wiped with a paper towel and then weighed and placed back on the sponge. This procedure was repeated after 4, 8, 24, 48, 72, 96, 144, 168 and 240 h. After the moisture absorption test, the samples were placed on a metal grid with one of the sealed narrow sides at a distance from each other to dry. After 1 h, the drying samples were weighed, followed by further measurements after 4, 8, 24, 48, 72, 96, 144, 168 and 240 h to determine the desorption behaviour. The moisture content based on the mass of the samples at each time interval (m_x) was calculated according to Equation (12):

$$\text{MC} (\%) = (m_x - m_{\text{modified}}) / m_{\text{modified}} \times 100 \quad (12)$$

The moisture content was then corrected by the WPG of the samples:

$$MC_R (\%) = MC \times ((1 + WPG) / 100) \quad (13)$$

2.7 Capillary water uptake

The capillary water uptake (CWU) was measured on samples measuring 10 mm × 5 mm × 100 mm (axial) using a custom-made measuring device. The samples, half of which were previously subjected to a leaching process in accordance with EN 84 (2020), were stored under normal climate conditions (20 °C/65 % RH) for two weeks prior to testing. Immediately before the test, one of the axial cut surfaces was very gently sanded to remove any chemical residue from the surface. The samples were then clamped in the device and the sanded cross-sectional surface was immersed 10 mm deep in a basin of water for 200 s. The CWU was then calculated from the weight of the samples before and after the test and their cross-sectional area:

$$CWU (\%) = (m_{200s} - m_{conditioned}) / A \quad (14)$$

3 Results and discussion

3.1 Modification

Table 1 shows the WPG and the CWB of the samples used for the tests described below. The samples treated with SorCA exhibited a significantly higher WPG at the same solution concentration – particularly in the high treatment levels. The CWB of the samples, on the other hand, was comparably high for both treatments, from which it can be concluded that a comparable proportion of both the chemicals is located in the cell wall. More detailed information on these properties of the modified wood can be found in the first part of this paper (Hötte and Miltz 2024).

3.2 Anti-shrink-efficiency

The ASE is an important measure of the dimensional stability of the modified wood. The higher the ASE, the lower the swelling of the modified wood compared to an unmodified reference. As Figure 1 shows, the ASE of the samples modified with CA increased with increasing chemical concentration of the impregnation solution and was highest at a treatment level of 30 %. In the samples modified with SorCA, ASE hardly increased from a treatment intensity of 10 % and

Table 1: Weight percent gain (WPG) and cell wall bulking (CWB) of the CA-modified and SorCA-modified samples and a heat-treated control group.

	Solution concentration (%)	WPG (%)	CWB (%)
CA	5	5.4 ± 0.5	2.8 ± 0.7
	10	11.2 ± 0.6	3.9 ± 0.4
	15	17.3 ± 0.5	5.3 ± 0.6
	30	34.0 ± 2.0	8.1 ± 0.4
SorCA	5	5.5 ± 0.5	2.4 ± 0.4
	10	13.3 ± 0.9	4.1 ± 0.6
	15	22.3 ± 1.3	5.4 ± 0.7
Reference _{heat treated}	30	46.6 ± 2.2	7.9 ± 0.4
	–	–0.6 ± 0.3	–0.1 ± 0.1

peaked at a treatment level of 15 %, decreasing again at higher treatment intensities (30 %). During the five water saturation cycles, the ASE decreased in both the samples modified with CA and those modified with SorCA. This is an indication of the leaching of chemicals from the cell wall.

Mubarok et al. (2020) also observed an initial increase in ASE on SorCA-modified beech wood with increasing treatment intensity followed by a significant decrease in ASE from a solution concentration of 30 %. They attributed this decrease to the swelling of incompletely reacted SorCA polyester and report that the decrease in ASE can be prevented by applying a higher curing temperature (160 °C), which cures the polyester completely.

The results show that modification with pure CA improves ASE significantly more than modification with SorCA, especially at high treatment levels: The ASE of CA samples treated with 10 % solution exceeded that of samples modified with 30 % SorCA solution. Vukusic et al. (2006) describe in this context that the ASE can already be improved very effectively with low citric acid concentrations. When

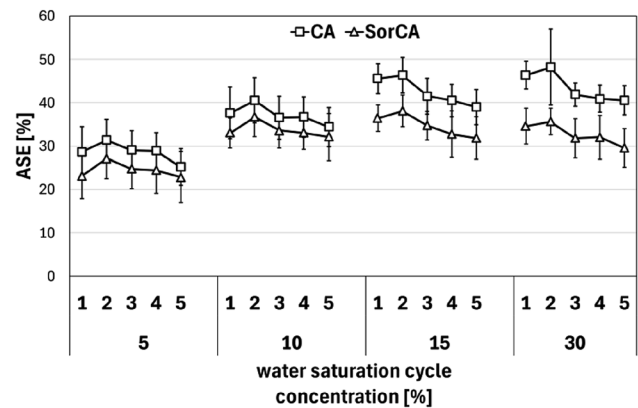


Figure 1: Anti-shrink efficiency (ASE) of the samples modified with CA (squares) and SorCA (triangles) as a function of solution concentration.

modifying with 2.3 % CA and 2.1 % sodium hypophosphite (SHP) as a catalyst, they describe an ASE of 29 % for fir wood (*Abies alba* Mill), and an ASE of 54 % when increasing the concentrations to 6.9 % CA and 6.5 % SHP, respectively. An increase in ASE can be due to both the bulking effect and the cross-linking of the cell wall (Hill 2006). However, since only a small bulking effect occurs at low treatment levels, the high ASE at low chemical concentrations indicates that the cross-linking effect plays an important role in modification with CA. This assumption is also supported by the fact that CA is an effective cross-linker for cellulosic textiles (Yang et al. 1997). The lower ASE of the SorCA-treated samples can thus also be explained by the fact that they contained slightly less CA in relation to the total solution due to the addition of sorbitol (the same solution concentration was used for both treatments).

Nevertheless, bulking and ASE also correlated significantly, albeit only for low treatment levels (Figure 2). From a treatment level of 10 %, the correlation decreased slowly for the CA-modified samples and drastically for the SorCA-modified samples, which shows that high treatment levels result in effects that have a negative impact on ASE. In this respect, the modified material behaves differently to wood modified with phenolic resins, for example, where there is a linear relationship between the CWB and the ASE (Karthäuser et al. 2024). Possible explanations include hygroscopic effects of unreacted citric acid and/or sorbitol.

3.3 Swelling behaviour

A closer look at the relative dimensions of the samples during the course of the experiment provides information about the cause of the higher ASE of the CA-modified samples on the one hand and about the decrease in ASE with

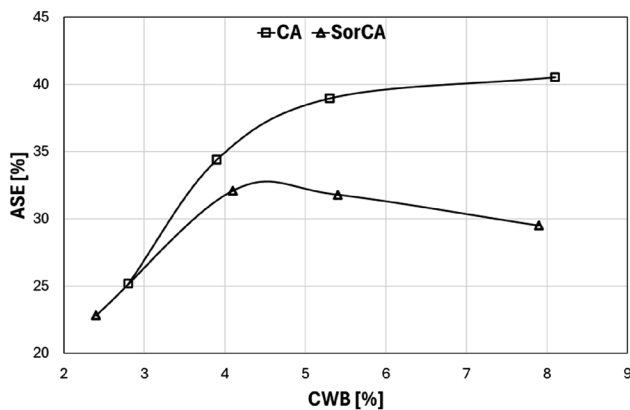


Figure 2: Anti-swelling efficiency (ASE) of the samples modified with CA (squares) and SorCA (triangles) as a function of cell wall bulking (CWB).

increasing chemical concentration on the other (Figures 3 and 4). The relative dimensions show the absolute cross-sectional area of the samples at any given time during the investigation in relation to their initial area. The figure thus shows the swelling – from the oven-dry to the water-saturated state – of the untreated samples between the dashed lines and the swelling of the modified samples between the solid lines. In the case of the samples modified with low chemical concentrations, there was only a slight difference in the swelling between the two modifications. However, from a chemical concentration of 15 %, a clear difference was recognisable and at a chemical concentration of 30 %, the swelling of the SorCA-treated samples exceeded that of the CA-treated samples to the greatest extent.

In addition, the swelling of the CA-treated samples initially decreased significantly with increasing chemical concentration; however, this decrease culminated at a solution concentration of 15 %. In the case of the SorCA-modified samples, on the other hand, the swelling initially decreased, but increased again for the samples treated with 30 % solution. A reduction in swelling compared to untreated samples – and thus an increase in ASE – can be caused by two mechanisms: 1) increase in oven-dry dimensions (cell wall bulking), 2) decrease in water-saturated dimensions (cross linking effect).

In the case of both modifications, bulking is mainly responsible for the decrease in the swollen dimension compared to the untreated test samples. This is represented in Figures 3 and 4 by the distance between the lower dashed line and the lower solid line. During the water saturation cycles, the bulking of the samples modified with CA and SorCA decreased slightly. This may be due to the leaching of unfixed or insufficiently fixed chemicals; also due to the leaching of wood components, as evidenced by the decrease in the oven-dry dimensions of the reference samples. If the decrease in the dry dimensions is accompanied by a decrease in the water-saturated dimensions, it can be assumed that thermally unstable wood components have been washed out (Hill 2006). However, if the decrease in the oven-dry dimensions occurs together with an increase in the water-swollen dimensions, the author suggests that the cause may be leaching of the modifying chemical. This can be seen in the samples modified with SorCA at high treatment levels.

However, because the CWB of samples modified with CA and with SorCA was comparably high (Table 1), the difference in swelling cannot be entirely explained by the cell wall bulking. Rather, the explanation for the difference in swelling (and thus also for the different ASE) can be found in the water-saturated dimensions of the samples. For both modifications, cross-linking of the cell walls can be seen in

CA

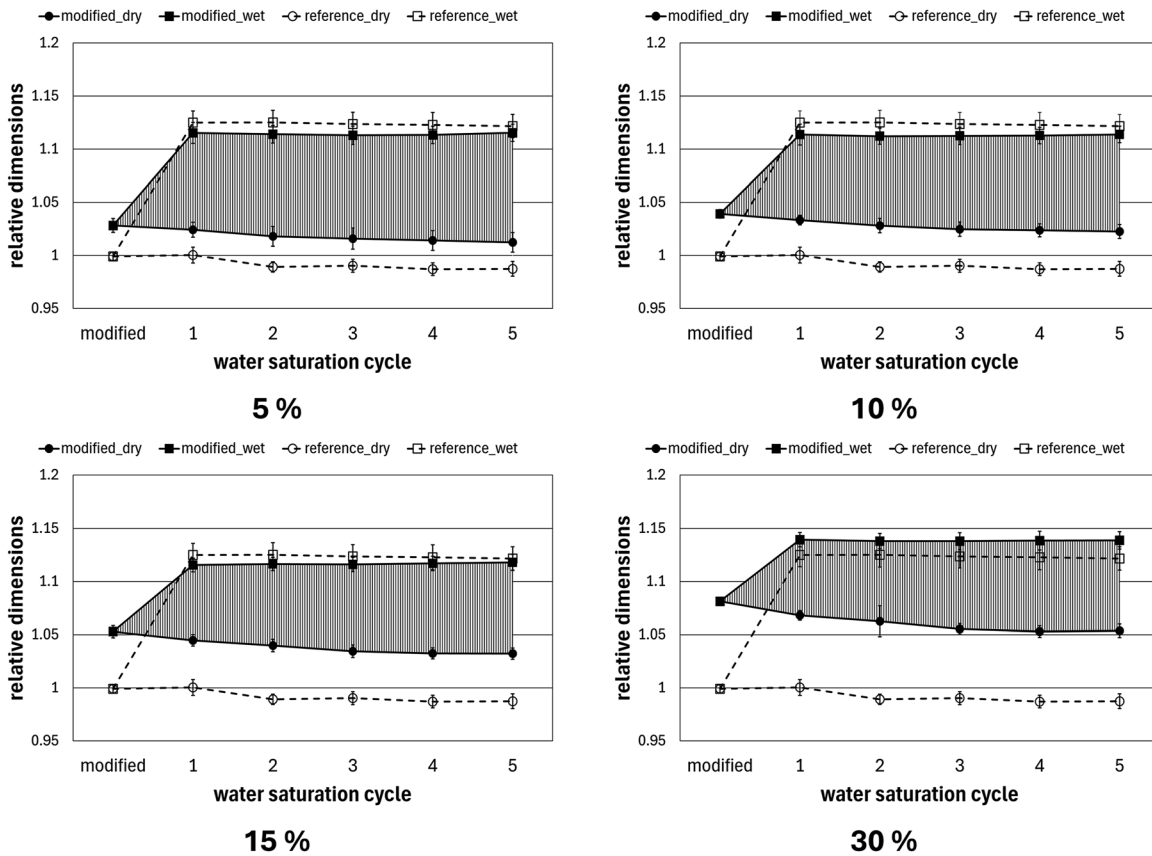


Figure 3: Relative dimensions of the CA-modified samples with different treatment levels.

Figures 3 and 4 at low chemical concentrations. The level of cross-linking is represented by the distance between the upper dashed line and the upper solid line. As can be seen in particular with the CA-modified samples with a low treatment level, cross-linking decreased slightly during the ASE cycles. In combination with the decrease in the bulking effect, this was the reason for the decrease in ASE over the course of the five water saturation cycles.

From a chemical concentration of 30 % in the case of the CA-modified samples and from a chemical concentration of 15 % in the case of the SorCA-modified samples, the water-saturated dimensions of the modified samples exceeded those of the untreated reference. This phenomenon, also known as super-swelling, has already been described in the literature for wood modified with SorCA (Beck 2020; Kurkowiak et al. 2021). Over-swelling of the modified samples compared to an untreated reference was also described for modification with DMDHEU (Emmerich et al. 2020). In this study, this effect was most pronounced for the samples modified with 30 % SorCA solution; this also explains the decrease in ASE for these samples compared to the next

lowest treatment level (15 %). However, over-swelling does not necessarily result in a decrease in ASE: if the increase in dry dimensions (CWB) exceeds the increase in samples wet dimensions due to over-swelling, ASE does not decrease. This was the case for the samples modified with 30 % CA solution. Beck (2020) assumes that the acidity of the impregnating solution already causes over-swelling during impregnation compared to the water-swollen dimensions. Due to the hygroscopicity of the polyester, this super-swollen state could then also be regained after curing as a result of water saturation. In addition, the author speculates that acidic hydrolysis products of the chemicals or unreacted citric acid could also cause the over-swelling. In our previous study, no increased swelling of the samples impregnated with CA or SorCA was found immediately after impregnation compared to a reference impregnated with pure water; in fact, the opposite was found: water-impregnated samples had a higher degree of swelling (Hötte and Militz 2024). Beck's (2020) assumption that the acidity of the solution was responsible for the over-swelling by permanently increasing the maximum swelling rate can therefore not be confirmed.

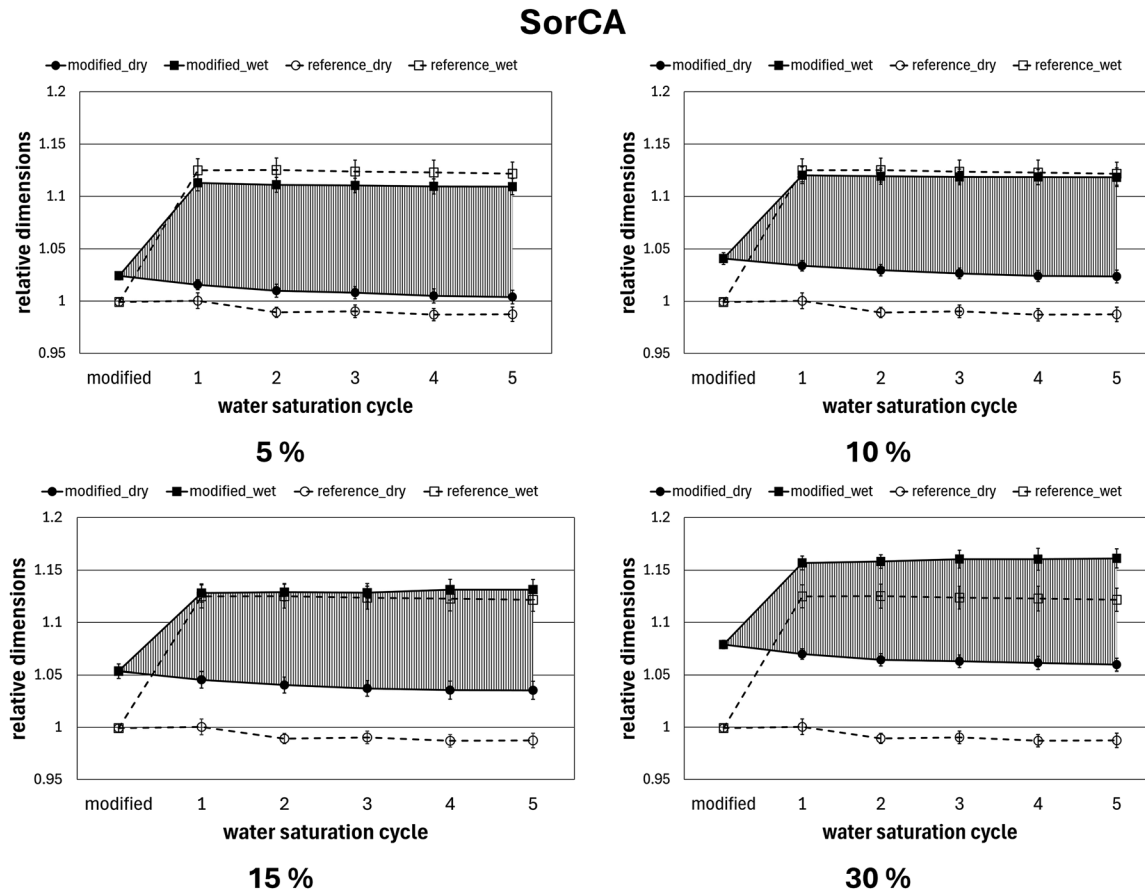


Figure 4: Relative dimensions of the SorCA-modified samples with different treatment levels.

On the basis of the present results, we assume that the over-swelling is the result of a combination of the degradation of the cell wall polymers, especially hemicelluloses and amorphous cellulose, and possibly also the hygroscopicity of the modifying chemicals. Degradation of the cell wall polymers is likely due to the high acidity of the impregnating solution (pH of the 30 % CA solution approx. 1.3) and has already been proven by Kurkowiak et al. (2021) for alpha-cellulose. The same authors were unable to demonstrate a decrease in the proportion of hemicellulose and attribute this to the fact that the citric acid mainly reacts with the hydroxyl groups of this cell wall component and thus increases its percentage by mass. Due to the sensitivity of hemicelluloses to hydrolytic degradation (Fengel and Wegener 1989), it can be assumed that they are partially hydrolysed by citric acid. The hygroscopicity of the modifying chemicals is probably caused in particular by unbound hydroxyl groups. These are present in greater numbers in the case of modification with SorCA, which could explain the stronger over-swelling.

By calculating the ASE', the different mechanisms that occur during modification can be determined more precisely (Hill 2006). The ASE' takes into account the influence of cell

wall bulking on the swelling of the modified wood and thus represents the ASE based only on dimensional change in the swollen state of the wood (Ohmae et al. 2002). ASE' becomes zero if the dimensional stabilisation is based only on the CWB. If there is a cross-linking effect, the ASE' becomes positive, but if the modification causes cell wall degradation – which increases the water-swollen dimensions – the ASE' becomes negative.

If the ASE is plotted against the ASE', it becomes clear that there is a cross-linking effect for both modifications at low treatment levels (Figure 5). From a chemical concentration of 10 % (SorCA) and 15 % (CA), however, the ASE' becomes negative. Following the explanations of Ohmae et al. (2002), cell wall degradation occurs above these concentrations.

However, it is unclear whether the negative ASE' in the case of modification with CA and SorCA is really based solely on the degradation of cell wall polymers, or which role the additional swelling of unreacted chemicals or the polyester plays. Following this argumentation, the significant increase in over-swelling (expressed in a negative ASE') with increasing chemical concentration could on the one hand be

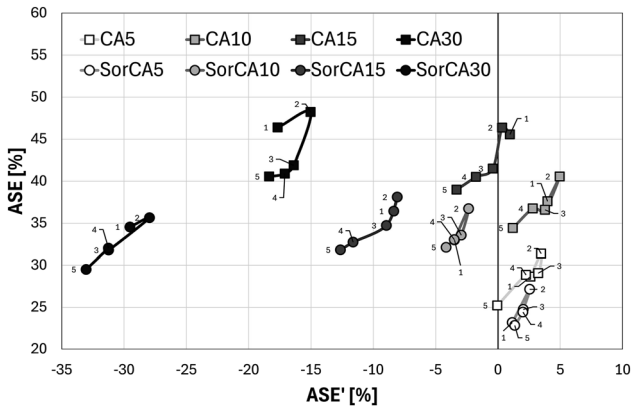


Figure 5: Relative changes in ASE and ASE' due to modification with CA and SorCA with different treatment levels.

attributed to the increase in acidity of the solution, which causes a stronger cell wall degradation. On the other hand, the proportion of unreacted acid groups presumably also increases with increasing solution concentration and could therefore cause over-swelling. However, it can be assumed that over-swelling occurs even in samples treated with low concentrations of chemicals, but that this is masked by the effect of cross-linking. In the same way, it can be assumed that cross-linking nevertheless exists for the samples with a high degree of treatment, in which the over-swelling occurred. Both effects are opposing, and their intensity depends on the degree of treatment, i.e. the chemical concentration used.

3.4 Dynamic vapour sorption measurements

The wood moisture content is, among other aspects, a determining factor for the durability and mechanical properties of the cell wall (Brischke and Alfredsen 2020; Kherais et al. 2024). Wood modification can influence the wood moisture content and thus also these properties (Thybring and Fredriksson 2021). DVS measurements are therefore an important tool for assessing the performance of modified wood under changing moisture regimes. The relationship between the relative humidity and the corresponding equilibrium moisture content of the wood is shown in Figure 6 as absorption and desorption isotherms. As is usual for wood and other cellulose-based materials, the sorption isotherms have a sigmoidal shape (Skaar 1988). The increase in equilibrium moisture content with increasing relative humidity is due partly to the hydroxyl groups present and partly to moisture-induced swelling of the wood matrix, which creates additional sorption sites (Malmquist and Söderström 1996).

In the case of the samples with the low treatment level (10 %), both modifications led to a similarly high reduction of the equilibrium moisture content compared to an untreated reference, so that the sorption isotherms of the samples treated with CA and SorCA were almost identical (Figure 6a). Both the samples modified with CA and the SorCA with high treatment intensity (30 %) exhibited a significantly lower EMC over the entire course of the sorption isotherms than the untreated reference samples. The CA-modified samples had a lower EMC than the SorCA-modified samples, especially in the high relative humidity range (Figure 6b). However, this could be due to the higher WPG of the SorCA-modified wood and thus an effect of the reference value for the EMC-calculation. When calculating the reduced EMC (EMC_R), the unmodified oven-dry mass is used as the reference value for the calculation, thus excluding the effects of differently high WPG. While the EMC_R hardly differs from the EMC actually measured in the case of samples with a low treatment concentration (Figure 6c), the differences are large in the case of samples with a high treatment concentration (Figure 6d): the EMC_R of the SorCA-modified wood was only lower than that of the untreated reference in the very high humidity range and in the case of the absorption isotherm. The EMC_R of the wood treated only with CA was significantly reduced over the entire RH range and for both the absorption and desorption isotherms. Thus, as the solution concentration was increased from 10 to 30 %, the EMC_R increased for the SorCA-treated samples and decreased for the CA-treated samples.

Wood modification can influence water vapour sorption – and thus the equilibrium moisture content – in various ways: (1) removal of the hydroxyl groups of the cell wall and reaction of the hydroxyl groups with the functional groups of the modifying agent, (2) cross-linking of the cell wall, (3) bulking effect due to the incorporation of the chemical into the cell wall, (4) degradation of cell wall components by the modification agent and (5) thermal degradation of cell wall components, possibly accompanied by condensation reactions (Thybring and Fredriksson 2021). All mechanisms have a reducing effect on the cell wall moisture content, on the one hand by removing or blocking the OH groups necessary for sorption (1, 3, 4 and 5), and on the other hand by increasing the stiffness of the cell wall matrix, which reduces the possibility of generating new sorption sites by swelling movements on cellular level (2 and 5).

For the modification with CA and SorCA, mechanisms 1–4 are conceivable as possible causes for a reduction in water vapour sorption. However, an increase in water vapour sorption compared to an untreated reference, as observed in the case of SorCA-treated samples with high

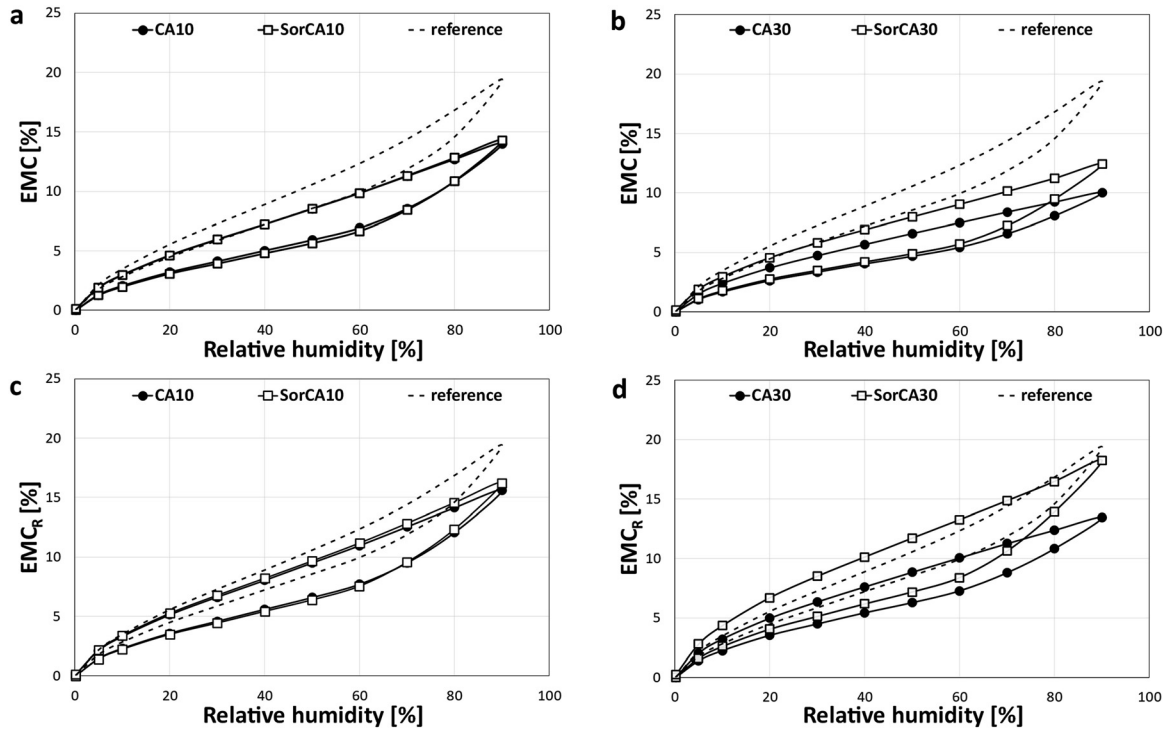


Figure 6: Moisture absorption and desorption isotherms for samples treated with 10 % CA and SorCA solution (a) and 30 % CA and SorCA solution (b) and untreated reference samples. The corresponding reduced moisture contents are shown in (c) and (d).

treatment intensity, cannot be explained by these mechanisms. Kurkowiak et al. (2021) also carried out DVS measurements on SorCA-modified wood. Largely independent of the molar ratio of the SorCA solution (1:1 or 1:3) and the solution concentration (20 or 30 %), the authors found no or only a slight decrease in the water vapour sorption of the modified wood compared to untreated reference samples. The authors attribute the largely unchanged sorption isotherms of the SorCA-modified samples to the water vapour sorption of the SorCA polyester inside the wooden matrix, whose high hygroscopicity from a relative humidity of approx. 50 % was demonstrated with sorption measurements on pure, cured polyester. They also assume that unreacted OH groups of the sorbitol or the hydrolysis of ester bonds may have been responsible for the high hygroscopicity of the SorCA-modified wood. Similarly, DMDHEU-modified wood shows no reduction in water vapour sorption over wide ranges of the sorption isotherm (up to 85 % RH) compared to unmodified wood (Emmerich et al. 2020). Additional OH groups inserted into the wooden structure by the DMDHEU polyester are also considered to be the cause in this case.

In line with the study by Kurkowiak et al. (2021), the water vapour sorption of the SorCA-modified wood increased with increasing treatment intensity of the wood.

The authors explain this by the fact that polyester localised in the cell lumen leads to a strong increase in sorption from a solution concentration of 20 %. Interestingly, the sorption of the wood modified only with CA behaved diametrically to these findings and decreased with increasing treatment intensity. Possible explanations for this decrease can be found in a lower deposition of CA in the cell lumen – and thus in a lower additional sorption by the polyester. This is consistent with the lower WPG of the samples treated only with CA. In this context, it would be interesting to investigate the sorption of the pure CA polyester. However, since it was seen that the *ex situ* cured polyester was completely water-soluble, a high water vapour sorption can be assumed. Other possible causes for the decrease in sorption at higher treatment levels are an increase in cross-linking or the reduction of OH groups due to the acidity of the solution.

The sorption isotherm of the reference samples showed a strong upward trend from a relative humidity of approx. 75 %. This is due to the increasing plasticisation of the hemicelluloses, as a result of which additional water can be stored in the cell wall (Thybring et al. 2022). This upward trend was less pronounced in the modified samples. A significant decrease was observed for the CA-modified wood with high treatment intensity: there, the desorption curves in particular were almost linear. Hosseinpourpia et al. (2018)

found a similar flattening of the desorption curve on acid-pretreated, thermally modified wood and describe an increase in the stiffness of the wood matrix due to cross-linking as a possible cause. Modification with glutaraldehyde, an effective cross-linker, also causes an increasing flattening of the isotherms in the high humidity range (Xie et al. 2011). Applied to the present results, however, this argument stands in contrast to the significant over-swelling of the modified wood, which should not occur as intensively with an increase in matrix stiffness due to cross-linking. We therefore assume that the flattening of the sorption isotherms, especially those of the CA-modified samples with high treatment intensity, in the high humidity range is rather due to the acid-induced degradation of the cell wall polymers and the associated reduction of the hydroxyl groups.

The EMC_R ratio represents the ratio of the equilibrium moisture content of the modified and untreated wood (Figure 7a and b). In the case of low treatment intensity, the EMC_R ratio of the absorption isotherms was almost constant after both modifications up to a relative humidity of approx. 70 %. In the high relative humidity range, the EMC_R ratio increased slightly before the curves bent downwards again from a humidity of approx. 80 %. A largely constant curve, i.e. a reduction in the equilibrium humidity over the entire humidity range, can be attributed on the one hand to bulking, i.e. the permanent occupation of cell wall space by the chemicals. This is also described by Himmel and Mai (2015) for the EMC_R ratio of acetylated wood, a modification that only causes cell wall bulking, but not cross-linking. In addition to cell wall bulking, the acid-induced degradation of hemicelluloses, which reduces the number of possible sorption sites in the cell wall, is also a possible cause for the reduction of the equilibrium moisture content over the entire humidity range. Although it was proven by Altgen and Rautkari (2021) that the reduction in equilibrium moisture content is not determined by the availability of the OH groups, but by the spatial availability for water – this would be an argument in favour of the bulking effect as the cause of the lower equilibrium moisture content due to the modification – it is possible that a significant reduction in the hydroxyl groups due to acidic hydrolysis causes a lower equilibrium moisture content even without a bulking effect. Hosseinpourpia et al. (2018) also attribute the reduction in the EMC_R ratio of acid-pretreated thermally modified wood to the degradation of the amorphous polysaccharides.

In the case of the high treatment level, the EMC_R ratios differ significantly between the two modifications. In the samples modified with SorCA, the EMC_R ratio of the absorption isotherm decreases slightly over a wide RH range and then rises sharply from an RH of 60 %. This upward bend

in the high humidity range can probably be attributed to a softening of the polyester itself and corresponds well with the increased water vapour sorption of the pure polyester in this humidity range (Kurkowiak et al. 2021). The course of the desorption isotherm then deviates significantly from that of the absorption isotherm and also exceeds the ratio of 1, which means that the sorption of the untreated samples is exceeded. This could be due to the delayed release of water from the newly created binding sites within the polyester.

The EMC_R ratio of the samples treated with 30 % CA was significantly different. Here, the EMC_R ratio of the absorption isotherm decreased over the entire RH range and also showed no significant upward trend in the high RH range. A constant decrease in the EMC_R ratio can possibly be attributed to cross-linking of the cell wall. The modification with formaldehyde, which leads to an intensive cross-linking of the cell wall, is also expressed in a constantly decreasing EMC_R ratio, as the modification hinders the swelling of the cell wall (Himmel and Mai 2015). Interestingly, in the case of treatment with pure CA, an increase in the chemical concentration did not lead to an increase in sorption in the high RH range, for example due to the additional sorption of polyester in the cell lumen. On the one hand, this can be explained by a lower deposition of polyester in the cell lumen (corresponding to the lower WPG compared to SorCA modified samples); on the other hand, any additional sorption may be compensated for and thus concealed by a more intensive acid degradation in the case of the higher treatment level. The 30 % CA solution had the lowest pH value and could therefore have caused the strongest acid degradation of the cell wall polymers.

The sorption hysteresis (Figure 8a and b) increased with both modifications in the case of the low treatment levels compared to that of the untreated reference. With the increase in treatment intensity, the hysteresis increased significantly in the case of the samples modified with SorCA; for the samples modified with CA, on the other hand, it decreased and even fell below that of the untreated reference in the high RH range.

The cause of sorption hysteresis in wood is considered to be the stiffness of the wood matrix, which results in a time delay between the removal of the water molecules and the relaxation of the matrix during desorption (Pignatello et al. 2006). This leads to different physical states during absorption and desorption (Pignatello et al. 2006; Hill et al. 2010). The stiffness of the cell wall and the resulting hysteresis effect on untreated wood is particularly influenced by the lignin (Hosseinpourpia et al. 2016; Hou et al. 2022). Wood modification, e.g. acetylation or modification with formaldehyde, reduce the hysteresis over the entire RH range (Himmel and Mai 2016). It is assumed that cross-linking

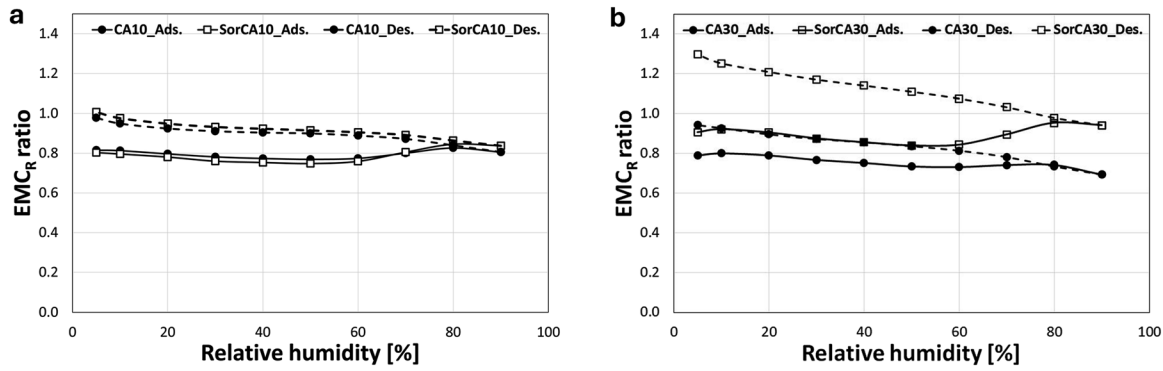


Figure 7: EMC ratio of the absorption and desorption isotherms for the samples treated with 10 % CA and SorCA solution (a) and 30 % CA and SorCA solution (b).

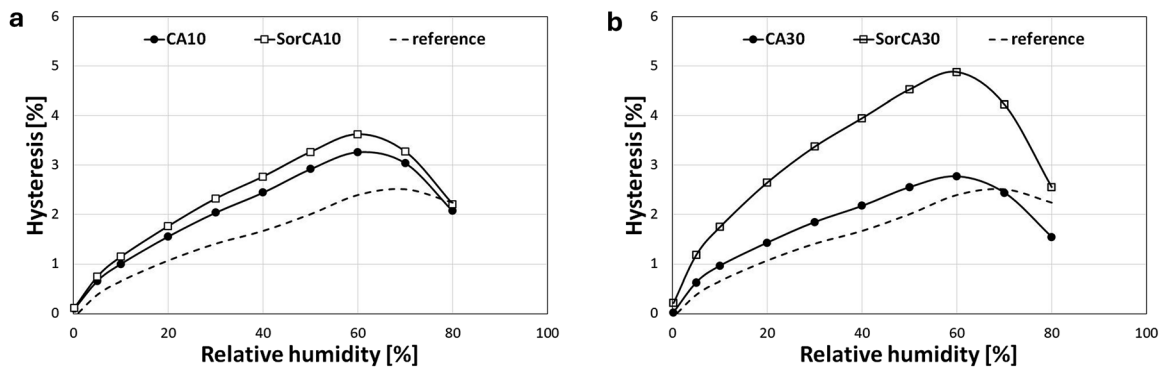


Figure 8: Hysteresis of the wood treated with 10 % CA and SorCA solution (a) and 30 % CA and SorCA solution (b).

reactions – by increasing the resistance of the cell wall to deformation (swelling) – lead to a decrease in the differences between the physical states of absorption and desorption and thus also to a decrease in hysteresis. Pre-swelling, i.e. the cell wall bulking effect, can also lead to a decrease in sorption hysteresis (Xie et al. 2011).

Modifications in which a resin is introduced into the cell wall increase the stiffness of the wood matrix (Emmerich et al. 2021a; Epmeier et al. 2004; Kielmann et al. 2013; Lang et al. 2022; Stamm and Seborg 1939). These resin forming treatments, such as modification with melamine and phenolic resins, result in a decrease in hysteresis especially in the higher RH-range of 70–90 % (Hosseinpourpia et al. 2016). This is somewhat contrary to expectations, because the introduction of rigid resins into the cell wall should increase the relaxation time of the wood matrix – and thus also the hysteresis – similar to what lignin causes in untreated wood. According to Hosseinpourpia et al. (2016), this increase in hysteresis is probably masked by the bulking effect of the modified wood. When modifying holocellulose, however, the authors were able to demonstrate an increase in hysteresis: although a bulking effect was also present here, the

auto-cross-linking of the resins was presumably much stronger than in untreated wood.

In consideration of the fact that the effects of bulking and presumably also cross-linking are present in the case of modification with CA and SorCA, the cause of the strong increase in hysteresis remains questionable. CA and SorCA also harden under heat to form a rigid, three-dimensional corset within the wood matrix and thus also cause an increase in stiffness or a decrease in flexibility (Hötte and Miltz 2024). It is possible that this decrease in flexibility is more pronounced than with other resin modifications, so that in this case it manifests itself in an increase in hysteresis. It is also possible that the acidic impregnation solution leads to a partial degradation of the hemicelluloses responsible for the flexibility of the matrix. In this case, however, the hysteresis should also increase for the samples modified with CA as the treatment level increases. In addition, Hosseinpourpia et al. (2018) describe a decrease in sorption hysteresis due to acidic pre-treatment of wood before modification.

It is unclear to what extent the hygroscopic polyester within the cell wall or in the cell lumen as well as

incompletely reacted chemicals also contribute to the increased hysteresis. Kurkowiak et al. (2021) compared the sorption hysteresis of SorCA polyesters with different molar ratios: they found that a cured 1:1 SorCA polyester exhibited significantly higher hysteresis than a 1:3 SorCA polyester. They attribute this result to a more intensive auto-cross-linking of the 1:3 polyester. In this study, the modification with SorCA could have led to increased autocondensation of the chemicals (which is also reflected in the lower ASE), whereby the hysteresis is more strongly influenced by the sorption properties of the pure polyester. In the case of modification with CA, on the other hand, it can be assumed that due to the lower number of available hydroxyl groups of the modification chemicals, less autocondensation has taken place and thus the hysteresis is less influenced by pure polyester. However, this should be verified by measuring the hysteresis of the pure polyester.

3.5 Liquid water absorption and release [adapted from CEN/TS 16818 (2018)]

Table 2 presents the WPG of the samples from the liquid water uptake test and their mass loss due to leaching according to EN84 (2020).

The liquid water absorption and release of the samples modified with CA or SorCA and untreated reference samples are shown in Figure 9. By plotting over the square root of time, the water uptake took on an almost linear course. With the exception of the samples treated with 5% citric acid, there was a decrease in the moisture content of the pine treated with pure citric acid compared to the reference samples. In particular, the samples with the highest treatment level (30%) showed significantly lower water uptake and correspondingly much lower wood moisture content. The samples leached before the water uptake test showed higher overall wood moisture contents, while at the same

time the difference between the wood moisture content of the reference samples and the samples modified with citric acid decreased; this was particularly true for the samples with the highest treatment level, where the maximum wood moisture content after 240 h increased from 11.5% before leaching to 40.9% after leaching.

The addition of sorbitol as a co-polymer changed the water absorption behaviour only insignificantly compared to the samples treated with pure citric acid on non-leached samples. In direct comparison, a slightly lower wood moisture content was observed in the samples with a treatment level of 10% and 15%, whereas the samples with the highest treatment level showed a slightly higher wood moisture content after modification with SorCA than after modification with pure citric acid. However, the water absorption of the samples that had been leached before the test was significantly different. Although the SorCA-treated samples also showed higher overall wood moisture levels after leaching than the non-leached samples, the difference was significantly less than for the pine modified with pure citric acid. This applies to the samples with treatment levels of 10% and 15% and especially those with the 30% treatment, where there was hardly any difference in wood moisture before and after leaching. Only the leached SorCA-treated samples with the lowest treatment level (5%) showed a higher wood moisture content than the corresponding variant treated only with citric acid.

There are substantial differences between the water vapour sorption that takes place in the hygroscopic area and the uptake of liquid water, both in terms of the underlying uptake mechanisms and the localization of the water within the wood matrix. While water vapour is absorbed into the cell walls via different mechanisms, the uptake of liquid water takes place in macropores and voids, especially in the cell lumina. As described in the DVS results, the wood moisture content in the hygroscopic range – depending on the chemical concentration and the addition of sorbitol – reached a maximum of 15%. This value approaches the so-called fibre saturation, in which the cell walls are completely saturated with bound water and any additional moisture is only present as free water in the cell lumina or other void structures. Because the wood moisture content was at least 10% at the start of the test, the observed variations in liquid absorption can be attributed primarily to modification-related changes in the macropore structure. These variations are presumably caused in particular by the blockage of the macropores, i.e. spots, cell lumina, etc., due to the incorporation of polymerized CA or SorCA. Accordingly, the water absorption or wood moisture content of the samples that were not leached before the start of the test decreased as the degree of treatment increased. The

Table 2: Weight percent gain (WPG) and mass loss after leaching according to EN 84 (2020) of the samples for the liquid water uptake test.

Treatment	WPG (%)	Mass loss_EN84 (%)
CA5	4.8 ± 0.2	0.9 ± 0.1
CA10	10.2 ± 0.5	1.1 ± 0.1
CA15	15.1 ± 0.6	1.4 ± 0.1
CA30	31.4 ± 0.7	1.6 ± 0.1
SorCA5	5.8 ± 1.3	1.9 ± 0.1
SorCA10	12.1 ± 0.5	1.3 ± 0.1
SorCA15	18.4 ± 1.4	1.2 ± 0.2
SorCA30	38.9 ± 2.6	0.6 ± 0.1
REF	–	0.5 ± 0.2

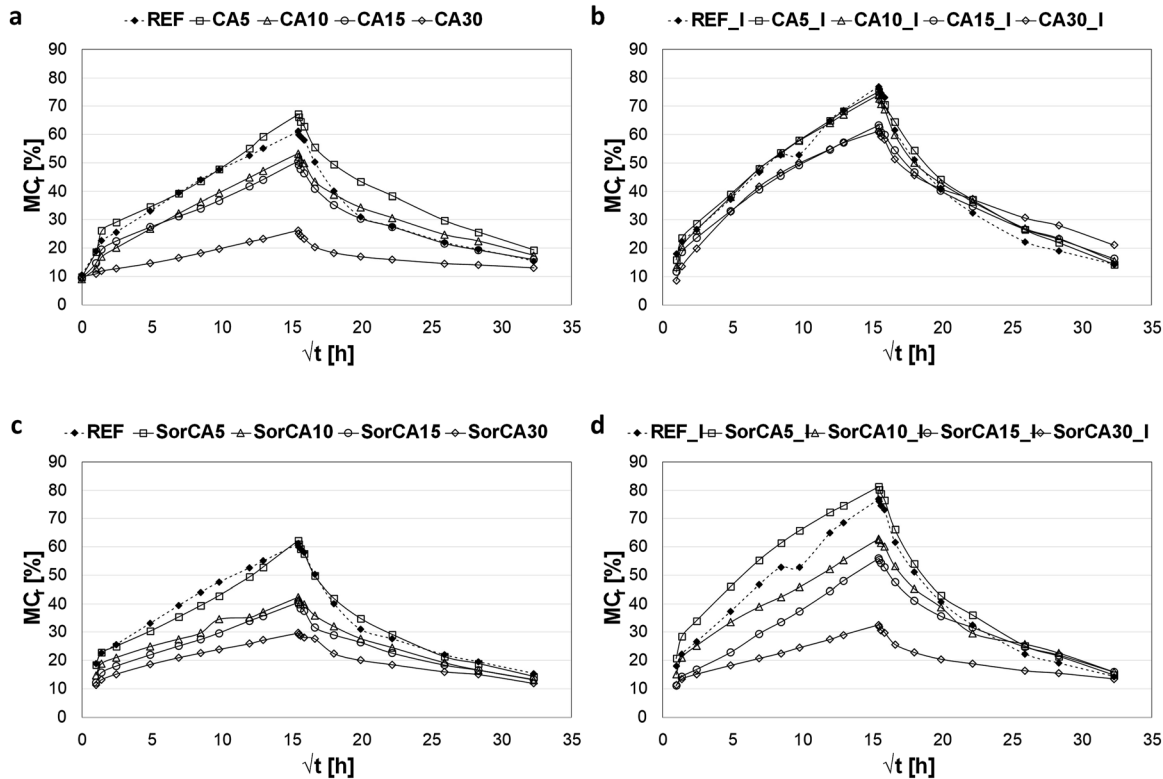


Figure 9: Wood moisture development during absorption (240 h) and desorption (805 h) as a function of the square root of time of the samples treated with CA before (a) and after leaching (b) as well as the samples treated with SorCA before (c) and after leaching (d).

significant decrease in wood moisture content between the samples treated with 15 % and 30 % citric acid is probably due to the increasing saturation of the cell wall with the chemicals, resulting in increased resin deposition in the cell lumina. According to Hötte and Militz (2024), the cell wall is saturated at a treatment level of between 15 and 30 %, and according to Kurkowiak et al. (2021) from a treatment level of 20 %.

Modification with the textile crosslinker DMDHEU also leads to a reduction in liquid water absorption (Emmerich et al. 2021b; Krause 2006). Dieste et al. (2009) attribute this to a decrease in the average pore diameter. This is also to be expected for the modification with citric acid, although counteracting effects due to the acidic effect cannot be ruled out. The acidic impregnation solution (pH approx. 1.2) during curing at 140 °C could well lead to conditions in which – similar to a mild thermal treatment – thermally unstable cell wall components are degraded. This could lead to an increase in permeability, as shown by Scheiding et al. (2016) for mildly thermally treated pine sapwood. It can be assumed that this effect is superimposed by the effects of resin incorporation as the degree of treatment increases. Such an effect can possibly be seen in the CA-modified samples before leaching and the SorCA-modified samples

after leaching, each with the lowest degree of treatment, which had a slightly increased moisture content compared to the reference samples.

The significant difference in water uptake between the samples of the highest treatment level modified with CA and SorCA after previous leaching is probably due to the differences in the efficiency of resin fixation in the cell lumina. Hötte and Militz (2024) explain the higher mass losses of pine treated with pure citric acid by the fact that it forms smaller polymer networks in the cell lumina due to fewer available OH groups, which are subsequently more prone to leaching. This was also evident from the EN84 mass losses: here, the mass loss of the samples modified with CA at the highest treatment level was more than twice as large as that of the samples treated with SorCA as a result of leaching. However, it must be mentioned that the overall mass losses are at a very low level.

3.6 Capillary water uptake

Table 3 shows the WPG of the samples from the capillary water uptake test and their mass losses due to leaching according to EN 84 (2020).

Table 3: Weight percent gain (WPG) and mass loss after leaching according to EN 84 (2020) of the samples for the CWU test.

Treatment	WPG (%)	Mass loss_EN84 (%)
CA5	3.8 ± 0.3	0.7 ± 0.2
CA10	9.6 ± 0.7	1.1 ± 0.2
CA15	15.3 ± 0.8	1.1 ± 0.3
CA30	29.9 ± 1.3	1.6 ± 0.4
SorCA5	5.2 ± 0.9	1.4 ± 0.5
SorCA10	10.5 ± 1.0	1.0 ± 0.4
SorCA15	16.6 ± 1.6	1.2 ± 0.2
SorCA30	38.0 ± 3.2	0.6 ± 0.3
REF	–	0.7 ± 0.3

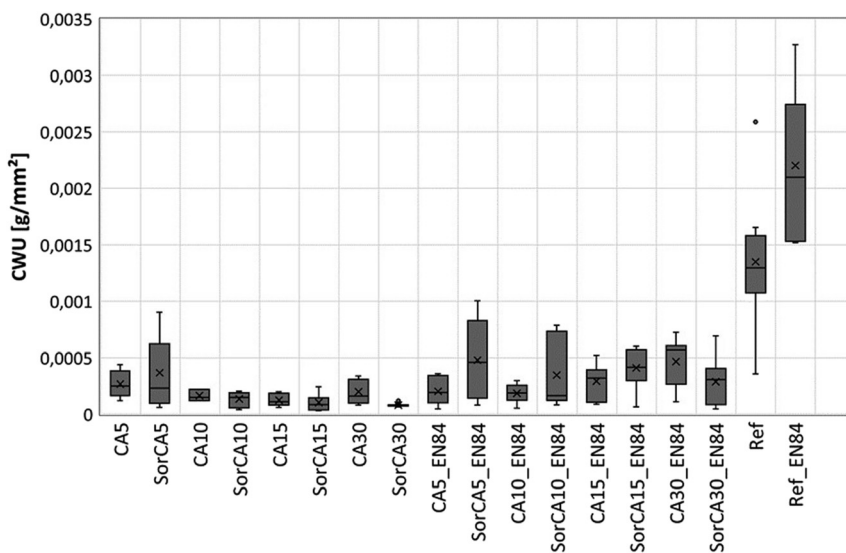
All treated samples had a significantly lower capillary water uptake than the untreated reference. Neither the addition of sorbitol as a co-polymer to the citric acid nor the treatment level significantly influenced the CWU (Figure 10). In the reference samples and in the SorCA-treated samples from a treatment level of 10 %, the CWU increased due to leaching. This was less pronounced in the samples treated exclusively with CA. An increasing CWU after leaching is probably a consequence of the increasing space for water in the cell structure due to the loss of modifying chemicals and was already described by Kurkowiak (2023).

It is noteworthy that even very low degrees of treatment lead to a significant reduction in the CWU, and that this was only slightly further reduced by the increase in the degree of treatment. According to Hötte and Militz (2024), the cell wall is saturated at a treatment level of between 15 and 30 %, and according to Kurkowiak et al. (2021) from a treatment level of 20 %. Accordingly, at low treatment levels, the cell wall

should predominantly be filled, while only a few chemicals should be present in the lumen. However, the very low CWU observed is an indication of the presence of chemicals in the cell lumen. This could possibly be the result of an inhomogeneous distribution of chemicals in the samples: it is conceivable that during curing, chemicals were transported to the axial cross sections with the water escaping axially from the samples and subsequently cured there. Such an effect is known from the curing of larger samples but could also apply here. To rule out this effect, it would be useful for future tests to shorten the specimens axially by a few millimetres before measuring the CWU.

4 Conclusions

This study investigated the water-related properties of wood modified with pure CA and in combination with sorbitol (SorCA) as a co-polymer. CA-modification resulted in significantly higher dimensional stability (ASE) compared to SorCA-modification, especially at high treatment levels. This might have been a consequence of the better cross-linking but could also have been due to the lower super-swelling of the water-saturated samples. While the results of the DVS measurements were very similar for the samples treated with 10 percent CA and SorCA solution, there were clear differences in terms of water vapour sorption in the case of the high treatment level (30 percent solution). In contrast to the wood modified with SorCA, which did not have a reduced EMC compared to the reference, treatment with CA led to a significant decrease in EMC and therefore also to a significantly lower EMC_R ratio. In addition, modification with

**Figure 10:** Capillary water uptake (CWU) of samples treated with CA and SorCA depending on the degree of treatment and of untreated references before and after leaching according to EN 84 (2020).

SorCA resulted in a significant increase in sorption hysteresis. In non-leached samples, liquid water uptake was relatively similar between CA- and SorCA-treated samples. However, after leaching, SorCA-modified samples exhibited significantly lower water uptake compared to CA-treated samples, especially at high treatment levels. This difference was likely due to the limited fixation of citric acid within the cell lumina.

Our results showed that the addition of sorbitol to citric acid in the sense of a copolymer did not bring any decisive advantages in terms of dimensional stability or water vapour sorption. On the contrary, the co-polymerization tended to negatively affect both properties, particularly at higher treatment intensities. However, the addition of sorbitol offered a clear advantage in reducing liquid water uptake, particularly after leaching. In a subsequent study, we will examine the durability of CA-modified wood and assess the impact of the copolymer on its resistance to biological degradation.

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