Artificially modified collagen fibril orientation affects leather tear strength

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ABSTRACT

BACKGROUND: Ovine leather has around half the tear strength of bovine leather and is therefore not suitable for high value applications such as shoes. Tear strength has been correlated with the natural collagen fibril alignment (orientation index, OI). It is hypothesized that it could

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be possible to artificially increase the OI of the collagen fibrils and that an artificial increase in OI could increase tear strength. RESULTS: Ovine skins, after the pickling and bating, were strained bi-axially during chrome tanning. The strain ranged from 2% to 15% of the initial sample length, either uniformly in both directions by 10% or with 3% in one direction and 15% in the other. Once tanned the leather tear strengths were measured and the collagen fibril orientation measured using synchrotron based small angle X-ray scattering. CONCLUSIONS: The OI increased as a result of strain during tanning, from 0.48 to 0.79 ($P = 0.001$), measured edge-on and the thickness normalized tear strength increased from 27 N/mm to 43 N/mm ($P < 0.001$) after leather was strained 10% in two orthogonal directions. This is evidence to support a causal relationship between high OI (measured edge-on), highly influenced by thickness, and tear strength. It also provides a method to produce stronger leather.

Keywords: collagen, fibril, orientation, strength, small angle x-ray scattering

INTRODUCTION

Skins possess a sophisticated stretch mechanism in which collagen fibers glide and align in the direction of strain resulting in the individual fibers equally absorbing the forces ^{1,2}. Collagen is a major component of skins and its structural arrangement greatly influences the strength of leather products ³. Increased collagen fiber alignment has been found to be associated with increased tear strength in leathers produced from a variety of animals and a linear relationship has been demonstrated between tear strength and the degree of collagen fibril alignment ⁴. It has been proposed that an important contribution to the greater tear strength of bovine leather than ovine leather is the greater collagen fibril orientation index (greater fibril alignment) in the plane of the leather ⁵. This lower strength of ovine leather means that it is not suitable for high value applications such as shoes and upholstery. Tear strength is also related to collagen fibril diameter to a small extent although there is species variation with a weak correlation between fibril diameter and tear strength for bovine leather but not ovine leather ⁶.

Mechanical methods have been used to influence alignment of component fibers in the production of a variety of materials to enhance strength. Laminated dough (or puff pastry) utilizes rolling to align gluten fibers to create sheets ⁷ and re-enforced concrete has strategically embedded steel fibers, placed in the direction of tensile stresses to enhance the tensile strength of concrete ⁸. In biological materials fiber arrangements are also mechanically influenced. Collagen is the most abundant fibrous protein in the body and it is the arrangement of these fibers that has

the greatest influence on the mechanical performance of connective tissue like tendons⁹ and skin^{1, 10} where fibers lie in the direction of stress forces.

The tanning process affects the alignment of collagen in skins¹¹ and has an impact on strength.. Drying of bovine leather under strain has been shown to increase the tensile strength of bovine leather¹². Tensile testing gives the ultimate material strength however having a large force distributed evenly over a segment of material is not common in practice. Tear testing, on the other hand, matches the mode of failure in practice where a puncture to the material experiences straining forces which then propagates into a tear¹ and is therefore a better measure of the performance of the material. Coupling these measurements with small angle X-ray scattering (SAXS) analysis provides further insights into the structural arrangements of the collagen fibrils and how these relate to the material strength of the material¹³.

Stretching leather while in the drying stage of manufacture has been used to increase surface area^{12, 14, 15} with a noted effect on the leather's stiffness and strength. Biaxial stretching on wet partially processed bovine hides found that there was a significant increase in the tensile modulus of leather and this was correlated to the collagen orientation perpendicular to the surface, as measured by wide angle X-ray diffraction¹⁶. The fiber planes that lay parallel to the surface were less affected by the biaxial stretching. Thickness and hydration state affects the collagen orientation during stages of the processing of ovine pelts to leather. An increase in thickness and hydration state increased alignment during the tanning stages while the application of mechanical stresses during the final staking stage increased the collagen fiber alignment¹¹.

Although tear strength has been correlated with the natural collagen fibril alignment (orientation index, OI) in leather^{4,5} and other materials^{17,18} it has not been shown either that this is a causal relationship (more than just a correlation), neither has it been shown that it is possible to increase strength by artificially increasing the orientation index. Here we investigate the hypothesis that a causal relationship exists between orientation and tear strength and to use this concept to create stronger materials.

EXPERIMENTAL

Leather preparation. Leather was prepared from ovine pelts which were expected to yield typical strength leather using conventional beamhouse and tanning processes. The ovine pelts were from 8 to 10 month old New Zealand Romney sheep. After rehydrating the skins, adhering fat and flesh was removed mechanically and conventional lime sulfide paint (140 g/L sodium sulphide, 50 g/L hydrated lime and 23 g/L pregelled starch thickener) was applied to the flesh side of the skin at a rate of 400 g/m². Following incubation at 20 °C for 16 hours keratinaceous materials were removed and the skins washed in water to remove the lime. Following the last wash ammonium sulfate was titrated into the water to lower the pH to 8 and a commercial bate enzyme, Tanzyme (0.1% (w/v)), was added before the skins were incubated at 35 °C for 75 min. Following further washing in water the skins were pickled in 20% (w/v) sodium chloride and 2% (w/v) sulphuric acid.

Control and test samples (each 200 x 200 mm) were obtained from the rehydrated and unhaired pelts at the official sampling positions with the orientation to the backbone noted for all samples.

The test squares were mounted in a biaxial stretching device which applied and maintained strain (10% and 10%; 3% and 15%; 2% and 7%) during the beamhouse and tanning process which was carried out in a bath that contained the stretching apparatus. This choice of strain was determined by: a) 10% and 10% strain was the maximum equal biaxial stretch possible determined by the strength of the operator; b) 3% and 15% strain was the maximum possible by the strength of the operator in the easier to stretch direction, perpendicular to the backbone, to reach 15% strain followed by the maximum possible of 3% strain in the direction normal to the first strain; c) for the 2% and 7% strain approximately half of the strains obtained in the maximum unequal biaxial strain. The control samples were processed as normal. Following pickling the control and test samples were degreased in 4% non-ionic surfactant (Tetrapol LTN, Shamrock, New Zealand) for 90 min and then washed. After being neutralized in a 1% disodium phthalate solution (Feliderm DP, Clariant, U.K) for 30 min. the samples were processed overnight at 25 °C in a 5% chrome sulphate solution (Chromosal B, Lanxess, Germany). The following day the samples were neutralized in 1% sodium formate and 0.15% sodium bicarbonate solution for 1 hour, washed in water, and retanned with 2% synthetic retanning agent (Tanicor PW, Clariant, Germany) and 3% vegetable tanning (mimosa) (Tanac, Montenegro, Brazil). Finally the skins were treated with a 6% fatliquor solution and fixed with 0.5% formic

acid for 30 min. After a final wash in cold water the stretched samples were removed from the biaxial stretching devices and left to dry with the control samples.

Tear strength. Tear strengths were measured according to standard methods (ISO 3377-2:2002) and normalized for thickness. Samples were cut from the official sampling position and treated at constant environment conditions (20 °C and 65% relative humidity) for 24 hours before tear strengths were recorded on an Instron 4467 instrument.

SAXS analysis. For SAXS analysis two types of samples were taken from both the stretched and control leather samples (Fig. 2). Circles (4 mm diameter) were punched from the leathers to perform measurements with the X-rays perpendicular to the surface, flat on. Nine diffraction patterns were recorded on each sample using a three by three grid with 0.25 mm spacing between points. Samples were measured at ambient humidity.

The second sample type, for edge-on analysis, consisted of thin strips of leather (1 x 5 mm) that were placed with the cross section (the cut edge) facing the X-ray beam. Measurements were made with 0.25 mm spacing between points in a vertical line down the cross section from the grain to the corium.

The diffraction patterns were recorded on the Australian Synchrotron SAXS/WAXS beamline. A high-intensity undulator source was utilized with an energy resolution of 10^{-4} from a cryo-cooled Si(111) double-crystal monochromator. The beam size (fwhm focused at the sample) was 250 x 80 μm with a total photon flux of about 2×10^{12} photons s^{-1} . All diffraction patterns were recorded with X-ray energy of 8 keV using a Pilatus 1M detector with an active area of 170 x 170 mm and a sample to detector distance of 3371 mm. The exposure time for diffraction

patterns was in the range of 1–5 seconds, and data processing was carried out using the Scatterbrain software. Intensities displayed are all absolute detector counts (one X-ray detected one detector count), except where stated otherwise.

The collagen orientation was determined from the azimuthal angle for the maximum intensity of the D-spacing diffraction peaks. The orientation index (OI) was the primary measure used where OI is defined as $(90^\circ - \text{OA})/90^\circ$, where OA, the orientation angle, is the minimal azimuthal angle range, centered at 180° , that contains 50% of the micro fibrils^{19, 20}. The OI range takes us from perfect anisotropic alignment which is represented by an OI of 1, through to an OI of 0 which represents isotropy. The OI was calculated from the spread in the azimuthal angle of the D-spacing peak at $0.059 - 0.060 \text{ \AA}^{-1}$. Each OI value presented here represents the average of 14 – 36 measurements of one sample.

RESULTS

Stretch tanned leathers. Three leather samples were prepared with biaxial stretching during tanning, each with a non-stretched counterpart which was cut from the same skin to act as the control.

Measured as a percentage of length gain relative to their original length, the following strains were used in the preparation of the tanned leather:

- 2% parallel to the backbone and 7% perpendicular to the backbone
- 3% parallel to the backbone and 15% perpendicular to the backbone

- 10% parallel to the backbone and 10% perpendicular to the backbone

It required less force to stretch the skins in the direction perpendicular to the backbone than parallel to the backbone. The resulting tanned leather did not shrink after strain was removed and had an area gain of 9%, 18% and 21% respectively.

SAXS. The leather samples gave scattering patterns with well-defined diffraction peaks (Figures 3 a, b). Choosing the fifth order D-period diffraction peak, and plotting the variation in the intensity of this peak with azimuthal angle, it is seen that there is a simple unimodal collagen fibril orientation distribution when measured edge-on (Fig.3 c, d).

Collagen fibril re-orientation. A change in orientation and a change in the orientation index are observed as a result of the strain during tanning (Table 1 and Fig. 4). The fibrils change orientation towards the direction of the applied strain, measured both edge-on and flat on, with the largest change occurring edge-on ($OI = 0.31$, $P = 0.001$). The fibrils become more oriented (the OI increases) with strain for orientation measured edge-on. However, for the OI measured flat-on the relationship between OI and strain is not simple. When the dominant strain is perpendicular to the direction of the initial preferred orientation of the fibrils (this initial direction is parallel to the backbone), the OI goes down with strain. When the strain is applied equally in two directions the OI doesn't change significantly ($OI = 0.02$, $P = 0.78$).

Model of OI change with thickness. If the collagen fibrils are not lying flat then as the thickness of the leather decreases on stretching the angle of these fibrils to the plane of leather will decrease. This will cause an increase in OI. Previously a model was developed for the change in OI with thickness changes¹¹ and the details are repeated here.

The range of fiber angles in a sample is given by the orientation angle, OA, which is defined as the subtended angle that contains half the fibrils, i.e. it satisfies eq 1.

$$0.5 = \frac{\int_{\theta=-OA/2}^{\theta=OA/2} \theta N d\theta}{\int_{\theta=-90^\circ}^{\theta=90^\circ} \theta N d\theta} \quad (1)$$

Where N is the number of fibrils, and θ is the fiber angle (relative to the plane of the leather). In practice this is determined from the SAXS diffraction pattern by the integrated intensity verses azimuthal angle for one of the D-spacing diffraction peaks, eq 2:

$$0.5 = \frac{\int_{\varphi=-OA/2}^{\varphi=OA/2} \varphi I d\varphi}{\int_{\varphi=-90^\circ}^{\varphi=90^\circ} \varphi I d\varphi} \quad (2)$$

where I is diffraction intensity of a selected D-spacing diffraction peak above a fitted background and φ is the azimuthal angle of the diffracted X-rays.

OI is derived from OA by eq 3.

$$OI = \frac{90 - OA}{90} \quad (3)$$

Therefore, for perfect alignment in the reference direction $OI = 1$ and for a completely isotropic arrangement of fibrils $OI = 0$.

If a sample of leather containing a fiber shrinks in thickness uniformly, and the fiber is at an angle θ_1 from the base, then the new angle of the fiber, θ_2 , depends on the change in thickness by eq 4.

$$\frac{T_2}{T_1} = \frac{\tan \theta_2}{\tan \theta_1} \quad (4)$$

Where T_1 is the original thickness, and T_2 is the new thickness.

Rearranging eq 4 for θ_2 gives the new angle of the fiber after the leather has decreased in thickness:

$$\theta_2 = \tan^{-1} \left(\frac{T_2}{T_1} \tan \theta_1 \right) \quad (5)$$

It is then possible to calculate a transformed OA after stretching. It is only necessary to calculate the transformation by eq 5 of the angle that is the OA to calculate the new OA that represents the new fiber distribution.

The change in the thickness in the leather produced as a result of stretching while tanning (compared with the unstretched material) can then be used to calculate the change in OI due to this affine transformation. It is found that the change in OI can be explained solely by the change in thickness (Table 2).

Strength changes from stretching during tanning. The absolute tear strength of the leather was less for leather tanned while stretching (Table 3). However, as a result of the thickness

change with stretching, a the tear strength normalized for thickness increased after tanning under strain (Table 3, Fig. 5). In leather processed without strain (the control samples) the tear strength when torn parallel (27 ± 0.4 N/mm) or perpendicular (29 ± 3.6 N/mm) to the backbone were not statistically different ($P = 0.73$). For the leather prepared by tanning under strain, the normalized tear strength increases in both directions (Fig. 5), showing that tanning under strain does cause a change in thickness normalized strength of the material as hypothesized. However, the relationship between strain and tear strength also depends on the relative directions of the applied strain and the measured direction of the tear strength. When the tear strength is measured in the same direction (where the “direction” means the direction of the initiated fracture, which is at right angles to the direction of the movement of the jaws used for tearing) as the strain had been applied during tanning, the maximum strength is achieved with the maximum strain in that direction (42.8 ± 4.2 N/mm for both of these parallel to the backbone, and 42.8 ± 2.4 N/mm for both of these perpendicular to the backbone). However, when the tear strength is measured perpendicular to the direction the strain had been applied during tanning the relationship is not as simple, with the tear strength increasing with greater strain when the strain is in the direction parallel to the backbone but staying relatively constant for increasing strain perpendicular to the backbone.

Structure – strength relationship. A relationship can be seen between OI and tear strength (Fig. 6). A greater in-plane OI produces greater tear strength in both the parallel and perpendicular tear directions. There is a strong linear correlation between strength and collagen fiber orientation measured edge-on (R^2 is 0.65 and 0.86 respectively for a least squares linear fit).

DISCUSSION

Collagen fibril structural changes. It is apparent that it is possible to modify the structural arrangement of collagen fibrils in leather by modification to the tanning process. The OI increases both as measured edge-on (so that the layered structure of collagen fibrils is enhanced) and as measured flat-on (Fig. 7). The increase in OI measured edge-on is approximately proportional to strain during tanning, in the range of strain used in these experiments. With an increase in fiber alignment edge-on there is a decrease in the OI measured flat-on (Fig. 4). The hides required less stress to strain them in the direction perpendicular to the natural fibril orientation. The reason for this is that the fibrils are strong along their length^{21, 22} but the connections between fibrils are weak²³ so that it is much easier to pull the fibrils apart than to stretch them.

The strain obtained in this work was limited by the force available with the apparatus, but it may be possible to strain the leather more and therefore increase the OI further.

Structure affects strength. Overlaying the orientation information with the tear strength has provided a basis to develop an understanding of the relationship between process-modified collagen fibril orientation and strength. Previously it had been seen that there is a correlation between the native OI and tear strength in leather made from the hides of different animals of the same species⁵ and between animals of different species⁴. This suggested the concept of

developing a structure with an artificially high OI to generate extra strength. This would achieve two purposes: firstly to support the concept that there is a causal relationship between OI and tear strength and secondly as a method to produce a manufactured material with modified or improved properties.

Utilizing this natural property of strong skin, here it has been shown to be a cause and effect relationship between collagen alignment and mechanical function by artificially creating a high OI material which resulted in a material with greater tear strength. It was found that the OI could be increased very substantially in-plane from 0.48 to 0.79. The edge-on OI is most influenced by the stretch forces applied perpendicular to the backbone.

Tear strength is affected by the collagen fiber orientation where a tear propagates more easily between the fibrils than across the fibrils (Fig. 8). Therefore changing the orientation affects the ease of tear differently in different directions. In cases where the fibers are aligned perpendicular to the movement of the jaws for the tear test (Fig. 8 a) the tear direction is along the path of least resistance which is perpendicular to the movement of the jaws. However, when fibers are aligned parallel to the direction of the movement of the jaws for the tear test (Fig. 8 b) the tear propagates in this same direction as the applied force, along the path of least resistance between the collagen fibrils. When fibrils are more highly aligned they display their greatest tear strength to forces applied perpendicular to the fibril direction.

Material application considerations. The ability to manipulate the collagen structures in skins to produce leathers with customized characteristics could prove valuable for industry

applications when producing skins with specialized mechanical properties. Understanding how the application of strain can change the collagen alignment, which ultimately determines a significant portion of the tear strength properties of the leather, allows manufacturers to introduce processing steps to align the collagen fibrils to tailor the leather to the properties they desire. This concept could be implemented to allow ovine leather to be used for a wider range of applications and thus offer a significant increase in value and it may also be possible to increase the tear strength of other leather (such as bovine) that is naturally stronger than ovine. Once stretched the tanned skins don't return to their original size allowing for a gain in surface area as well as stronger leather. A surface area gain of up to 21% was achieved here. Leather is sold by surface area so the increase in surface area increases revenue. The thickness of the leather is important for each application and leather is split or shaved to achieve the desired thickness. Therefore the thickness normalized strength is the primary tear strength consideration, rather than the absolute tear strength of leather prior to splitting. Although the absolute tear strength decreased on stretching during tanning, the strength for any given thickness of leather produced by this method will be stronger than for a corresponding leather made without stretching during tanning. A further understanding of the natural collagen fiber alignments found in skins would provide a useful basis for more strategic stretching to produce certain properties in the leather.

CONCLUSIONS

Evidence has been provided to support a causal relationship between a high edge-on collagen fibril OI and tear strength. A relationship is found between the amount of strain applied during tanning and resultant thickness normalized tear strength. The tear strength depends on the relative directions of strain applied during tanning and the measured direction of tear strength. A greater in-plane OI produces greater tear strength in both the parallel and perpendicular tear directions to give a strong linear correlation between strength and collagen fiber orientation measured edge-on. Previously this relationship had been seen in a range of natural collagen materials but in this instance a material has been manufactured with improved properties demonstrating both the causal relationship and the ability to use this to modify natural materials. This concept could be implemented to allow ovine leather to be used for a wider range of applications and thus offer a significant increase in value.

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Table 1. Stretched samples and their orientation index measured flat-on and edge-on and fiber orientation.

Stretch parallel to backbone (% of original length)	Stretch perpendicular to backbone (% of original length)	Orientation Index (flat-on $\pm$ SD)	Orientation Index (edge-on $\pm$ SD)	Fibril Orientation where 0° is perpendicular to the backbone (°)	P values for t test for different mean to the control (flat on, edge on)
2	7	0.37 $\pm$ 0.07	0.66 $\pm$ 0.26	-1	0.48, <0.001
3	15	0.32 $\pm$ 0.14	0.79 $\pm$ 0.04	-3	0.06, 0.001
10	10	0.42 $\pm$ 0.09	0.65 $\pm$ 0.11	-17	0.78, 0.001
0	0	0.40 $\pm$ 0.08	0.48 $\pm$ 0.01	-10	n/a

Table 2. Adjusted orientation index based on thickness change.

Stretch perpendicular to backbone (% of original length)	Stretch parallel to backbone (% of original length)	Thickness change T2/T1	OI measured	OA measured	Thickness adjusted OA	Thickness adjusted OI	Difference between measured and thickness adjusted OI
2	7	0.57	0.66	30.6	31.3	0.65	-0.01
3	15	0.46	0.79	18.9	26.3	0.71	-0.08
10	10	0.50	0.65	31.5	28.0	0.69	0.04
0	0	1	0.48	46.8	46.8	0.48	0

Table 3. Tear strength for tanned leather parallel and perpendicular to the backbone.

Stretch perpendicular to backbone (% of original length)	Stretch parallel to backbone (% of original length)	Thickness (mm $\pm$ SD)	Parallel Tear Strength N ($\pm$ SD)	Parallel Normalized Tear Strength N/mm ($\pm$ SD)	Perpendicular Tear Strength N ($\pm$ SD)	Perpendicular Normalized Tear Strength N/mm ($\pm$ SD)	P values for t test for different mean to the control (parallel, perpendicular)
2	7	1.6 $\pm$ 0.2	54	34 $\pm$ 3	61	38 $\pm$ 3	<0.001, <0.001
3	15	1.3 $\pm$ 0.1	49	38 $\pm$ 1	56	43 $\pm$ 4	<0.001, 0.005
10	10	1.4 $\pm$ 0.2	60	43 $\pm$ 2	53	38 $\pm$ 1	<0.001, <0.001
0	0	2.8 $\pm$ 0.4	76	27 $\pm$ 0.4	81	29 $\pm$ 4	n/a

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