



INFLUENCE OF GLYCERIN ON DENATURATION TEMPERATURE OF CHROME- AND VEGETABLE-TANNED LEATHER

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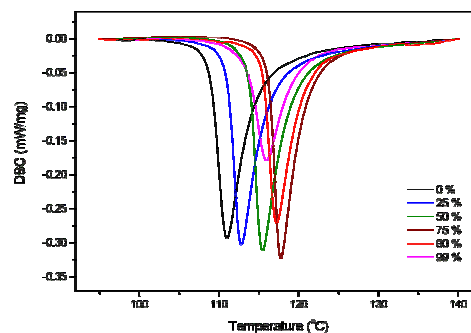
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The aim of this preliminary study was to observe the effect of glycerin on the denaturation (shrinkage) temperature of leather. For this, samples of chrome- and vegetable-tanned leathers were analyzed by DSC measurements while immersed in pure water, glycerine-water solutions of different concentrations (25, 50, 75, 90%) and pure glycerin, in pressure-tight crucibles. The denaturation temperature, T_d , of chrome-tanned leathers has shown an increase when measured in glycerin solutions up to 75 – 90% concentration, and a slight decrease in pure glycerin. Quite interestingly, for vegetable-tanned leathers measured in similar conditions, an opposite behavior was observed. These results indicate that glycerin alters the denaturation process of both types of leather, but in a different way. A possible explanation for this phenomenon was proposed.



INTRODUCTION

The denaturation (or shrinkage) temperature (hereinafter noted T_d) is of great importance in the leather industry, being used in quality-control of finished leathers. Its value reflects the hydrothermal stability, *i.e.* the resistance to wet heat. When this temperature is reached, the collagen protein of a wet leather sample denatures, this process being physically reflected by a significant shrinkage of the sample's dimensions. The value of T_d is routinely determined by observing the length variation of the sample which is immersed in water and heated with a constant rate (usually between 2-5 °C min⁻¹). For chrome-tanned leathers the shrinkage temperature is generally above 100 °C and these tests are usually conducted in glycerin-water solutions. Most

standards (including ASTM D 6076 – 03), specify a 75% glycerine solution, while other few standards mention a different concentration or even undiluted glycerine. The correct approach would be however the use of an apparatus with water under pressure for working in true hydrothermal conditions, as pressure-tight instruments are recently commercially available and allow measuring of the leather samples in water up to 115 °C.

The aim of our study was to observe whether glycerin affects the denaturation temperature of chrome-tanned leather as compared to true hydrothermal conditions. For this, samples of chrome-tanned leathers were analyzed by DSC measurements while immersed in pure water, glycerine-water solutions of different concentrations and pure glycerine, in pressure-tight crucibles. We

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also performed a similar study on a vegetable-tanned leather for making a comparison of the effect of glycerine on both types of leathers.

RESULTS

The DSC curve of chrome-tanned leather immersed in water displayed a peak of denaturation with a maximum at 111.2 °C (Fig. 1a), which agrees well with the shrinkage temperature of this type of leathers.¹ With increasing glycerin concentration a progressive shift of this peak to higher temperatures is observed, up to 75% glycerin (the corresponding T_d is 116.7 °C). At the same time, the height of the peak constantly increases, and the peak becomes narrower (the halfwidth is reduced from 3.5 °C for water-immersed sample to 2.9 °C for the sample immersed in 75% glycerin solution). The corresponding enthalpies of these peaks are in the range 50–54 J/g. Interestingly enough, on further increasing in glycerin content, the variation of T_d shows an opposite trend. Thus, for sample immersed in 90% glycerin solution a slight shift of T_d to a lower value is noticed, while for the sample immersed in pure glycerin a further decrease in T_d , accompanied by a significant broadening and lowering of the peak (halfwidth value of 3.8 °C and an enthalpy of 41 J/g), is observed. For vegetable-tanned leather, the denaturation peak in water exhibits a minimum at 82.8 °C, which is typical for such kind of leathers (Fig. 1b).²⁻⁴ The corresponding enthalpy of denaturation is 28.3 J/g,

in very good agreement with literature data,⁴ almost a half of that of chrome-tanned leather. When measured in glycerin solutions, an opposite behavior was observed, as compared to the chrome-tanned leather. Thus, on increasing the glycerin content of the solution up to 75%, the denaturation peak shifts to lower temperatures from 82.8 to 75.2 °C, then, at high glycerin content (90 and 99%) reverts its trend showing a slight increase in T_d , up to 77.5 °C (in pure glycerin). The overall variation of T_d versus glycerin concentration, for vegetable tanned leather, is thus of the same magnitude with that observed in the previous case, but has almost a mirror-reflected shape (Fig. 2a).

A gradual decrease in peak height and a peak broadening, which becomes larger with the increase of glycerin concentration, is observed for vegetable-tanned leather samples. Thus, the halfwidth of the peaks increases from 3.3 °C (in water) to 5.8 °C (in glycerin), a variation which is larger than in the previous case. The enthalpy which remains rather constant between 0 – 50% glycerin, then decreases sharply, reaching a value of 17 J/g for the sample immersed in pure glycerin. The enthalpy variations for both types of leather have thus similar shapes (Fig. 2b). However, the reduction in ΔH at high glycerin concentration is more pronounced in vegetable-tanned leather than in chrome-tanned one, suggesting a stronger destabilizing effect of glycerin on the former.

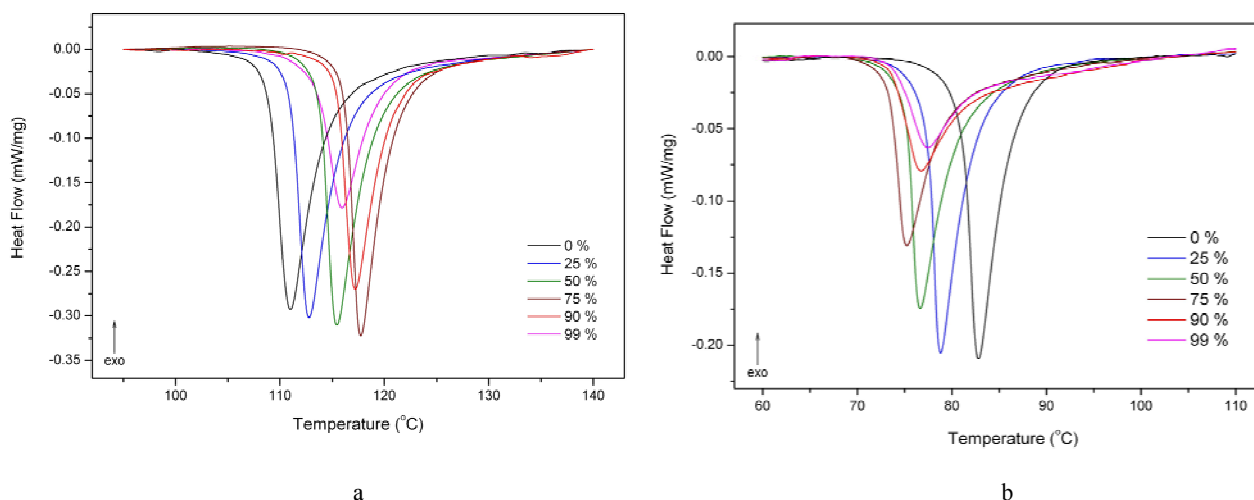


Fig. 1 – DSC curves in glycerin-water solutions for: (a) a chrome-tanned and (b) a vegetable-tanned leather. Glycerin concentration is given (0 and 99% stand for pure water and glycerin, respectively).

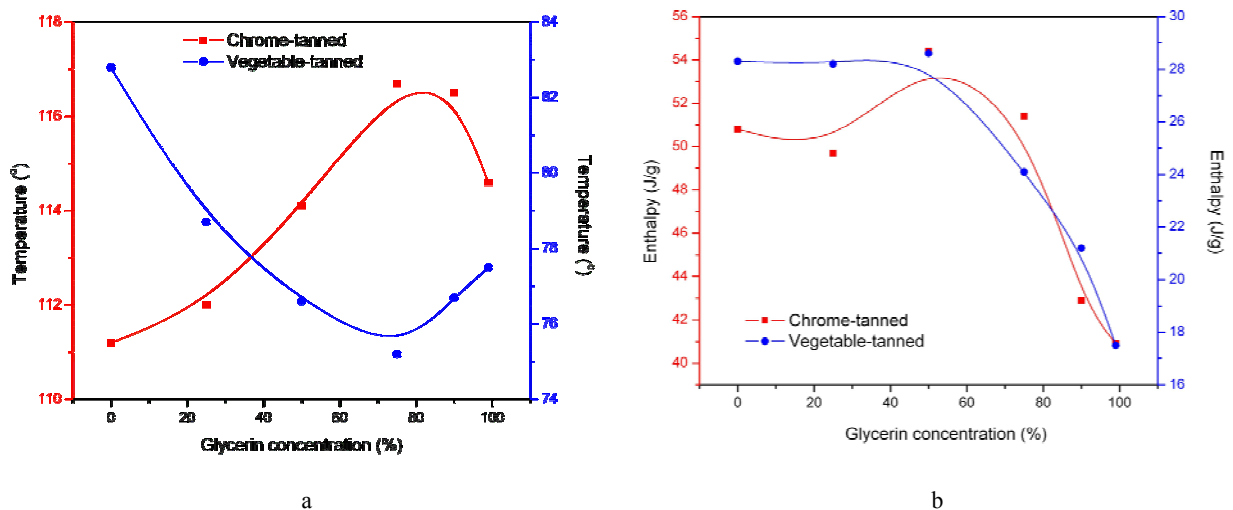


Fig. 2 – Plot of (a) denaturation temperatures, T_d , and (b) enthalpies of chrome- and vegetable-tanned leather vs. glycerin concentration.

DISCUSSION

Leather is a complex material, being mainly composed of a matrix of collagen, fibrils, fibers and bundles, crosslinked with tanning agents. Hence, interactions are expected to occur between the leather's components and glycerin. These interactions can have a decreasing or increasing effect on the denaturation temperature of leather.

The first one is the interaction of glycerin with collagen protein, the main constituent of leather. There are several studies in the literature concerning this type of interaction, performed mainly on solutions of collagen.⁵⁻⁸ The general observation was that glycerin stabilizes triple-helical structure of solubilized collagen, as reflected by an increase in the denaturation temperature. This was explained by the binding of glycerin molecules to the surface of the collagen molecule through incorporation of its hydroxyl groups into the water-chain structure.⁸ However these studies were performed with glycerin solutions of low to intermediate concentrations (up to 6M, ~50% by mass). At higher concentrations, the reduction in water content of the sample will result in a shift of T_d toward higher temperatures, according to the “polymer-in-a-box” mechanism proposed by Miles and Ghelashvili.⁹ The strongest effect is expected to occur in pure glycerin. It must be mentioned, however, that leather contains about 10-20% water as moisture, and thus, even if an anhydrous solvent would be used (which was not the case in our study), a quite significant water amount would still be present in the sample.

The second interaction is that between glycerin and tanning agents, which are chromium ions (in chrome-tanned leather) and plant polyphenols (in vegetable-tanned leather). Glycerin is expected to interact with both types of them due to its three hydroxyl groups, thus acting as a ligand toward chromium ions and as hydrogen bond donor toward polyphenols. This interaction most probably will lead to a decrease of T_d by weakening the bonds between collagen and tanning agents.

In the light of these suggested mechanisms, the increase of T_d for chrome-tanned leathers may result as a consequence of binding of glycerin to the surface of the collagen molecule through incorporation of its hydroxyl groups into the water-chain structure, in the same way as proposed for solubilized collagen. At very high glycerin concentrations, glycerin may remove chromium(III) ions from leather by complexing them, thus decreasing the T_d .

For vegetable-tanned leathers, one expects that glycerin will remove the vegetal tannins from leather by dissolving them. This will deprive the leather of tannins, yielding a less crosslinked collagen matrix. As a consequence, the denaturation temperature will tend to decrease toward a value corresponding to that of native collagen (which is about 65 °C). This mechanism could be responsible for the shifting of T_d of these samples to lower temperature for glycerin solutions up to 75%. At very high glycerin concentrations, the low water content of the remaining collagen would decrease its denaturation temperature, as expected by the “polymer-in-a-box” theory.

For both vegetable- and chrome-tanned leathers the enthalpy of denaturation significantly decreases at glycerin concentrations above 50%, reaching the

minimum value in pure glycerin. This suggests a disruption of the network of hydrogen bonded glycerin molecules surrounding the collagen.

Research is under way in order to complement, verify and explain the results obtained in this preliminary work.

EXPERIMENTAL

Materials and methods

Chrome and vegetable tanned leathers processed with chromium basic salts and respectively, with mimosa were manufactured at Leather Research Department from Leather and Footwear Research Institute (Bucharest, Roumania), by usual procedures. Glycerin solutions with 25, 50, 75 and 90% volumetric concentrations were prepared by thoroughly mixing appropriate volumes of glycerin and distilled water.

The DSC measurements were performed using a DSC 204 F1 Phoenix instrument (Netzsch, Germany). Samples typically weighing 6–7 mg were placed in pressure-tight stainless steel crucibles (~ 40 μ l) which were filled with the corresponding glycerin solution, closed with stainless steel lid provided with PTFE seal, left for about 1 hour for equilibration, then heated from room temperature to 160 °C at 2 °C min⁻¹. The reference was a closed empty crucible.

CONCLUSIONS

The present study shows that measuring the denaturation (shrinkage) temperature of a chrome-tanned leather in a glycerin solution yields a higher value (by several degrees °C) as compared to true

hydrothermal conditions. The magnitude of this effect depends on the glycerin concentration, being maximum at about 75-90% glycerin. Measurements in water and pressure-tight vessels for this kind of materials would thus be recommended for obtaining actual T_d values. For vegetable-tanned leather, the observed opposite effect suggests a different mechanism of action, most probably due to different nature of tannin agents.

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