INFLUENCE OF TANNING TECHNOLOGIES ON DRY LEATHER SHRINKAGE

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ABSTRACT
The shrinkage of leather under the influence of alternate climate conditions, especially under the influence of dry heat, restricts the usability of leather e.g. in the automotive sector. Leather shrinkage results in either a loss of dimension or, if the leather is tightly fitted, isometric strength development.
In the present study, some key factors affecting the leather shrinkage of chrome-free leathers were investigated.
It was found, that reversible dimensional changes occur due to adsorption and desorption of moisture under changing environmental conditions. Irreversible shrinkage of leather, however, is caused by changes at the molecular level of the collagen triple helix. Under dry heat conditions, a partial denaturation of the collagen triple helix can be observed, but without leading to the complete coiling known from hydrothermal denaturation.
The higher the degree of crosslinking of the pretanning, the higher the leather shrinkage.
The retanning agents have the greatest influence on leather shrinkage.
The influence on shrinkage correlates with the influence on molecular stability to dry heat and changing moisture content.
In the study, the relationship with the chemical structure of the retanning agents will be discussed in more detail. Fatliquors have only a minor influence on leather shrinkage.
With the knowledge gained, leathers were produced that showed excellent results in terms of shrinkage force.

Key words: Leather shrinkage, Climate change test, Shrinkage force

1. Introduction

During its use, leather is permanently exposed to changing temperature and humidity. Drastic values can be reached, e.g. in automobiles or in shoe manufacturing. Both the exposure to relatively high temperatures and the change in humidity and temperature lead to temporary and permanent changes in the leather, which limit its usability.

Macroscopically, the structural changes manifest themselves as dimensional changes (the dry leather shrinkage), changes in softness, bending stiffness or in force developments under isometric conditions. This leads to major problems, for example, in the use of leather in the automotive sector, especially when covering dimensionally stable components (e.g. instrument panels).

Until now, there are only a few works in the literature addressing the phenomenon of dry leather shrinkage.

In their investigations into the influence of changing climatic conditions on mass, thickness and bending stiffness, Scheibe and Wolf (Scheibe and Wolf 1997) found that the measured changes are dependent on the type of previous treatment. For the first time, isometric force measurement under changing climatic conditions was used in this work.

Kellert et. al (Kellert et al. 2000) investigated the increase in bending stiffness over time after temperature stress to determine the thermal stability of chrome and chrome-free tanned leathers in dry state. They show that chrome leather is less resistant to dry heat than chrome-free tanned leather. On the other hand, when exposed to moist heat, the chrome-free leather is altered much faster. They also found that the

water absorption capacity decreases after reclimatization depending on the level of temperature exposure.

A more detailed evaluation of isometric force measurements on dry leathers of different tannins under the influence of isothermal moisture changes can be found in work by Tuckermann (Tuckermann et al. 2001)). When lowering the ambient humidity at room temperature, the isometric force development in leather is explained by desorption of water with capillary contraction, and a corresponding model is developed.

A recent study (Masic et al. 2015) shows the relationship between the removal of water molecules by lowering the ambient humidity and interfibrillar and intermolecular geometries and isometric force development on rat tail tendons using X-ray diffraction and Raman spectroscopy. In the range from 90 % rH to 0 % rH, the length of the D-bands (cross striation of collagen visible in Atomic Force Measurement (AFM), X-ray diffraction and electron microscopy, caused by the staggered arrangement of collagen molecules within the fibril) and the spacing of the molecules are continuously reduced. This occurs by shortening the gap region or gap and overlap region between the collagen molecules within the fibril with eventual sliding of the molecules past each other.

In (Bajza and Vrcek 2001), the influence of the fatliquor concentration on the area shrinkage during static heat storage is investigated as a function of temperature. According to this study, the area shrinkage decreases with increasing fatliquor concentration in the liquor.

In the automotive sector, chrome-free tanned leathers are used for dimensionally stable parts because it is known that the dimensional stability of chrome leathers under changing climatic conditions is considerably lower than that of chrome-free leathers. However, chrome-free leathers can also develop very high dimensional losses and forces under unfavorable climatic conditions, e.g. in desert regions, so that components covered with leather can be destroyed or even break. In leather production, attempts are being made to produce shrinkage-optimized leathers for the automotive interior. However, there is currently a lack of strategies to specifically vary the parameters that are relevant for the shrinkage behavior. In particular, the influence of leather auxiliaries has not yet been systematically investigated. In the present study, the influence of retanning agents and fatliquor on dry leather shrinkage after pretannage with glutaraldehyde is investigated. Particular attention is paid to the question of whether there are systematic effects of retanning agents on leather shrinkage that correlate with their chemical classification. The effects of retanning agents and fatliquors is investigated at both the macroscopic and molecular levels.

2. Materials and Methods

Model leathers

Cattle hides (mass class 20-25 kg) were soaked, limed, pickled to pH 3, tanned with Relugan GT 50 with an offer of 6 % and basified with sodium hydrogencarbonate to pH 4.2. The Wet Whites were shaved to thickness of 1.4 mm. The Wet Whites were divided in four quarters:

A: Wet (Dry) white

B: Wet-white+ retannning

C: Wet White + faliqouring

D: Wet White+retanning+ fatliquoring

The offer of retanning agents was 25 %. Retanning was done over two days. The offer of fatliquor was 10 %. The quarters were dried on air with clamping. No mechanical post-treatment was applied.

Vegetable tannins used:

Hydrolzyble tannins; Tara extract, Sumac milled, Valonea extract, chestnut extract Condensed tannins: Quebracho extract, Mimosa extract

Furthermore, syntans with varying OH/SO_3H-content were used wich have a uniform structure in the basic body (condensation product of phenylsulfonate and phenylsulfone) (Table 2). As fatliquor, a sulfonated plant based oil with an offer of 10 % was used. Every model leather was produced in duplicates.

Table 1: Syntans

	Content of organic matter in %	Total-phenolic content / organic matter in %	OH/SO_3H
Syntan 1	22.8	11.2	
Syntan 2	28.1	12.2	
Syntan 3	32.2	7.4	
Syntan 4	26.2	5.2	

Climate change test (CCT)

Climate change tests were performed in a climate chamber (Typ 3633/18 Feutron, Germany).
The climate change was programmed as follows:

- 4 h 23°C, 50 % rH,
- 3 h at 110 °C, temperature increase 0.725 °C/ min
- 4 h 23°C, 90 % rH, temperature decrease 0.725 °C/ min
- 24 h 23°C, 50% rH
- Step 2 and 3 are repeated 10 times.

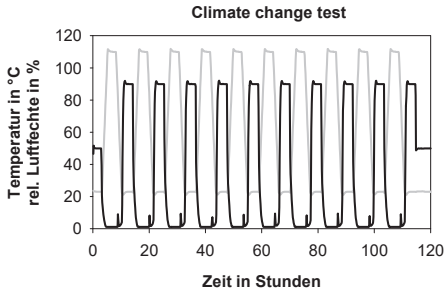


Figure 1: Climate change test, black: temperature, grey: relative humidity

The determination of shrinkage force was done according to the climate change test Porsche PPV5002B

Area shrinkage

The model leathers were punched into pieces of 100 x 100 mm. An area of 80 x 80 was marked and measured before and after the climate change test (CCT). The area shrinkage was calculated as 100* (area before CCT - area after CC)T/ area before CCT. The area shrinkage was determined as duplicates each in separate climate change tests.

Length and force measurement during climate change test

The force measurement was performed with samples of 150 x 50 mm. The specimens were fixed between two clamps firmly installed in a rack. The lower clamp is connected to a force sensor (Typ 8431, burster Germany). For the length measurement inside the climate chamber samples of 130 x 50mm are used. The sample is mounted between two clamps, one is fixed, the other one can move freely. A length sensor (Typ 87245, burster, Germany) is connected with the moveable clamp. Length and force are recorded continuously during climate change test.

Differential scanning calorimetry (DSC)-measurement

The DSC-measurements were done with a heat flow-DSC device (DSC 1, Mettler Toledo, Switzerland). Before and after the climate change test the model leather samples were cut into pieces of appr. 10 mg and soaked in a phosphate-buffer at pH 7 for 16 h. The buffer was replace with DI-water. After 4 h the excess water was removed with a tissue. Samples were then placed in aluminum pans (pan volume 40 µl) and hermetically sealed. Temperature scans were run from 0 – 125 °C with a rate of 5 $Kmin^{-1}$. After the measurement, the pans were pierced and dried at 105 °C and 100 mbar over night. After cooling in an exsikkator, the pans were weighed. From the endotherms, temperature of denaturation (TD_{onset}) was calculated. The decrease of denaturation temperature ΔTD was calculated as difference of TD before and TD after climate change test. From the area under the denaturation curve (heat of denaturation, Q) the enthalpy of denaturation was calculated according to ΔH = Q/ m dry mass collagen. Dry mass collagen = Dry mass leather * collagen content.

Determination of collagen content of the model leather

The determination of collagen contend of the model leathers was determined according to ISO 5397 (Determination of nitrogen content and "hide substance"; Titrimetric method)

Organic matter of syntans

Syntans were placed in a platinum container und heated up to 800 °C in a muffle oven. The residue was weighed, and the ash content was calculated as thepercentage of the mass of the residue relative to the mass of the Syntan. The content of organic matter was calculated as 100 minus ash content.

Phenolic content of Syntans

0.2 ml of tannin solution (approx. 5 mg/ ml) was mixed with 5 ml of Folin-Ciocalteu's phenol reagent (Merck) (10-fold dilution). After 4 min, 4 ml of a 7.5% sodium carbonate solution is added. After 90 min, the absorbance is measured photometrically at 760 nm. Calibration is performed with sodium 4- hydroxybenzenesulfonate dihydrate (98%, aldrich) in the concentration range 2 - 200 mg/ml.

Statistic

t-test with p = 0,05

3. Result and Discussion

Principle mechanism of leather shrinkage

The process of leather shrinkage under changing climate conditions can be divided into two sub- processes: reversible shrinkage and irreversible shrinkage. Reversible shrinkage occurs through desorption of water molecules in the hot part of a climate change test, caused by a decrease in ambient humidity and an increase in temperature. After re-adsorption of water molecules in the wet part of climate change test, this shrinkage recedes again.

However, during the hot phase, a second process is initiated, which is a partial denaturation of the triple helix of collagen. This is the irreversible part of leather shrinkage, which remains after reclimatization to a normal ambient climate. Leather shrinkage, whether reversible or irreversible, can manifest itself as dimensional loss or isometric force development on the macroscopic level.

The behavior of leather under changing climatic conditions can be simulated and investigated with the aid of a climate change test in a climate test chamber equipped with special sensors for length and force measurement. Figure 2b-f shows examples of what can be measured macroscopically when leather is subjected to a climate change test. The changes in humidity and temperature during the climate change test are presented infigure 2a. Figure 2b shows the course of the mass of a FOC-leather during the climate change test. Figure 2d shows the length change of the same FOC-leather during climate change test measured with length sensors (figure 2c). Figure 2f shows the isometric force that can be measured in the hot phase of the climate change test when the leather is tightly clamped between two clamps to which a force sensor is attached which is shown in figure 2c.

As can be seen in figure 2b, slightly less water is adsorbed from cycle to cycle in the wet phases of the climate change test. However, this is not in proportion to the reduction in length (figure 2d). The length does not return to the initial level in the moist phase of the climatic change test. This is the irreversible part of leather shrinkage. The irreversible dimensional loss is usually determined also as area shrinkage with defined areas on extra punched pieces (Figure 3a).

On a molecular level, the cause of irreversible leather shrinkage under dry heat conditions is a partial denaturation of the triple helix of collagen. The partial denaturation, however, does not lead to the complete coiling known from hydrothermal denaturation. The degree of partial denaturation can be estimated by Differential Scanning Calorimetry (DSC) by measuring the denaturation temperature (TD) and denaturation enthalpy (ΔH) before and after the climate change test in the fully hydrated state (figure 3b). The decrease of denaturation enthalpy is thereby a measure of the percentage of broken hydrogen bonds stabilizing the triple helix of collagen. , although the denaturation enthalpies in particular are difficult to determine with increasing degradation degree. The breaking of hydrogen bonds also leads to a decrease of thermal stability which can be measured as a decrease in denaturation temperature (ΔTD).

With the help of atomic force microscopy (AFM) one can see, that although a decrease of the denaturation enthalpy can be measured by DSC, the typical cross striation of collagen fibrils is still visible (figure 3c). What is remarkable, however, is the shortening of the distances between the D bands of the collagen fibrils after the climate change test.

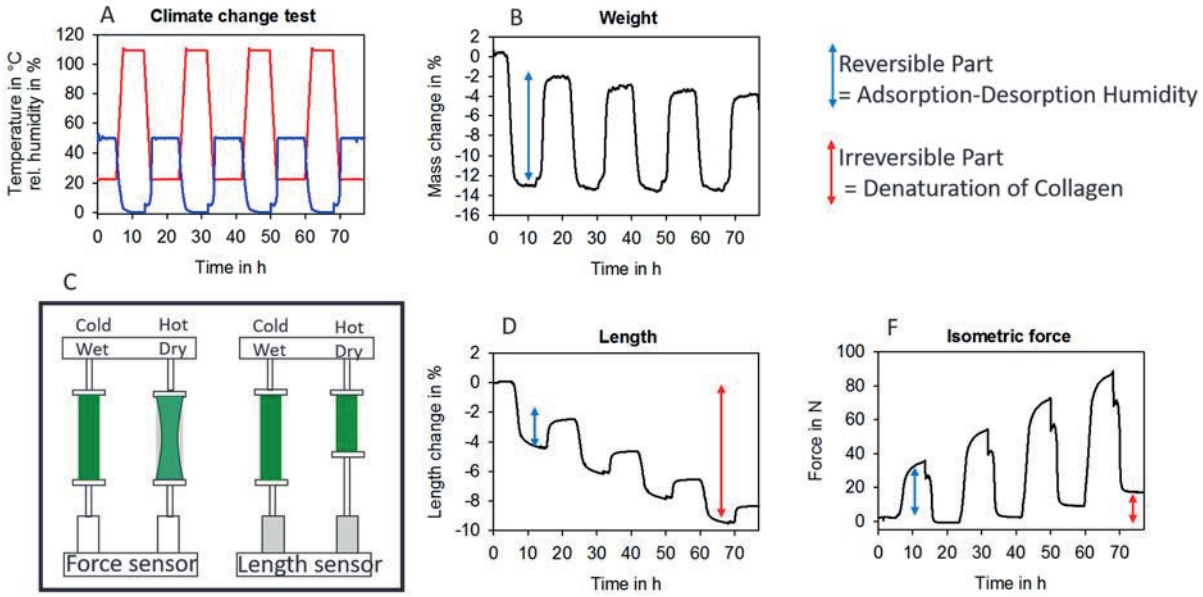


Figure 2: Principle tools and parameters for the characterization of leather during climate change test: a) course of a climate change test (blue: relative humidity, red: temperature), b) weight change during climate change test of FOC-leather, c) scheme of force and length measurement device implemented in the climate chamber, d) Length change of FOC- leather during climate change test, f) Isometric forces of FOC-Leather during climate change test. FOC= Free of chrome leather

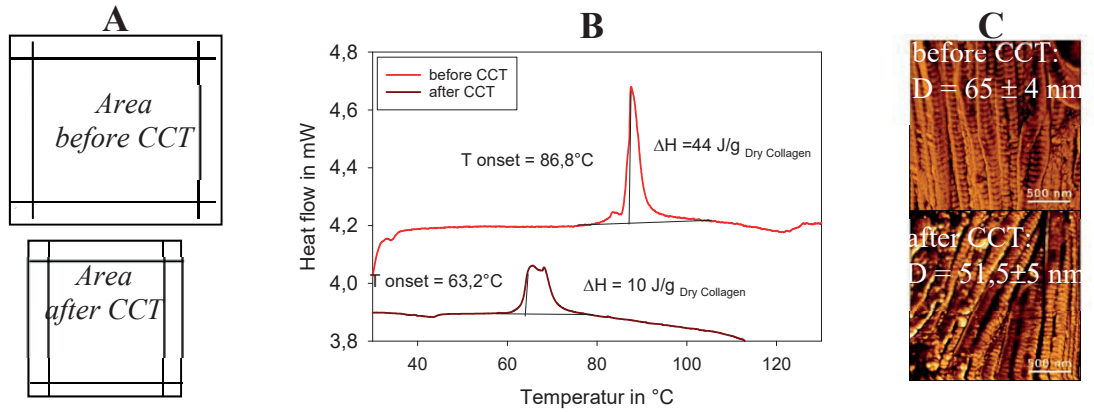


Figure 3: Irreversible changes after climate change test: a) area loss, b) DSC-Thermogramm of fully hydrated FOC-leather before and after climate change test, c) Atomic force microscopic (AFM) images of fibers from the FOC-leather before and after climate change test with D = distance of characteristic D-banding of collagen

Influence of retanning agents on irreversible dry leather shrinkage

In order to investigate the effect of retanning agents on irreversible leather shrinkage and on molecular stability, model leathers were prepared with a glutaraldehyde pretannage. The semifinished products were quartered. One quarter was dried (Dry white A), one quarter retanned and dried (B), one quarter greased only before drying (C) and one quarter retanned and greased (D) (see "Model leathers" in section 2.). The retanning agents were selected to cover a broad spectrum of chemically different classes.

The model leathers were punched into squares and subjected to the climate change test.The areas are measured before and after the climate change test and the area shrinkage was calculated. The denaturation temperature was meausered by DSC before and after climate change test in the fully hydrated state and the decrease of the denaturation temperature was calculated from the difference. The denaturation enthalpy was calculated from the area under the denaturation heat peak in DSC-curve.

In contrast to the varying denaturation temperatures, the denaturation enthalpy before the climate change test does not differ significantly between the different retanning agents (40 J/g +7). Therefore, only the enthalpies after the climate change test are compared to estimate the degree of denaturation. For thermal stability, on the other hand, the difference between TD before and TD after the climate change test is used.

Figure 4a shows the area shrinkage of the model leathers variant A (Dry White) and the retanned Wet Whites (variant B) with different retanning agents for variant B. To better illustrate the effects, differences between area shrinkage of variant B and A are calculated. Figure 4b shows this differences for all retanning agents investigated.

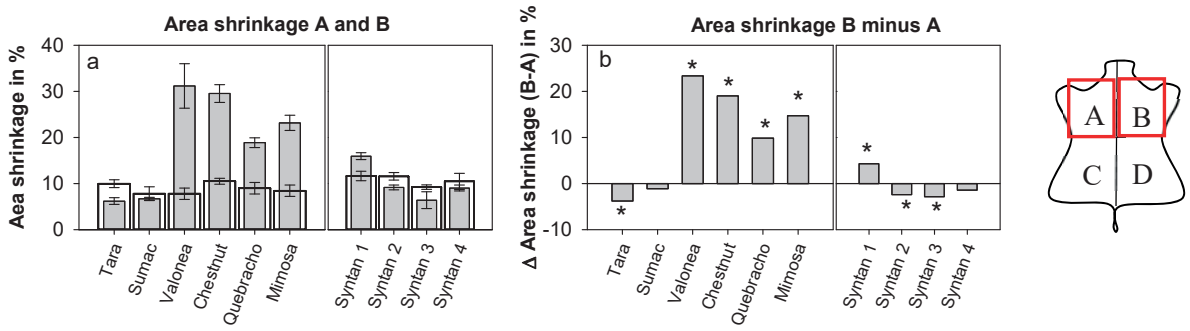


*Figure 4: a) Area shrinkage, denaturation enthalpy and decrease of denaturation temperature of model leathers. Dry white (A), transparent , Wet white + **different retanning agents (B), grey***
*b) Area shrinkage B minus A, n= 2 samples * 2 hides, Asterisk: differences are significant (t-Test, p = 0.05)*

The retanning agents have a significant influence on the area shrinkage. The effects goes in different directions: Tara and sumac reduce the area shrinkage, all other vegetable tanning agents investigated lead to a (in part drastic) increase in area shrinkage. In the case of the synthetic retanning agents, the syntan with the highest OH/ SO_3H ratio increases the area shrinkage. Syntanes 2, 3 and 4 with lower OH/SO_3H ratio decrease the area shrinkage.

Compared to a mean area shrinkage of 9.7 ± 1.7 % of the Dry Whites A, the area shrinkage increases by a factor of 4 to 37 % in the case of valonea as retanning agent. Retanning with tara , however, leads to a reduction of the area shrinkage by a factor of 2 to 4 %.

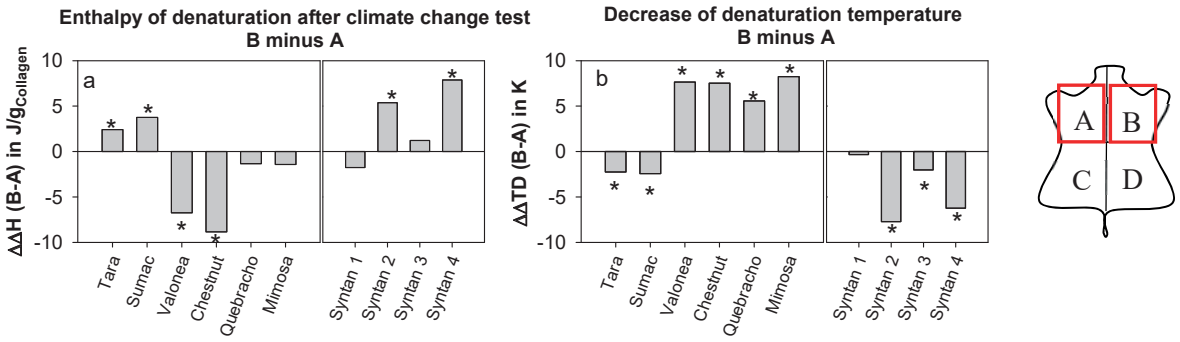


Figure 5: a) Denaturation enthalpy and b) decrease of denaturation temperature of model leather variant B minus variant A

Subtracting the denaturation enthalpies after the climate change test from the retanned variant B from the denaturation enthalpies of the pretanned variant A (Figure 5a), the effects show the following: The more the retanning agent increases the surface shrinkage, the more it decreases the enthalpy during the climate change test. The same applies to the decrease in denaturation temperature (Figure 5b).

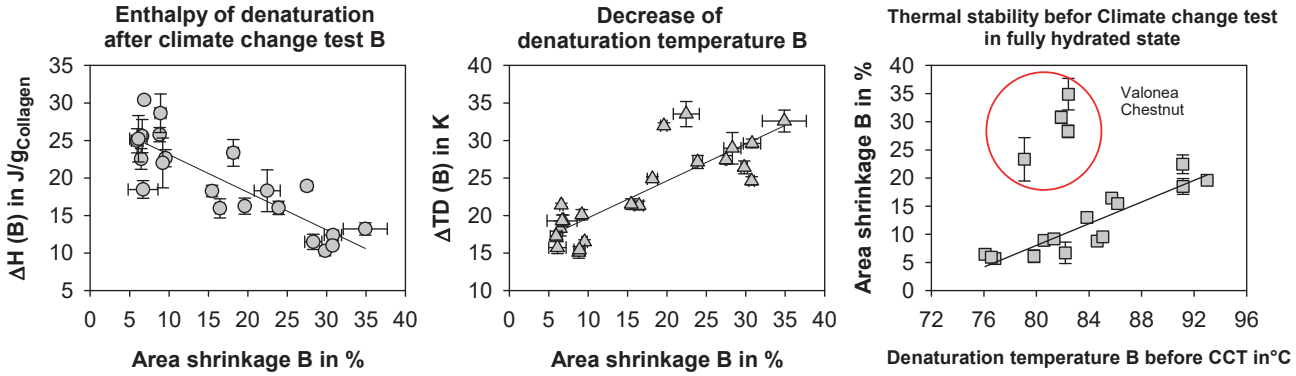


Figure 6: a) Correlation between area shrinkage and denaturation enthalpy after climate change test b) decrease of denaturation temperature of model leather variant B (wet white + retanning) and c)Correlation between denaturation temperature in fully hydrated state before climate change test and area shrinkage after climate change test of model leather B (WW + retanning)

Looking at the absolute denaturation enthalpies and the decrease in denaturation temperature of the retanned samples (variant B) after the climate change test, a correlation to the area shrinkage can be seen (figure 6a and 6b): The higher the area shrinkage, the lower the denaturing enthalpy and the higher the drop in denaturing temperature. This strengthens the hypothesis, that the molecular cause of the irrecversible area shrinkage is to be found in the partial denaturation of the triple helix and the shortening of the fibrils. On the other hand, this means that the retanning agents considerably influence the molecular stability against the stress of the climate change test with dry heat.

A correlation between the chemical classification of the vegetable retanning agents and the described effects cannot be clearly seen. The hydrolyzable tanning agents can cause a strong increase in area shrinkage and a decrease in molecular stability, as in the case of valonea and chestnut, or an increase in molecular stability and a decrease in area shrinkage, as in the case of tara and sumac. The condensed tannins all cause a decrease in molecular stability and an increase in area shrinkage. A certain trend can be seen with regard to the decreasing tanning effect of the syntans. The syntan 1 with the highest OH/SO_3H ratio, which exhibits a strong tanning ability, has a shrinkage enhancing effect. As the OH/SO_3H ratio decreases, the syntans have a shrinkage-reducing effect, similar to tara and sumac.

Interestingly, an inverse trend was found for thermal stability before the climate change test in the fully hydrated state and are shrinkage of retanned variant B (figure 6c): The higher the denaturation temperature of the retanned model variant B in the fully hydrated state **before** climate change test, the higher the area shrinkage and the lower the molecular stability against climate change test with dry heat. Similar observations were made when investigating the shrinkage behavior in the climate change test of semi-finished products, tanned with Glutaraldehyde and Chromiumsulfate(Dry White, Dry Blue) as a function of the degree of crosslinking: the higher the degree of crosslinking and the hydrothermal stability befor climate change test, the higher the shrinkage and the lower the molecular stability against dry heat in the climate change test (Schröpfer and Meyer 2012). An explanation for this phenomenon is currently still being worked on.

Influence of fatliquor on irreversible leather shrinkage

In order to investigate the influence of the fatliquor alone and in interaction with retanning, one quarter of the pretanned Wet Whites (A) was only fatliquored (C) and a second quarter retanned and fatliquored (D), The same vegetable oil-based fatliquor with the same supply was used in all experiments.

Looking at the behavior of the model leather variants A and C in climate change test (figure 7), it can be seen that the fatliquoring of Wet White (C) leads to an increase in area shrinkage and a decrease in molecular stability compared to the only preretanned variants (A). The average fat content of all leathers of variant C is 12.6 % ± 2.7.

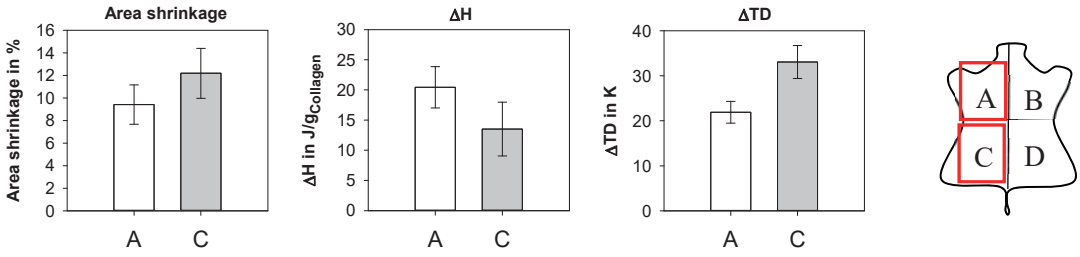


Figure 7: Area shrinkage, denaturation enthalpy and decreas of denaturation temperature of model leather A (Dry White) and C (Wet White + fat)

The effect of the fatliquor on the retanned variants B is presented in figure 8 as the difference D minus B. Various effects can be seen. However, for the area shrinkage, these are considerably smaller than the effects of the retanning agents on the only pretanned variants. With the hydrolyzable retanning agents and the moderate binding syntans, the area shrinkage is slightly increased by the fatliquor and the molecular stability decreased. For the condensed vegetable tannins and the strong binding syntans, there is no effect on area shrinkage and no significant effect on molecular stability.

In addition, the effect of different fatliquors of different chemical nature (silicones, vegetable, animal and synthetic) on the irreversible area shrinkage of a uniformly retanned leather was investigated. Synthetic fatliquors produced slightly higher area shrinkage than fatliquors based on natural oils (approx. 2 -3%).

An explanation for the destabilizing effect of the fats against dry heat could be the increase in mobility of the collagen chains by the fats, which act as a lubricant or spacer between the structural elements similar to water.

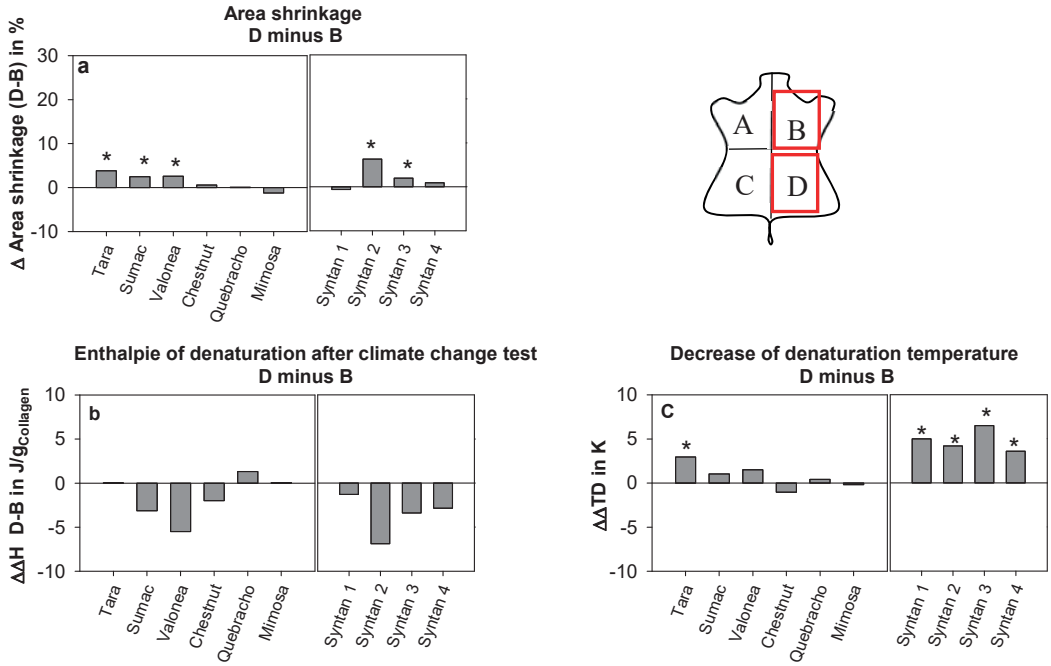


Figure 8: Effect of fatliquoring on retanned Wet Whites: a) *Area shrinkage, b) denaturation enthalpy and c) decrease of denaturation temperature after climate change test D minus B*

Influence of retanning on isometric shrinkage force

For some years now, the isometric shrinkage force of leather has been part of the tests to be fulfilled by an automotive manufacturer for leather used in automotive interiors.

As described above, two processes must be considered in isometric force development: The reversible adsorption and desorption of moisture caused by the changing ambient humidity and temperature causes reversible forces and

length change. This force build-up and reduction is superimposed by the irreversible shrinkage processes, which are based on the irreversible partial denaturation due to the influence of heat. The reversible force in the hot part of the climate change test is influenced to some extent by the thickness and stiffness of the leathers (own unpublished results). Nevertheless, the forces at the end of the climatic change test are significantly influenced by the effect of the retanning agents Figure 9 shows the course of the isometric forces, the lenght change and the mass change of leathers (variant D) retanned with tara and chestnut during the climate change test according to PPV 5002B. As described above, tara causes a shrinkage-reducing effect and chestnut causes a shrinkage-increasing effect as far as irreversible shrinkage is concerned. Leathers retanned with tara therefore show absolutely a low area shrinkage in contrast to leathers retanned with chestnut. This also has an effect on the isometric forces. If the leathers can move freely, as is the case when measuring the change in length (figure 9, middle), the irreversible part increases with different slope comparing both leathers, but the reversible part (difference of length between hot and cold cycle of climate change test) of the shrinkage is independent of the irreversible part and thus independent of the retanning.

Slightly less water is adsorbed from cycle to cycle, but the course of adsorption and desorption does not differ significantly between the two leathers (figure 9, right).

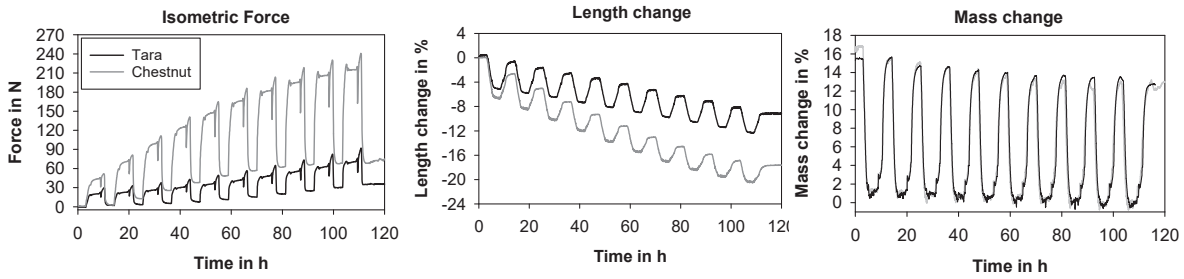


Figure 9: Course of shrinkage force, length change and mass change of model leathers Variant D according to PPV 5002B,. black: retanning with tara extakt, grey: retanning with chestnut extract

If the leather are clamped isometrically as in the case of force measurement (figure 9, left), the reversible forces, increase with increasing irreversible portion. The resistance of the leather and thus the force generated by the adsorption and desorption of moisture increases disproportionately from cycle to cycle. This behavior can also be significantly influenced by the choice of retanning agent. In the example shown in the figure 9, the minimum length at the end of the hot phase in the 10th cycle differs between the two leathers by a factor of 1.5, and the maximum forces by a factor of 3. Thus, only the choice of retanning agent can produce a difference in the maximum forces of 60 N with tara retanning and 250 N with chestnut retanning.

With regard to the absolute force values of 60 N of the tara retanned leather, not all parameters have yet been optimized for the model leathers: The thickness is 2.4 mm (almost twice as much as a normal leather) and the leathers are not mechanically processed, i.e. they are very stiff.

Based on the results of the preceding investigations, a FOC-leather for automotive interior was produced that was retanned using only Tara and Syntan 4. The thickness was 1.6 mm. The leather was milled. Samples of leather were subjected to the climate change test according to PPV 5002B. The averaged maximum forces of three samples at the end of the 10th cycle was 9 ± 1 N. Thus, the requirements of a maximum of 40 N specified in the PPV5002 B standard are fulfilled.

4. Conclusions

In the present work, the influence of retanning agents and fatliquors on irreversible leather shrinkage and on the shrinkage force of glutaraldehyde pretanned leathers in climate change test was investigated. It was shown that retanning agents in particular can influence shrinkage significantly. The cause of irreversible leather shrinkage is the partial denaturation of the triple helix of collagen, which leads to a shortening of the triple helix. The retanning agents influence the molecular stability to changing climatic conditions and thus the irreversible area

shrinkage. In particular, tara and syntans with moderate OH/SO_3H ratios can be used to produce leathers with low area shrinkage and good molecular stability. This effect is opposite to the effect that retanning agents have on hydrothermal stability in the fully hydrated state (except for valonea and chestnut). This is also true for the degree of crosslinking of the pretannage with glutaraldehyde. An explanation for this has yet to be found. Fatliquor lead to a slight deterioration of the molecular stability and increase of irreversible area shrinkage towards climate change test and dry heat. However, this depends on the retannage.

The effects of retanning agents on irreversible area shrinkage are very clearly reflected in the shrinkage forces under isometric conditions, although these are reversible to a large extent. Due to the steadily increasing irreversible shrinkage, the reversible forces increase disproportionately.

With the knowledge gained, it should be possible, through the choice of retanning materials, to produce low-shrinkage leathers that also meet the high requirements of shrinkage force tests.

5. Acknowledgment

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References

Bajza, Z., & Vrcek, I. V. (2001). Fatliquoring agent and drying temperature effects on leather properties.

Journal of materials science, *36*(21), 5265–5270.

Kellert, H., Hummel, A., & Germann, H. (2000). Das Alterungsverhalten von Leder. *Leder und Häutemarkt*, (3), 25.

Masic, A., Bertinetti, L., Schuetz, R., Chang, S.-W., Metzger, T., Buehler, M., & Fratzl, P. (2015).

Osmotic pressure induced tensile forces in tendon collagen. *Nature communications*, *6*.

Scheibe, R., & Wolf, H. (1997). Eigenschaftsänderungen von Chromleder bei Klimawechsel. *Das Leder*, *4898*, 134.

Schröpfer, M., & Meyer, M. (2012). Dimensional and structural stability of leather under alternating climate conditions. *J. of Aqeic*, *63*(2), 1–9.

Tuckermann, M., Mertig, M., Pompe, W., & Reich, G. (2001). Stress measurements on chrome-tanned leather. *Journal of materials science*, *36*(7), 1789–1799.

Note