Fatliquor Effects on Collagen Fibril Orientation and D-spacing in Leather During Tensile Strain

by

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Abstract

Strength is a very important property of leather and is known to depend on the arrangement of the collagen fibrils within the material. The addition of fatliquor (penetrating oils) is an essential part of the manufacture of leather and enhances the strength and feel of leather. However, the mechanism by which fatliquor leads to increased strength is not understood. Here we use synchrotron based small angle X-ray scattering (SAXS) to monitor the collagen fibril rearrangement and internal strain of leather during tension. Differences in internal structural changes under strain with varying levels of fatliquor are investigated. It is found that when a strain of up to 40-70% was applied to leather, the orientation index (OI) of the collagen fibrils changed up to 21.8% and the d-spacing changed by up to 1.8% with no consistent differences at different levels of fatliquor. The extensibility of leather increases by 11.3% with as little as 2% fatliquor addition and the elastic modulus decreases with fatliquor addition but not in proportion to the amount of fatliquor. This change in extensibility is not reflected in differences in OI or d-spacing changes during strain. As reported previously, the fatliquor modifies the d-spacing of collagen. While fatliquor is traditionally considered to lubricate the fibers in leather, here the evidence suggests that this does not occur at the level of collagen fibrils. This provides an insight in the action of fatliquor in leather manufacture.

Introduction

The physical properties of leather result from a combination of the native characteristics of the skin or hide from which the leather is prepared and from the chemical and mechanical processing of leather manufacturing. Strength, flexibility, elasticity, and appearance are all important for the applications of leather. The major structural component of leather is type I collagen and it is the mechanical properties of the collagen fibrils [1-3] and the interactions between the fibrils [4-8] that make the major contribution to the physical properties of leather. Interactions between collagen fibrils in leather consist of hydrogen bonding, hydrophobic bonding, and cross-linking introduced by tanning with chromium salts or tannins. Cross-linking agents can alter the arrangement of collagen fibrils [8] and the mechanical properties of the material[9]

At a later stage in the processing of skins to leather, penetrating oils, known in the industry as fatliquor, are added to improve the feel of the leather and to increase the strength. It is believed that fatliquor acts to lubricate the fibers in leather. [10] Recently it has been shown that fatliquor penetrates to the level internal to collagen fibrils and alters the structure of the fibrils, increasing the d-spacing. [11] This is believed to be a result of shielding of the hydrophobic interaction between individual collagen molecules or tropocollagen units.

A powerful method to investigate the structure of collagen materials is small angle X–ray scattering (SAXS) that can provide detailed structural information on the microfibril orientation, d-spacing and the collagen fibril diameter in leather and other tissues. [12-17]

To understand the physical properties of leather, changes to the structure and arrangement of the collagen fibrils during mechanical strain has been investigated. [3,18-20] It has been found that with strain of the leather the collagen fibrils first re-orient and then stretch.

We wished to investigate the effect that fatliquor has on leather during mechanical strain. It is believed that fatliquor lubricates the fibers in leather and it has been shown that

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fatliquor penetrates beyond the level of collagen fibrils, so does the fatliquor lubricate at the level of collagen fibrils?

EXPERIMENTAL

Ovine skins were obtained from 5-month-old, early season Romney cross lambs. Conventional beamhouse and tanning processes were used to generate leather. The skins were depilated using a caustic treatment comprising sodium sulfide and calcium hydroxide. The residual keratinaceous material was then removed in a 1.2% solution of sodium for 16 h at 20°C. The skins were then washed and treated with a proteolytic pancreatic enzyme (Tanzyme, Tryptec Biochemicals, Ltd.) at 0.1%, followed by pickling in a 2% sulfuric acid and 10% sodium chloride solution. The pickled skins were then pretanned using oxazolidine, degreased with an aqueous surfactant, and then tanned using chromium sulfate. The resulting "wet blue" was then retanned using a mimosa vegetable extract.

Fatliquoring was carried out using Lipsol EHF (Schill + Seilacher). This product contains a mixture of lanolin, bisulfited fish oil, and 2-methyl-2,4-pentanediol. Lanolin, or wool wax, consists primarily of long chain waxy esters and some hydrolysis and oxidation products of these esters. The fatliquor offered was 0–10% by weight of wet leather prior to drying and mechanical softening.

The fatliquor content of samples processed with offerings of 0-10% fatliquor was determined using standard method ISO 4048. Briefly, 10 g of ground leather was extracted with at least 30 changes of dichloromethane in a Soxhlet extraction apparatus. The extract was dried in an oven at 102°C for at least 4 h and the resulting grease was cooled in a desiccator and weighed.

Samples for synchrotron-based small angle X-ray scattering (SAXS) analysis were prepared by cutting strips of leather 1 × 30 mm from the official sampling position (OSP) [21] from skins processed to leather with 0, 2, 4, 6, 8, and 10% Lipsol EHF offered. Diffraction patterns were recorded on the Australian Synchrotron SAXS/WAXS beamline using a high-intensity undulator source. Each sample was mounted without tension in the X-ray beam to obtain scattering patterns from an edge-on direction. Measurements were made every 0.25 mm through the cross section from the grain to the corium. Energy resolution of 10^{-4} was obtained from a cryo-cooled Si (111) double-crystal monochromator, and the beam size [full width at half maximum (fwhm) focused at the sample] was 250 × 80 μm, with a total photon flux of about 2×10^{12} photons s^{-1}. All diffraction patterns were recorded with an X-ray energy of 11 keV using a Pilatus 1 M detector with an active area of 170 × 170 mm and a sample–detector distance of 3371 mm. Exposure time for diffraction patterns was 1 s, and data processing was carried out using the SAXS15ID software. [22]

A custom built stretching apparatus was built for in-situ small angle X-ray scattering (SAXS) measurements as described by Basil-Jones. [18] Each strip of leather was mounted without tension in the X-ray beam and measurements were made every 0.25 mm through the cross section to obtain scattering patterns through the full thickness of the leather. The sample was stretched by 1 mm and was maintained at this extension for 1 minute before diffraction patterns, force, and extension data were recorded. This process was repeated with the sample stretched a further 1 mm each time until the sample failed.

Orientation index (OI) is used to give a measure of the spread of microfibril orientation and can be any number within the range 0–1. An OI of 1 indicates anisotropic microfibrils or fibrils that are completely parallel to each other; an OI of 0 indicates isotropic microfibrils or fibrils that are completely randomly oriented. OI is defined as (90° – OA)/90° where OA is the azimuthal angle range that contains 50% of the microfibrils centered at 180° and is calculated for one of the most intense d-spacing peaks (at around 0.059–0.060 $Å^{-1}$) for every diffraction pattern. [1]

The d-spacing of collagen was determined for each spectrum from Bragg's Law by taking the central position of several collagen peaks, dividing these by the peak order (usually from $n = 5$ to $n = 10$) and averaging the resulting values.

Tear strengths of the crust leathers were tested using standard methods. [23] Samples were cut from the leather at the official sampling position (OSP). [21] The samples were then conditioned by holding at 20°C and 65% relative humidity for 24 hours then tested on an Instron tensile tester using jaws placed in a standard eye-shaped cutout. Stress and strain measurements were recorded on an Instron mechanical test system using a standard tensile strength test. [24]

RESULTS

Fatliquor Addition.

The offer of fatliquor to the leather ranged up to 10% however the actual uptake of fatliquor was not quite the same as the offer. We therefore refer to the offer as the "nominal fatliquor". An analysis of the fat content of the fatliquored leather showed a higher fat content than the offer, because of some initial fat content in the leather, with a saturation occurring at 8% offer (Table I).

Scattering Patterns

The X-ray scattering patterns recorded for the leather samples show clear diffraction rings (Figure 1 a, b) which

are due to the collagen d-banding. The integrated intensity for these patterns shows these as well defined peaks from which the d-banding can be identified (Figure 1c, d). The variation in intensity with azimuthal angle (Figure 1e) can be used to calculate the orientation index of the collagen fibrils. It can be seen that when the leather is stretched the OI increases and a portion of the fibrils which are oriented in the direction of the strain become highly stretched with the d-spacing increasing substantially.

Tear Test

The tear force observed had an initial drop in the tear strength with the addition of a small amount of fatliquor followed by a general increase in tear strength with further fatliquor additions (Figure 2). Generally therefore leather is stronger when this fatliquor is present.

When the variation of d-spacing with strain is plotted it becomes apparent that the d-spacing increases with fatliquor

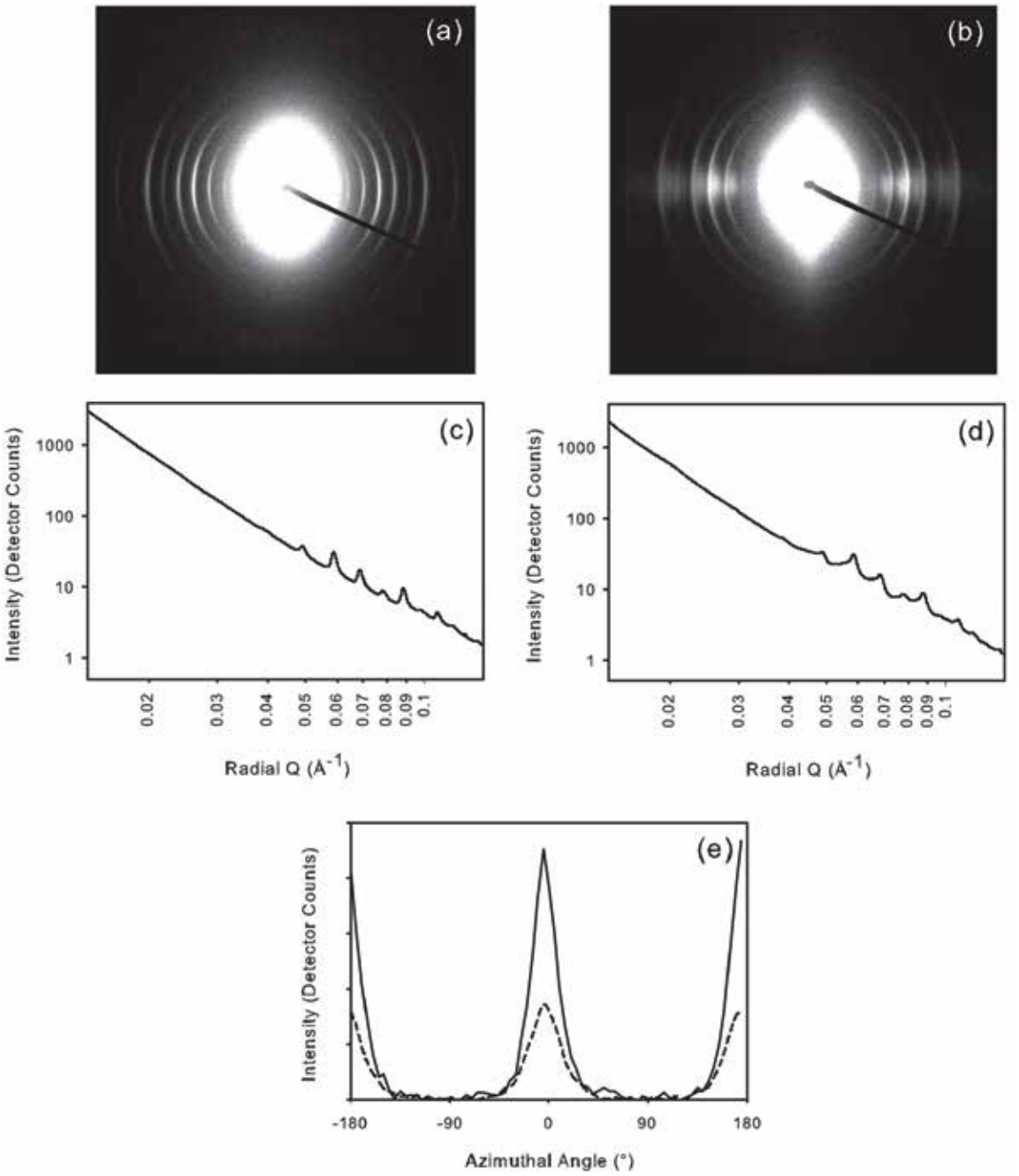

Figure 1. Example of SAXS of leather: (a) raw SAXS pattern static; (b) raw SAXS pattern after stretching; (c) integrated intensity profile of static sample; (d) integrated intensity profile of sample after stretching; (e) intensity variation with azimuthal angle for the 5th order diffraction peak (dotted line static, solid line stretched).

content (as reported elsewhere [11]) and increases with strain (as seen with ovine leather [18]) (Figure 3.). There is no difference between 8% and 10% fatliquor offered samples as these had saturated and had the same uptake of fatliquor.

Orientation Index

The OI increases with strain for all samples (Figure 4). No correlation was found between fatliquor and OI when the samples were not under tension (R^2 = 0.47, P = 0.13) (Figure 5a). Similarly, when stretched, after the increase in OI which happens for all samples, the OI measured at maximum strain before the samples broke does not correlate with fatliquor addition (R^2 = 0.08, P = 0.60) (Figure 5b).

TABLE I
Nominal addition of fatliquor and measured content of fat in leather samples.

Nominal Addition of Fatliquor (%)	Measured Fat Content (%)	Measured fatliquor added (%)
0	1.0	0.0
2	3.8	2.8
4	5.7	4.7
6	8.8	7.8
8	9.8	8.8
10	9.9	8.9

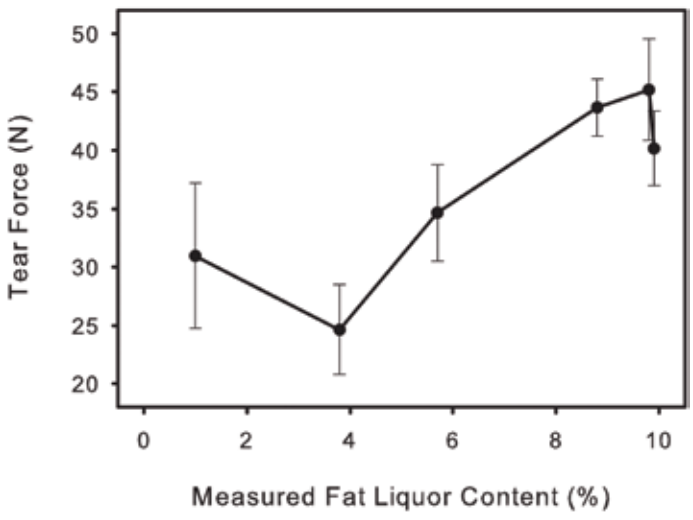

Figure 2. Tear force of leather with measured fatliquor content.

The samples with different fatliquor content do not all stretch the same amount. Therefore a plot of the change in d-spacing and OI at a strain of 0.4 is also shown (Figure 6). This provides a fair comparison between the changes that take place to fibril rearrangement and fibril extension under tension when different levels of fatliquor are present. This shows no trend when stretched with fatliquor content of the sample in either the amount that d-spacing changes or in the OI change with stretching (Figure 6).

Stress-strain

The stress-strain curves (Figure 7) show that the elasticity varies with fatliquor content. With fatliquor added, leather has

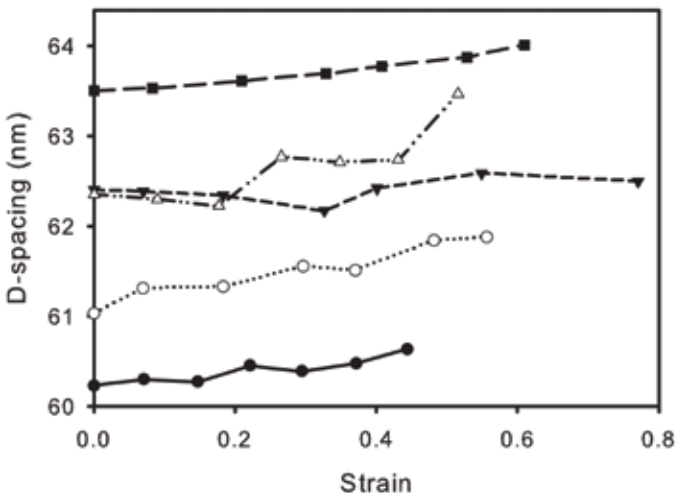

Figure 3. Variation in d-spacing with strain and fatliquor content: (●, _____) no fatliquor, (○, ·····) 2.8% fatliquor, (▼, – – – –) 4.7% fatliquor, (Δ, – ·· – ·· –) 7.8% fatliquor, (■, ———) 8.8% fatliquor.

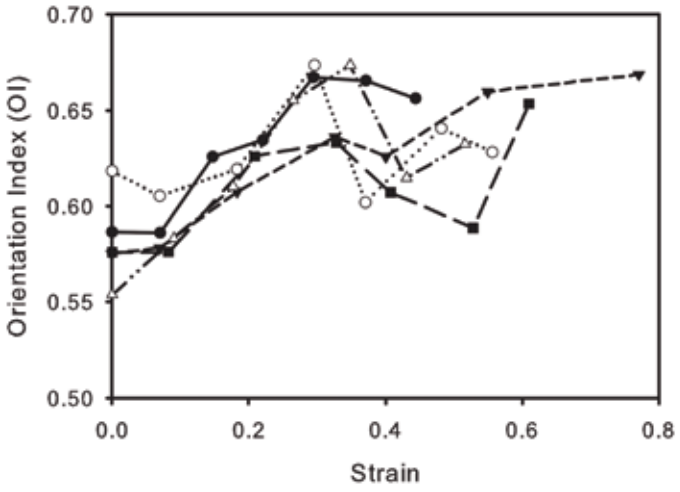

Figure 4. Variation in orientation index (OI) with strain and fatliquor content: (●, _____) no fatliquor, (○, ·····) 2.8% fatliquor, (▼, – – – –) 4.7% fatliquor, (Δ, – ·· – ·· –) 7.8% fatliquor, (■, ———) 8.8% fatliquor.

a longer region of low elastic modulus (stretchier material) before the leather starts to resist stretching. Full stress-strain curves for the small samples measured in-situ during X-ray analysis are shown in Figure 7a but these were small samples and must not be over-interpreted. Elastic modulus obtained from these curves show the initial drop in elastic modulus with an addition of a small amount of fatliquor followed by a general increase in elastic modulus with further fatliquor additions (Figure 7b). The total extensibility of the leather is also shown but does not follow an easily rationalized trend (Figure 7c).

OI of Cross Sections

The variation of OI through sections of leather with different amounts of fatliquor at different levels of strain (Figure 8) show the strain is taken up throughout the thickness of the leather and that this is similar with or without fatliquor added. There is no obviously different mechanism of responding to strain with or without fatliquor present.

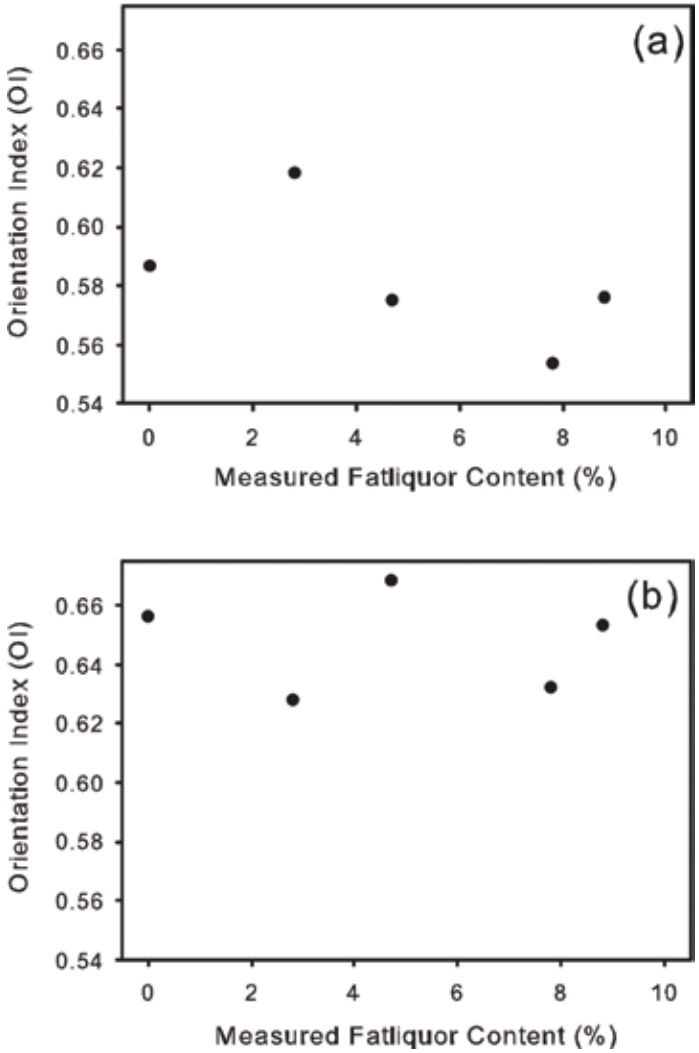

Figure 5. Variation of OI with measured fatliquor content (a) for unstrained leather; (b) for leather strained to Maximum, orientation is calculated by taking the average OI of the sample after each stretching increment (from no stretch up to the maximum amount stretched) and averaging these values.

DISCUSSION

While it can be seen that the fatliquor penetrates to the collagen fibrils and changes some aspect of the structure of the fibrils, the d-spacing, as reported elsewhere, [11] there does not appear to be any difference in the change in the orientation of the fibrils during strain with or without fatliquor. Therefore the rearrangement of fibrils in the leather is not greater with fatliquor added than without. In addition, the amount of force individual fibrils experience (evidenced by d-spacing change during stress) is not less with fatliquor than without.

If the fatliquor acted to lubricate the collagen fibrils so that they slide more easily past one another then it would be expected that the OI would change much more with strain when fatliquor is added because as the fibrils slide past each other they would be able to rearrange their positions to become more oriented in the direction of strain. If this is the mechanism of action of fatliquor then it would also be expected that once highly oriented the fibrils should be able to stretch more as they are oriented with the direction of force. Neither of these is seen, neither a greater change in OI nor a larger increase in d-spacing. Therefore, there is no evidence of lubrication of the collagen fibrils, even though we know that the fatliquor penetrates not just to the fibrils but also within the fibrils (as evidenced by the change in d-spacing).

From the stress-strain data, and as is well known already, fatliquor does improve the bulk properties of leather and increases the extensibility and decreases the elastic modulus of leather. Therefore fatliquor does have an effect on the leather. Since the lubrication by fatliquor does not appear to occur at the fibril level the mode of action may be lubrication between fibril bundles or fibers which is at a different scale to the fibrils.

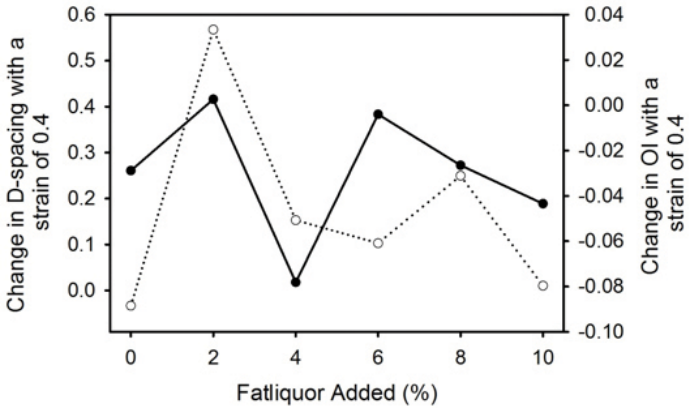

Figure 6. Change in OI and d-spacing upon strain to 0.4 for measured fatliquor contents: (●, _____) change in d-spacing, (○, ·····) change in OI.

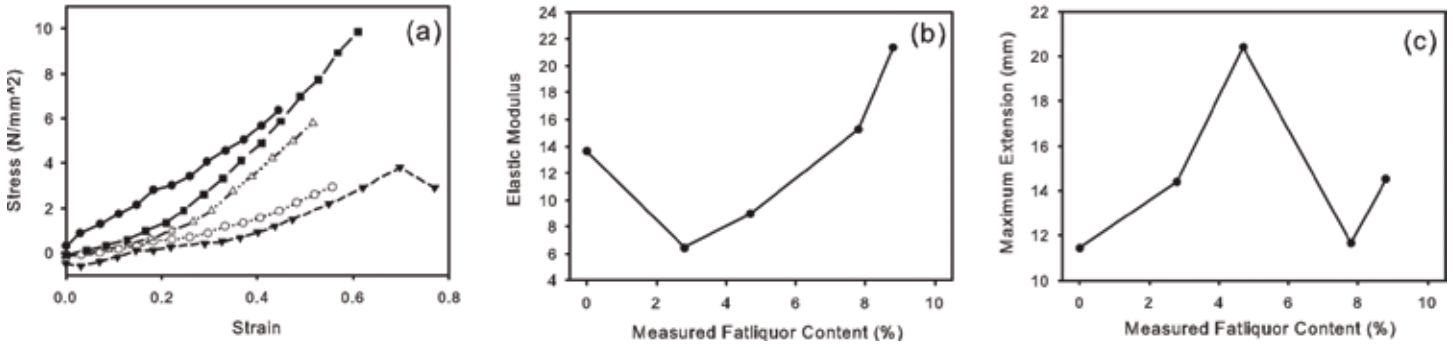

Figure 7. (a) Stress-strain on small leather samples recording during SAXS measurements: (●, _____) no fatliquor, (○, ·····) 2.8% fatliquor, (▼, – – – –) 4.7% fatliquor, (Δ, – ·· – ·· –) 7.8% fatliquor, (■, ———) 8.8% fatliquor; (b) Elastic modulus taken from curves in (a); (c) maximum extension of sample before break occurred versus measured fatliquor content.

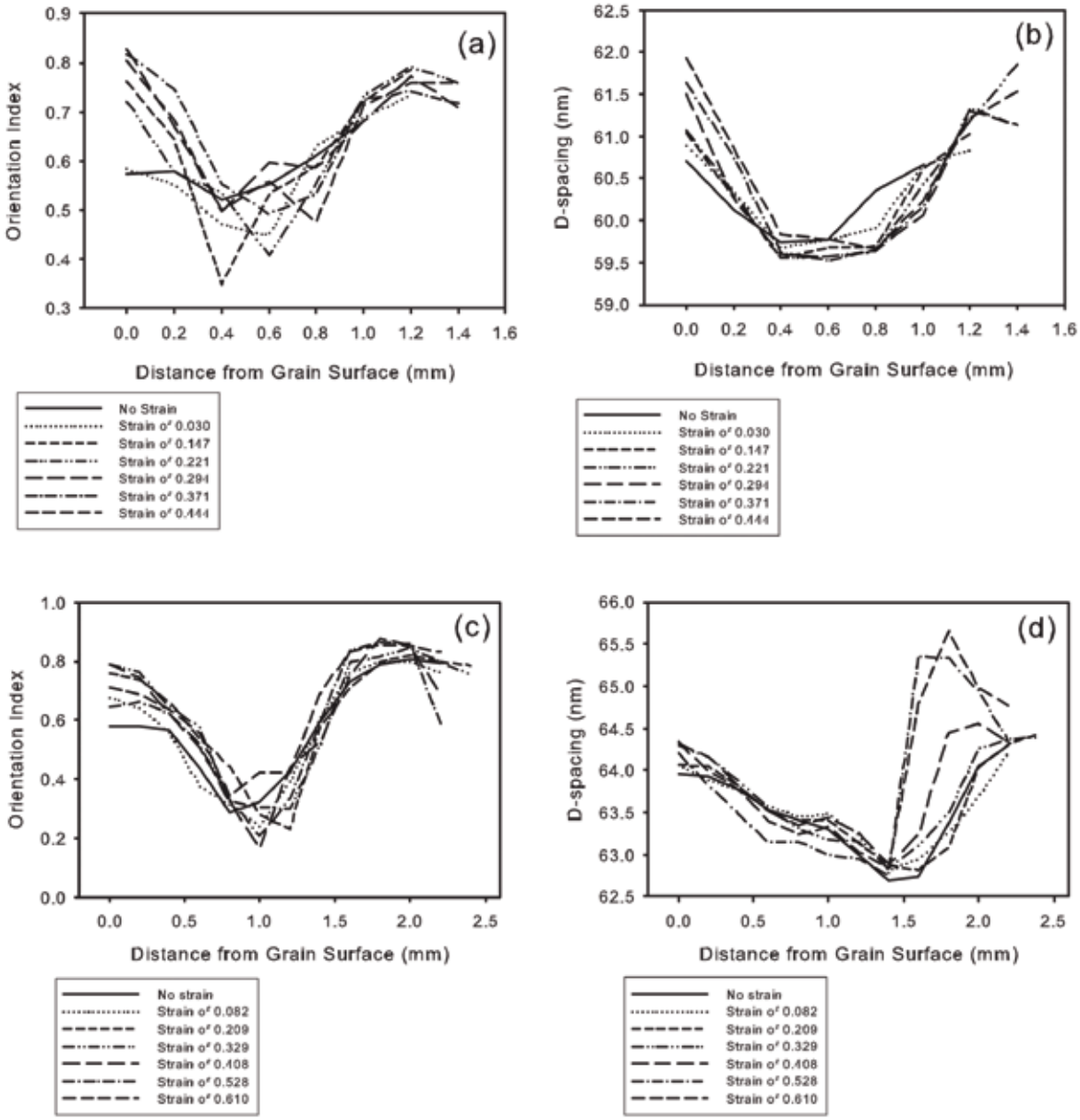

Figure 8. Cross sections of leather under strain. No fatliquor (a, b), 8.8% measured fatliquor content (c, d). Variation of OI with strain (a, c), variation of d-spacing with strain (b, d).

Leather takes up strain at a variety of scales, both within the fibril (d-spacing), between fibrils (OI) and at the fibril bundle and fiber level (possibly contributes also to OI). Fatliquor affects the larger scale processes such as drying of the leather and is the most important step in making soft leather. However, it was observed that the arrangement of fibers is mostly unaffected by fatliquor with no change in the spread of orientation.

CONCLUSIONS

Using small angle X-ray scattering to analyze leather, differences in collagen fibril orientation and d-spacing with different levels of fatliquor addition and at different levels of strain were investigated. Both the orientation index and d-spacing changed during strain however there were no consistent differences in these behaviors with different levels of fatliquor. While fatliquor is traditionally considered to lubricate the fibers in leather, here the evidence suggests that this does not occur at the level of collagen fibrils, even though there is evidence that the fatliquor penetrates to the level of the fibrils and changes the structure of the fibrils. We have been able to provide more knowledge on the mechanism of action of fatliquor to the elasticity of leather to inform the leather making process.

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