Paper A17

Dimensional and structural stability of leather under alternating climate conditions

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1. Introduction

The change of properties under the influence of alternate climate conditions and especially under the influence of dry heat restricts the usability of leather. This includes area loss, loss of softness, development of stress under isometric conditions (i. e. dash board in automotives) and degradation of molecular structure. It is known, that big differences exist in the dimensional stability of chrome tanned leathers and chrome free leathers. SCHEIBE AND WOLF [1] first measured the forces of chromium leather observed during climate changing as well as they analysed thickness, mass and bending stiffness before and after treatment in climate change tests. Their results demonstrated, that the forces of leather held isometrically increased with increasing number of climate changing cycles. Thickness as well as mass varied with the humidity of the applied climate and stiffness increased with increasing number of cycles even at temperatures above 60°C. This was interpreted as sticking together of the fibers. KELLERT ET AL. [2] showed, that leather differs in its susceptibility against heat depending on the type of tanning and the climate exposed. At the same temperature, chrome free leather is more stable at dry conditions whereas chrome leather shows higher stability (measured as bending stiffness) at high humidity. Furthermore, the authors showed, that the ability of the samples to take up humidity by reclimatisation is reduced depending on the temperature of treatment. Already at 40°C this ability is reduced. The authors explained this increase in stiffness with sticking together of the fibers.
At IULTCS Congress 2005, TROMMER AND MEYER [3] presented results about the dimensional stability of chromium and chrome free tanned leather during changing climate conditions. The results of SCHEIBE AND WOLF were confirmed. Chrome tanned leather showed an increase of forces during the climate change test, whereas for chrome free leather such an increase was not observed. Furthermore, a decrease of shrinkage temperature was found.
In 2006, MEYER ET AL. [4] showed that the differences in shrinkage behaviour of chrome and chrome free leather are correlated with differences in the denaturation rate during climate change tests.

The aim of this work was to find a possible explanation for the cause of leather shrinkage and for the differences between chrome and chrome free leather, respectively. The influence of tanning agents on the dimensional stability as well as the influence of crosslinking degree was investigated.

2. Materials and Methods

2.1 Materials

- Dry Blue and Dry White with different crosslinking degrees
- Model-leathers after different technological steps where only one chemical component was changed

2.2 Methods

- Climate change tests according to VolkswagenTL 52064 (40°C, 90% rH-110°C, 0% rH, Plateaus 6 h)

- Measurement of length change during climate change test with a length sensor inside the climate chamber. The samples are fixed with a non-moveable clamp on one side and with a movable clamp on the other side which is connected with the length-sensor
- Determination of permanent area shrinkage by measuring defined pieces of leather before and after climate change test with reclimatisation in norm-climate (23°C, 50% rH)
- Determination of denaturation temperature (T_D) and denaturation enthalpy (ΔH_D) before and after climate change test with differental scanning calorimetry (DSC) in fully hydrated state in hermetically sealed aluminium pans (DSC7, Perkin Elmer)
  $\Delta T_D = T_D$ before climate change test – T_D after climate change test
  Degree of denaturation: 100x(ΔH_D before climate change test / ΔH_D after climate change test)
- Determination of porosity with a gas pycnometer (AccuPyk, Micromeretics)
- Atomic force microscopy AFM (Nanowizard, JPK)
- Thermally crosslinked lysine groups: Derivatisation with trinitrobenzensulfonic acid followed by hydrolysis and photometrical detection of derivatised lysine groups before and after climate change test

3. Results

3.1 Influence of crosslinking degree on shrinkage

In principle, the shrinkage of leather can be divided in two segments: If the temperature rises or/and humidity decreases, water is desorbed from the leather structure. If the water is also removed from the mesopores, capillary forces evolve that cause a contraction of the fibre structure leading to shrinkage of the leather or development of forces if the leather is fixed isometrically [5]. This first step is partly reversible: If the temperature decrease or/and humidity increases again, water is reabsorbed and the original length is restored until a remaining rest of irreversible shrinkage if the temperature during resorption is high. Figure 1 and figure 2 show the length change of semi-finished Dry Whites and Dry Blues, respectively, with different degrees of crosslinking during a climate change test.

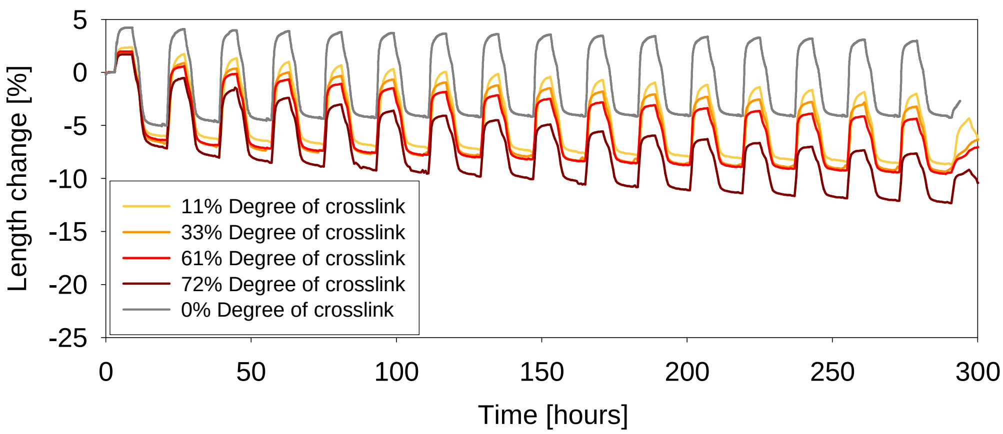


Figure 1: Length change of semi-finished Dry Whites with different degrees of crosslinking during a climate change test

Figure 3 shows the permanent area shrinkage after 16 cycles of climate change test and reclimatization for Dry Blues and Dry Whites comparing air dried and acetone-dried samples.

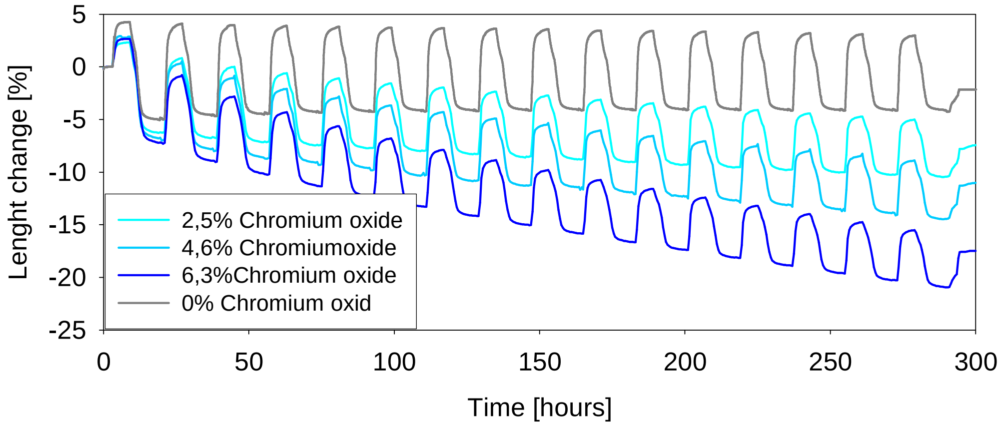


Figure 2: Length change of semi-finished Dry Blues with different degrees of crosslinking during a climate change test

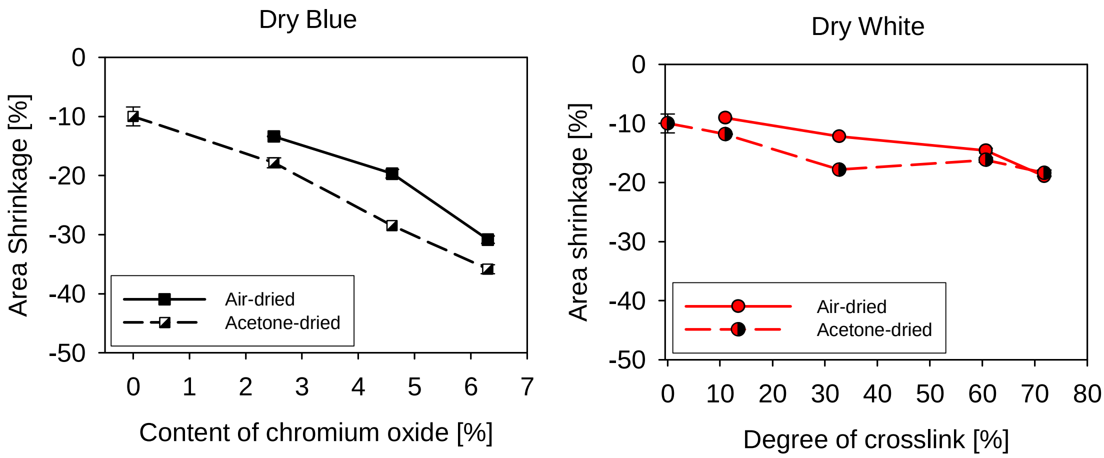


Figure 3: Permanent area shrinkage of Dry Blue and Dry White with different degrees of crosslinking after 16 cycles of climate change test

The permanent area shrinkage strongly depends on the degree of crosslinking. With increasing degree of crosslinking, the percentage of permanent area shrinkage increases. Chrome tanned hides show more permanent area loss than glutaraldehyde tanned hides. The higher degree of fibre isolation in the case of acetone-dried samples causes a small increase of shrinkage, but the influence of the chromium oxide content is more dominant. At crosslinking degrees above 30 %, the glutaraldehyde tanned hides show no further area shrinkage. In the past, the degree of porosity was discussed as one reason for the shrinkage of leather. Figure 4 shows, that the porosity of air dried hides increases with increasing chromium content or increasing crosslinking degree of glutaraldehyde tanned hides. Tannage prevents the fibres from collapsing during drying (Figure 4). However, if the hides are dried by acetone no influence of the chromium content and only little influence of the crosslinking degree of Dry Whites on porosity was found. Nevertheless, the area shrinkage strongly depends on the crosslinking degree.

To investigate the stability of the molecular structure, we measured the hydrothermal shrinkage temperature and denaturation enthalpy before and after climate change tests. In this way, the degree of partial denaturation in the triple helix can be calculated as explained in the material section. ΔT_D decreases similarly for chromium and glutaraldehyde tanned hide with increasing crosslinking degree (Figure 5 left). However, the degree of denaturation differs between both materials (Figure 5 right). The partial denaturation, that can be observed, occurs slowly depending on the surrounding conditions and is a consequence of the action of dry heat on the leather structure.

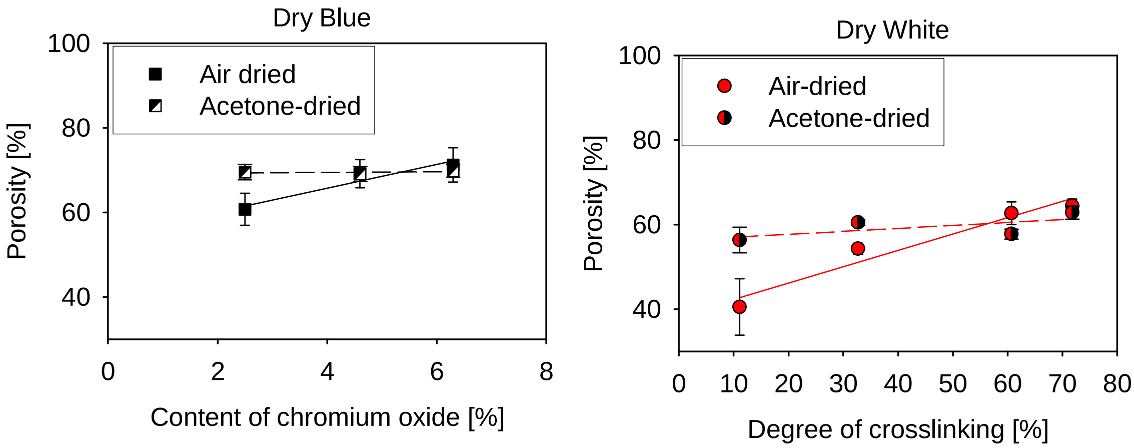


Figure 4: Porosity of Dry Blue and Dry White with different degrees of crosslinking after air drying and acetone drying

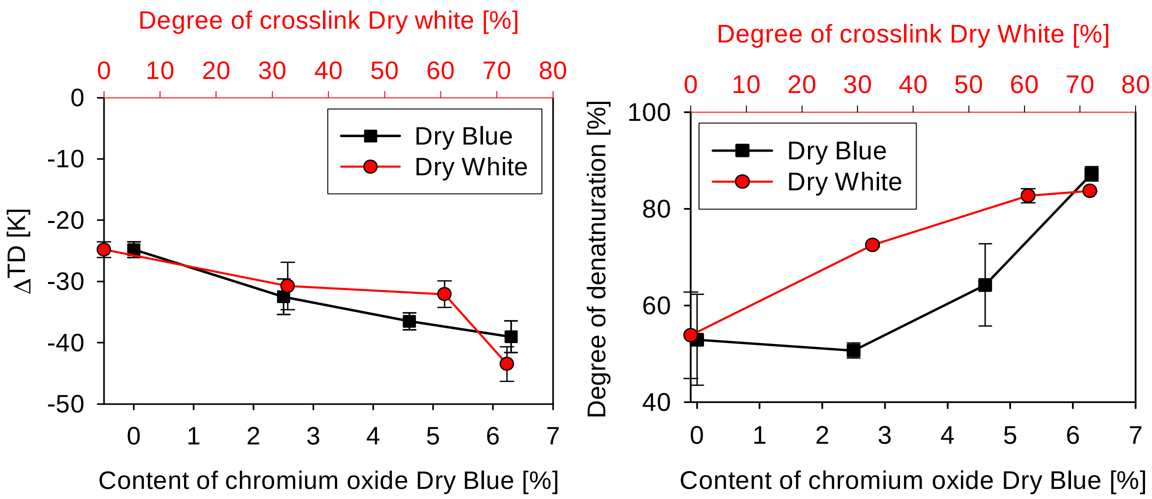


Figure 5: Decrease of hydrothermal denaturation temperature (left) and degree of degradation (right) of Dry Blue and Dry White with different degrees of crosslinking after 16 cycles of climate change test

AFM was used to resolve the structural level of the fibrils and to measure the distance of D-periodicity. If this distance is compared between fibrils before and after thermal treatment, a shortening
of the D-periodicity after climate change test can be determined (Figure 6).

3.2 Influence of tanning agents on shrinkage

To investigate the influence of different tanning agents on the shrinking behaviour of leather, model leathers were produced following the scheme in figure 7.

The hides were either pre-tanned with chrome or glutaraldehyde. In every case, three variations of retanning agents were used: Basyntan SW, Tara or polyacrylate. Other parameters like fatliquoring agent, time, concentration and temperatures were kept constant.

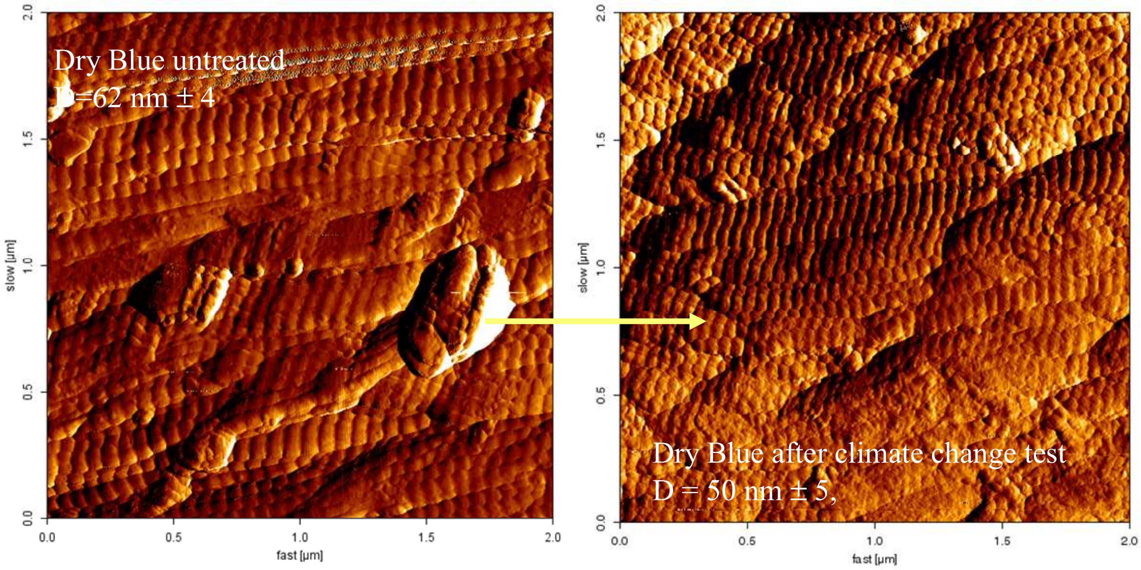
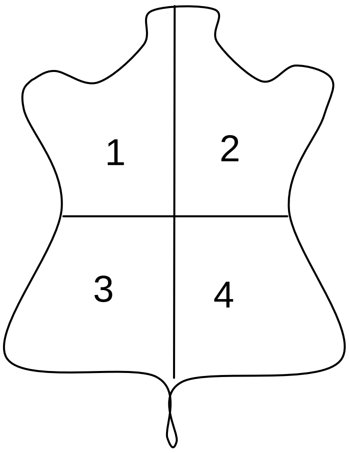


Figure 6: AFM measurements of Dry Blue before and after 16 cycles of climate change test



1: Pre-Tannage (Chrome or Glutaraldehyde)

2: Pre-Tanning + Retanning

3: Pre-Tanning + Fatliquoring

4: Pre-Tanning + Retanning + Fatliquoring

As Retanning agents Tara, Syntan and Polyacrylate were used.

Figure 7: Scheme for the production of model leathers

In figure 8 it can be seen that shrinkage follows a 1st order kinetic. Every retanning agent, that was used, has a significant influence on the amount of shrinkage depending on the kind of pretannage: Basyntan decreases the amount of shrinkage in both cases. Polyacrylate has no influence on the shrinkage of Wet White leather whereas the shrinkage of chrome leather with polyacrylate is increased. The most interesting results are obtained using Tara as the retanning agent. In combination with chrome pretannage Tara leads to an extensive increase of shrinkage while with glutaraldehyde pretannage shrinkage is decreased.

Considering the parameters of partial denaturation, which follows a first order kinetic too, there is a good correlation between the degree of denaturation and the amount of area shrinkage (
Figure 9).

The fatliquoring agents do not influence the shrinkage of chrome pretanned hides if the chrome content is high (Figure 10 left). If the chrome content is lower the fatliquoring agent increases the shrinkage. Using glutaraldehyde for pretannage, addition of fatliquoring agent increases the shrinkage, in some cases even until the sample is completely destroyed (Figure 10 right).

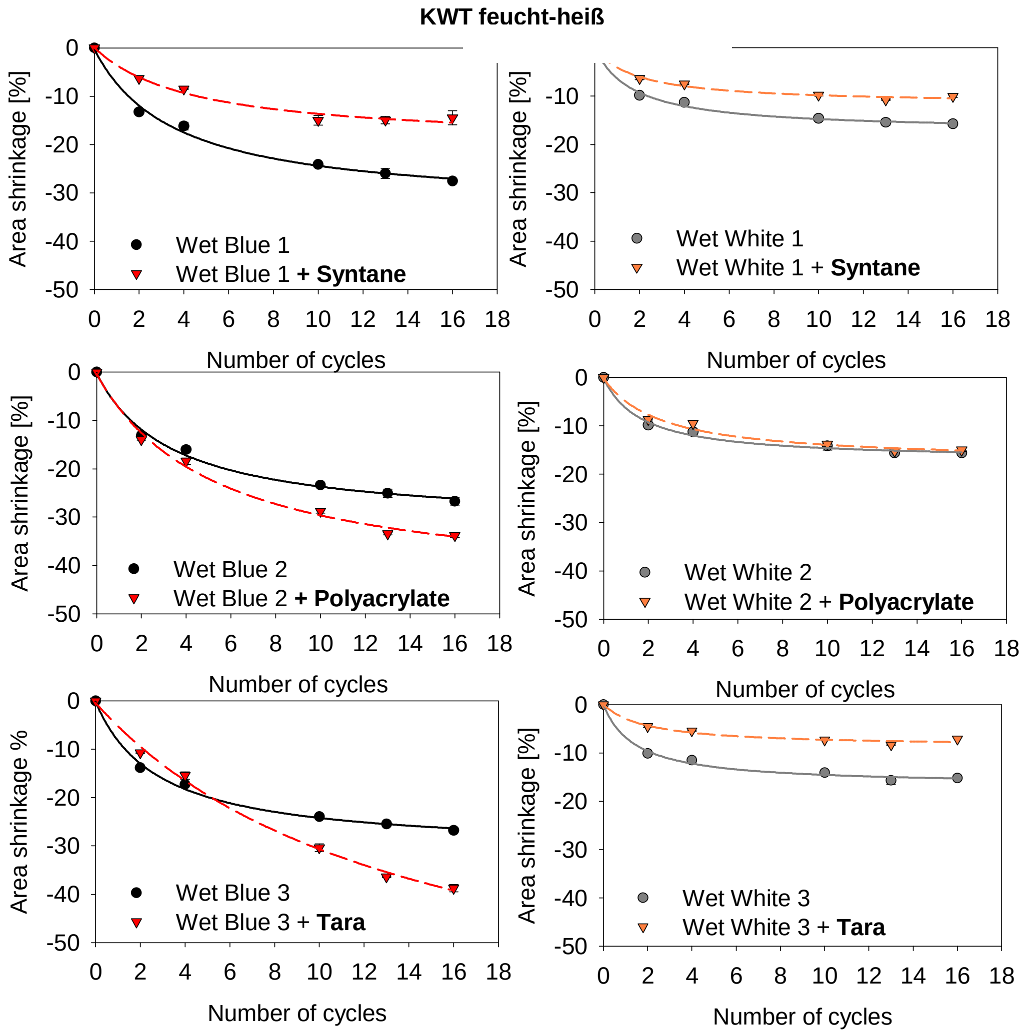


Figure 8: Area shrinkage of pretanned and retanned model leathers

Determination of the thermodynamic parameters after climate change test shows an acceleration of the decline of denaturation temperature induced by the addition of fatliquoring agent (Figure 11). However, the degree of denaturation, e. g. the denaturation enthalpy, does not decrease faster after fatliquoring when compared to the pretanned Wet Blue. In contrast, the denaturation enthalpy of Wet White decreases faster than that of the pretanned hide (Figure 12). Again, this correlates well with the kinetic course of the area shrinkage during climate change test.

4. Conclusions

The results of this study lead to the conclusion that the permanent area shrinkage of leather is caused by a partial denaturation of the tripelhelix occuring at a low rate under the action of dry heat and/or changing climate conditions and depending on the surrounding conditions. Hydrogen bonds are broken during the thermal treatment and the structure is compressed in an axial direction. The latter is supported by the shortening of D-periodicity measured by AFM as well as the decline in denaturation enthalpy determined calorimetrically. A complete coiling as observed during hydrothermal shrinkage cannot proceed because the approach of the structural elements that is caused by capillary forces during water desorption in the hot state induces a steric hindrance. With increasing crosslinking degree, which is usually correlated with an increase in hydrothermal stability, the molecular stability against dry heat decreases and at the same time the permanent area shrinkage increases.

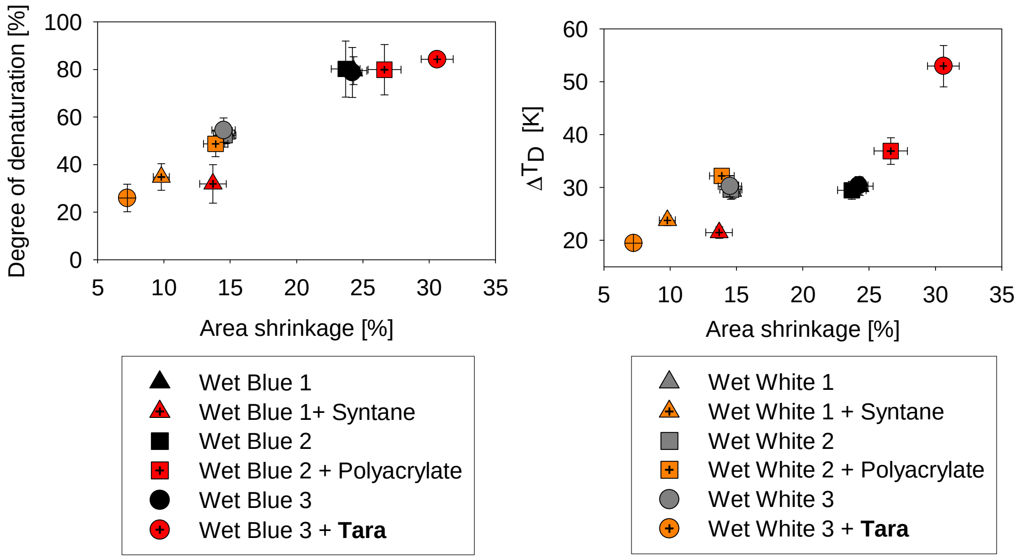


Figure 9: Correlation of area shrinkage between degree of denaturation (left) and decrease of denaturation temperature (right) for different pre- and retanned model leathers. Values are taken from the shrunken samples after 10 cycles of climate change test.

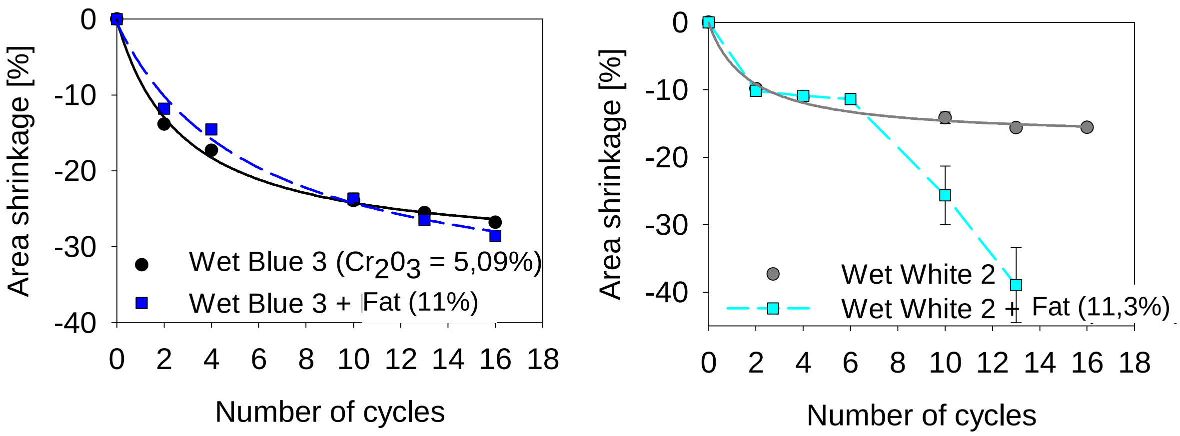


Figure 10: Area shrinkage of pretanned and fatliqoured model leathers: Chrome pretannage (left), glutaraldehyde pretannage (right)

Retanning agents have significant influence on the shrinkage behaviour as well as the molecular stability against dry heat. Especially Tara acts in opposite manner depending on the kind of pretanning. In combination with chrome it destabilizes the molecular structure and enhances the area shrinkage. However, the combination of Tara and glutaraldehyde results in higher molecular stability against dry heat and low area shrinkage. Hence, the different behaviour of chrome and glutaraldehyde tanned leathers is not only caused by the single action of the different pretanning agents but also by synergistic effects of pretanning and retannig agents.
Addition of fatliquoring agent leads to lower molecular stability against dry heat and to increased area shrinkage compared to non fatliqoured hides.

Acknowledgements

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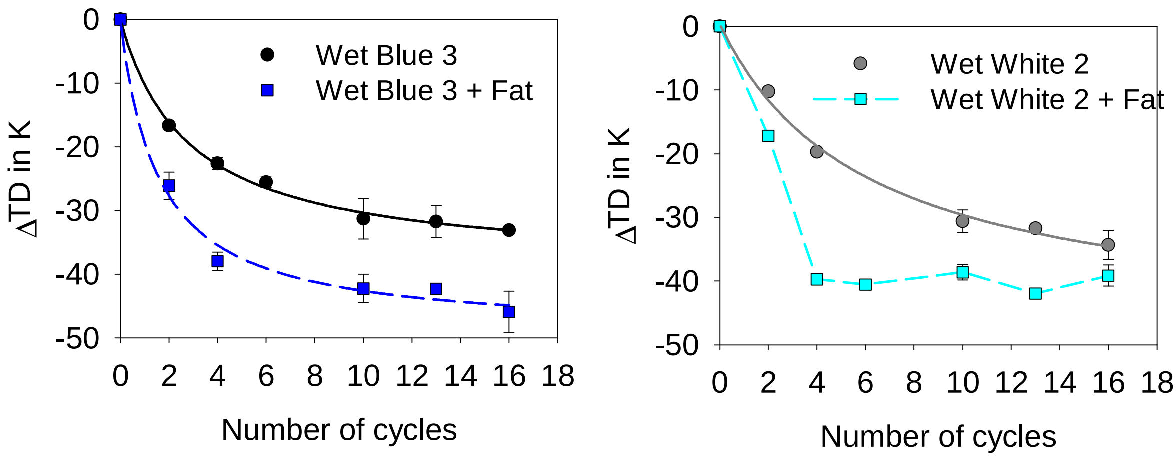

Figure 11: Decline of denaturation temperature T_D of pretanned and fatliqoured Wet Blues (left) and Wet Whites (right) during climate change test

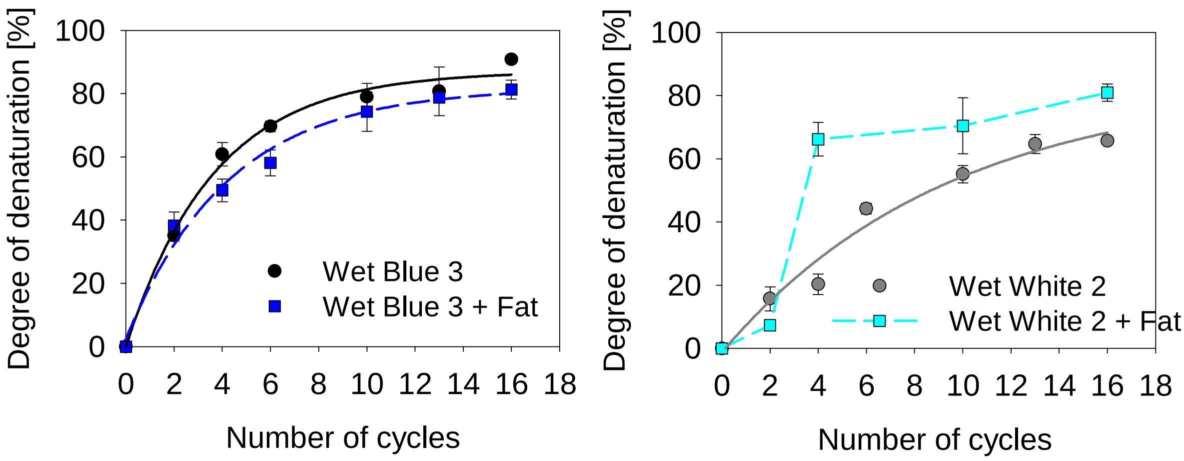

Figure 12: Degree of denaturation of pretanned and fatliquored Wet Blues (left) and Wet Whites (right) during climate change test

5. References

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