Research Article

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# A small angle X-ray scattering study of the structure and development of looseness in bovine hides and leather

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## Abstract

**BACKGROUND: Some bovine hides produce poor quality leather, termed loose leather. The structural characteristics of hides and the intermediate processed stages that lead to loose leather are not well understood. In the present study, synchrotron-based small angle X-ray scattering (SAXS) is used to investigate collagen fibril orientation at the different stages of processing (i.e. from hide through to leather) that result in both tight and loose leathers.**

**RESULTS: Tight leather of a relatively isotropic texture has a lower orientation index (OI) than loose leather of a more pronounced stratified texture; conversely, tight pickled hide and wet blue have a higher OI than loose pickled hide and wet blue. There is a greater increase in OI on processing from pickled hide to dry crust (leather) for loose material. This is largely the result of a greater increase in hide thickness prior to pickling for loose hide than tight hide, followed by a greater decrease at the dry crust stage. The collagen fibrils in loose leather and wet blue more readily orient under stress than do those in tight leather. Loose leather has a more pronounced layered structure than tight leather, although this difference is not apparent from SAXS measurements of hide prior to the dry crust stage; it develops during processing.**

**CONCLUSION: The greater swelling of the loose hide during processing disrupts the structure and leads to a more layered collagen arrangement on shrinking at the final dry crust stage.**
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**Keywords:** leather; looseness; collagen; small angle X-ray scattering; orientation

## INTRODUCTION

'Looseness' is the term used in the leather industry for a defect that results in a greatly reduced value for leather. It causes wrinkles and creases in the finished product and may be present in 5–10% of finished bovine leather hides (C. Thiele, Tasman Tanneries, personal communication). The loss to the New Zealand bovine leather industry alone is estimated at $50 million per annum. The measure of looseness is known as the 'break' and is defined in an ASTM standard[1] where a coarse break (high number) is a loose (poor quality) material. Looseness may also develop in leather produced from the skins of other animals.

Relatively recent research found that, in loose leather, the grain layer tends to be separated into sheet-like structures and also that there are larger gaps between the collagen fibers than in tight leather.[2] A weak layer exists in the lower grain layer or at the grain–corium boundary, allowing the surface grain to partially detach and therefore wrinkle when bent inwards (towards the grain).[3,4] 'Tight leather' is the term applied to leather that does not have these deficiencies.

It is possible to use ultrasonic imaging to identify looseness in dry crust.[3] The characteristic features identified in images of loose leather are also present in images of wet blue and pickled hide that subsequently develop into loose leather even though looseness is not apparent in these materials when subjected to the break test.[5]

Small angle X-ray scattering (SAXS) studies of loose and tight leather support the idea that, in loose leather, the collagen fibrils are more layered, exhibiting a higher orientation index (OI) than in tight leather when the OI is measured with the X-rays edge-on to the leather.[3] SAXS has been shown to be valuable in improving our understanding of the structure of leather and its relation to other physical properties, such as tear strength and the response to strain.[6–9] The overall goal of the present study is to determine how looseness develops during the processing of bovine hides to dry crust. SAXS was used to monitor the collagen fibril arrangement during various stages of processing, and to compare hides that developed into loose and tight leathers. One specific aim

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was to investigate whether looseness is an inherent property of a hide and, if not, to what extent it results from processing. Another aim was to investigate why looseness is not detectable in a break test during the early stages of processing and is obvious only at the final dry crust stage. The present study also investigated how the collagen fibril structure of loose and tight crust and partially processed hides responded to strain, using a similar approach to that employed in studies of other leather and collagen-based materials[8,10] to address the question: is there a difference in the behavior under strain that may partially explain separation of the grain?

## MATERIALS AND METHODS

### Sample selection

A range of hides was selected from the lime-splitting machine at a local tannery, Tasman Tanning Ltd (Wanganui, New Zealand), with the intention that some might become loose leathers and some tight leathers. As noted above, it is not possible to accurately pre-determine whether a hide will develop looseness; however, some hides that appeared to have more draw were considered to be likely candidates and were included.

### Leather preparation

At the time of selection, the hides were part-processed (from a production run). Each hide weighed approximately 35 kg and had been green fleshed and processed using a conventional recipe. This recipe is based on sodium sulfide, sodium hydrosulfide and lime to both depilate and open-up the structure to allow the removal on non-collagenous proteins. Processing involved loading approximately 8500 kg of hides at a time into drums (diameter 4 m, width 3.8 m), which were rotated at $0.0179 \times g$ (units of radial acceleration) during the liming stage and $0.0716 \times g$ during washing. Hides were taken from the drums after 8 h of liming and returned to the Leather and Shoe Research Association for onward processing in its pilot tannery to leather using a conventional recipe for shoe leather production. The next day, the horsed-up leather was sammed and sett to achieve a moisture content of 650 g $kg^{-1}$ and toggle dried at 40 °C on a tunnel drier until dry in all regions. The crust leathers were conditioned heavily with water on the flesh side and held under these conditions for 24 h. The next day, moisture was measured to ensure a moisture content of 140–160 g $kg^{-1}$ in all areas prior to Molissa staking on settings of 4 and 5 (Svit Machinery, Zlin, Czech Republic).

From the dry crust, samples showing looseness were taken from the shoulder region, just above the axilla, which is the region normally most prone to looseness, and tight samples were cut from areas adjacent to the affected region. The results reported in the present study are from three hides processed through to leather.

### Standard test of looseness

Looseness was evaluated using the standard break test method,[1] which involves folding the leather grain side in, and quantifying the wrinkles against a standard scale. Samples were considered tight if the break measurement was $\leq 2$ and loose if the break was $\geq 4$.

### Thickness assessment

A sample's thickness was measured using calipers closed to a light pressure with minimal compression of the leather or hide. Because the range of samples prepared for SAXS did not include initial fresh hides and subsequent interpretation of the SAXS results revealed that the thickness changes from fresh hide stages are important, a separate batch of hides was processed from fresh through to dry crust with thickness recorded at each stage. In this separate batch, splitting did not occur so that data for each stage were derived from the full-thickness raw hide, whereas, for the SAXS samples, splitting occurred post liming. One limitation of the 'unsplit' hides was that the tanning chemicals might not have penetrated to the centre of the hide's thickness.

### SAXS measurement

To prepare the samples for SAXS, 1–2-mm thick strips of loose and tight leather were cut at the wet blue and pickle stages. For the static tissue analyses, the samples were mounted edge-on to the incoming X-rays. Diffraction patterns were recorded every 0.2 mm, with the samples being analyzed from the grain to the corium. For the SAXS analyses of samples under strain, each $1-2 \times 33$-mm strip was mounted on a purpose-built frame attached to a linear motor (Linmot PS01 $48 \times 240/30 \times 180$-C; NTI AG, Spreitenbach, Switzerland).[8] Clamps fitted between the motor and a L6D OIML single-point load cell (Hangzhou Wanto Precision Technology Co., Zhejiang, China) held the samples. The samples were mounted without tension and stretched in 1-mm increments until the slack was taken up and tension was just registered by the load cell. This was the starting point for each analysis. An initial diffraction pattern was recorded, and the sample was stretched in 1-mm increments until it failed. After each extension, the sample was allowed to stabilize for 1 min before the diffraction pattern was recorded.

Diffraction patterns were recorded on the SAXS/WAXS beam line at the Australian Synchrotron and the X-ray Nanoprobe Beamline at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan,[11] which have similarly configured beamlines. The Australian beamline uses a high-intensity undulator source from which an X-ray energy of 12 keV was used. An energy resolution of $10^{-4}$ (e.g. $1 \times 10^{-4}$ for 1 radiation) was used from a cyro-cooled Si(III) double-crystal monochromator with a beam size of $250 \times 80$ µm (full-width at half-maximum focused at the sample) and a total photon flux of approximately $2 \times 10^{12}$ $phs^{-1}$. A Pilatus 1 M detector (Dectris, Baden-Daettwil, Switzerland) with an active area of $170 \times 170$ mm was used with a sample-to-detector distance of 3371 mm. The 23A SWAXS beamline of the Taiwan Light Source provides an energy range of 5–23 keV. A 12-keV beam was used for the leather samples, with an energy resolution $(1.2-1.8) \times 10^{-2}$ from a double-multilayer crystal monochromator for a flux of $2.8 \times 10^{11}$ ph $s^{-1}$. A beam size of 0.25 mm in diameter and a Pilatus 1 MF detector was used for data collection, with an exposure time of 1–2 s. Diffraction patterns for the unstrained and strained samples of pickle, wet blue and dry crust (leather) were recorded on the Australian Synchrotron and diffraction patterns of a separate set of unstrained and strained samples of loose and control leather were recorded on the NSRRC SWAXS beamline. Representative examples of diffraction patterns of the leather samples are presented in Fig. 1.

SAXS data were analyzed using SAXS15ID software.[12] D-spacing of the collagen fibrils was found by integrating the intensity plots from the azimuthal range of 45° to 135°, fitting a Gaussian curve to the sixth-order diffraction peak and determining the position of the centre of the curve. The OI is defined by:

$$\mathrm{OI} = \frac{90° - \mathrm{OA}}{90°}$$


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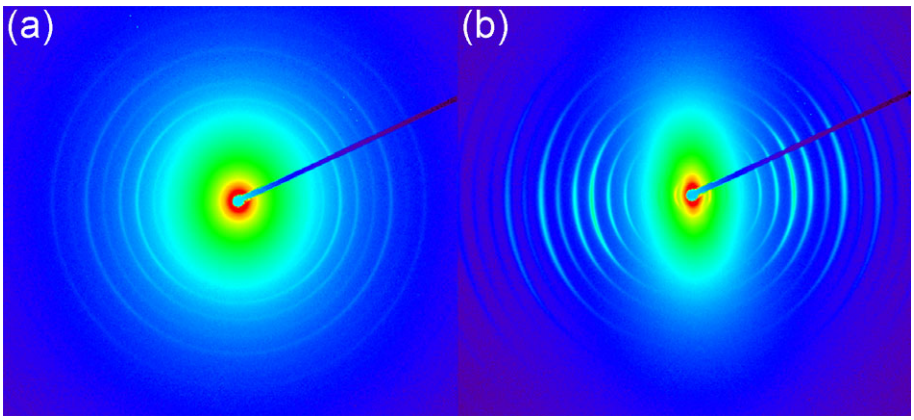


**Figure 1.** Representative scattering patterns of (a) poorly aligned leather with a low OI and (b) leather under tension and therefore highly aligned with a high OI.

where OA (orientation angle) is the minimum azimuthal angle range centered around 180° that contains 50% of the collagen fibrils, based on the method of Sacks for light scattering but converted to an index[7] using the spread in azimuthal angle of D-spacing diffraction peaks. The OI is a measure of spread of collagen fibril orientation in a sample, where an OI of 1 indicates the fibrils are parallel to each other and an OI of 0 indicates the fibrils are randomly oriented.

## RESULTS

### Sample selection

Sample selection was successful, with both loose and tight leather being included in testing, according to data from break testing of the samples at the dry crust stage.

### Thickness

The hide thickness data (Table 1) revealed that, as it passes from the pickled to the wet blue stage, a hide swells, and that loose leather swells more (132%) than tight leather (42%). By contrast, from the wet blue to dry crust stage, a hide shrinks in thickness, more so for loose leather (20%) than for tight leather (5%).

### Orientation index through sample cross-sections

Average collagen fibril OI for each sample type (Table 2) was derived from measurements along two or three cross-sections of each sample type (Fig. 2). There is good consistency between the replicates. Dry crust had the highest OI (fibrils were the most highly oriented), whereas wet blue had the lowest OI, with pickled hide showing an OI just slightly higher than the wet blue. Loose leather had an average OI higher than tight leather and this was especially evident in the central and corium regions. However, the same OI relationship between tight and loose material was not apparent in the wet blue and pickled hide; rather, the opposite relationship was observed. The cross-sections revealed a region of very low OI in the corium for loose wet blue, in contrast to loose leather, and the loose pickled hide had a lower OI than the tight pickled hide across much of the thickness.

### D-spacing through sample cross-section

From the plots of data for collagen fibril S-spacing through cross-sections (Fig. 3), it is apparent that D-spacing decreased as the hides went from the pickled to wet blue stages and decreased further to dry crust. The loose pickled hide had a significantly lower D-spacing than did tight pickle. There was no large variation in D-spacing with depth through the samples and D-spacing and OI were not correlated.

**Table 1.** Thickness of materials at different process stages. Average of two hides each

| | Thickness (mm) | |
|---|---|---|
| Process stage | Tight (OSP) | Loose (lower axilla) |
| Raw | 4.10 | 2.40 |
| Pickle | 3.83 | 1.85 |
| Wet blue | 4.23 | 2.31 |
| Wet crust | 5.43 | 4.30 |
| Dry crust | 5.15 | 3.43 |

**Table 2.** Average OI measured edge-on at different stages ($n = 18–41$)

| Average OI | Pickle | Wet blue | Leather |
|---|---|---|---|
| Loose | 0.31 | 0.30 | 0.61 |
| Tight | 0.45 | 0.38 | 0.54 |

$P < 0.003$ for $\alpha = 0.05$ in all comparisons between loose and tight.

### Changes in OI and D-spacing with strain

The OI and D-spacing were determined for strained samples with the X-rays edge-on (Fig. 4) and with the X-rays normal to the surface (Fig. 5). Edge-on measurements indicate the degree of fibril layering, whereas the normal-to-the-surface data give a measure of the 'weft/weave' nature of the fibrils as viewed looking down on a flat surface.

Measured edge-on, the fibrils of the loose wet blue and leather oriented more readily than those of tight materials on stretching (Fig. 4); measurements normal to the surface did not exhibit this pattern (Fig. 5). This difference shows that, in loose leather and wet blue, the collagen formed into parallel layers on stretching more than it did in tight leather. However, pickled hide did not behave this way.


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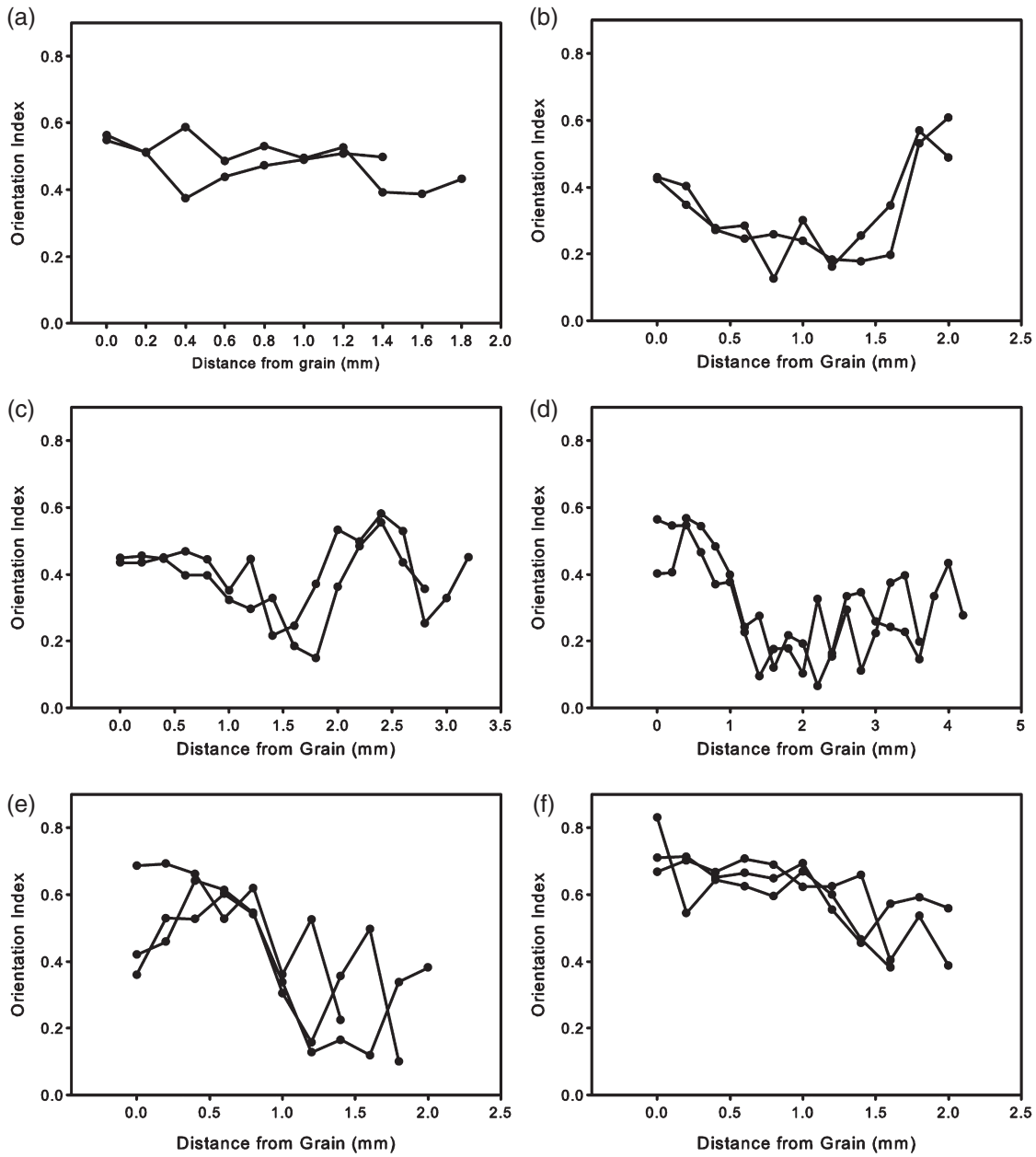


**Figure 2.** SAXS OI data from cross-sections of loose and tight hide and leathers. (a) Tight pickled hide; (b) loose pickled hide; (c) tight wet blue; (d) loose wet blue; (e) tight leather; and (f) loose leather. The two or three lines in each plot represent duplicate separate measurements (at different positions).

Measured normal to the surface, the OI changes on stretching of loose and tight materials were similar. Pickled hide and wet blue underwent a large change in OI and became highly oriented (0.8–0.9), whereas leather, which also underwent a large change in OI, reached an OI of only approximately 0.7, having started from a lower initial value.

The D-spacing changes in leather were similar for tight and loose leathers measured edge-on, although the changes were greater in tight than loose leather in normal measurements. For wet blue measured both edge-on and normal, the D-spacing changed less in tight than in loose, although this was reversed in all the data for pickled leather. Because D-spacing changes indicate the stress experienced by individual collagen fibrils in a leather, acting as an internal stress or strain gauge,[12,13] the D-spacing data suggest that individual fibrils undergo greater strain for tight compared to loose in leather examined in the weft/weave dimension and in pickled hide examined in any dimension. Only in wet blue did fibrils of loose samples undergo increased strain compared to tight samples (in any dimension).

## DISCUSSION

The present study aimed to further our understanding of the structural basis of looseness in bovine leather and how it develops as hides are processed from raw hide to leather. Using this knowledge, it might be possible to develop processing strategies that minimize the likelihood of looseness developing.

The degree of collagen fibril orientation changed as hides were processed to leather, and the thinnest material, dry crust, had the highest OI, measured with the X-rays edge-on. This has been


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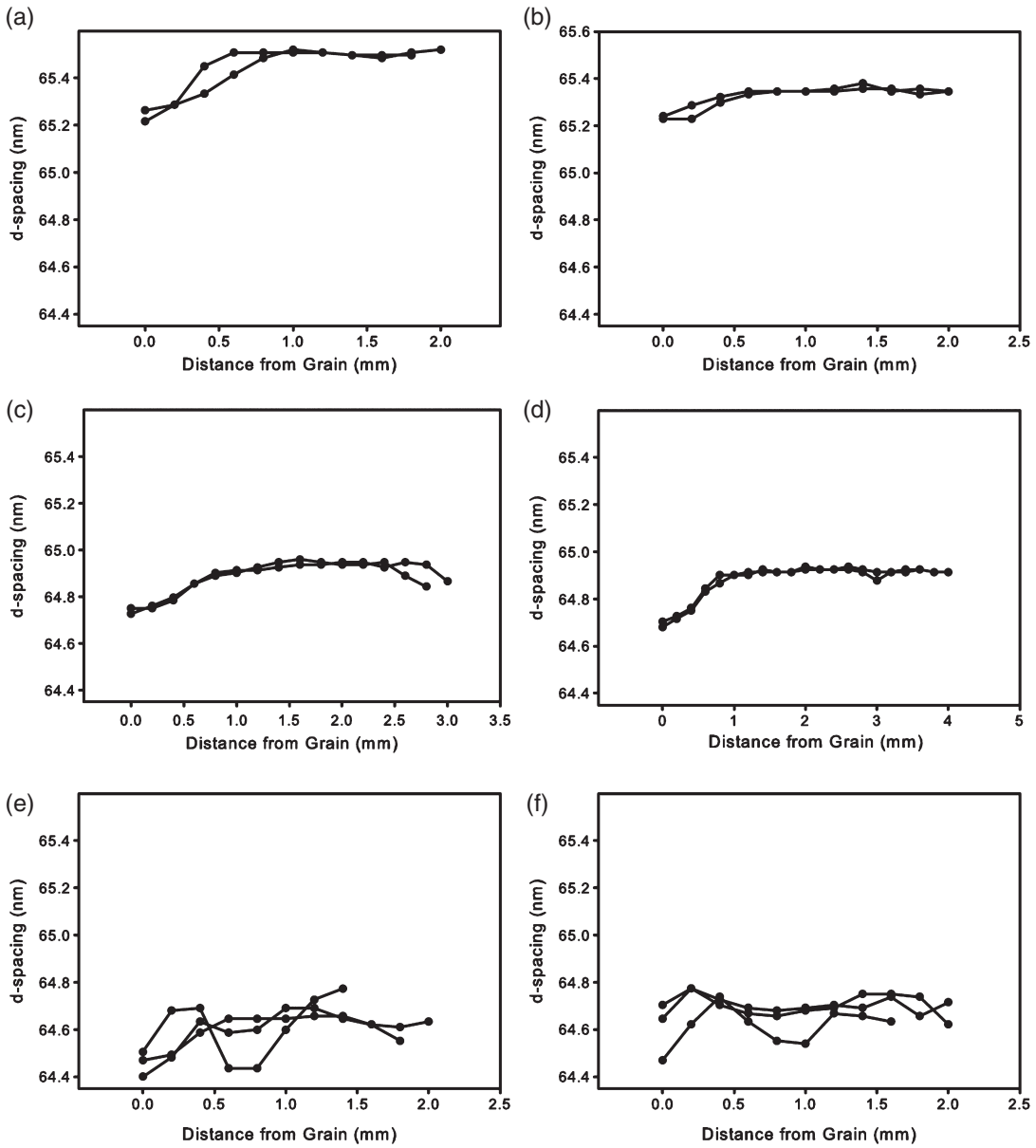


**Figure 3.** D-spacing measured edge-on through cross-sections of (a) tight pickled hide; (b) loose pickled hide; (c) tight wet blue; (d) loose wet blue; (e) tight leather; and (f) loose leather. The two or three lines in each plot represent duplicate separate measurements (at different positions on the same sample).

described previously[14] and can be modeled by considering a sample of leather containing a fiber that expands uniformly in thickness (from original thickness $T_1$ to new thickness $T_2$), and its $\theta_1$ from the base changes to a new angle $\theta_2$, depending on the change in thickness:

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

From this equation, the change in OI can be calculated because OI is related to orientation angle, OA, by the relationship:

$$\mathrm{OI} = \frac{90° - \mathrm{OA}}{90°} \quad (2)$$

The change in OI resulting from a change in thickness (where $\mathrm{OI}_2$ is for $T_2$ and $\mathrm{OI}_1$ is for $T_1$) is obtained by substituting OA for $\theta_1$ in Eqn (1) to give Eqn (3):

$$\theta = \tan^{-1}\left(\frac{T_2}{T_1}\tan\theta_1\left[90\left(1-\mathrm{OI}_1\right)\right]\right) \quad (3)$$

Although the loose pickled hide and loose wet blue had a higher OI than did tight material at the same stages, dry crust had a higher OI in the loose leather because of the greater change in thickness it underwent compared to tight leather. This change, when corrected for Eqn (3), does not account well for the higher OI of the final dry crust (Table 3). Therefore, some other mechanism is acting to increase the fibril OI between the wet blue and the dry crust stages.

One possible additional contributor to the changes in fibril orientation could be the cross-linking between collagen fibrils. It is considered that collagen cross-links are responsible for mechanically

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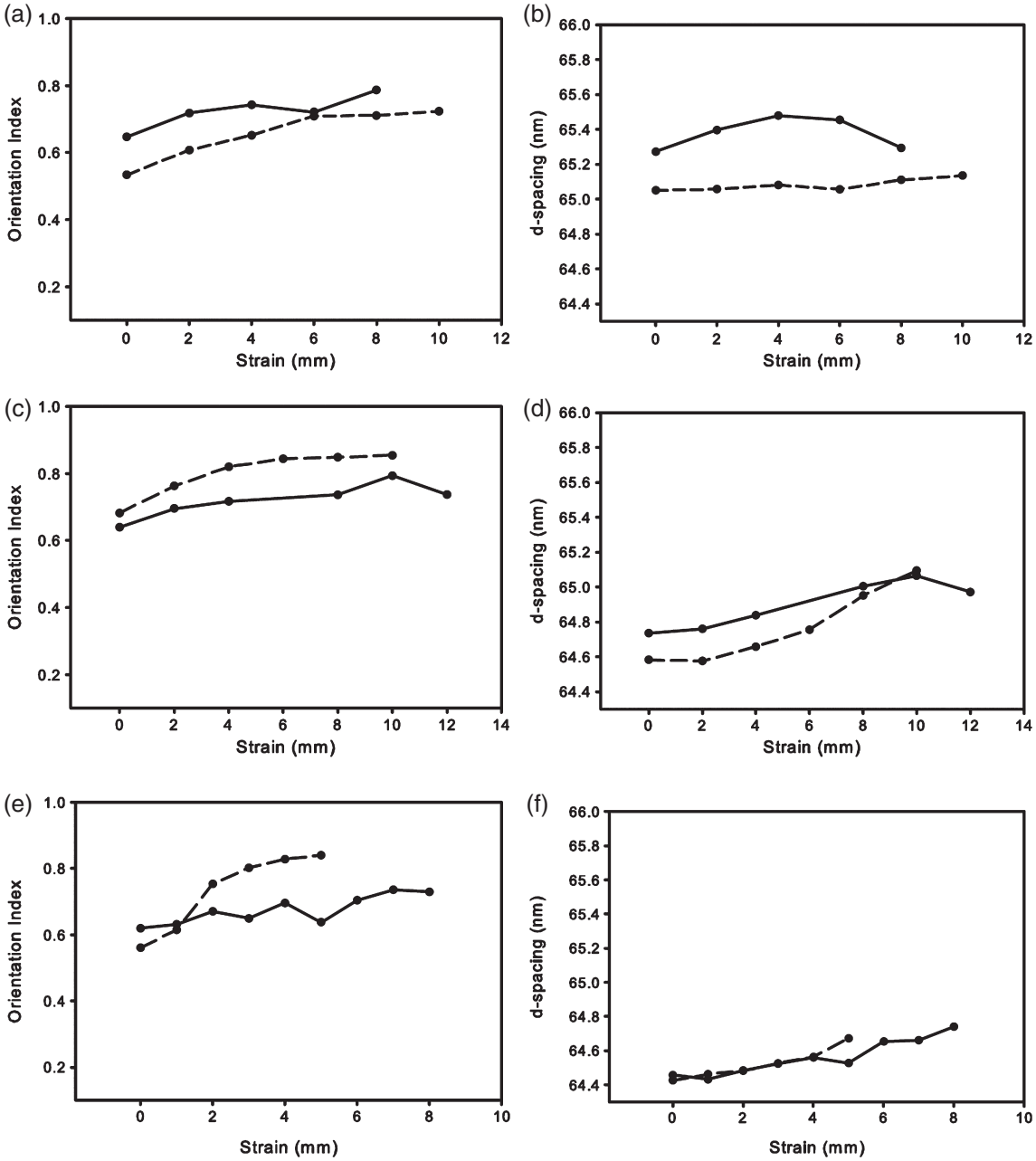


**Figure 4.** OI and D-spacing measured edge-on during strain (average values). Solid lines: tight materials, dashed lines: loose. (a, b) Pickled hide; (c, d) wet blue; and (e, f) leather. Each point on the plots is the average of eight to 16 diffraction patterns, representing a full cross-section of the sample. The two lines in each plot represent duplicate measurements on separate samples (at different positions).

coupling fibrils to restrict fibril sliding[15] and collagen cross-links can affect fibril orientation in some collagen-based materials.[16] However, the overall effect of cross-linking on collagen fibril structure has been shown to be only minor[16] and so changes in cross-linking are not sufficiently significant on their own to explain the structural difference seen between loose and tight hides and leathers in the present study. Between the wet blue and dry crust stages, there are other chemical and physical processes that hides are subjected to, such as filling, fatting and staking. These other factors could contribute to the differences in OI.

The change in thickness during processing between loose and tight materials can explain both the development of looseness and some of the OI differences. When a hide swells 'too much', the connections between (virtual) layers of collagen fibrils in the hide are broken by the physical expansion (Fig. 6). From pickled hide to wet blue, swelling was found to be greater in loose material (132%) than in tight leather (42%). This greater swelling in the hides that went on to develop looseness would be associated with the much greater destruction of the inter-layer connections. It may be that there are also differences in swelling between loose and tight with liming, although that was not measured in the present study. The second consequence of the greater swelling (the lower OIs observed in loose pickled hide and wet blue compared to OIs of comparable tight material) reflects the fact that, as hide swells, the collagen fibrils become increasingly tilted out of the plane of the leather.


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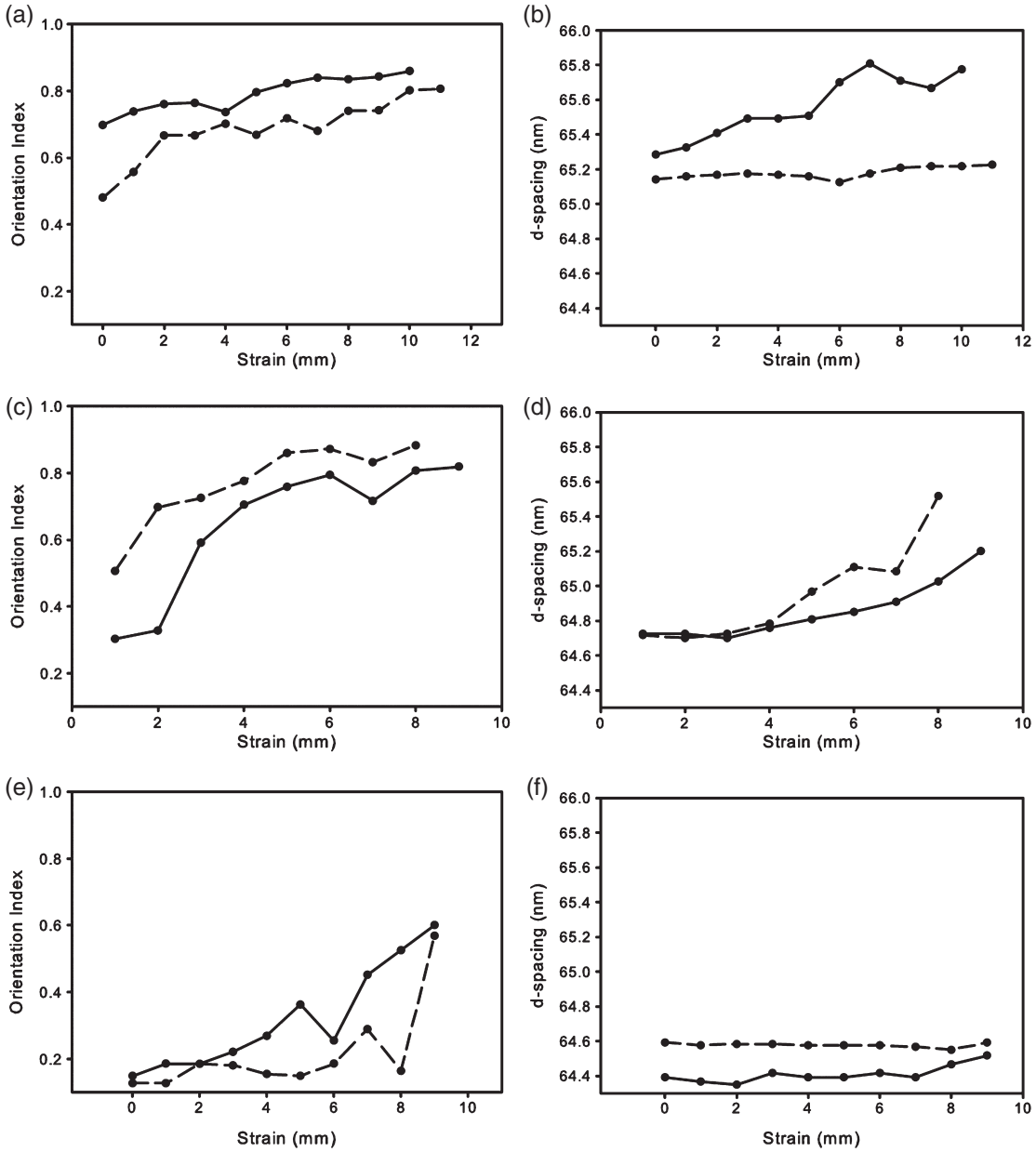


**Figure 5.** OI and D-spacing measured normal to the surface during strain. Solid lines: tight materials, dashed lines: loose. (a, b) Pickled hide; (c, d) wet blue; and (e, f) leather. Each point on the plots is the average of eight to 16 diffraction patterns, representing a full cross-section of the sample. The two lines in each plot represent duplicate measurements (at different positions).on separate samples.

Once these inter-layer connections have been broken, during further processing of the hide to dry crust, the hide shrinks and these layers are compressed back together. From wet blue to dry crust, the hide shrank more for loose leather (20%) than for tight leather (5%). The high OIs at the dry crust stage indicate that the collagen was well oriented in these layers, and there was little connection between the layers in the loose leather (Fig. 6). In tight leather, the connections might be in the form of some fibrils traversing the layers or branching of some fibrils. The lack of connection between the layers in loose material results in a weakness between the layers, which permits the layers to slide over each other, particularly near the lower part of the grain. Once the grain layer detaches from the corium, it bunches up as it is bent inward on the grain side. This disconnection in the lower grain region for loose leather is apparent in ultrasound imaging.[3,5]

These findings raise the question of why hides prone to looseness swell more than those that yield tight leather. Two possibilities are that either loose hides have a pre-existing weakness between layers so that there is less resistance to swelling (i.e. swelling is a result of looseness) or that some other factor, such as a differing affinity to water, perhaps as a function of a differing fat content, results in greater swelling and therefore looseness (i.e. swelling is a cause of looseness).

A third possibility is that elasticity and shrinkage in the grain differ from those in the corium, and that the differential shrinkage produces looseness. If the expansion and contraction was in area (i.e. laterally) and was markedly different between these regions, it might force these two layers to become disconnected, regardless of how well they were initially bonded to each other. Although, in the present study, only changes in hide thickness were measured,


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**Table 3.** OI corrected for changes in thickness and dryness

| Process stage | Thickness (mm) | OI as measured | OI, thickness corrected (relative to pickled hide OI)* |
|---|---|---|---|
| Tight | | | |
| Pickled hide | 3.83 | 0.45 | 0.45 |
| Wet blue | 4.23 | 0.38 | 0.41 |
| Dry crust | 5.15 | 0.54 | 0.63 |
| Loose | | | |
| Pickled hide | 1.85 | 0.31 | 0.31 |
| Wet blue | 2.31 | 0.30 | 0.36 |
| Dry crust | 3.43 | 0.61 | 0.77 |

*'Thickness corrected' represents what the OI would be had thickness not changed.

and these were found to be greater in the material that became loose, it is plausible that the lateral expansion, and therefore grain–corium shear forces, would also be greater in material that becomes loose. However, this is not necessarily consistent with the SAXS OI data. Lateral expansion would be expected to increase OI, whereas an expansion in thickness would decrease the OI. As discussed above, the OI changes during processing can be largely attributed to thickness changes, and the fractional change in thickness (up to 132%) is much greater than the fractional change in area (not measured in the present study but believed to be typically approximately 2%). The hypothesis of lateral shear causing looseness does not appear to be supported by the SAXS analysis during strain of these materials.

The response of the processed hides to strain revealed information on the structure of these materials and the differences between material that develops into loose and tight leathers. In pickled hide, the fibrils in loose material oriented with strain more readily than did those in tight material when measured with X-rays normal to the surface (but not measured with X-rays edge-on to the hide). For the pickled hide, the D-spacing of tight material changed much more than that of loose material when measured both edge-on and normal to the surface. This behavior suggests that the tight pickled hide has a more constrained fibril network, with stress developing on the fibrils but no movement resulting in reorientation; in loose material, the network does not appear to be as constrained. This further suggests that the loose pickled hide did not initially have or had already lost some of its connecting network structure and was therefore destined to produce loose leather. Alternatively, it could be that, in loose material (which was more swollen with water), the strain was taken up by water being squeezed out rather than much movement of fibers.

In wet blue, loose material reoriented under strain more readily than tight material, again suggesting that the fibrils of it had less network-like arrangement and so were less constrained (because the network had been damaged by swelling). However, the greater D-spacing changes of loose wet blue with increasing strain, measured both edge-on and normal to the surface, compared to tight wet blue suggests that the collagen fibrils in loose material experienced more stress for a given strain. This observation supports the idea that swelling breaks the connections between layers; it is not consistent with pre-existing weak connections between the layers causing swelling. The extra D-spacing increase shows that extra force was required to break the inter-layer connections.

In the dry crust, the loose leather reoriented more readily under strain than did tight leather, and the D-spacing changes were similar for the two types of leather when measured edge-on, and larger for tight leather when measured normal to the surface. This suggests that a collagen fibril network is more constrained in tight leather than in loose leather; hence, individual layers of collagen fibrils are freer to move or separate in the loose leather.

The interpretation of the observed behaviors of the materials under increasing strain, and in terms of the structural differences between loose and tight leather, is consistent with the analyses of samples not under strain.

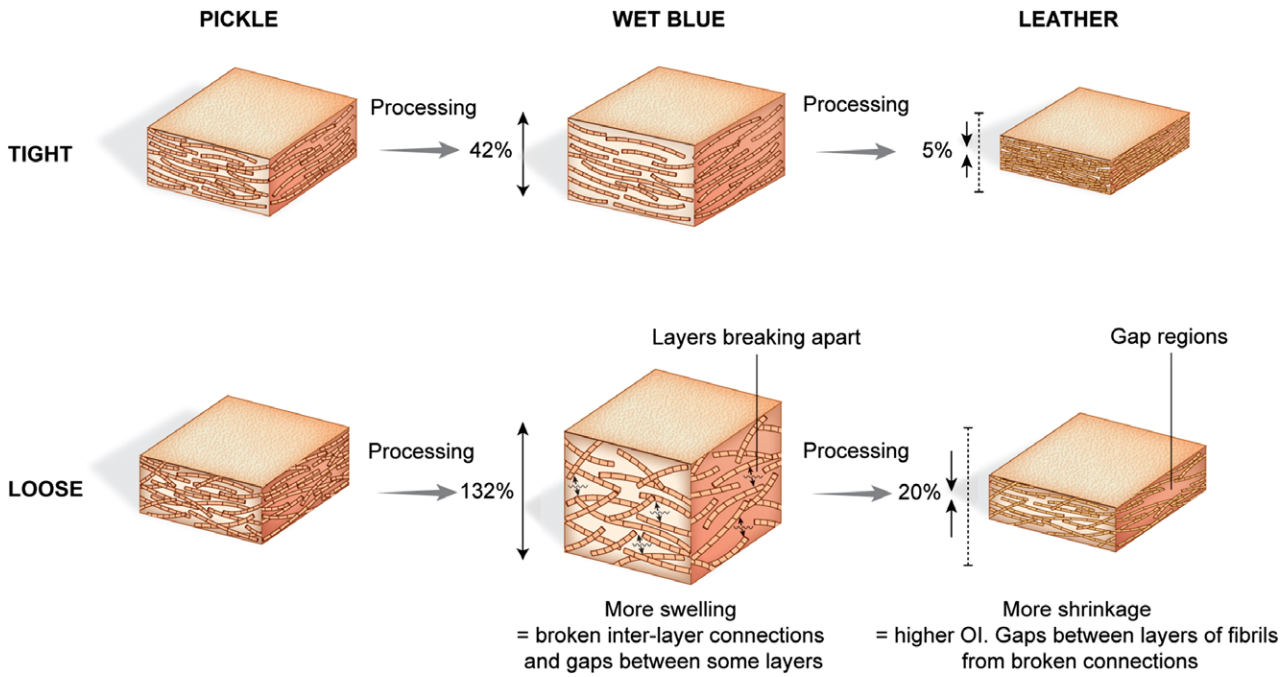


**Figure 6.** Illustration of the different behavior of loose and tight leathers during processing.


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If looseness develops during processing from the excessive swelling of some hides, it may be possible to alter processing strategies for these hides (if they could be identified at the raw hide stage) to inhibit the swelling. This might then prevent the development of looseness.

The material with more highly oriented fibrils that eventually exhibits looseness was reported elsewhere to be stronger in the standard tear test.[3] This strength is therefore clearly not dependent on bonding or on a network structure between the layers but, rather, on the number of collagen fibrils in the plane of the leather. This relationship is similar to that found in studies of a large number of ovine and bovine leather samples[7] and a range of different animal leathers.[9] However, tear strength is only one consideration in leather value; looseness degrades appearance and perhaps also serviceability and therefore also devalues leather.

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