

Evaluation of (re)tanning effect of leather chemicals in a model and a real system

Yujie Ma, Roberto Rumnit, Wouter Hendriksen
Smit & Zoon

In the large portfolio of retanning chemicals, it is important to distinguish between the effect of different chemicals on leather in order to effectively develop new products that can deliver differentiated functionalities. However, the traditional route for such a process is very tedious and costly due to the fact that:

1. Tests need to be done on leather, which is a natural material that presents inevitable variations making comparison tests rather difficult to reproduce;
2. Reliable results require large amount of starting material (leather) and work since full wet-end recipes need to be applied for each set of tests;
3. Wet-end leather application recipes are rarely standardised in a simplified manner to ensure that the obtained results will have a real predictive character.

In order to effectively and efficiently screen newly developed leather chemicals in a less costly manner, we set out to develop an affordable, standardised model system that can simulate the natural substrate of leather. Accompanying analytical tests can provide direct correlations of what can be expected when certain retanning chemicals are applied.

The Model System

Since the basic component of leather is collagen, it was hypothesised that it would be logical to use gelatin as the base material for the model system due to its origin and resemblance to native collagen⁽¹⁾. Gelatin is made through heat treatment of animal parts and, from a chemical point of view, gelatin can be considered as the hydrolysed form of collagen. Widely used in many areas such as food, film and paper as well as pharmaceutical industries, gelatin can be made presenting different properties, but generally gelatin dissolves in hot water and forms a gel upon cooling. Starting from collagen, the extraction process of gelatin changes the molecular organisation of the collagen structure. The gelling properties of gelatin upon cooling are believed to be a kinetic process, which is related to the partial recovery of collagen's helix fibre structure (coil – triple helix transition).

In this paper, a model system based on glycerol containing gelatin films is described to simulate the real substrate of leather. To simplify the research, a series of synthetic polyphenolic retanning chemicals with known difference in their retanning performance in the wet-end is used as the test chemicals on the model system. After applying varying amounts of test chemicals, the mechanical properties of the gelatin films are measured and compared.

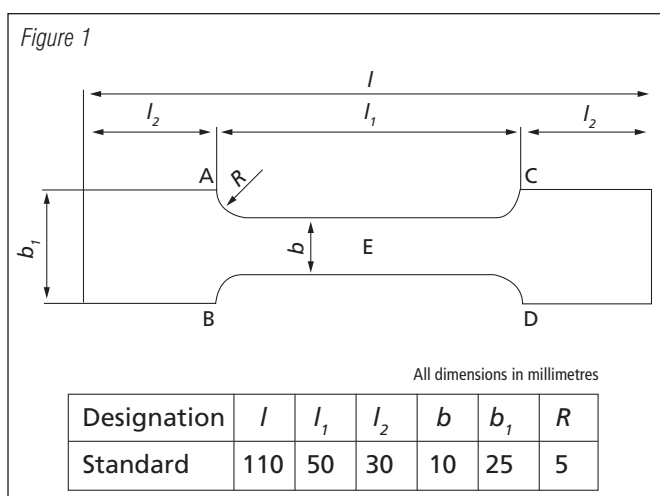
The Real System

In parallel, the same set of phenolic syntans are applied at the same amounts onto glutaraldehyde (GA) pre-tanned leather and the increases of shrinkage temperature (Ts) of the leather are measured. The differences of the measured mechanical properties of the model system of gelatin films are compared to the differences of Ts increase, to determine whether obvious correlations between the two systems can be observed.

Materials and Methods

Model system of gelatin films

Gelatin films are made from bovine gelatin (type B; Sigma Aldrich, Saint Louis, Missouri) with a Bloom strength of 225g. Glycerol (>99.5%, Sigma Aldrich, Saint Louis, Missouri) is used as a plasticiser for the preparation of the gelatin films. The films are cast in 12 cm² polystyrene square petri dishes by starting with a 10% (w/w) aqueous solution (demi water) of gelatin in a beaker with varying amounts (0-50% w/w of gelatin) of glycerol added. This is left to swell at room temperature for 30 minutes before raising the temperature to 55°C under mechanical stirring (100rpm). At 55°C (re)-tanning agents are incorporated into the mixture (0-5-10-20-30% w/w of gelatin) and the mixtures are set to react for 30 minutes under mechanical stirring at 100-140rpm. Afterwards 45 ± 0.2 grams of the mixture is poured into the petri dishes and settled on a steady surface until cooled to room temperature. To further settle the structure of gelatin, it is refrigerated at 4°C for 30 minutes, followed by 30 minutes of re-heating at 30°C to reduce the amount of water (in order to create a better film). The samples are further brought to equilibrium in a Wekk 028 climate chamber (Weiss Technik, Belgium) at 23°C and 50% relative humidity for a minimum



duration of 36 hours before testing, by which time most of the water has evaporated leaving a thin gelatin film that is then manually separated from the petri dish. A standard dumbbell shaped mold (Figure 1) is used to cut 3 strips from each 12cm² sample. 9-12 pieces of gelatin film of each composition are prepared and measured.

Mechanical properties of the film such as elongation at break (Eb), tensile strength (Tn), maximum force (Fmax) and elastic modulus (E-mod) are measured using a tensile testing machine (Zwick/Roell, s/n: 196335, 2010 equipped with a 2.5 kN loading cell). The tensile testing machine is set with a pre-load of 0.2 N, a test speed of 10 mm/min and a grip to grip separation at the start position with a value of 50.00 mm. All measurements are performed at temperatures between 20-25°C and a relative humidity between 30-50%.

Via the plot of stress versus strain from the tensile testing machine, four parameters are obtained. The tensile strength Tn/Ts is calculated by dividing the maximum load by the initial cross-sectional area of the specimen. Elongation at break Eb is calculated by dividing the extension at rupture of the specimen by the initial gauge of the specimen (50 mm). Elastic modulus E-mod is obtained as the slope of the linear range of the stress-strain curve. This is calculated via the following formula:

$$E - mod = \frac{[L_0 \cdot (X_H - X_L)]}{[A \cdot B \cdot (L_H - L_L)]}$$

With L_0 being the initial gauge length (mm)

X_H : the end of tensile modulus determination (N)

X_L : the beginning of tensile modulus determination (N)

A: Specimen thickness (mm)

B: Specimen width (mm)

L_H : Strain at X_H (mm)

L_L : Strain at X_L (mm)

It should be noted that this is an estimate of the elastic modulus due to not having a perfect linear range (as a result of the grips available for this test).

The solid content of the gelatin films is determined via a halogen moisture analyser (HR73, Mettler Toledo, Ohio, US). A minimum of 2 grams used as this is recommended to reach a repeatability of $\pm 0.1\%$.

Table 1: Phenolic retanning chemicals selected for this study.

Phenolic syntan	Mw (g/mol)
A1	20, 288
B16	13, 241
C28*	N/A
L33**	10, 072

* C28 is a semi-finished product, the Mw of which is expected to be lower than that of A1 and B16.

** L33 is prepared from a base recipe that is different from the rest of the samples, and its Mw weight is measured following a slightly different analysis protocol and therefore it cannot be directly compared to Mw of the other samples.

Selected phenolic syntans

Four different phenolic syntans synthesised from the same basic polycondensation chemistry, but with varying molecular weights (Mw) produced by Smit & Zoon's factory in the Netherlands from different chemical processes are used for the study, see Table 1.

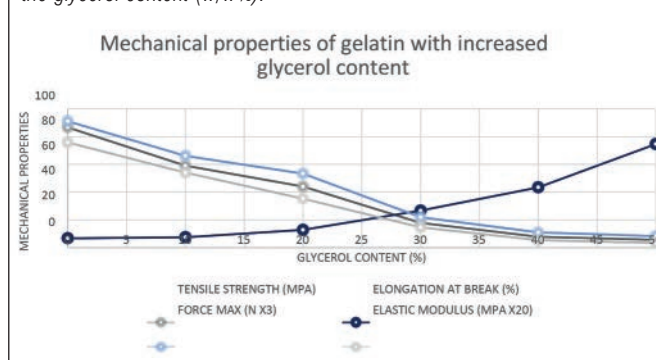
Real system of wet-white leather

Leather pieces from Italian bulls, pre-tanned with glutaraldehyde are used. Shrinkage Temperature (Ts) of the leather pieces are measured according to ISO 3380/IUP16 using standard equipment⁽²⁾. After retanning treatment with the selected syntans, leather samples with dimensions of 50 ± 2 mm (for a thickness < 3 mm) are immersed in a vessel filled with de-ionised water in order to properly "wet" or soak the leather for a duration of 5 minutes. Afterwards the leather pieces are punctured to fit into the piece holders and submerged into the beaker of the standard equipment. The temperature of the heating element is increased at a regular rate (often at 2°C/minute) from a starting point at 10°C below the actual Ts. Intervals of 30s are taken to record the temperature and the distance shrunk. The recorded shrinkage temperature is considered the point at which 1% of the total length of the specimen shrinks.

Dependence of mechanical properties of gelatin films on glycerol content and other experimental conditions

Glycerol has been used as the plasticiser for the gelatin films in order to overcome the brittleness and enhance the flexibility and peelability of the films^(3,4). The most suitable gelatin film composition is determined by comparing the

Figure 2: Dependence of tensile strength Tn, elongation at break Eb, maximum force Fmax and elastic modulus E-mod of the gelatin films on the glycerol content (w/w%).





mechanical properties of gelatin films with varying amounts of glycerol content ranging from 0-50% (w/w). In general, it is observed that the higher the glycerol content, the more flexible the film becomes, which is illustrated by changes in the following mechanical parameters: Fmax, Tn, Eb and E-mod. As an example, the trend in changes of the tensile properties of the films as a function of the glycerol content are shown in Figure 2. Very similar trends are also observed in Fmax and E-mod of the film. The elongation at break Eb of the film followed an exactly opposite trend.

For all tests on retanning chemicals, a film composition containing 30% (w/w) glycerol is used as the fixed recipe due to the fact that both the Eb and the E-mod of the films have sufficient space to be manipulated at this glycerol concentration.

It is also found that pH and salt concentration can affect the mechanical strength of the gelatin films. For example, Fmax, Tn and E-mod show a consistent increase in the acidic pH range of 3-5.5.

After applying varying amounts of syntans from 1-30% (w/w of gelatin), all the mechanical property parameters are measured again. Results in terms of Eb and E-mod are shown in Figure 3. Compared to data obtained from blanco gelatin films, when no phenolic syntans have been applied,

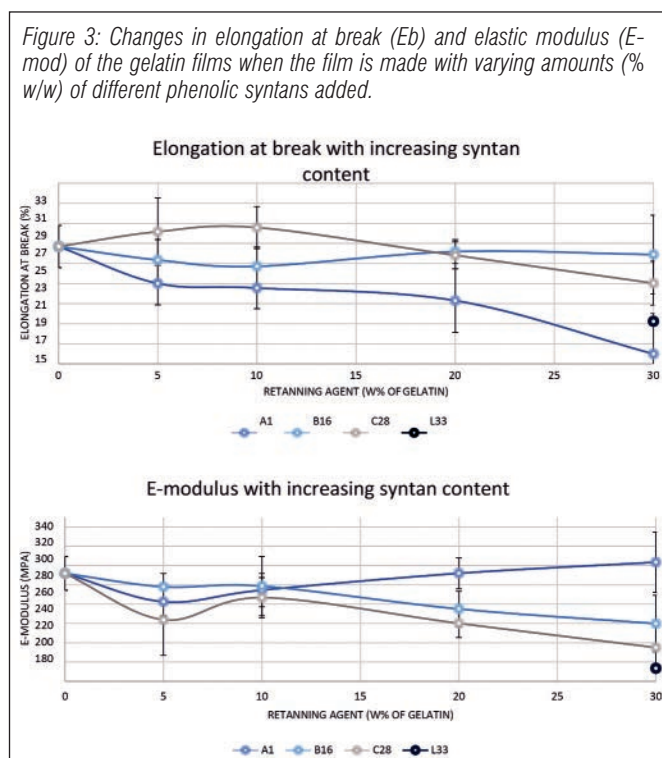


Table 2: Highest relative changes (in percentage as compared to data obtained on blanco gelatin films without phenolic syntans) of various mechanical parameter of the gelatin film with different amounts of phenolic syntans applied.

	Syntan A1 (%)	Syntan C28 (%)	Syntan B16 (%)
Fmax (N)	+26.3	-27.9	-6.3
Tn (MPa)	+6.4	-37.7	-22.9
Eb (%)	-80.0	+62.9	-1.3
Emod (MPa)	-12.0	-42.5	-29.0

Table 3: Shrinkage temperature changes of wet-white leather with varying amounts of phenolic syntans applied (10- 30% w/w of the starting material).

Ts (°C)	Additive	ΔT (°C)
68.0 ± 1.0	none	0
73.5 ± 0.5	Syn A1 (10%)	5.5
79.0 ± 1.0	Syn A1 (20%)	11
80.5 ± 0.5	Syn A1 (30%)	12.5
74.5 ± 0.5	Syn B16 (20%)	6.5
74.5 ± 0.5	Syn B16 (30%)	6.5
78.0 ± 0.5	Syn C28 (30%)	10
75.5 ± 0.5*	none	0
69.0 ± 0.5	L33 (10%)	3.5
74.0 ± 0.5	L33 (20%)	8.5
76.5 ± 0.5	L33 (30%)	11

* for this set of experiments a different blanco reference has been taken and measured.

Fmax, Tn and E-mod of films containing varying amounts of syntan A1, C28 and B16 in general show a rather consistent initial decrease when the syntans are introduced at amounts of 0-5% meaning that the films becoming more elastic at this composition range, beyond which a different trend until the application amounts reach 30%. As can be expected Eb shows an opposite trend. Significant changes in the mechanical properties of the gelatin films are seen when syntans are added at more than 20-30% of the weight of the gelatin, which is likely due to a big change in the nature of the films. Table 2 lists the maximum percentages of change seen on different parameters of the mechanical properties of the films containing the different syntans.

Table 3 shows the shrinkage temperature changes of wet-white leather pre-tanned with glutaraldehyde and then treated with varying amounts of different phenolic retanning agents. An increasing trend in shrinkage temperature can be seen with increasing amounts of applied syntans, but the effect seems to level off at higher amounts of syntan application (20-30%).

While the mechanical properties of the gelatin films containing the retanning chemicals do not show consistent trends with increasing amounts of the chemicals added, the shrinkage temperature changes follow the same trend: the higher the amount of each retanning chemical used, the higher the shrinkage temperature of the leather becomes. However, due to the slight structural differences between the different phenolic retanning chemicals, their effect on shrinkage temperature increase indicating their (re)tanning effects also show differences. From the samples that were chosen for this study, the most significant (re)tanning effect is shown by syntan A1, followed by C28, L33, and the least effect is observed for syntan B16.

Observations, conclusions and recommendations

The objective of the present study was to correlate shrinkage temperature changes of wet-white leather, pre-tanned with glutaraldehyde and treated with various phenolic syntans, to changes of the mechanical properties of gelatin films when different phenolic retanning chemicals are incorporated at similar weight percentages. Overall,



employing a model system using gelatin, valuable insights were obtained. For each specific phenolic syntan, an individual trend could be seen in both the increase of shrinkage temperature and the changes in mechanical properties (F_{max} , T_n , E_b , E_{mod}) when an increasing amount is used in the range of 5-30%. However, the differences observed for the mechanical properties of gelatin films containing different syntans are not consistently following the same trend, whereas the shrinkage temperature changes are. In conclusion, the developed gelatin film system as such cannot be directly used as a model system for evaluating the (re)tanning effects of different syntans on leather.

A possible explanation for the above-mentioned conclusion is that known parameters that can influence the mechanical properties of gelatin films are pH and salt concentrations. All selected syntan products have different characteristics such as 10% pH, acid values and ash values, which can affect the pH and salt concentrations of the gelatin system, therefore leading to changes in mechanical properties that cannot be directly linked to the effect of the phenolic polymeric ingredients alone.

In order to verify this theory, it would be recommended to perform a study in which a new series of experiments using, for example, syntans with similar structures and varying Mw but not formulated to contain additional chemical ingredients. In addition, all experiments in the present study do not take into account any unbound chemicals which should be

considered in future experiments. Furthermore, rheology may be used to follow the mechanical properties of the gelatin system with varying compositions under different temperatures, the result of which to be compared with dynamic mechanical thermal analysis of leather^(5,6) with the same amounts of chemicals applied to see if additional information and correlations can be obtained on the viscoelastic transitions of the two systems. ☺

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