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Effects of temperature and humidity on different crosslinked collagen structures

1 Introduction

Dimensional stability of leather while changing temperature and humidity is an important characteristic especially for the automotive industry. Due to its unfavourable position in the car this leather can be exposed to temperatures up to 120°C at the day, followed by moderate temperatures and high humidity in the night. This climate changing causes high stress development in leather and could lead to material rupture. Therefore the automotive industry developed stability tests, leathers have to be overcome to be used in an automotive. Two important tests in this regard are a climate changing test and the storage test in dry heat. During these tests effects are observed which are not easy to explain. One of these effects is reversible and permanent area loss as well as tension, which are developed during these tests. Furthermore clear differences are found between chromium tanned leathers and leathers which are chromium free.

Tension of leathers had been an objective of a couple of investigations already especially in connection with drying [1][2] or as tension development during hydrothermal shrinkage [3]. SCHEIBE AND WOLF [4] first measured the forces of chromium leather during climate changing as well as thickness, mass and bending stiffness before and after treatment in climate changing tests. They found, that the forces of leathers held isometrically increased with increasing number of climate changing cycles. Thickness and mass of the leathers varied with the humidity of the applied climate. The stiffness increased with increasing number of cycles partially at temperatures higher than 60°C. This was interpreted as sticking together of the fibers.

KELLERT ET AL. [5] showed, that leather differs in its susceptibility against heat, depending on the type of tanning and the climate exposed. At the same temperature chromium free leather is more stable at dry conditions, whereas chromium 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 reclamation 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 [6] showed results about the dimensional stability of chromium and chromium free tanned leathers during changing climate conditions. The results of SCHEIBE AND WOLF were confirmed. Chromium tanned leather showed an increase of the forces during climate changing test, whereas chromium free leather did not show this increase. Furthermore a decrease of the shrinkage temperature was found.

The aim of this investigation is to discuss reasons for the different behaviour of chromium tanned and chromium free tanned materials under heat exposition and climate changing, respectively. In this regard three aspects are particularly interesting, which are firstly the decrease of the shrinkage temperature and secondly the permanent area loss during heat storage as well as thirdly reasons for the increasing forces developing during climate changing.

2 Materials and methods

As semi finished raw materials commercial wet blue (chromium tanned) and commercial wet white were used, the latter tanned by glutaraldehyde and synthan (chromium free tannage). The leathers investigated were crust leathers for the use in automotives (before finishing). These leathers were also made from wet white and wet blue, both retanned synthetically in different ways, dyed and fatted.

Ts (fully hydrated) of semi finished products were found to be 110°C for chromium tanned and 79,3°C chromium free tanned, that of the leathers were 87,5°C for chromium free and 118°C chromium tanned.

Determination of shrinkage temperature Ts

After rehydration under standard climate conditions (23°C, 50% RH) the samples were cut, weighed and immersed in water for 24 hours. The test pieces were put into a high pressure DSC pan and closed tightly. Scans were performed from 2°C to 150°C at 5K/min with DSC 7 from Perkin Elmer. The denaturation temperature was set to be equal with the onset temperature of the recorded DSC peak.

Climate changing test

The climate changing tests were performed in a climate test chamber (Fa. Feutron, Langenwetzendorf) with a special equipment to measure forces under isometric conditions and changes in length of sample pieces. Thereto, the samples were cut in pieces of 150 x 50 mm and fixed into the clamps of the force and length measurement device. The climate changed between 40°C/90% r.H. and 110°C and 0% r.H.

Permanent area loss

Samples were cut in pieces of exactly 100 mm x 100 mm. Before and after thermal treatment the samples were stored under standard climate conditions. Area loss was calculated from the relationship of the area determined before and after thermal treatment.

3 Results and discussion

Decrease of denaturation temperature after storing in permanent heat

Different semi-finished products and leathers, chromium tanned as well as chromium free, were exposed to dry heat at different temperatures as described above. From the samples exposed to permanent heat shrinkage temperatures (Ts) were measured as well as the permanent area loss depending on the time. In all cases the shrinkage temperature decreased with time. This decrease was accelerated with increasing exposure temperature.

To compare the decrease of different samples, Ts at time t was subtracted from the corresponding shrinkage temperature Ts (t=0) at the beginning of the test to give ΔT_s . The semi-finished products showed almost no difference of ΔT_s in this decrease (Fig.1), whereas in leathers a markedly difference was found between chromium tanned leather and chromium free leather especially at 120°C (Fig. 2).

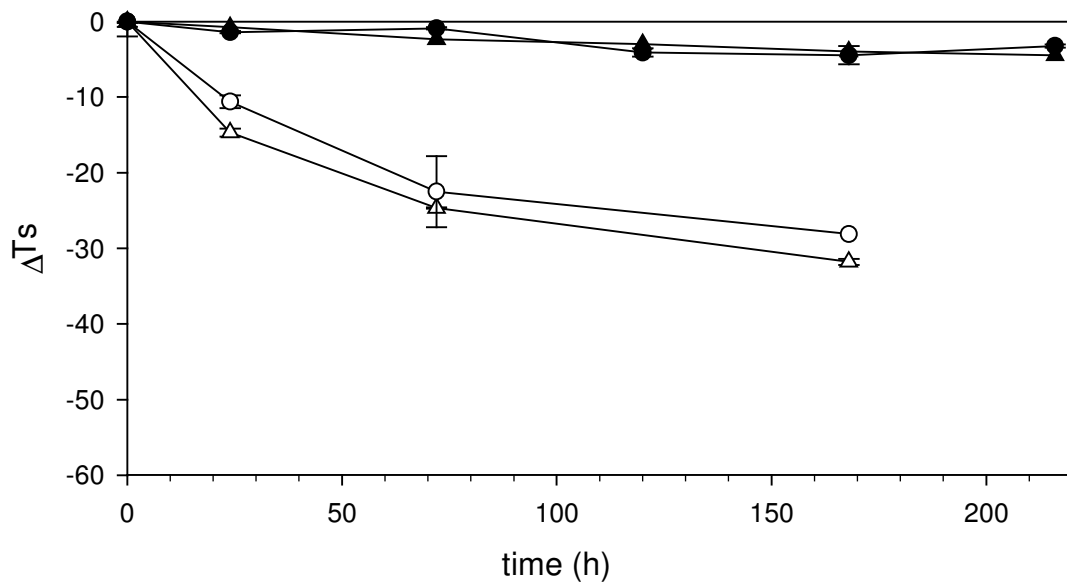


Fig.1: Storage of semi-finished products at permanent heat; ▲..chromium free; ●..chromium tanned (80°C); △..chromium free; ○..chromium tanned (120°C); $\Delta T_s = T_s(t) - T_s(t=0)$; T_s ...denaturation temperature fully hydrated)

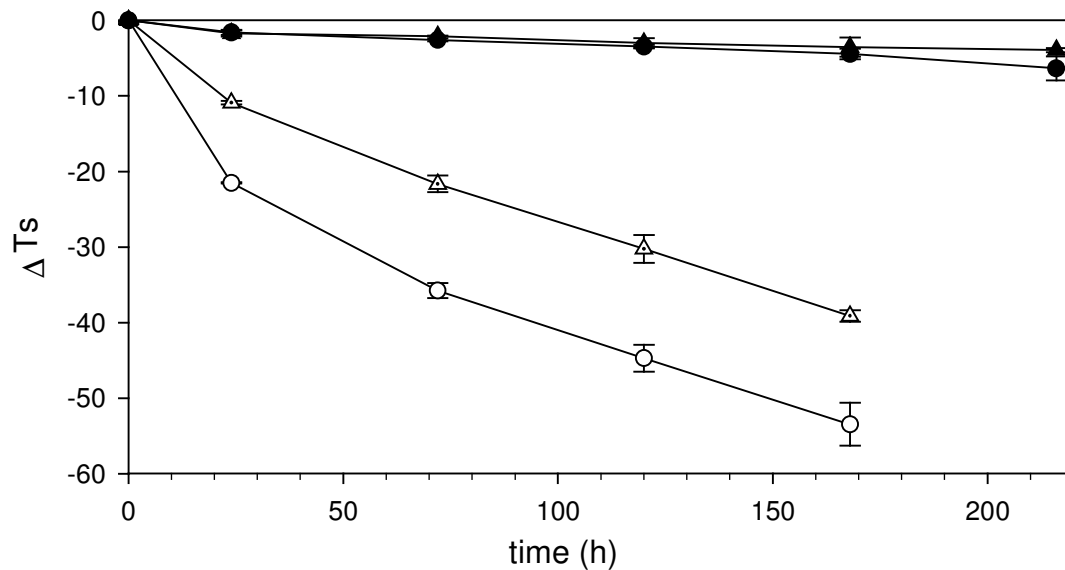


Fig. 2: Storage of leathers at permanent heat; ▲..chromium free; ●..chromium tanned (80°C); △..chromium free; ○..chromium tanned (120°C); T_s ...denaturation temperature fully hydrated)

How to explain this decrease?

In case of fibrous collagen, other than collagen solution, denaturation of the triple helix is an irreversible rate process [7][8][9]. The denaturation rate, which is corresponding to the denaturation temperature, depends on enthalpic and entropic contributions. The enthalpic part, the intrinsic stability of the helix, depends on the hydroxyproline content, pH, addition of hydrotropic agents and salts. That means, this is the sum of the energy of the bonds stabilizing the triple helix. The entropic part describes the chain mobility. To explain this entropic contribution MILES AT AL. [10] applied the theory of a “polymer in a box” on collagen.

Focusing on one triple helix, they postulated a lattice surrounding this helix. This lattice is stiffening the chains and reduces its configurational entropy. The chain mobility strongly depends on interactions with other triple helices of the collagen fibrils. These interactions depend on the swelling state, the volume fraction of water of the collagen molecule and this volume fraction of water highly depends on crosslinking as well as dehydration. Furthermore, the authors showed, that the enthalpy of the triple helix is not affected by covalent crosslinking [11].

COVINGTON [9] had previously expanded some aspects of this theory on different other tanning mechanisms, especially chromium tannage and organic tannage. He summarised that high hydrothermal stability of tanned collagen is created by a rigid matrix around the collagen molecule, partly displacing supramolecular water. This water may also be incorporated in the matrix structure, however. In case of organic tanning like covalent crosslinking of tannins, oxazolidine or mimosin, a matrix out of organic molecules is formed around the triple helix. By this lattice the entropy is reduced and the shrinkage temperature increases.

Chromium tannage is different from all other (especially organic) tannages, however. Up to today a satisfying explanation of the theory of chromium tannage is still missing. COVINGTON (2000) speculated, that the chromium ions form a lattice surrounding the collagen molecules. Part of this lattice is supramolecular water, which is further stabilised by sulfate ions to give high hydrothermal shrinkage temperatures of 110°C [12].

Beside the decrease of the shrinkage temperatures as shown above, we found, that in case of chromium tannage the denaturation enthalpy is reduced by heat storage of chromium tanned leathers whereas chromium free leathers did not show this decrease (data not shown). The latter finding confirms the results of MILES ET AL. [11].

Therefore, in case of chromium free tannage heat storage affects preferably the entropic part of the shrinking rate and the chain mobility is increased. In case of chromium tannage heat storage influences both, enthalpy and entropy, the former decreasing, the latter increasing. This explanation requires that heat storage has to affect the lattice.

The shrinkage temperature of collagen samples strongly depend on the hydration level [11][13][14]. We now precede, that one triple helix can only be denatured or not denatured. It cannot be partly denatured. If the testing material is not homogenous on the molecular level, especially if the lattices of tanning molecules or if dehydration of the material is not homogeneously distributed over the sample, different shrinkage temperatures would result. This would lead to a distribution of shrinkage rates over the sample. Then, during heat storage parts of the samples, this means some triple helices are able to denature while others still remain stable. Lower enthalpies as well as lower entropies could be a result of these partly denatured samples.

Permanent area loss during storage in permanent heat

In further experiments, permanent area loss was measured from the samples. The measurements were performed after reconditioning at 23°C and 50% rel. humidity. Just as the shrinkage temperature the permanent area loss was temperature dependent (Fig 3 and Fig 4).

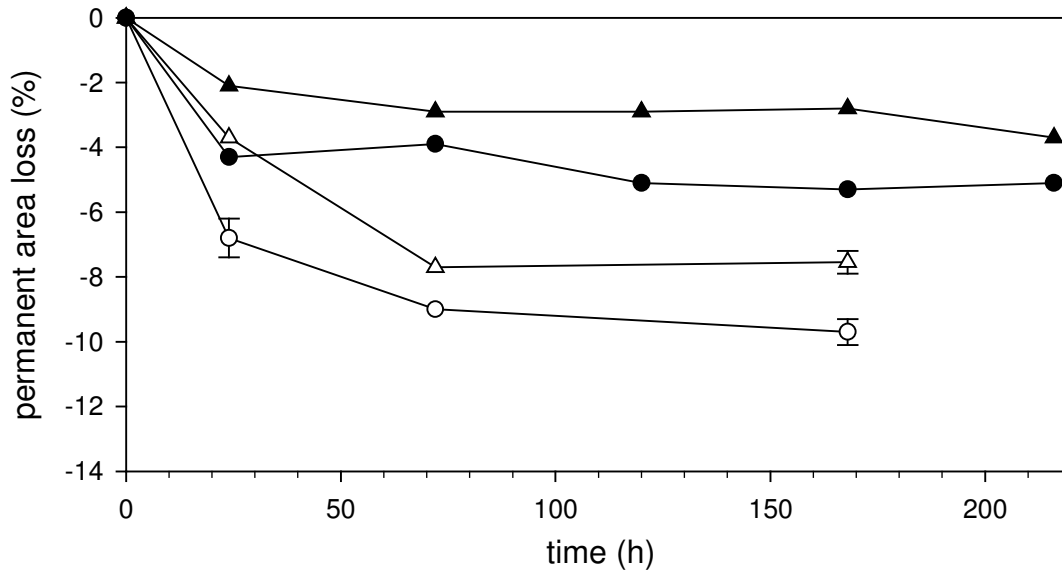


Fig.3: Heat storage of semifinished products; ▲..chromium free; ●..chromium tanned (80°C); △..chromium free; ○..chromium tanned (120°C)

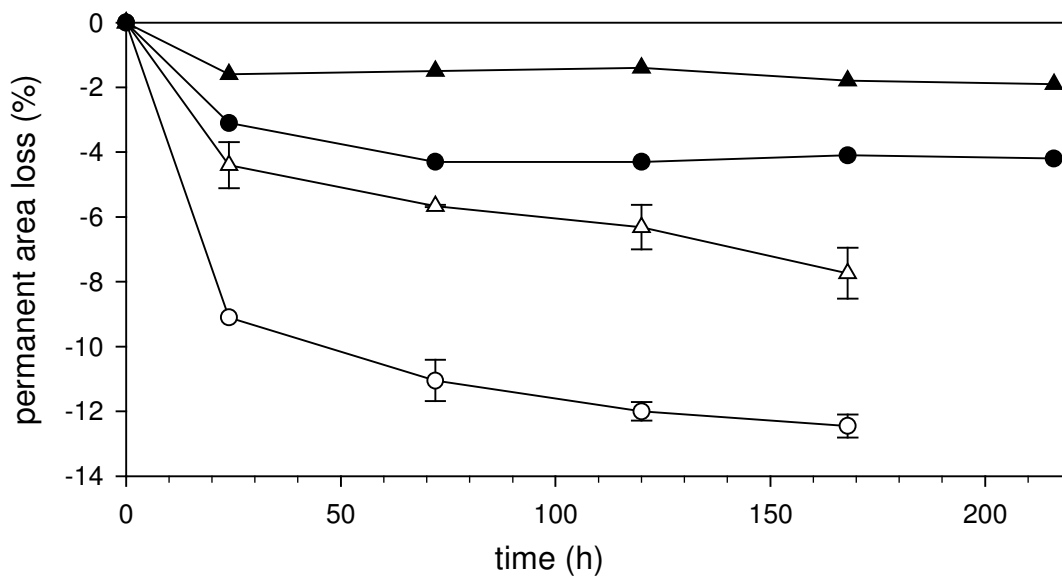


Fig 4: Heat storage of leathers; ▲..chromium free; ●..chromium tanned (80°C); △..chromium free; ○..chromium tanned (120°C)

At 80°C the semi finished products behaved similar to the leathers. Merely the chromium free samples showed a permanent area loss something lower than that of the chromium tanned samples. At 120°C heat storage the chromium free semi-finished product showed lower permanent area loss than the chromium tanned samples.

Preceding, that the permanent area loss is connected to the denaturation of the triple helix, it is surprising, that the amount is different between the chromium free leathers compared to the chromium tanned leathers. This means, that on one hand only parts of the collagen are denaturing beside other parts, which are resting stable. By measuring the permanent area loss the sum of this shrinkage is determined. On the other hand, it was found by other authors [4][5] that the leathers stiffness was increasing with storage in dry heat. The reason for this they speculated are new bonds formed during heating. The stiffening was different between samples which had been chromium tanned and others chromium free samples. If the

formation leads to an alteration of the lattice surrounding the collagen molecules or the collagen molecules itself form the stiffening of the lattice by sticking together, the triple helix would be hindered to denature.

Climate changing tests

The samples were exposed to changing climates, which means a cyclic change of dry heat (110°C, ~0% rel. humid.) and wet climate at lower temperature (40°C, 90% rel. humid.). The samples to be tested were fixed isometrically and the forces were measured. Others were let to shrink or expand and the lengths were measured continuously.

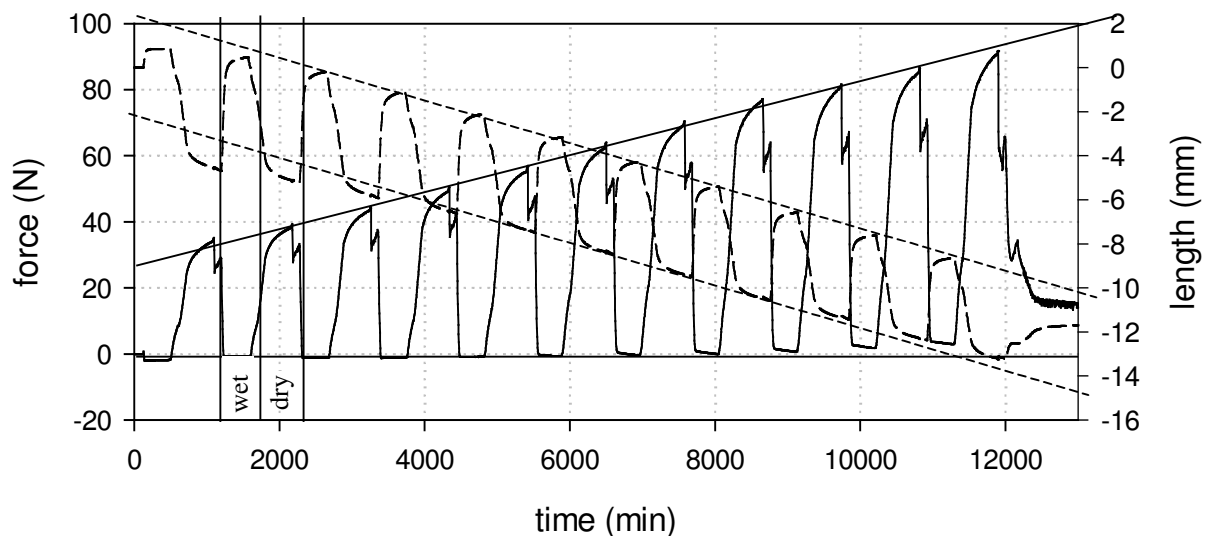


Fig.5: Force (—) measured isometrically and length (---) of a sample of chromium tanned leather during 11 cycles of a climate changing test (110°C; ~ 0% r.H./40°C 90% r.H.). During one cycle the forces are changing because of drying and wetting. The maxima of the forces are increasing with each new cycle. The length shows changing inside of each cycle and a permanent decrease with increasing number of cycles.

All samples, the chromium free, the chromium tanned as well as leathers and semi finished showed changes in length and of the forces during each cycle (Fig. 5 and Fig. 6). This led to a cyclic changing of length and force of the samples. The alteration of force and length inside one cycle is a result of wetting and drying. To confirm this, the influence of temperature was excluded by only changing humidity (25% r.h.; 50% r.H.) at constant temperature (Fig. 7). It could be observed, that the semi finished showed the highest forces up to around 50 N. The leathers showed low values around one tenth of this. This means, that semi finished is very sensible to changes of humidity, whereas leather is more robust.

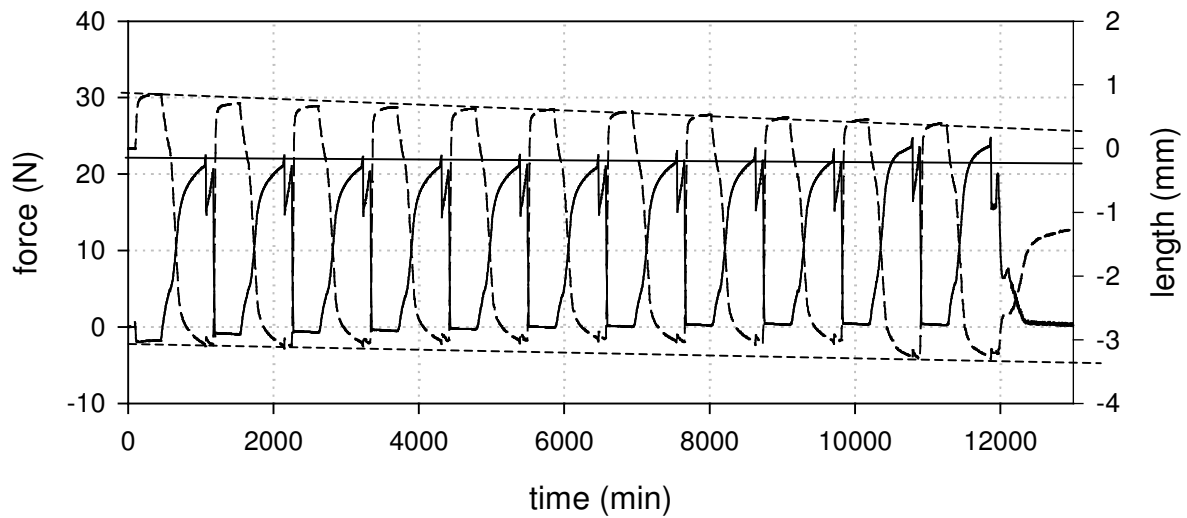


Fig.6: Force (—) measured isometrically and length (---) of a sample of chromium free tanned leather during 11 cycles of a climate changing test (110°C; ~ 0% r.H./40°C 90% r.H.). Length and forces are again changing during each cycle. The length of the samples in dry state is only slightly decreasing during 11 cycles, the maximum forces show no increase.

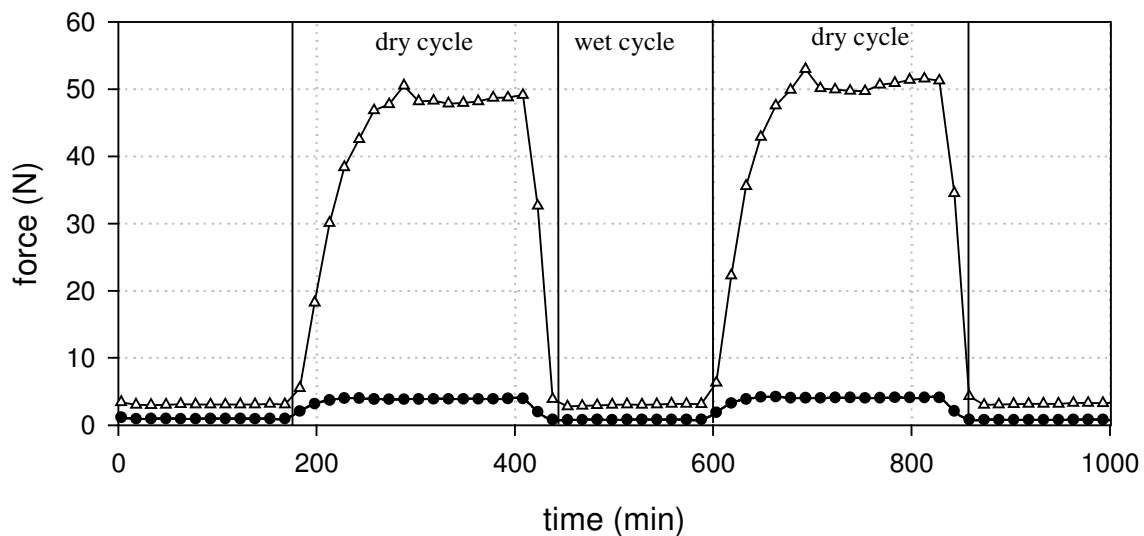


Fig. 7: Forces of leathers and semi-finished products under climate changing conditions (23°C, 50% r.H.; 23°C, 25% r.H.; Δ ..chromium free semi-finished; \bullet chromium free tanned leather

Shrinkage of collagen and leather because of drying is a phenomenon which has already been widely described and discussed. LI ZHIGIANG ET AL. [1] and RENTARIA AND HEIDEMANN [2] investigated the influence of different technological parameters on softness and tension of leathers after drying. They found, that leather generally generated a tension when reaching a water content lower than ~25%. If these leathers were not fixed, they were shrinking during drying. At temperatures higher than 35°C they found, that the leathers began to loose their softness. These leathers were difficult to rehydrate. WRIGHT AND ATTENBURROW [15] and

STURROCK ET AL. [16] investigated set, mechanical behaviour and fiber orientation of chromium tanned semi finished after drying under strain. They observed, that the deformed state of these materials was fixed during drying under monoaxial strain, so that this set was not completely reversible by rewetting of the samples. Application of biaxial strain while drying led to stiffening of the samples.

As reason for the reversible shrinkage capillary forces are discussed, generated in the capillaries of the leather structure during drying [17][18]. These capillary forces are generated only when removing the water in liquid state, not by freeze drying or drying after soaking in organic solvent (“Acetonblösse”).

Furthermore, our results show however, that the force maxima of chromium leather (Fig 5) increased in dry state from cycle to cycle during climate changing and the length decreased permanently, whereas chromium free tanned leathers showed no increase in maximum force and lengths (Fig. 6). Under the conditions applied here, the forces were completely reversible in wet state of the cycle for both leathers.

The reason for the increase of the forces of chromium leather, with increasing cycle number remains unclear. It can neither be a result of thermal shrinkage of the triple helix nor a result of fibre orientation, because then no difference would be expected to chromium free samples. Up to now the only possible explanation is a change of the molecular structure of the chromium-water lattice, which would have to lead to other capillary structures. Furthermore these structure would have to alter more and more with each cycle of the climate changing test.

Conclusions

The decrease of denaturation temperature during heat storage may be explained by alteration of the enthalpic and entropic contribution of the shrinkage rate by this heat storage. Presumably these alterations do not happen homogenously. Therefore, on the molecular level these alterations lead to distributions of the shrinkage rates inside a sample. This concept may also explain the slowly occurring shrinkage of the samples (permanent area loss) during heat storage as well as during climate changing test. A satisfying explanation for the increasing forces during climate changing especially in the case of chromium tanned leather is still missing, however. Up to now, the shrinkage of leather is explained by capillary forces. One can speculate, that the increase is caused by changing of the pore distribution.

References

- [1] Renteria, L, Heidemann, E, Das Leder 34 (1983) 188
- [2] Zhiqiang, L, Renteria, R, Heidemann, E, Das Leder 34 (1983) 170
- [3] Covington, AD, 3rd Freiberg Collagensymposium 2004
- [4] Scheibe, R, Wolf, H, Das Leder 6/7 (1997) 134
- [5] Kellert, J, Hummel, A, Germann, HP, Leder und Häutemarkt 3 (2000) 25
- [6] Trommer, A, Meyer, M, IULTCS Congress Florence (2005)
- [7] Weir, CE, JALCA 44 (1949) 108
- [8] Miles, CA, J Mol Biol 245 (1995) 437
- [9] Covington, AD, 2nd Freiberg Collagensymposium
- [10] Miles, CA, Ghelashvili, M, Biophysical Journal 76 (1999) 3243
- [11] Miles, CA, Avery, NC, Rodin, VV, Bailey, AJ, J Mol Biol 346 (2005) 551
- [12] Covington, AD, JSLTC 85 (2000) 24
- [13] Miles, CA, Burjanadze, TV, Biophys J 80 (2001) 1480
- [14] Kopp, J, Bonnet, M, Renou, JP, Matrix 9 (1989) 443
- [15] Wright, DM, Attenburrow, GE, J Mat Sci 35 (2000) 1353
- [16] Sturrock, EJ., Boote, C, Attenburrow, GE, Meek, KM, J Mat Sci 39 (2004) 2481
- [17] Komanovski, M, JALCA 86 (1991) 269
- [18] Mertig, M, Tuckermann, M, Pompe, W, Reich, G, 2nd Freiberg Collagensymposium (2000)