Collagen structure and strength in leather

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Abstract

Strength is an important property of leather. However the structural basis of strength in leather is not well understood. We have used synchrotron based small angle X-ray scattering to investigate the structure and strength of collagen materials under a variety of conditions. This enables changes in the extent of orientation of the collagen fibrils to be quantified and the internal stress on the individual collagen fibrils to be measured. We have found that collagen alignment in the plane of the leather correlates strongly with strength in bovine and ovine leather and across a range of other mammals. Strong leather is better able to distribute applied stress across the full thickness of leather than weak leather. Collagen fibril diameter has a slight correlation with strength in bovine leather. Changes in thickness and dryness during processing affect fibril orientation. Fat liquor modifies the structure of the collagen in a systematic way but lubricates at a structural level above the fibril size. These factors provide a better understanding at the nanostructural level of strength in leather.

Keywords: Small angle X-ray scattering, collagen, fibril orientation, fibril diameter.

1 – Introduction

A large portion of leather produced globally is used for the production of footwear, upholstery and clothing, and many of these applications require good quality leather. One important property of leather is its strength. The strength of leather is largely dependent upon the properties and behaviour of the fibres that make up the material. Leather consists of long collagen fibres that interlink to form a mesh-like structure. The collagen fibres are held together in the mesh-like structure through cross-links, either natural or synthetic.

Small angle X-ray scattering has been used to determine structural characteristics of various leather materials with ranging strengths. The manner in which collagen provides strength to leather and the reason strength varies in different leather materials is the subject of this paper.

2 – Materials and Methods

Ovine, bovine and other animal leathers were prepared using conventional beamhouse and tanning processes with chrome tanning.
Synchrotron based small angle X-ray scattering was used to investigate the collagen structural arrangement (Basil-Jones et al. 2010). This enables changes in the extent of orientation of the collagen fibrils to be quantified and the internal stress on the individual collagen fibrils to be measured (Basil-Jones et al. 2011). Diffraction patterns were recorded on the Australian Synchrotron SAXS/WAXS beamline, utilizing a high-intensity undulator source. Energy resolution of $10^{-4}$ was obtained from a cryo-cooled Si (111) double-crystal monochromator and the beam size (FWHM focused at the sample) was $250 \times 80 \mu m$, with a total photon flux of about $2 \times 10^{12} \text{ph} \cdot \text{s}^{-1}$. All diffraction patterns were recorded with an X-ray energy of 11 keV using a Pilatus 1M detector with an active area of 170 x 170 mm and a sample-to-detector distance of 3371 mm. Exposure time for diffraction patterns was 1 s and data processing was carried out using the SAXS15ID software (Cookson et al. 2006). The partially processed leather samples were mounted onto a sample plate and sealed using kapton tape to prevent drying during X-ray analysis.

Orientation Index (OI) is used to measure the spread of orientation of the collagen fibrils. It is calculated from the azimuthal angle spread of the most intense Bragg’s peak at around 0.058–0.060 $\text{Å}^{-1}$. OI is defined as $(90° – OA)/90°$ where OA is the minimum azimuthal angle range, centered at maximum peak intensity, that contains 50% of the fibril scattering intensity. An OI value of 1 indicates that the fibrils are completely parallel to each other, while a value of 0 indicates orientation of the fibrils is completely isotropic.

Tear strengths were determined using standard methods for double-edge tear testing (IULTCS 2002; Williams 2000). Samples were cut and stored at 20 °C and 65% relative humidity for 24 hr before the tear strength was measured using an Instron 4467. Thickness was measured using method BS EN ISO 2589:2002.

**Figure 1.** The SAXS experimental setup. Meridional and equatorial scattering from a sample containing well-oriented collagen fibrils.
3 – Results and Discussion

The collagen alignment in the plane of the leather is found to correlate strongly with strength in bovine and ovine leather (Basil-Jones et al. 2011) and across a range of other mammals (Sizeland et al. 2013) (Figure 2). Collagen fibrils are strong in the direction of the length of the fibril but connections between fibrils determine the strength of a collagen based material in the direction at right angles to the fibrils. These connections are relatively weak. These connections in green hide are largely glycosaminoglycans but these are removed during tanning and cross-links between fibrils are probably chromium complexes. The strength of these linkages is apparently much less than the strength of the collagen fibrils, and therefore collagen materials are stronger in the direction in which the majority of fibrils are oriented.

![Figure 2](image-url)

**Figure 2.** a) Orientation index versus tear strength for the averages of each of the leather types measured through the edge parallel to the backbone. Error bars for one standard deviation.; b) Orientation index versus tear strength for a range of animals. a) from J. Agric. Food Chem. 59(18) 9972-9979 ©American Chemical Society; b) from J. Agric. Food Chem. 61(4) 887-892 ©American Chemical Society.

It is possible with SAXS analysis to take points through the thickness of leather and observe the behavior of the collagen fibril orientation and strain during strain of the leather. We have found that there is a difference in the response to strain of strong and weak leather. Strong leather is better able to distribute applied stress across the full thickness of leather, and the load is taken up fairly evenly by the collagen fibrils throughout, whereas in weak leather there are points of high and of low stress within the leather. Failure therefore is likely in weak leather at lower overall stress because it will be initiated at the regions where stress is concentrated (Basil-Jones et al. 2012).

Collagen fibril diameter as been shown to have some influence on strength in tendons (Parry et al. 1978). We have found a correlation of collagen fibril diameter with strength in bovine leather where for larger diameter fibrils are present in stronger leather (Wells et al. 2013) although the correlation is not very strong (Figure 3).
Figure 3. Collagen fibril diameter versus tear strength for bovine leather $r^2 = 0.59$, $t = 3.4$, $P = 0.009$ (for slope). Each point is the average value from 12–20 diffraction patterns. From *J. Agric. Food Chem.* 61(47) 11524-11531 ©American Chemical Society

Other factors have been shown to affect the orientation of collagen fibrils in leather. In particular, changes in thickness during processing results in a change in measured orientation index, with thicker stages having lower OI, but without fundamentally altering the structural arrangement of the collagen (Sizeland et al. 2015a).

Figure 4. Collagen D-spacing versus measured fat liquor content for ovine leather. Each point is taken from the average of about 20 scattering patterns. Adapted from data presented in *J. Am. Leather Chem. Assoc.* , 110(3) 66-71 with the difference that here we show measured fat content rather than offered fat.

One of the final stages of leather manufacture is the addition of fat liquor to increase strength and impart suppleness to leather. We have investigated the action of fat liquor and find that it penetrates to the level of collagen fibrils and penetrates the fibrils to alter the structure of individual fibrils. This is evident in linear change in D-spacing with fat liquor content (Figure 4) (Sizeland et al. 2015c). However, despite the penetration within the collagen fibrils, the lubrication action of fat liquor appears to apply only at a structural level of fibers not fibrils (Sizeland et al. 2015b).

The contribution of the mechanical properties of individual collagen fibrils to the mechanical properties of the tissue which they comprise has also been studied (Wells et al. 2015), using pericardium as the test material. Measuring the ratio of fibril diameter changes to d-spacing changes (elongation) it was found that the collagen fibrils under tension exhibit a high Poisson’s number, greater than 0.5. This means that as a fibril is stretched the diameter contracts at an unusually high rate, resulting in a diminishing overall volume of the fibril. This is likely to impart a particular
resistance to strain and could be a contributing mechanism to the strong and elastic properties of collagen.

4 – Conclusions

Fibril orientation was found to have a significant influence on the overall strength of leather, with higher fibril alignment in the plane of the leather leading to higher strength in that direction. Weak interactions exist between fibrils at right angles to the length of fibrils. Strong leather, with highly aligned fibrils in the plane of the leather, distributes an applied load more evenly through the thickness of the material compared with weak leather. Weak leather tends to have regions of high and low stress, which leads to failure at a lower load. Collagen fibril diameter was also shown to have a small influence on overall strength in bovine leather. When fibril diameters were combined with d-spacing values to calculate the Poisson’s ratio, it was found that collagen exhibits a high Poisson ratio under stress, a characteristic that is unlike most engineering materials. By studying the collagen fibril component of leather including the orientation of the fibrils, the diameter, the changes with processing and chemistry and the behaviour under strain, it has been possible to understand better some of the strength and mechanical properties of leather.

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6 – References


