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Understanding the Molecular Basis of the Strength Differences in Skins Used in Leather Manufacture

A dissertation presented in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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New Zealand

RAFEA MUSTAFA NAFFA

2017

1 Dedication

To my mother

To Haifa, Lilian and Maya

for giving me the confidence and love to keep going

and not give up

2 Acknowledgements

I would like to thank my supervisor Gillian Norris for her guidance and advice throughout the project, help with skin preparation when time was at a premium, and their unfailing optimism. Thank you for encouraging me to follow and develop my own ideas, and to make contact, and discuss my work, with experts in different fields. Also thanks to my co-supervisors Richard Haverkamp and Meekyung Ahn for their support.

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3 Abstract

Although skin structure and its physical properties have been extensively studied, little research has been devoted to understanding the links between them. A comprehensive study of the molecular components of four animal skins commonly used to manufacture shoes, clothing and furniture was therefore undertaken in order to attempt to identify a common indicator of skin strength. The molecular architecture of the protein components of each skin was analysed using polarising, confocal and transmission-electron microscopy (TEM), small angle X-ray scattering (SAXS) and amino-acid and cross-link analysis; glycosaminoglycans were quantified and visualised using TEM; and, for the sake of completeness, total carbohydrate and lipid content were measured using a colorimetric assay and thin layer chromatography respectively. Differences in these properties were then related to different physical characteristics of each skin.

The results showed that an individual mechanical property of skin such as tensile strength is complex and related to different combinations of molecular properties. For example, deer and cow skins are the strongest of the skins examined, however they derive their strength from different combinations of molecular properties. Cow skin collagen fibrils have the largest diameter, but deer skin fibrils have the smallest. On the other hand, the fibrils in deer skin frequently change direction, and have a “wavy” or crimped appearance in contrast to the fibrils in cow skin which are aligned in two main directions approximately 60 and 90 degrees apart, differences that are also reflected in the types and amount of their collagen crosslinks. Deer skin fibrils contain a higher proportion of trivalent crosslinks while cow skin fibrils contain a higher proportion of tetravalent links. For the two weaker skins, goat skin fibrils are more crimped than those of sheep skin, but both fibrils have diameters intermediate between those of cow- and deer skins and have lower mature to immature crosslink ratio. In deer skin, glycosaminoglycans are observed by TEM to link fibrils in

regular arrays and are present in higher concentrations than in cow, sheep and goat skins. This study showed the relationship between the molecular structure of skin and its mechanical functions is complex, arising from different combinations of molecular features rather than just one.

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