INVESTIGATING THE CELL ROTARY CONDITIONING MECHANISM USING DYNAMIC MECHANICAL THERMAL ANALYSIS

by

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ABSTRACT

Jeyapalina *et al*. established that dynamic mechanical thermal analysis (DMTA) can be used to gauge the progression of leather drying.[1] This work has now been advanced in order to understand the mechanism surrounding sorption/desorption of moisture during cell conditioning, e.g., cell rotary conditioning (CRC). This paper will demonstrate how the use of DMTA could be used to monitor changes in leather stiffness. A gravimetric moisture analysis was performed on identical leather samples to gauge the progression of desorption. The change in storage modulus (E') was coupled to the moisture content (leather moisture and atmospheric relative humidity) to obtain a better understanding of the physical properties (specifically stiffness) of leather during a drying process. The research presented illustrates how DMTA can indicate leather fiber response to changes in atmospheric humidity and facilitate real-time adaptation of drying conditions during leather dehydration. The use of a cell conditioning system allows a tanner to control the flexibility of the material through the tension applied and the drying conditions. DMTA shows that the favorable conditions inside a CRC unit result in detectable changes to the leather fiber, similar to findings by Abrahamson and Williams-Wynn.[2] Using this technique a researcher can dry chromium-containing and chromium-free leathers in a manner that is highly customizable to produce desired physical properties. Difficulties experienced in chromium-free leathers can also be investigated in detail using this technique.[3]

INTRODUCTION

Drying Literature

Drying literature within the leather industry is divided into three main eras where the emphasis is placed on different topics that were relevant to the technology at the time. In the 1930s and 40s the research focused on shoe comfort and the movement of water (as vapor) through the leather substrate. From 1950-70 the emphasis was on trying to determine the simultaneous flow of heat and moisture, into/out of leather, in the hopes of modeling drying so that tanneries could optimize their drying parameters. The research is well summarized in Lamb *et al*.[4] From 1990 to 2015, Liu *et al*. worked to understand the mechanism of drying and the resulting leather physical properties.[5-13] Liu *et al*. established a mathematical model in low pressure conductive drying that is given in Equation 1 that allows a tannery to predict their vacuum drying rates from their drying parameters.[14,15]

$$\omega = K \times W_O \times \left(\frac{T}{T_b}\right) \times \sqrt{\frac{1}{t}} \times \sqrt{\frac{1}{d}} \times \sqrt{1-f} \quad (1)$$

Where *K* is a drying constant based on the leather type (*K* = 0.17 for chromium-containing leathers[14]; K = 0.32 for chromium-free); W_o is the initial water content; *T* is the drying temperature and T_b is the boiling point of the water; *d* is the thickness of leather; *t* is the drying time and *f* is the amount of fatliquor (as fraction of tanned hide mass).

Lamb illustrates (see Figure 1) a drying profile of leather, a hygroscopic and porous material.[16,17] From the figure, one can see a constant drying rate followed by two or more variable drying rate periods.

It is commonly understood 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 replenishment rate of water to the leather surface (see Equation 2). Water-carrying capacity is affected by temperature, the relative humidity and the flow speed of air over the leather.[18]

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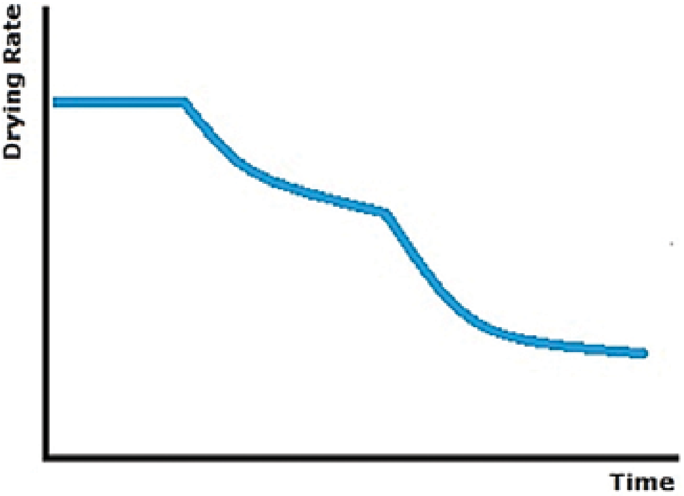

Figure 1. Starting with constant rate drying, the curve moves into the first variable rate drying sequence that is lower than the first phase of drying. A slower third phase of drying shows a marked tailing of the drying rate that is often attributed to removal of bound water. [16]

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 (shrinkage) of the fiber spaces.[19,20] Humphreys considers this to be highly detrimental in the processing of not only thick, but also vegetable tanned leather.[21]

$$\frac{dW}{d\theta} = \frac{hAT}{\lambda} \quad (2)$$

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.[21,22]

In convection drying, evaporation dominates the mechanism. Evaporation is a vaporization process that takes place at air/liquid interfaces.[23] Inside a liquid, vaporization can only take place if the vapor pressure of the liquid is greater than the atmospheric pressure (as is commonly the case in boiling). Evaporation at the leather surface will result in movement of liquid from the inside out until the rate of replenishment cannot match the rate of evaporation. Movement of liquid, governed by Fick's second law of diffusion, is mainly through interfibrillary spaces, but 1-3% of water does move through the fibers themselves.[24]

As the evaporative surface recedes into the leather structure the surface area available for evaporation rapidly increases. Possibly, the rate of drying would then increase, were it not due to the fact that evaporation is slowed down by slow moisture transfer rates out of the leather capillary structure. Variable rate or falling rate drying is typified by slow internal evaporation. During drying, water can be re-absorbed onto the fiber because water vaporization is an equilibrium phenomenon.

Drying Methods

The drying of leather is largely divided into three main types and combinations of those main types are common industrial practice. Convective, conductive and radiation type drying methods are now universal throughout the industry with a lot of focus on the conductive drying methods due to the short drying times they provide.

Vacuum drying of leather is the most typical conductive system.[25] Toggle drying, hang drying and suspension drying being the most common convective type of drying.[26-28]

Paste drying is a typical hybrid drying method where the grain of the leather is glued to a hot plate. Conductive heat transfer takes place from the plate to the leather as well as convective drying taking place from the flesh side.

Recently, the industry has paid attention to the use of conditioning systems at the end of drying to ensure the moisture content is uniform across the leather substance. CRC is a hybrid technology that couples elements of toggle drying together with leather conditioning.[29] The drying method allows the simultaneous drying and conditioning under tension to achieve a variety of leathers, with very comparable drying times.

Cell rotary conditioning exhibits major advantages in drying as the leather is contained in a drying cell with highly defined conditions and can be held at differing degrees of tension during the drying/conditioning cycle.

The degree of tension, i.e., the amount of strain (that may be translated into set) is achieved using various methods, ranging in descending order of set from paste, toggle, vacuum, hang/suspension and all will result in very different physical properties in the final leathers.

Sorption/Desorption of Water

Models of interface adsorption and its corollary (evaporation) are vital in understanding drying rates and is best described using either one of the two models: the Brunauer, Emmet and Teller sorption isotherm equation (BET) and the Guggenheim, Anderson and de Boer sorption equation (GAB). BET and GAB sorption profiles indicate how moisture interacts with collagen and provide an inverse model of how drying proceeds.[30] If a dry fiber starts to take up moisture, the most active sites of the collagen will take on water first and this will give off a large amount of energy in the process. Heats of wetting for the most active groups of the collagen at 0% moisture give off 167 J/g for vegetable tanned and 96 J/g for chromium containing leathers.[31,32] Conversely, when water is desorbed it pulls energy from the drying boundary layer and the surface cools. The surface of the leather is always significantly cooler than the surrounding air.

Effects of Heat and Moisture on Leather

The simultaneous movement of heat and moisture has been studied in depth by various authors to investigate the optimal conditions for shoe leather lasting.[33-37] At low moisture contents, leathers follow Henry's theory of coupled diffusion, with heat penetrating in two waves.[38] Henry's model is unhelpful at high moisture values.

Attenburrow relates the material science features of leather to the rheological performance of a block copolymer, in which there are crystalline and amorphous regions.[39] It has been established that collagen does exhibit a glass transition temperature (T_g): above the T_g, the structure is more relaxed, so that area and softness are increased. Water as a plasticizer has the effect of lowering the T_g in collagen as it does in other hygroscopic polymers. Jeyapalina *et al*. showed that tanning (and retanning) materials (especially fatliquor and vegetable tannins) also plasticize the collagen.[2]

Komanowsky investigated the changes occurring in leather during drying and confirmed the relationship between shrinking during drying and the moisture content: he showed that a critical point occurs at about 50% moisture (on wet weight basis), when linear fiber shrinkage is initiated.[19] As shrinking proceeds, the fiber structure collapses to a greater and greater extent, eventually causing the elements of the structure to approach closely enough to allow the formation of new crosslinks by means of several reactions, including the Maillard reaction.[40]

Dynamic Mechanical Thermal Analysis

Collagen exhibits viscoelastic properties, i.e., it can be modeled as a mixture of elasticity (E' -associated with energy storage) and viscous liquid (E" - associated with heat loss).[41] Tan δ is the damping of the sample, i.e., the dissipation of energy during a cyclic load (E''/E').[42]

Jeyapalina *et al*. addressed the effects of drying leather under different conditions using dynamic mechanical thermal analysis (DMTA). This work was able to define a generic drying curve, in which there are critical tan δ inflections: drying to about 60% moisture on wet weight of collagen content caused an increase in tan δ, as the bulk or freezable water is removed, drying to about 30% moisture on wet weight of collagen content caused a decrease in tan δ as partially associated water is removed, further drying by removing the associated water caused an increase in tan δ.[2] The scale of inflections are independent of tanning chemistry and rate of drying, however it shows that the viscoelasticity of leather is lower if drying is conducted under conditions of controlled humidity.

Properties of Leather After Drying

Liu in a number of papers examined the physical properties of chromium-free and chromium containing leathers.[7-9,15] The research also looked at the properties of the leathers produced by differing drying methods.[3,5,6,9,10,12,13] Fiber separation by any means whether it is liming, bating, over-drumming, solvent drying, staking, milling, or slow drying will result in leather with a low apparent density.

High apparent density, from whatever cause, results in lower flexibility; variable elongation at break; higher Young's modulus and higher toughness. Liu and McClintick showed that toughness has a strong correlation with fracture energy.[5] Brittle leather that often results from rapid drying, has fibers that may be strong but has fibers glued together in tight bundles (high compactness).

Fast drying methods will increase the compactness, especially if the capillary force during drying is high, but if combined with high drying tension will result in low angle of weave and possibly low apparent density. Wang and Attenburrow reported poor physical properties in goatskins that had low apparent density.[43] Collapsed structures, loss of thickness and loss of area are also associated with harsh drying conditions.[13]

Loose grain can result from many reasons, including migration of lubricants to the grain junction, especially stable oils (e.g., sulfited fatliquors). Another source of loose grain caused by drying could be a result from over-tension during drying (especially at <30% moisture content) and harsh drying conditions, e.g., high drying temperature and low humidity.

Liu *et al*. established that high residual moisture content in leather after drying gave rise to a higher loss of area.[15] It is well established that the area of leather is highly dependent on the moisture content.[44] However, it is less well understood how the area of leather can be controlled and maximized by the way in which the leather is dried. It has been shown that area can be gained and retained by stretching leather in the wet and warm state:[45-47] this is different to the retention of 'set', obtained by drying leather under tension,[39] and is the basis of the current interest in wet staking.

The aim of this work was to examine whether viscoelasticity (using the DMTA) could be used as an indicator of the progression of drying. The change in stiffness (using storage modulus), while simultaneously checking the gravimetric moisture content, allowed conclusions to be drawn about drying rates.

EXPERIMENTAL

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[48]. 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[49] to leather.[50]

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 allowed to equilibrate for a week before sample testing commenced.

TABLE I
The cabinet conditions of leather samples prior to testing showing the saturated salt (or water) used to ensure thatatmosphere 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 $mol.dm^{-3}$)

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.[51] 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 majority would be water and for the sake of simplicity, this research refers to the removed volatile components as water.

BS EN ISO 4684:2005 calculates the volatile content, according to Equation 3 which expresses the leather on a wet-basis, whilst the volatile content of this research is expressed on a wet-basis as calculated from Equation 3.

$$\textit{Volatile matter (wet basis} - \Delta M_w) = \frac{100 \times (M_1 - M_2)}{M_1} \qquad (3)$$

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 mode used and then loaded into the dynamic mechanical thermal analysis tester (DMTA) and allowed to 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.[51]

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.

Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) of all upholstery leather types was performed on a Mettler-Toledo DSC 822e (Mettler-Toledo, Leicester, UK) using an empty aluminum pan as a reference. The DSC test was done to measure the static thermal properties. A flow of 70 mL/min of nitrogen gas was maintained over the sample in the furnace during the scan. Peak area and onset/peak temperature data from integrations of the thermal profiles were performed using the STARe v. 9.1 software (Mettler-Toledo, Leicester, UK). Samples weights (3.0±0.5 mg) for DSC were fully hydrated and enclosed in a sealed pan. The heating rate of each scan was 5°C/min.

DSC shrinkage temperatures were cross-checked using a shrinkage temperature apparatus according to BS EN ISO 3380:2002 at a heating rate of 2°C/min.[52]

RESULTS/DISCUSSION

Leather Raw Materials (Gravimetric Analysis)

Pre-conditioning of leathers to produce leathers of differing moisture content using conditioning chambers and saturated salt solutions produced moisture profiles that were similar to those reported by other authors.[30,50,53,54] Figure 2 shows that leathers conditioned at 98% RH give leathers with a moisture content (on a dry basis) of 68.1±4.3%; 76% gave 24.2±5.0% and 47% gave 13.4±2.4%.

The post-tanned chromium leathers that were pre-conditioned showed variable levels of moisture content even though precautions were taken to prevent this.

Static Thermal Studies

The four leather types were measured on a DSC according to the method given above. Results given below in Table II show that the leathers that did not receive post tannage had onset temperatures (an indication of shrinkage temperature) that were within the expected range for the type of tannage used.

The retannage/dyeing and fatliquoring operations of the chromium tanned leather seems to lower its thermal stability. One of the likely explanations for this is the removal of some of the sulfate by washing and chemical replacement from the chromium complexes.

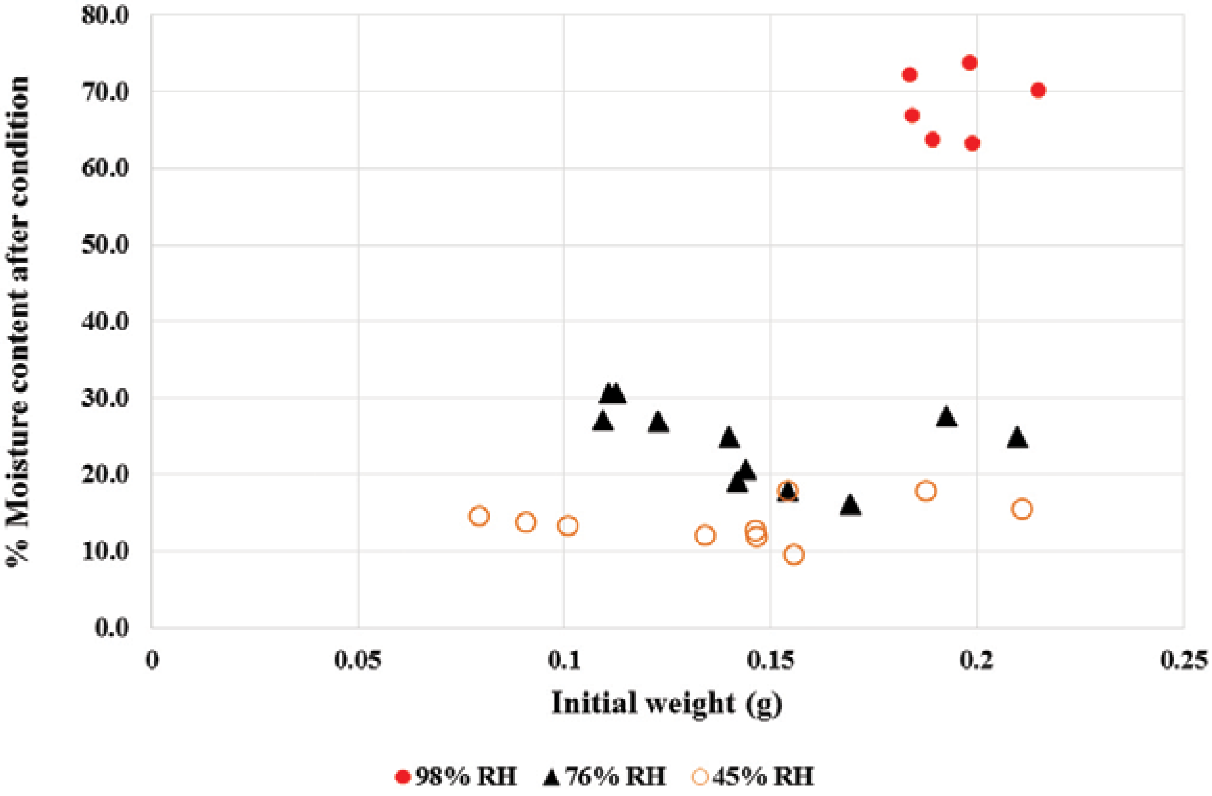

Figure 2. Moisture profiles of post tanned chromium leathers pre-conditioned at 98%, 76% and 45% relative humidity in constant environment chambers. Drying was performed at 23°C.

Dynamic Thermal Studies

Leathers were analyzed using DMTA in DC bending mode. Acquiring good information about what is taking place during drying is possible when using the DMTA in dual cantilever bending mode. As the drying progresses the storage and loss modulus increase, see Figure 3. The increase in moduli is not always proportional so a researcher can also see any changes in the tan δ value.

TABLE II
Differential scanning calorimetry data obtained from thermal scans of the four types of leathers used in this study.

Leather type	Onset temperature (°C)
Chromium tannage only	104.95
GTA tannage only	75.16
Cr tanned and post tanned	93.89
GTA tanned and post tanned	78.24

Generally, researchers use the moduli values to ascertain whether the material is becoming more viscoelastic or "stiffer". In general, the leathers lost their flexibility and became stiffer. The rate of viscoelasticity change differed according to drying method and it is these variations that the research is highlighting.

Figure 3 and 4 show the DC bending mode at 40 and 60°C and it shows the effect that drying temperature and drying humidity exert together on the drying profile. As the temperature is raised, the storage modulus is increased, see Figure 3 and 4. Stiffer/drier leather is expected in leather, as higher temperatures result in faster moisture removal from the interfibrillary spaces and additionally provides more activation energy for fiber cohesion.

Figure 4 shows that the plasticising effect of water on the post tanned pieces is higher, due to both the retanning chemicals having a higher hydrophilicity and a chemistry that allows increased molecular volume and rotational freedom. The post tanned leather seems to release its water rapidly in a manner different to non-post tanned material and this may be attributed to the retanning and fatliquor content as suggested by Liu *et al*.[14] There is not a large difference between chromium and non-chromium tanned material that has been post tanned, in terms of their drying profile at 60°C.

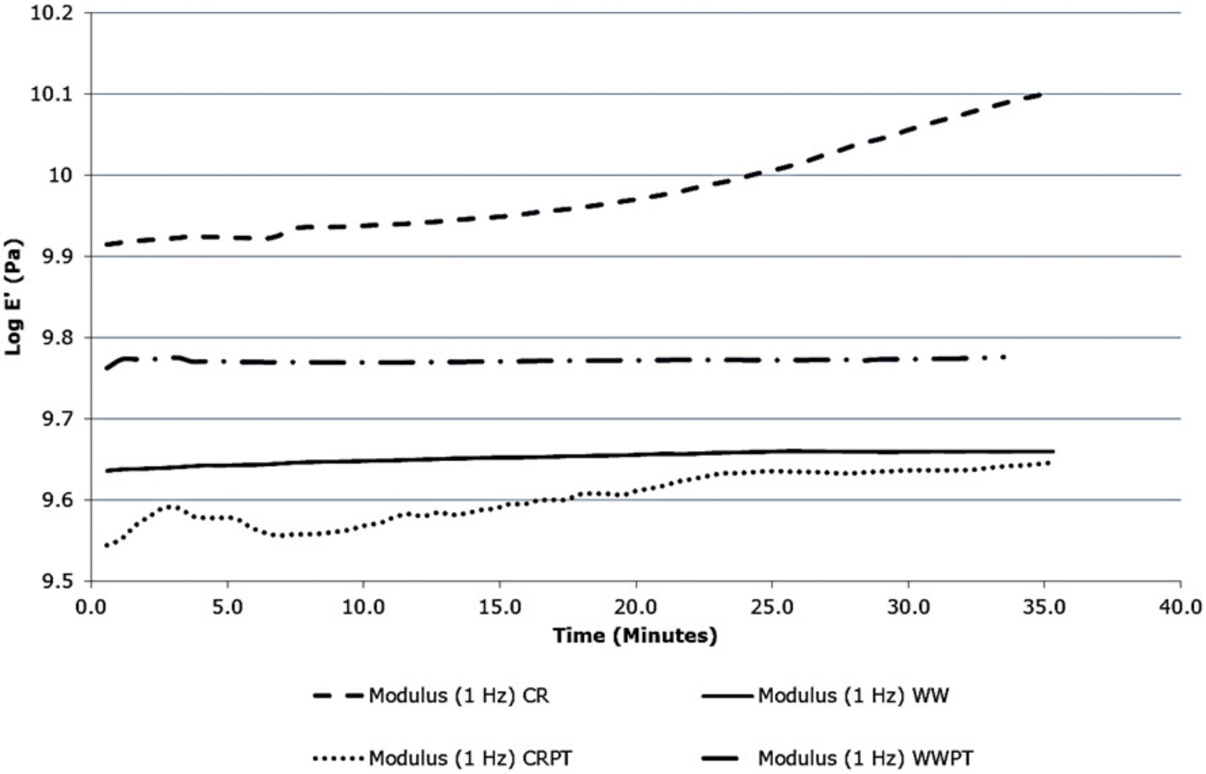

Figure 3. Four damp leather types dried at 40°C in a DMTA instrument and their storage modulus measured at 1 Hz showing variable change in modulus. The leathers were dried where the relative humidity began at 85% and decreased to 45% at 10%/min. The starting moisture content for all leathers was 65% and did not go past 35% in any of the leathers after 40 minutes.

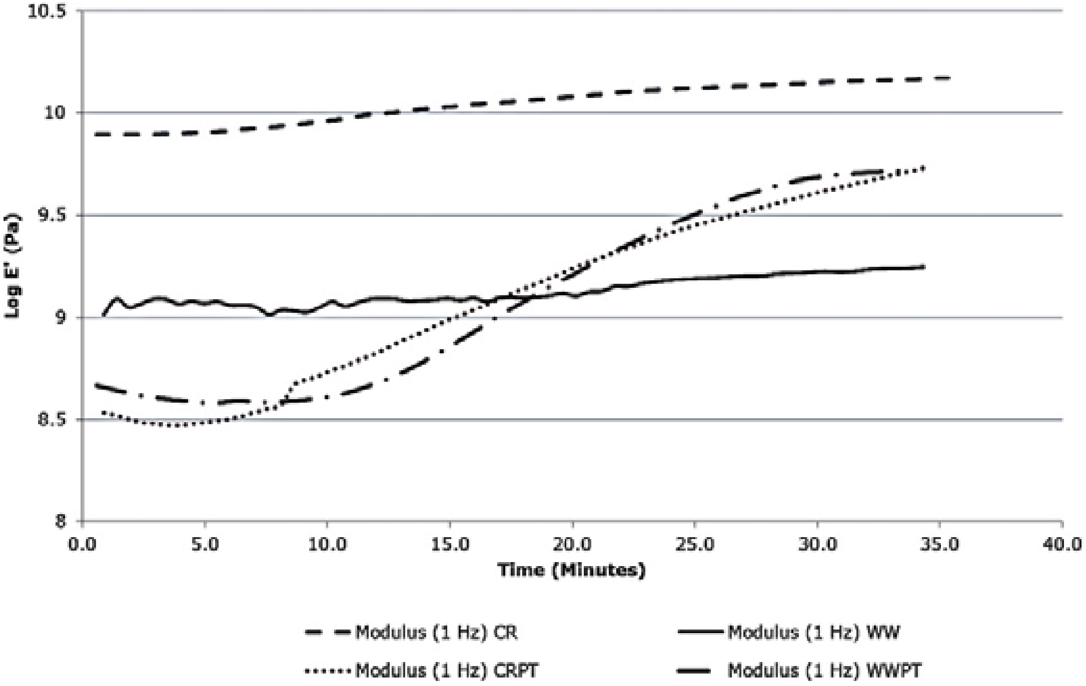

Figure 4. Four damp leather types dried at 60°C in a DMTA instrument and their storage modulus measured at 1 Hz showing variable change in modulus. The leathers were dried where the relative humidity began at 85% and decreased to 45% at 10%/min. The starting moisture content for all leathers was 65% and the post tanned leathers dried to below 10% moisture after 40 minutes.

Rapid increase in viscoelasticity is undesirable in leather manufacture as the resulting leather has a higher E' value (giving firmness to soft leather) and can often leave the leather fibers brittle. It is also known from many sources that very rapid drying affects area yield.[1,5,33,37,41,55-57] DMTA in DC bending mode does not give data that inform what happens to the area yield.

CONCLUSIONS

Analysis using DMTA drying of the four leathers has shown that storage modulus during leather drying changes at rates governed by the drying parameters used.

The research conducted did not corroborate findings, where Liu et al. suggest the tannage itself changes the rate of drying, but indicates that leathers with different tannages end with different stiffness values because they start with different viscoelasticity values.[8,9] However, it has shown that post tanned leathers do differ in their rate of drying, but it seems the leather tannage forms the basis for how the post tannage chemicals interact with the tanned leather collagen, so ultimately influence the degree of plasticization and the viscoelasticity of the resulting leather.

Covington in an updated theory on tannage suggests that the role of water in the thermal stability is crucial. An additional effect of tannage on the water content of the collagen is its combined influence that it (and other plasticizers) have on the storage modulus. This research found that the role of post tannage has a greater effect than the tanning chemicals in drying in terms of storage modulus.[58]

It has been seen that the two (possibly even all three) phases of drying should be seen as separate considerations. First-phase drying temperature is governed by a modification of Regnault's formula. Second-phase drying is dominated by temperature and humidity transfer. Third-phase drying is dominated by collagen desorption mechanics.

The viscoelasticity that can be measured by DMTA allows insight directly into what is taking place in terms of leather elasticity and set. More research needs to be performed on exactly how the post tannage and the combined effects of drying temperature/humidity affects the drying rates, physical properties as well as the area yield.

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