

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Nanostructure and Physical Properties of Collagen Biomaterials

Katie Sizeland

2015

Nanostructure and Physical Properties of Collagen Biomaterials

A thesis presented in partial fulfilment of the requirements for the
degree of

Doctor of Philosophy

In

Engineering

at Massey University, Manawatu, New Zealand.

Katie Sizeland

2015

Abstract

Collagen is the main structural component of leather, skin, pericardium, and other tissues. All of these biomaterials have a mechanical function and the physical properties are partly a result of the structure of the collagen fibrils. The architecture of the collagen network and how it changes when different chemical and mechanical processes are applied is not fully understood and forms the foundation of this thesis. Synchrotron-based small angle X-ray scattering has been used to quantify aspects of the collagen structure, specifically the orientation index (OI) and D-spacing of the collagen biomaterials investigated. In leather, the nanostructural changes of the collagen network and the strength of the material across a range of different animals, through each stage of the leather-making process, and when model compounds are added or the fat liquor addition is varied has been investigated. Both the D-spacing and fibril orientation were found to change with leather processing. The changes to the thickness of the leather during processing impacts the fibril OI and, once taken into account, the main difference in OI is due to the hydration state of the material with dry materials being less oriented than wet. Model compounds urea, proline, and hydroxyproline were found to increase D-spacing. It was found that as the fat liquor addition is increased, the D-spacing increased. Pure lanolin resulted in a similar increase in D-spacing. The collagen fibril structure and strength of both adult and neonatal pericardium was also investigated. Significant differences were observed with the neonatal tissue having a higher modulus of elasticity and being significantly more aligned than adult pericardium. Neonatal pericardium is advantageously thinner for heart valve applications. This research proves it has the necessary physical properties required. By understanding the hierarchical structure of collagen and its mechanisms for modification when subjected to different chemical and mechanical processes, we gain valuable insight in understanding the performance of leather and skin in biological, medical, and industrial contexts. This will lead to better comprehension of current processes and informs future processing developments.

Acknowledgements

This work has been made possible by a number of people whom I would like to thank.

Thank you to my supervisor and mentor, Professor Richard Haverkamp - without you none of this would have been possible. I greatly appreciate your positive attitude and enthusiastic approach to the projects we have worked on. You inspired me to start my PhD in the first place and you showed me how much fun research can be so thank you.

I would like to thank Mum, Dad, Jacqui, Tom, Nate, and Charlie. Your love and support means the world to me and I couldn't have achieved this without you there every step of the way. Thank you to my friends and everyone who has believed in me and supported me along the way.

I would like to thank the fantastic team on the SAXS/WAXS beamline at the Australian Synchrotron and the ongoing support from Nigel Kirby, Adrian Hawley, and Stephen Mudie. Thanks to you our requests have never been impossible and your knowledge and expertise have been a tremendous help. I am absolutely certain that my PhD and all the research projects I am involved in would not have gone so smoothly without your input. I look forward to continuing to work with you in the future and will continue to try and find any excuse to come back to the synchrotron - it feels like a second home now! Thank you to the New Zealand Synchrotron Group for providing travel funding for the synchrotron trips.

I would like to thank the New Zealand Leather and Shoe Research Association (LASRA) who, supported by the Ministry of Business, Innovation, and Employment on grant number LSRX0801, financially backed this research project. In particular I want to thank Richard Edmonds, Sue Cooper, and Geoff Holmes from LASRA for providing their knowledge and expertise throughout my PhD.

Thank you to Associate Professor Gillian Norris for your input throughout much of this research project.

Table of Contents

Chapter 1: Introduction	1
1.1 A Perspective on the Leather Industry.....	1
1.2 Aims and Objectives.....	2
Chapter 2: Literature Review	5
2.1 Skin.....	5
2.1.1 The Epidermis.....	6
2.1.2 The Dermis.....	9
2.1.3 Accessory Structures of the Skin	12
2.1.4 Functions of the Skin.....	14
2.2 Collagen	15
2.2.1 Amino Acid Structure of Collagen Type I	16
2.2.2 Alpha Helix Structure of Collagen Type I.....	17
2.2.3 Tropocollagen Structure of Collagen Type I.....	18
2.2.4 Fibril Structure of Collagen Type I.....	20
2.2.5 Macro Organisation of Collagen	24
2.3 Leather	23
2.3.1 Leather Structure.....	24
2.3.2 Leather Processing.....	26
2.4 Pericardium and Heart Valves	33
2.4.1 Structure of the Heart	34
2.4.2 Heart Valves.....	37
2.5 Small Angle X-ray Scattering for Nanostructural Measurements	39

2.5.1 Synchrotron Radiation	42
2.5.2 General Theory of SAXS.....	47
2.5.3 Bragg's Law	48
2.5.4 SAXS of Collagen Biomaterials.....	53
Chapter 3: Collagen Orientation and Leather Strength	54
3.1 Introduction.....	55
3.2 Experimental Procedures	56
3.2.1 Leather Processing and Sampling	56
3.2.2 Small Angle X-ray Scattering.....	61
3.2.3 Tear Strength Testing	67
3.3 Results.....	68
3.4 Discussion.....	71
3.5 Conclusions	77
Chapter 4: Collagen D-spacing and the Effect of Fat Liquor Addition	78
4.1 Introduction.....	79
4.2 Experimental Procedures	81
4.3 Results.....	82
4.4 Discussion.....	84
4.5 Conclusions	86
Chapter 5: Changes to Collagen Structure During the Processing of Skin to Leather	88
5.1 Introduction.....	89
5.2 Experimental Procedures	91
5.3 Results.....	95
5.4 Discussion.....	103
5.5 Conclusions	111

Chapter 6: Modification of Collagen D-spacing in Skin by Model	
Compounds	112
6.1 Introduction.....	112
6.2 Experimental Procedures	115
6.3 Results.....	117
6.4 Discussion.....	120
6.5 Conclusions	122
Chapter 7: Fat Liquor Effects on Collagen Fibril Orientation and D-spacing in Leather During Tensile Strain	123
7.1 Introduction.....	124
7.2 Experimental Procedures	126
7.3 Results.....	127
7.4 Discussion.....	136
7.5 Conclusions	137
Chapter 8: Age Dependent Differences in Collagen Alignment of Glutaraldehyde Fixed Bovine Pericardium	138
8.1 Introduction.....	139
8.2 Experimental Procedures	142
8.3 Results.....	147
8.4 Discussion.....	154
8.5 Conclusions	157
Chapter 9: Conclusions	159
Chapter 10: Appendices	162
10.1 Appendix 1	162
10.2 Appendix 2.....	236
10.3 Appendix 3.....	301
Chapter 11: References	350

List of Figures

Figure 2.1. Epidermal layers	6
Figure 2.2. Ovine skin anatomy showing the thinner epidermis at the surface and the thicker dermis underneath	9
Figure 2.3. Cross section of skin showing the main structures in the dermis	11
Figure 2.4. Components of the integumentary system.	12
Figure 2.5. Single hair follicle	13
Figure 2.6. Primary structure of collagen is the sequence of amino acids in the polypeptide	16
Figure 2.7. Three domains of a peptide showing variation in helical twist	17
Figure 2.8. The collagen triple helix	18
Figure 2.9. Hydrogen bonding network showing the regular pattern of direct hydrogen bonds and how water mediated hydrogen bonds are formed	20
Figure 2.10. Tropocollagens assemble into collagen fibrils with a 67 nm D-spacing that includes an overlap and a gap region.....	21
Figure 2.11. Main structural features of the heart.....	35
Figure 2.12. Layers of the heart wall	36
Figure 2.13. Interior of the heart	37
Figure 2.14. Replacement heart valve folded up and inserted via a stent.....	38
Figure 2.15. Electromagnetic spectrum with real life objects to illustrate scale lengths	40

Figure 2.16. Synchrotron radiation emitted from charged particles spiraling in a magnetic field.....	42
Figure 2.17. The Australian Synchrotron.	43
Figure 2.18. Components of a synchrotron: 1) electron gun; 2) linac; 3) booster ring; 4) storage ring; 5) beamline; 6) end station.....	44
Figure 2.19. A bending magnet changing the path of an electron	45
Figure 2.20. (a) a wiggler and (b) an undulator enhancing the intensity of the synchrotron radiation.	46
Figure 2.21. Basic SAXS experimental configuration.....	47
Figure 2.22. Illustration of Bragg's Law	48
Figure 2.23. Friedich and Knipping's improved experimental set-up	49
Figure 2.24. Zinblende Laue photographs along (a) four-fold and (b) three-fold axes	50
Figure 2.25. Change of shape of X-ray reflections as the photographic plate was moved further away from the crystal.....	51
Figure 3.1. Structure-strength relationship of leather: (a) sheep leather with a lower orientation with more crossover within planes, weaker material; (b) deer leather with a higher orientation with less crossover within planes, stronger material.....	54
Figure 3.2. Representation of a hide or skin showing the sampling location for whole hides, skins and sides: (a) From Williams where B is the root of the tail, AD is a line perpendicular to BC, $AC=2AB$, $AF=FD$, $JK=EF$, $GE=EH$, $HL=LK=HN$, and $AE=50\text{ mm} \pm 5\text{ mm}$; (b) simplification of hide showing the OSP in relation to anatomical features of the animal	58
Figure 3.3. Sample cut from the OSP will either be cut as a square for flat on analysis or will be cut along the dotted lines of the square for samples that are parallel or perpendicular to the backbone of the hide	59

Figure 3.4. An example of the leather samples in plastic and glass vials for storage and transportation.....	60
Figure 3.5. SAXS/WAXS beamline at the Australian Synchrotron	61
Figure 3.6. Direction of beam on the sample for edge on and flat on sample directions.....	62
Figure 3.7. (a) edge on samples mounted on the plate ready to be inserted into the beam; (b) wet edge on samples sandwiched between kapton tape on the plate and ready to be inserted into the beam	63
Figure 3.8. (a) SAXS diffraction pattern; (b) plot of intensity versus q	64
Figure 3.9. Tear test on a leather sample: (a) at start of test; (b) part way through test	67
Figure 3.10. SAXS analysis of leather. a) A raw SAXS pattern; b) integrated intensity of a whole pattern	68
Figure 3.11. Collagen d-spacing and tear strength for leather from different animals	68
Figure 3.12. Azimuthal variation in intensity at one value of q (one collagen peak)	69
Figure 3.13. Collagen fibril orientation and tear strength for leather from different animals: (a) measured flat-on; (b) measured edge-on	70
Figure 3.14. Three dimensional modelled OI' based on normalised integral of $\cos^2\theta \cos^2\phi$	73
Figure 3.15. The relationship between collagen orientation index (OI) and strength of skin. Edge-on measurements with orientation indices that result in leather that is: a) very weak (vertical fibre defect); b) medium strength (low OI); c) strong (high OI). Arrow indicates direction of applied stress in tear measurements	74

Figure 3.16. The relationship between collagen orientation index (OI) and strength of skin. OI measured on the flat with orientation that results in leather that is a) weak (high OI); b) fairly weak (high OI); c) strong in all directions. Arrow indicates direction of applied stress in tear measurements.....	75
Figure 4.1. Increase in collagen D-spacing when fat liquor is added	78
Figure 4.2. Example of SAXS of leather: (a) raw SAXS pattern; (b) integrated intensity profile.....	83
Figure 4.3. Collagen D-spacing versus fat liquor percentage for ovine leather: (●, ---) corium, (▼, ⋯) grain, and (○, —) average. Each point for the corium and grain is taken from the average of about 10 scattering patterns. Pure lanolin at 8% also shown (■)	83
Figure 5.1. D-spacing of collagen fibrils and orientation of collagen fibres: (a) dry materials have a smaller D-spacing and a lower OI; (b) wet materials have a larger D-spacing and a higher OI.....	88
Figure 5.2. Schematic of custom built stretching apparatus	92
Figure 5.3. Leather sample held by the stretching machine and mounted in the beamline.....	93
Figure 5.4. (a) SAXS diffraction pattern; (b) plot of intensity versus q	94
Figure 5.5. Variation in orientation index for all stages of processing: (▲, ---) corium, (■, ⋯) grain, (●, —) average	95
Figure 5.6. Fibril orientation index versus thickness.....	96
Figure 5.7. Variation in D-spacing and pH between different stages of processing prior to stretching: (Δ, ---) corium, (□, ⋯) grain, (●, —) pH	97
Figure 5.8. Variation of D-spacing with pH (wet blue and retanned points are coincident)	97
Figure 5.9. Correlation of OI with pH.....	98

Figure 5.10. D-spacing versus OI for samples of different stages of processing when held without tension.....	99
Figure 5.11. Stress strain curves for each process stage, performed in situ concurrently with the SAXS measurement (not normalized for sample width or thickness): (●, —) Fresh green, (●,) salted, (▼, - - - -) pickled, (▲, - · - · -) pretanned, (■, - -) wet blue, (■, - · - · -) retanned, (◆, - - -) dry crust, (◆, —) dry crust staked	99
Figure 5.12. Changes in collagen D-spacing as samples of partially processed skin are stretched: (●, —) Fresh green, (●,) salted, (▼, - - - -) pickled, (▲, - · - · -) pretanned, (■, - -) wet blue, (■, - · - · -) retanned, (◆, - - -) dry crust, (◆, —) dry crust staked	100
Figure 5.13. Changes in collagen fibril OI as samples of partially processed skin are stretched: (●, —) Fresh green, (●,) salted, (▼, - - - -) pickled, (▲, - · - · -) pretanned, (■, - -) wet blue, (■, - · - · -) retanned, (◆, - - -) dry crust, (◆, —) dry crust staked.....	101
Figure 5.14. Illustration of the change in collagen fibril angle θ to the plane of leather as the thickness T of the leather changes	103
Figure 5.15. Fibril orientation index versus thickness: (▲) measured OI, (■) calculated OI adjusted for thickness changes (relative to salted).....	107
Figure 5.16. D-spacing versus thickness corrected OI for samples of different stages of processing when held without tension.....	108
Figure 5.17. Variation of thickness corrected OI with pH.....	109
Figure 6.1. Example of SAXS of collagen: (a) SAXS pattern; (b) integrated intensity profile.....	117
Figure 6.2. Collagen D-spacing versus additive percentage for processed skin: (●) no additives, (▼) lanolin, (◆) hydroxyproline, (■) proline, and (▲) urea. Each point is the average value taken from 11–17 scattering patterns, except the 0% sample, which is the average of 6 patterns	118

Figure 6.3. Collagen orientation index (OI) versus additive percentage for processed skin: (●) no additives, (▼) lanolin, (◆) hydroxyproline, (■) proline, and (▲) urea. Each point is the average value taken from 11-17 scattering patterns, except the 0 % sample which is the average of six scattering patterns 119

Figure 7.1. Increase in fibre sliding upon stretching of leather after the addition of fat liquor..... 124

Figure 7.2. 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) 129

Figure 7.3. Variation in d-spacing with strain and fat liquor content: (●, —) no fat liquor, (○,) 2% fat liquor, (▼, - - - -) 4% fat liquor, (Δ, - · - · -) 6% fat liquor, (■, — —) 8% fat liquor, (□, - · - · -) 10% fat liquor 129

Figure 7.4. Variation in orientation index (OI) with strain and fat liquor content: (●, —) no fat liquor, (○,) 2% fat liquor, (▼, - - - -) 4% fat liquor, (Δ, - · - · -) 6% fat liquor, (■, — —) 8% fat liquor, (□, - · - · -) 10% fat liquor 130

Figure 7.5. Variation of OI with measured fat liquor 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 130

Figure 7.6. Change in OI and d-spacing upon strain to 0.4 for each measured fat liquor content 131

Figure 7.7. (a) Stress-strain on small leather samples recording during SAXS measurements (●, —) no fat liquor, (○,) 2% fat liquor, (▼, - - - -) 4% fat liquor, (Δ, - · - · -) 6% fat liquor, (■, — —) 8% fat liquor, (□, - · - · -) 10% fat liquor; (b) Elastic modulus taken from curves in (a); (c) amount stretched by sample versus measured fat liquor content..... 133

Figure 7.8. Tear force of leather with measured fat liquor content..... 134

Figure 7.9. Cross sections of leather under strain. No fat liquor (a,b), 8% fat liquor (c, d). Variation of OI with strain (a,c), variation of d-spacing with strain (b,d) ...	135
Figure 8.1. Adult pericardium with a lower OI is a weaker material, neonatal pericardium with a higher OI is a stronger material.....	138
Figure 8.2. (a) neonatal and (b) adult pericardium prior to cutting into a butterfly shape	143
Figure 8.3. Flattened pericardium held with weights around the edge following cutting.....	144
Figure 8.4. Beam direction for SAXS analysis with relation to pericardium butterfly	145
Figure 8.5. Pericardium stained with picosirius red and imaged through cross polarized light to highlight collagen: a) adult pericardium; b) neonatal pericardium. The parietal side is toward the left, the fibrous side toward the right of each image. Scale bar is 0.1 mm.....	147
Figure 8.6. SAXS spectra of pericardium: a) a poorly oriented tissue; b) a highly oriented tissue.....	149
Figure 8.7. SAXS profile of an example bovine pericardium integrated around all azimuthal angles. The sharp peaks due to collagen d-spacing of various orders are visible (order 5 is just below 0.05 \AA^{-1} , order 6 at just below 0.06 \AA^{-1} , etc.).....	150
Figure 8.8. Plots of the intensity of a selected collagen peak at varying azimuthal angles for bovine pericardium samples. a) a poorly aligned tissue; b) a highly aligned tissue. The central peak at 180° (and other peaks at 0 and 360°) is the variation in intensity of collagen d-spacing whereas the lower peaks at 90° and 270° are due to the scattering from the thickness of the fibrils and fibril bundles	150
Figure 8.9. Variation of orientation index through the thickness of glutaraldehyde fixed pericardium a) neonatal; b) adult. Each figure shows two profiles for each of two samples.....	153

List of Tables

Table 2.1. Leather usage	24
Table 3.1. Leather tear strength compared with orientation index (OI) of collagen fibrils ^a	71
Table 5.1. D-spacing changes in processing stages of leather with strain.....	102
Table 5.2. OI changes in processing stages of leather with strain OI.....	102
Table 5.3. Calculated change in orientation index of collagen fibrils for different thicknesses of material.....	106
Table 6.1. Statistics for orientation index (OI) and D-spacing values when comparing samples with no additives (0%) to samples with added model compounds. All <i>t</i> -tests were calculated using an alpha of 0.05.....	119
Table 7.1. Nominal addition of fat liquor and measured content of fat in leather samples.....	127
Table 8.1. Mechanical properties of adult and neonatal glutaraldehyde fixed bovine pericardium	149
Table 8.2. Orientation index (OI) for pericardium samples measured perpendicular and edge on to the surface for samples cut vertically or horizontally from the pericardium.....	152

LIST OF PUBLICATIONS

Journal Articles

Sizeland, K. H., Edmonds, R. L., Basil-Jones, M. M., Kirby, N., Hawley A., Mudie S. T., & Haverkamp R. G. (2015). Changes to Collagen Structure during Leather Processing. *Journal of Agricultural and Food Chemistry*, 63(9), 2499-2505.

Wells H. C., **Sizeland K. H.**, Kirby N., Hawley A., Mudie S. T., & Haverkamp R. G. (2015). Collagen Fibril Structure and Strength in Acellular Dermal Matrix Materials of Bovine, Porcine, and Human Origin. *ACS Biomaterials*, 1, 1026-1038.

Sizeland K. H., Holmes. G., Edmonds R. L., Kirby N., Hawley A., Mudie, S., & Haverkamp, R. G. (2015). Fatliquor Effects on Collagen Fibril Orientation and D-spacing During Tensile Strain. *Journal of the American Leather Chemists Association*, 110, 355-362.

Kayed H. R., **Sizeland K. H.**, Kirby N., Hawley A., Mudie S. T., & Haverkamp R. G. (2015). Collagen Cross Linking and Fibril Alignment in Pericardium. *RSC Advances*, 5(5), 3611-8.

Wells H. C., **Sizeland K. H.**, Kayed H. R., Kirby N., Hawley A., Mudie S. T., & Haverkamp R. G. (2015). Poisson's Ratio of Collagen Fibrils Measured by Small Angle X-ray Scattering of Strained Bovine Pericardium. *Journal of Applied Physics*, 117(4).

Sizeland K. H., Wells H. C., Norris G. E., Edmonds R. L., Kirby N., Hawley A., Mudie, S., & Haverkamp, R. G. (2015). Collagen D-spacing and the Effect of Fat Liquor Addition. *Journal of the American Leather Chemists Association*, 110(3), 66-71.

Wells, H. C., **Sizeland, K. H.**, Edmonds, R. L., Aitkenhead, W., Kappen, P., Glover, C., Johannessen, B. & Haverkamp, R. G. (2014). Stabilizing Chromium from Leather

Waste in Biochar. *ACS Sustainable Chemistry & Engineering*, 2(7), 1864-1870.

Sizeland, K. H., Wells, H. C., Higgins, J., Cunanan, C. M., Kirby, N., Hawley, A., Mudie, S. T., & Haverkamp, R. G. (2014). Age Dependant Differences in Collagen Alignment of Glutaraldehyde Fixed Bovine Pericardium. *BioMed Research International*.

Sizeland, K. H., Wells, H. C., Basil-Jones, M. M., Edmonds, R. L., & Haverkamp, R. G. (2014). Leather Nanostructure and Performance. *International Leather Maker*, 30-34.

Sizeland, K. H., Basil-Jones, M. M., Edmonds, R. L., Cooper, S. M., Kirby, N. (2013) Collagen Orientation and Leather Strength for Selected Mammals. *Journal of Agricultural and Food Chemistry*, 61, 887-892.

Conference Papers

Sizeland, K. H., Edmonds, R. L., Norris, G. E., Kirby, N., Hawley, A., Mudie, S., & Haverkamp, R. G. (2014). "Modification of collagen d-spacing in skin", *Proceedings of the 28th International Federation of the Societies of Cosmetic Chemists Congress*, (pp. 1222-1235), Palais des Congrès, Paris, France, 27th-30th October, 2014.

Sizeland, K. H., Wells, H. C., Norris, G., Edmonds, R. L. & Haverkamp, R. G. "Collagen D-spacing Modification by Fat Liquor Addition". *Proceedings of the 65th Leather and Shoe Research Association Conference*, Wellington, New Zealand, 13th-14th August, 2014.

Wells, H., **Sizeland, K. H.**, Edmonds, R. L., Aitkenhead, W., Kappen, P., Glover, C., Johannessen, B., & Haverkamp, R. G. 2014. "Biochar and Other Solid Waste Minimisation Options". *Proceedings of the 65th Leather and Shoe Research Association Conference*, Wellington, New Zealand, 13th-14th August, 2014.

Sizeland, K. H., Basil-Jones, M. M., Norris, G. E., Edmonds, R. L. Kirby, N., Hawley, A., & Haverkamp, R. G. "Collagen Alignment and Leather Strength", *Proceedings of*

the International Union of Leather Technologists and Chemists Societies XXXII Congress, (Paper 110), Istanbul, Turkey, 29th-31st May, 2013.

Haverkamp, R. G., Basil-Jones, M. M., **Sizeland, K. H.**, & Edmonds, R. L. "Synchrotron Studies of Leather Structure", *Proceedings of the International Union of Leather Technologists and Chemists Societies XXXII Congress*, (Paper 109), Istanbul, Turkey, 29th-31st May, 2013.

Sizeland, K. H., Basil-Jones, M. M., Edmonds, R. L., & Haverkamp, R. G. "Implications of Synchrotron Analysis for Leather Manufacturing", *Proceedings of the 63rd Annual Leather and Shoe Research Association conference*, (pp. 28-37), Wellington, New Zealand, 16th-17th August, 2012.

Conference Presentations and Posters

Haverkamp, R. G., **Sizeland, K. H.**, Wells, H. C., Kayed, H. R. "Strength in Collagen Materials." *Poster presented at the Materials Research Society Spring Meeting*, San Francisco, USA, 2015.

Haverkamp, R. G., **Sizeland, K. H.**, Wells, H. C., Kayed, H. R., Edmonds, R. L., Kirby, N., Hawley, A., & Mudie, S. "Orientation of Collagen Fibrils in Tissue." *Symposium presented at the 1st Matrix Biology Europe Conference*, Rotterdam, Netherlands, 2015.

Wells, H. C., **Sizeland, K. H.**, Edmonds, R. L., Kirby, N., Hawley, A., Mudie, S., & Haverkamp, R. G. "Poisson Ratio of Collagen Fibrils." *Poster presented at the 1st Matrix Biology Europe Conference*, Rotterdam, Netherlands, 2015.

Sizeland, K. H., Edmonds, R. L., Kirby, N., Hawley, A., Mudie, S., & Haverkamp, R. G. "Chemical Processing and Leather Strength", *Poster presented at the Fourth International Conference on Multifunctional, Hybrid, and Nanomaterials*, Barcelona, Spain, 9th-13th March, 2015.

Sizeland, K. H., Haverkamp, R. G., Wells, H. C., Kayed, H. R., Edmonds, R. L., Kirby, N., Hawley, A., & Mudie, S. “Strength in Collagen Biomaterials”, *Poster presented at the Fourth International Conference on Multifunctional, Hybrid, and Nanomaterials*, Barcelona, Spain, 9th-13th March, 2015.

Wells, H. C., **Sizeland, K. H.**, Kayed, H. R., Kirby, N., Mudie, S., & Haverkamp, R. G. “Poisson Ratio of Collagen Fibrils Measured by SAXS”, *Poster presented at the Fourth International Conference on Multifunctional, Hybrid, and Nanomaterials*, Barcelona, Spain, 9th-13th March, 2015.

Sizeland, K. H., Basil-Jones, M. M., Edmonds, R. L., Kirby, N., Hawley, A., Mudie, S., & Haverkamp, R. G. “Changes to the Nanostructure of Collagen in Skin During Leather Processing”, *Poster presented at the Australian Synchrotron Users Meeting*, Melbourne, Australia, 20th-21st November, 2014.

Sizeland, K. H., Edmonds, R. L., Norris, G. E., Kirby, N., Hawley, A., Mudie, S., & Haverkamp, R. G. “Modification of Collagen Structure in Skin”, *Poster presented at the 28th International Federation of Societies of Cosmetic Chemists*, Palais des Congrès, Paris, France, 27th-30th October, 2014.

Sizeland, K. H., Wells, H., Norris, G. E., Edmonds, R. L., & Haverkamp, R. G. “Collagen D-spacing Modification by Fat Liquor Addition”, *Symposium presented at the 65th Annual Leather and Shoe Research Association Conference*, Wellington, New Zealand, 13th-14th August, 2014.

Wells, H., **Sizeland, K. H.**, Edmonds, R. L., Aitkenhead, W., Kappen, P., Glover, C., Johannessen, B., & Haverkamp, R. G. “Biochar and Other Solid Waste Minimisation Options”, *Symposium presented at the 65th Annual Leather and Shoe Research Association Conference*, Wellington, New Zealand, 13th-14th August, 2014.

Sizeland, K. H., Edmonds, R. L., Norris, G. E., Kirby, N., Hawley, A., Mudie, S. & Haverkamp, R. G. “Effects of Model Compounds on the Nanostructure of Skin”, *Poster presented at the 65th Annual Leather and Shoe Research Association Conference*, Wellington, New Zealand, 13th-14th August, 2014.

Wells, H. C., **Sizeland, K. H.**, Edmonds, R. L., Kirby, N., Hawley, A., Mudie, S., & Haverkamp, R. G. “Poisson Ratio of Collagen Fibrils”, *Poster presented at the 1st*

Matrix Biology Europe conference (XXIVth FECTS meeting), Rotterdam, Netherlands, 21st-24th June, 2014.

Haverkamp, R. G., Wells, H. C., **Sizeland, K. H.**, Edmonds, R. L., Aitkenhead, W., Kappen, P., Glover, C., & Johannessen, B. "Biochar from Leather - the Fate of Chromium", *Symposium conducted at the 117th Society of Leather Technologists and Chemists Annual Conference*, Northampton, United Kingdom, 26th April, 2014.

Sizeland, K. H., Norris, G. E., Edmonds, R. L., Kirby, N., Hawley, A., & Haverkamp, R. G. "Collagen Fibril Axial Periodicity and the Effects of Polyol Addition", *Poster presented at the 12th International Conference on Frontiers of Polymers and Advanced Materials*, Auckland, New Zealand, 8th-13th December, 2013.

Sizeland, K. H., Norris, G. E., Edmonds, R. L., Kirby, N., Hawley, A., & Haverkamp, R. G. "Polyol Modification of Collagen Fibril Axial Periodicity", *Poster presented at the Australian Synchrotron Users Meeting*, Melbourne, Australia, 21st-22nd November, 2013.

Kayed, H. R., **Sizeland, K. H.**, Kirby, N., Hawley, A., Mudie, S., & Haverkamp, R. G. "Cross Linking Collagen Affects Fibril Orientation", *Poster presented at the Australian Synchrotron Users Meeting*, Melbourne, Australia, 21st-22nd November, 2013.

Sizeland, K. H., Basil-Jones, M. M., Norris, G. E., Edmonds, R. L., Kirby, N., Hawley, A., & Haverkamp, R. G. "Collagen Alignment and Leather Strength", *Poster presented at the 64th Annual Leather and Shoe Research Association Conference*, Wellington, New Zealand, 15th-16th August, 2013.

Sizeland, K. H., Basil-Jones, M. M., Norris, G. E., Edmonds, R. L., Kirby, N., Hawley, A., & Haverkamp, R. G. "Collagen Alignment and Leather Strength", *Poster presented at the International Union of Leather Technologists and Chemists Societies XXXII Congress*, Istanbul, Turkey, 28th-31st June, 2013.

Haverkamp, R. G., Basil-Jones, M. M., **Sizeland, K. H.**, & Edmonds, R. L. "Synchrotron Studies of Leather Structure", *Symposium conducted at the International Union of Leather Technologists and Chemists Societies XXXII Congress*, Istanbul, Turkey, 28th-31st June, 2013.

Sizeland, K. H., Basil-Jones, M. M., Edmonds, R. L. & Haverkamp, R. G. "SAXS of Leather Reveals a Structural Basis for Strength", *Poster presented at the Australian Synchrotron Users Meeting*, Melbourne, Australia. 28th-29th November 2012.

Haverkamp, R. G., Basil-Jones, M. M., **Sizeland, K. H.**, & Edmonds, R. L. "SAXS Structural Studies of Collagen Materials", *Symposium conducted at the Australian Synchrotron Users Meeting*, Melbourne, Australia, 28th-29th November, 2012.

Poddar, D., Ainscough, E. W., Freeman, G. H., Ellis, A., Glover, C. J., Johannessen, B., **Sizeland, K. H.**, Singh, H., Haverkamp, R. G., & Jameson, G. "Preliminary characterization by XAS of Mn hyperaccumulated by probiotic *Lactobacillus* sp.", *Poster presented at the Australian Synchrotron Users Meeting*, Melbourne, Australia. 28th-29th November, 2012.

Haverkamp, R. G., Basil-Jones, M. M., **Sizeland, K. H.**, & Edmonds, R. L. "Implications of Synchrotron Analysis for Leather Manufacturing", *Symposium conducted at 63rd Annual Leather and Shoe Research Association Conference*, Wellington, New Zealand. 16th-17th August, 2012.

Papers I am Acknowledged in

Beattie, I. R., & Haverkamp, R. G. (2011). Silver and gold nanoparticles in plants: sites for the reduction to metal. *Metallomics*, 3(6), 628-632.

Luangpipat, T., Beattie, I. R., Chisti, Y., & Haverkamp, R. G. (2011). Gold nanoparticles produced in a microalga. *Journal of Nanoparticle Research*, 13(12), 6439-6445.

Basil-Jones, M. M., Edmonds, R. L., Cooper, S. M., & Haverkamp, R. G. (2011). Collagen fibril orientation in ovine and bovine leather affects strength: A small angle X-ray scattering (SAXS) study. *Journal of agricultural and food chemistry*, 59(18), 9972-9979.

Basil-Jones, M. M., Edmonds, R. L., Norris, G. E., & Haverkamp, R. G. (2012). Collagen Fibril Alignment and Deformation during Tensile Strain of Leather: A Small-Angle X-ray Scattering Study. *Journal of agricultural and food chemistry*, *60*(5), 1201-1208.

Owe, L. E., Tsytkin, M., Wallwork, K. S., Haverkamp, R. G., & Sunde, S. (2012). Iridium–ruthenium single phase mixed oxides for oxygen evolution: Composition dependence of electrocatalytic activity. *Electrochimica Acta*, *70*, 158-164.

Haverkamp, R. G. (2013). The Australian Synchrotron - A Powerful Tool for Chemical Research Available to New Zealand Scientists. *Chemistry in New Zealand*, *76*(1).