Use of Viscoelastic Changes to Demonstrate the Relationship Between Drying Parameters – A Preliminary Study

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Abstract

Dynamic mechanical thermal analysis (DMTA) is routinely used for mechanical analysis by the polymer industry to provide information on the viscoelastic properties of a material. This report reveals how DMTA has been used to further previous studies by providing insight into the differences between post-tanned leathers (chromium and chromium-free). It demonstrates the potential to correlate the results with an industrial application such as optimization of the drying conditions during cell rotary conditioning (CRC). DMTA can indicate leather fiber response to changes in atmospheric humidity and temperature, potentially facilitating real-time adaptation of conditions during leather drying. Initial DMTA results show that post-tanning, particularly fatliquoring, changes the rate of drying and allows scientists to advise on optimal leather drying conditions based on viscoelastic changes.

Introduction

The drying of leather is arguably one of the more crucial steps in leather manufacture and can be a source of leather damage and area loss (or a reduction in area gain).[1] This is partly illustrated by the plethora of drying technologies available on the market that cater for a multitude of needs.

Liu *et al*. are continuing work to elucidate the mechanism of drying leather[2-5] and its resulting physical properties.[6-9] The understanding of water movement in leather during drying has improved: it is now known that during constant rate drying (first-phase drying) the mechanism of water removal is evaporative and is rate-governed by the water-carrying capacity of the air, surface area of drying interface and rate of replenishment of water to the leather surface (see Equation 1). Water-carrying capacity is affected by temperature, the relative humidity and the flow speed of air over the leather.[10]

$$\frac{dW}{d\theta} = \frac{hAT}{\lambda} \qquad (1)$$

Where $dW/d\theta$ is the rate of drying, h is the heat transfer coefficient, A is the surface area, T is the temperature difference between the surface and air stream and λ is the latent heat of evaporation.[11,12]

The replenishment rate of the water at the drying surface is affected by the surface area requiring that water, the porosity of the leather and the tortuosity factor of the leather. If a high replenishment is required the force of the capillary action may result in a rapid narrowing of the fiber spaces[13,14] which is observed as shrinking.

The mechanistic understanding does not address the issue of real time measurement of mechanical property changes which has been less well defined and in addition the intricacies of leather manufacture that result in different leathers make it unclear how this affects the drying conditions/parameters required to obtain maximal performance from the leather.

The leather industry has long known of and manipulated the different processing parameters that impart different viscoelastic properties to the leather,[15] however this is normally judged qualitatively by touch/ feel or an investigation using a range of instruments and has been difficult to quantify quickly. Previous research has probed dynamic mechanical thermal analysis (DMTA) as a possible solution to this issue and more recent work has addressed the limits of this apparatus.[16]

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DMTA is widely used in the polymer industry as an analytical method for quantifying the viscoelastic behavior of materials under various environmental conditions, however its use in leather research and industry has been less widely publicized. However DMTA lends itself to studying the complex polymeric matrix of tanned collagen as well as quickly quantifying the effect of water content on the system.

As with all polymers, collagen exhibits viscoelastic properties which can be studied using DMTA, by applying a sinusoidal stress to a sample and measuring the resultant strain. The material can be modeled as a mixture of elasticity (E' – associated with energy storage) and viscosity (E'' – associated with energy loss).[17] It is more common to refer to the ratio of these two moduli (tan δ) which demonstrates the damping of the sample, i.e., the dissipation of energy during a cyclic load (E E''/E').[18]

Jeyapalina *et al*. addressed whether DMTA was a suitable technique to study the effects of drying leather under different environmental conditions.[19] This work helped to define a generic drying curve and identified some critical tan δ inflections that supported previous work by Lamb and Liu.[20-22] Although the scales of inflections are independent of tanning chemistry and rate of drying, the work demonstrated the applicability of DMTA in addressing the viscoelastic behavior of leather.

Work recently presented by Flowers *et al*. continued this research.[23] Using DMTA, tan δ inflections were followed whilst varying the surrounding environmental atmosphere. The presentation (and forth coming publications) demonstrate how the changing environmental conditions influenced the water absorbance and desorbance from leather. Further (as yet unpublished) DMTA work and analysis has provided some unexpected, but important, preliminary results to scientifically demonstrate the differences in drying behavior between tanned and post-tanned leathers as well as differences between tannages. The observed differences between these leathers could have important implications on the newest drying technologies and the debate of area gain during the drying step.

MATERIALS AND METHODS

Leather Raw Materials

The leathers used in this research were obtained from domestic upholstery processes currently in use in Italy. The bovine hide was of European origin. The samples were sourced from one hide to eliminate inter-hide variation. A hide was taken through a conventional beamhouse, which included lime splitting, and was processed to pickle. The hide was sided at the pickle stage and was sent to different drums for tannage, either by chromium or by glutaraldehyde/ syntan tannage.

After tannage the hide was further cut into quarters. A chromium-containing and chromium-free quarter were treated with fungicide and sealed (damp) in plastic bags for storage and transportation. The remaining quarters were treated using separate post tannage recipes. After the respective post tannage treatments, the quarters were treated with fungicide, sealed (damp) in plastic bags and transported to ICLT for analysis. The post tannage of each quarter had different quantities of syntan and fatliquor to suit the type of tannage.

ICLT re-split the tan-only quarters to 1.2 to 1.4 mm to make them more uniform in thickness. The post tanned quarters were not split upon arrival. The official sampling position on the four quarters was ascertained using BS EN ISO 2418:2002.[24] Samples 5mm x 300mm were clicked out (parallel to the backbone) and then conditioned in different environments that differed only in relative humidity.

Conditioning

The wet moisture content of leather can be manipulated by the relative humidity of the atmosphere in which the leather is stored. Saturated solutions of salts have been used to maintain an atmosphere (above them) of known relative humidity (RH). Solutions have been used in a range of applications from biological[25] to leather.[16]

Table I shows how the four conditioning atmospheres were constructed to ensure leathers of varying moisture content were prepared. The relative humidity of the atmosphere was checked using of a Fischer hair hygrometer, model no. 111 (Feingerätebau K. Fischer GmbH, Drebach, Germany). The cabinet atmosphere was circulated using fans.

Analytical grade salts were used (Fisher Scientific, Loughborough, UK). Basins of the saturated solutions were placed into the conditioning cabinets and the atmospheres were allowed to equilibrate for a week before sample testing commenced.

The samples for testing were placed in the humidity chambers and allowed to equilibrate for a week. Weights before and after conditioning were measured. Leather samples from each pre-condition atmosphere were dried according to BS EN ISO 4684:2005 to check the volatile content of the leather [26]. The volatile content of the leather comprises a number of chemicals that would be removed by drying at 105°C for 8 hours, but the major one would be water and, for the sake of simplicity, this paper refers to the removed volatile components as water.

BS EN ISO 4684:2005 calculates the volatile content expressed on wet-basis according to Equation 2.

$$Volatile\ matter\ (wet\ basis - \Delta M_w) = \frac{100 \times (M_1 - M_2)}{M_1} \qquad (2)$$

Where M_1 is the mass of the sample before drying and M_2 is the mass of the sample after drying.

Data taken from the post-tanned chromium samples were plotted to show the change in weight relative to the starting weight, in conditions of differing relative humidity. The pre-conditioned samples (or damp non-conditioned leather) were further cut according to the DMTA mode used and then loaded into the dynamic mechanical thermal analysis tester and run for 35-40 minutes while the viscoelastic properties were recorded.

Dynamic Mechanical Thermal Analysis

DMTA was run (in triplicate) on damp leather samples representing the four tannage/post tannage types. The DMTA program used was a declining, ramped, relative humidity profile (85 to 45% RH, 10%/min), at an isothermic temperature (40°C or 60°C). A declining ramp rather than a static RH prevented case-hardening. Start and end wet moisture contents were measured using BS EN ISO 4684:2005.[26]

The DMTA equipment used in this research was a Tritec DMTA 2000 (Triton Technology). The heating/cooling unit was a Grant Optima TX150 (Grant Instruments, Shepreth, UK). The humidity chamber was a Lacerta humidity chamber (Lacerta Technology limited, Keyworth, UK).

The DMTA was used in dual-cantilever (DC) bending mode (narrow disk orientation, free length 15 mm): DC bending mode was used even though the sample modulus and thickness were, at times, out of range of the preferred method. Dynamic displacement of sample during runs was always set at 64 µm and scans were run at 1 Hz unless stated otherwise.

Software control of DMTA scans was managed using a Microsoft Excel® 2003 plugin from which the data was exported. The storage modulus (E') and damping ratio (tan δ) were the main data values used in the characterization of leathers.

RESULTS AND DISCUSSION

The range of parameters possible in this research is large and it is important to understand that as a preliminary study it was not possible to address all of them. This work has therefore not attempted a large multi-factorial analysis; instead it uses a statistical approach (Taguchi) and focused on four parameters: temp, humidity, leather type, and how the leathers were preconditioned. Table 2 shows the effect of preconditioning.

Preconditioning with precision may not be compatible with modern day industrial practises; nevertheless this area of study is necessary to ensure reproducibility of results. However preconditioning is already possible in some more modern machinery such as the cell rotary conditioning (CRC) system manufactured by Fratelli Carlessi.[1]

Although Figure 1 unsurprisingly demonstrates that limited drying takes place at 20°C, it does clearly establish some

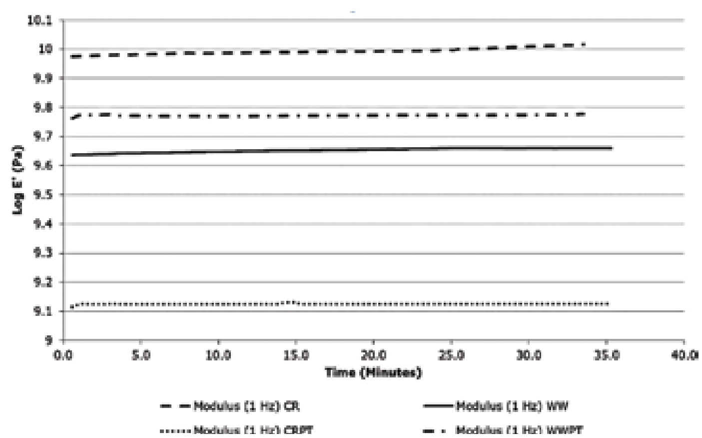

Figure 1. Four leather types dried at 20°C in a DMTA instrument and their storage modulus measured at 1 Hz showing little change in modulus. The leathers were dried where the relative humidity began at 85% and decreased to 45% at 10%/min. The starting moisture content for all leathers was ~150% and did not go past 100% in any of the leathers after 40 minutes.

TABLE I
The cabinet conditions of leather samples prior to testing showing the saturated salt (or water) used to ensure that atmosphere and the relative humidity of that atmosphere.

Relative Humidity of Atmosphere (%RH)	Solution used
45	$K_2CO_3.2H_2O$ (8.10 mol.dm^{-3})
76	NaCl (6.14 mol.dm^{-3})
98	KNO_3 (3.13 mol.dm^{-3})

significant differences between the leathers tested. The chromium tanned leather is the stiffest, which is supported by what most tanners feel when working with the material. Interestingly, there is a large difference in storage modulus between the chromium tanned material and the chromium tanned leather that had also been through a post-tanning process, with the chromium post tanned leather being the least stiff of all four leathers tested.

It is noteworthy that in contrast to the chromium tanned leathers the wet white post-tanned material is actually stiffer than wet white leather that was not post-tanned. Further investigation is needed to understand this, however it is possibly related to the amount of retannage used and the level of filling from the post tanning recipe.

Perhaps unsurprisingly there is a marked difference between Figures 1 and 2: comparing the two shows the effect that the temperature has on drying the leather. Whilst Figure 1 demonstrates virtually no drying takes place, in Figure 2 (80°C) it does. Figure 2 exhibits a sigmoidal curve, which shows that there is a lag in the drying process followed by a

TABLE II
The gravimetric analysis of leathers dried according to a Taguchi DOE.

Experiment	Temp (°C)	Humidity (RH)	Leather Type	Condition %	$\log_{10}E'_{end}$	*Start Moisture*	*Change in moisture*
					Mean	M_s (%)	ΔM (%)
1	40	45	Cr	D	9.3	210.2	174.5
2	40	65	CrPT	47	9.1	10.7	0.9
3	40	85	WW	98	9.2	84.4	57.6
4	40	85	WWPT	76	9.2	18.5	4.2
5	50	45	CrPT	98	9.4	50.1	39.6
6	50	65	Cr	76	9.6	25.9	10.2
7	50	85	WWPT	D	8.8	170.5	101.6
8	50	65	WW	47	10.3	16.6	1.1
9	55	45	WW	76	10.0	26.3	11.6
10	55	65	WWPT	98	9.2	65.2	48.8
11	55	85	Cr	47	9.7	13.9	-0.5
12	55	45	CrPT	D	9.4	156.4	142.0
13	40	45	WWPT	47	9.3	12.4	2.0
14	55	65	WW	D	9.3	177.7	138.3
15	50	85	CrPT	76	9.1	18.4	4.0
16	40	85	Cr	98	9.2	140.2	88.5

*where; Cr – chromium tanned leather with no post tannage, CrPT – chromium tanned leather with a defined (see experimental) post tannage, WW – chromium free tanned leather with no post tannage, WWPT – chromium free tanned leather with a defined (see experimental) post tannage. Conditioning was either; D – 'damp' as off the sammy setting machine, numbers in % - conditioned at [specified% relative humidity (RH).

more rapid drying phase and finally a reduction in the drying rate which, may indicate approaching the limit of the drying phase. It is probable that this matches the 'drying phases' that Lamb has previously published.[11]

The graph also demonstrates a clear difference in the drying of the two post-tanned leathers. The chromium tanned leather starts off with a lower storage modulus than the chromium free leather and whilst it initially dries more rapidly it does not reach the apparent maximum storage modulus as quickly as the chromium free leather. Whilst the direct reason for the shape change of this graph is easy to explain, explaining the mechanistic reasons is much more difficult. However the difference in drying rates and subsequent changes in the viscoelastic properties of the leather has ramifications outside the laboratory. New machines such as the CRC apply a stress to a system primarily in order to gain area. These results demonstrate that in order to maximize area gain the stress should be applied to different leathers at different times. For example in the systems shown in Figure 2, due to the more rapid drying of the chromium tanned leather the stress would need to be applied earlier than it might in a chromium free system.

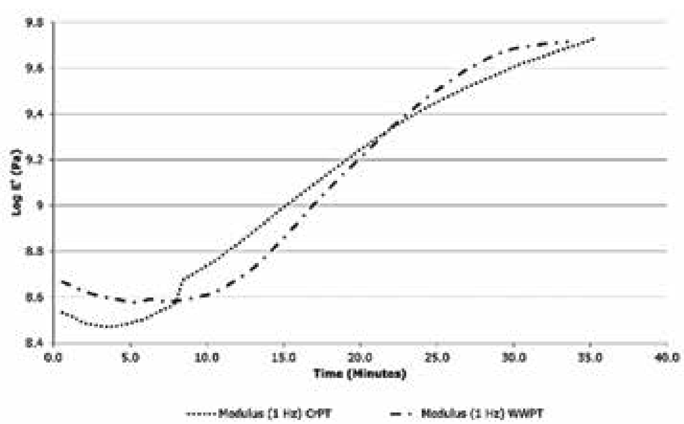

Figure 2. Chromium and chromium-free leathers (post tanned) dried at 80°C in a DMTA instrument and their storage modulus measured at 1 Hz (80 to 45% RH ramp). The starting moisture content for all leathers was ~150% and were both under 10% after 40 minutes. It can be noted that the chromium-free leather rapidly reached maximum viscoelasticity and then plateaus.

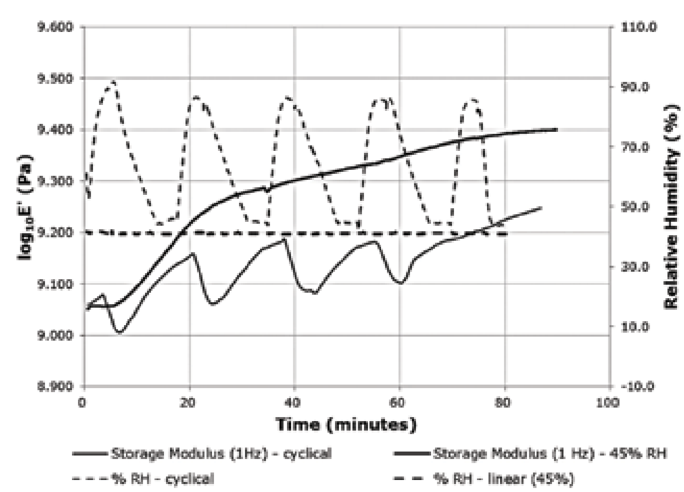

Figure 3. Preconditioned, chromium-free crust (115% moisture) dried at 55°C using either a relative humidity cycle (cycled between 80% and 45%) or a linear relative humidity set at 45%. Dashed lines indicate the relative humidity curves.

Figure 3 shows effect of humidity. Unsurprisingly the higher the humidity the slower the leather dries, because the surrounding air has less 'water carrying capacity' as per Equation 1. What is most interesting however is that whilst a constant humidity results in a constant drying of the leather, cycling the humidity has a direct correlation with a cycling of the storage modulus of the leather.

This suggests a point for 'safe' area gain during second stage drying. A strain could be applied, which would involve inherent stress, then by administering an increase in humidity the stress will drop whilst the strain remains. This process can be cycled until the maximum area gain is achieved (without detrimentally affecting the leather). The reduction in stress with an increase in humidity could be due to a degree of plastic flow within the leather which is facilitated by an increase in interfibrillary water.

This independent work was carried out in conjunction with similar research that Fratelli Carlessi was conducting on a larger scale. They have built the equivalent of a large 'tension only DMTA' to see if the results in the ICLT lab are reflected when applied to a whole hide. So far, results obtained by Fratelli Carlessi seem to support fully the observations presented in this work. Work is on-going to develop a machine that can interpret these real time measurements and utilize them to adjust the environmental conditions and tension applied to a hide in the newest iterations of their CRC machine.

CONCLUSION

It should be reiterated that the results published in this paper are only preliminary and whilst the authors have demonstrated the possible impact, more thorough experimentation exploring more parameters needs to be performed to confirm these findings unequivocally.

These experiments have used the laboratory technique, DMTA, to assess quickly the effect of the drying environment on leather and determine difference in drying characteristics between four different leathers. The results demonstrate the industrial applicability of this research, which might be translated into machinery developments. It is hoped that presentation of these results combined with further research will allow the development of such machinery, which can substantially increase area yield without detrimentally affecting the integrity, properties and performance of the leather.

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