

The glass transition temperature of leather and its implications to the leather industry

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A comprehensive understanding of the physical and mechanical behaviour of leather is essential within leather processing and leather goods manufacture. Glass transition is the single most important thermal property to study because it is directly linked to molecular flexibility, thus affecting leather performance in all temperature related operations.

The polymeric behaviour of leather

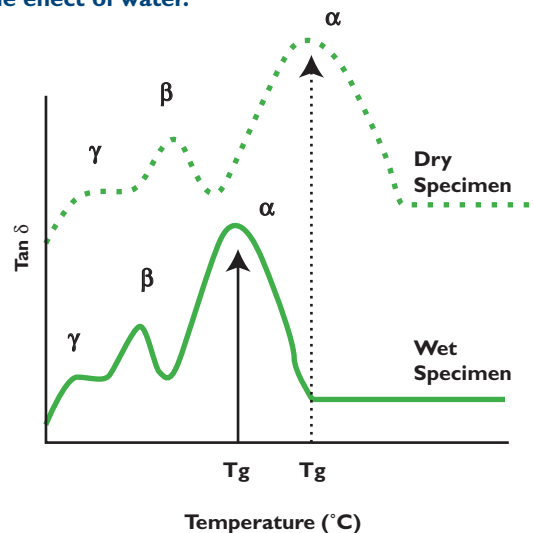
Leather shows both flow-like behaviour as found in a liquid, and elastic spring-like behaviour as found in a solid, and can be described as a non-linear viscoelastic material. Because of this behaviour, mechanical energy applied to a piece of leather will partially dissipate through liquid-like deformation, and be partially stored within the elastically deforming molecules. When the applied energy is released, the stored energy will be used to recover part of the original shape. Changes in viscoelastic properties with respect to time or temperature can be studied by a thermo-mechanical technique called Dynamic Mechanical Thermal Analysis (DMTA).

For a non-crystalline polymer, as the temperature increases from cold additional chain movements can occur at specific temperatures, which is called a relaxation process. These are said to be softening/viscoelastic transitions. The major softening transition of an amorphous polymer is known as the glass transition (T_g). Sometimes the T_g can be viewed as the onset of greater molecular flexibility, giving liquid-like behaviour to the solid. Eventually, such liquid-like behaviour is constrained only by cross-links between the long molecular chains. However, the major thermal softening transition of a structured/crystalline polymer is melting. Due to the semi-crystalline nature, leather displays transitions that are characteristics of both materials.

The existence of these transitions becomes apparent when the modulus, representing the stiffness of a given material, is plotted as a function of temperature. Furthermore, such transitions can also be studied by the ratio of energy lost to energy stored per deformation cycle ($\tan \delta$) in a dynamic mechanical experiment. DMTA is a unique tool because it can measure both parameters over a wide range of temperature. These changes can be represented mathematically as a storage modulus (E') or a tangent to the loss angle ($\tan \delta$).

Changes in $\tan \delta$ with temperature can be expressed as a graph,

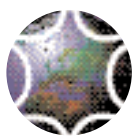
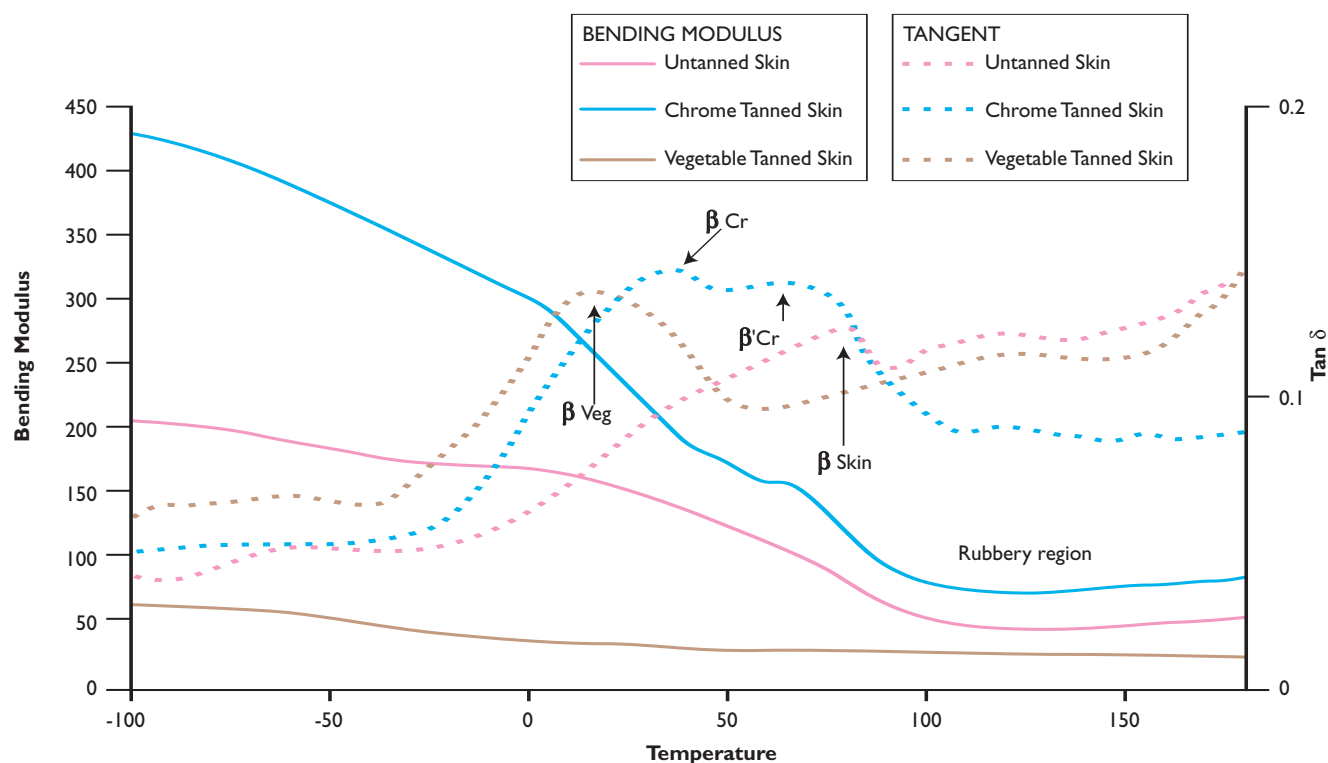
Figure 1: Temperature dependence of loss tangent for hydrophilic amorphous polymers in wet and dry state (modulus — and loss tangent --- line), demonstrating the effect of water.



and Figure 1 shows a generic plot for an amorphous polymer. The peaks in $\tan \delta$ identify the individual relaxation processes. The presence of water shifts the transition temperature to a lower temperature. This is due to the plasticisation of polymer by the water molecules.

The temperature related behaviour of leather

Thermally induced shrinkage is the most studied transition in leather science, and this is associated with the non-crystalline ➤

**Figure 2: Dynamic thermal analysis: Untanned, chrome and vegetable tanned skin, conditioned at 0% RH.**

The plotted results show the bending modulus (as energy stored E , and the loss in angle ($\tan \delta$), as a function of temperature. The β -peak represents the glass transition of the skin in its raw and tanned conditions.

DMTA thermograms of chrome tanned skin, vegetable tanned skin and untanned skin, pre-conditioned at 0% RH. Showing storage modulus E' and loss tangent of the phase angle, $\tan \delta$, as a function of temperature. The β -peak represents the glass transition of the material

molecular regions of the collagen backbone structure. However, leather may be seen as a semi-crystalline biopolymer, having both regions of order and regions of disorder. For this reason it shows thermal properties associated with both crystalline and amorphous materials, but to date the glass transition of tanned collagen—being associated with the amorphous region—has not been studied at all.

The shrinkage temperature gives information regarding thermal stability, but it does not give any useful information regarding other aspects of the leather performance. For example, the shrinkage temperature of leather gives no indication of its combustion temperature or its rheological properties. On the other hand, it is known from polymer science that those viscoelastic transition temperatures and, in particular, the glass transition temperature, is the key determinant of the performance of a material.

The dynamic mechanical properties of leather as a function of temperature are illustrated in Figure 2. In this example the samples were dry calfskin being dehydrated by conditioned at 0% RH. This is to eliminate the plasticising effect of water molecules on the leather fibres.

It can be seen that the untanned skin and chrome and vegetable tanned leathers all show viscoelastic transitions within the studied temperature range of -100°C to 100°C . The β -peaks represent the T_g of these three materials. It is clear that untanned skin shows T_g at higher temperature than those of tanned leathers.

This lowering of T_g indicates the ability of the tanning agent to decrease the softening transition temperature. This softening effect is actually well known, as is the fact that vegetable tanning produces a softer leather than chrome tanning, as shown in Figure 2. However, for the first time these facts can be explained by scientific principles.

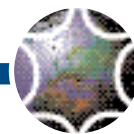
The plasticising effects of tanning agents and water molecules

One can view the tanning process as a plasticisation of the collagen molecule. In this event tanning molecules interpose themselves between the collagen chains, thus reducing the

Panel I

The viscoelastic character of leather

The viscoelastic characteristics of leather like other polymers change with temperature. Because of the complex structure of collagen fibres, leather has a broad viscoelastic transitional region, during which, collagen molecules have freedom to move readily. Above the so called "glass transition temperature" segmental rotations of collagen molecules are probable and the molecules may dissipate mechanical energy more quickly and display profound relaxation.



Panel 2

Viscoelastic behaviour

The rheological behaviour of materials can be examined in terms of their ability to react to applied mechanical energy. When a specimen is made to deform, work is done on each point in the body by the applied force over the distance that point has travelled. A perfectly elastic solid stores this energy, and upon release of this deformation, the stored energy is used to recover its original geometry. In fluids, the work of deformation is immediately dissipated and transformed into heat. Most polymeric materials, including leather, exhibit viscoelastic behaviour, a combination of elastic and energy dissipative behaviour.

The glass transition temperature

The glass transition temperature, T_g , of a polymer defines where the polymer changes from a glassy to a rubbery state. In this event, polymer chains gain enough mobility to move relative to each other. T_g is important for polymer performance, as glassy polymers show markedly different behaviour above and below T_g .

Dynamic Mechanical Thermal Analysis (DMTA)

In DMTA, the temperature of the sample is altered while continuously applying an oscillating strain or force to it. This allows measurement of the rheological properties of the sample over a wide temperature range. It has been much used in the characterisation of viscoelastic materials.

Water as a plasticiser

A good plasticiser shields inter- and intra-molecular interaction and can reduce some macromolecular associations within the crystalline regions. Here solvation shells increase the distance between chain segments and decrease the activation energy for segmental motion. Many hydrophilic compounds of low molecular weight can act as plasticisers, however, none is as effective as water.

Panel 3

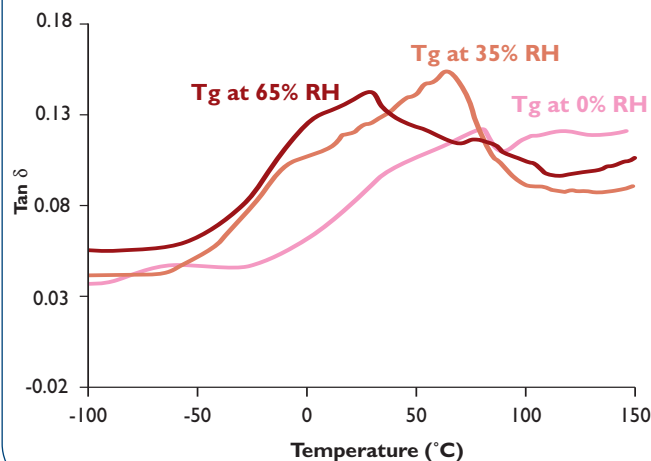
Other uses for DMTA

DMTA may also find a use in quality control measurements, including determination of the glass transition temperature, shrinkage temperature and stiffness properties. Modulus values, in the so-called rubbery region (the region above the T_g) will give a direct measurement of the molecular stiffness of leather. This technique may even be used as a diagnostic tool in determining the type of leather since different types of tanning show different splitting behaviour of the glass transition peaks.

forces holding the chains together. As a result, viscoelastic transitions (including T_g) are depressed to a lower temperature.

As stated earlier, the transition temperatures of polymers are sensitive to moisture content, and this applies to both untanned and tanned skin. Figure 3 presents DMTA thermograms of the untanned skin, where $\tan \delta$ (the loss tangent) as a function of temperature of samples conditioned

Figure 3: Loss tangent, $\tan \delta$, as a function of temperature for acetone-dried skin samples pre-conditioned in a given relative humidity environment (0, 35, 65% RH).



in various relative humidities are given. It is clear that the glass transition temperature (T_g) is highly sensitive to moisture content. Even though the data is not given in this article, at ambient conditions (65% RH and 20°C), most of the tanned leathers are above the T_g , hence showing flexible properties.

The physical properties of many polymers depend on the position of the glass transition temperature in relation to the ambient temperature. This is because polymers are more flexible at temperatures above the glass transition temperature, while below this temperature they are inflexible and glassy. For this reason the physical properties as a function of temperature differ greatly.

It is known that the physical properties of leather are altered by the presence of moisture. This is probably due to the relative position of the glass transition temperature to the ambient conditions. In order to predict the physical behaviour of leather one must therefore look closely at its dynamic mechanical properties.

The softening of leathers in process by temperature increase

Whilst detection of the glass transition of leather has previously not been a subject of much interest, it has been now conclusively demonstrated that DMTA is able to detect the glass transition of leather quite clearly. This has important practical implications, and it may be concluded that processing above the glass transition temperature will be beneficial. This is especially so where temperatures can be raised without causing structural damage, such as in post tanning operations. This is because the leather fibres are much more flexible above T_g , thus the uptake and fixation of dyes, fatliquor and other chemicals will be optimised. 

Acknowledgements

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