TOWARDS A MOLECULAR LEVEL UNDERSTANDING OF CHROME TANNING: INTERPLAY BETWEEN COLLAGEN STRUCTURE AND REACTIVITY

Yi Zhang, Jenna K. Buchanan, Geoff Holmes and Sujay Prabakar

Leather and Shoe Research Association of New Zealand, P.O. Box 8094, Palmerston North, 4472, New Zealand

a) Corresponding author: sujay.prabakar@lasra.co.nz

Abstract. Synchrotron based small-angle X-ray scattering (SAXS) technique is a powerful technique that has helped us understand the changes in molecular-level collagen structure during tanning and denaturation (shrinkage). Based on SAXS results from real-time denaturation experiments on leather samples, we established a mechanistic model of chrome tanning indicated by the structural changes of collagen. It suggests that only low level of chromium species is effectively involved in the cross-linking with collagen, highlighting the overuse of chrome during conventional tanning processes. Any extra amount of chrome added, however, can support the stabilisation of collagen possibly via a non-covalent mechanism. Such mechanism points towards a more environment-friendly tanning method by using suitable supplementary reagents to benefit tanning effect non-covalently instead of chrome. Also, by pre-treating with complexing agents such as sodium formate and disodium phthalate, as well as nanoclay (sodium montmorillonite), the uniformity through bovine hide collagen matrix can be improved significantly. These pre-treatments effectively reduce the reactivity of chromium during its cross-linking reaction with collagen while retaining its bound water. However, collagen pre-treated with a covalent cross-linker (glutaraldehyde) results in a decrease in both chromium-collagen cross-linking and bound water while improving uniformity. These molecular-level insights can be developed into metrics to guide us towards a more sustainable future for the leather industry. Further, coating on collagen fibrils can provide a pseudo-stabilisation effect of increasing the heat resistance of collagen. Overall, synchrotron SAXS provides valuable information about collagen structure changes that could lead to more efficient use of chrome (or other tanning agents) in the global leather tanning industry.

1 Introduction

Conventional chrome tanning processes utilize 6% to 8% of basic chromium sulphate by weight relying on a concentration gradient to drive penetration.[1,2] While an uptake of 40% to 70% is typical depending on the nature of animal hides and skins, the poor chrome uptake results in environmental stress relating to hexavalent chromium exposure, leading researchers to reassess the case of chromium sulphate in modern tanning.[1-4] Studying molecular level changes can reveal the mechanism by which chromium stabilizes collagen, and could lead to more efficient use of chrome during the tanning process.[5-10] Collagen molecules are aligned in a quarter stagger structure, resulting in repeating gap/ overlap regions within the fibrils.[14] Because of its ordered arrangement, mechanistic information can be acquired by X-ray diffraction techniques from changes in the periodicity of the gap/overlap regions (D-period), fibril size and the intensity of the scattering peaks.[11-14] This paper will review some of our recent work on synchrotron based SAXS to minimize and effectively use chrome in leather processing.

2 Results and Discussion

Many studies have focused on the use of less chrome with higher uptake by involving nanocomposites, pre-tanning agents, or novel processing methodologies.[15-20] However, the evaluation of properties remains superficial with lack of molecular level insights, hindering researchers from finding comprehensive solutions to sustainable chrome tanning. Considering that collagen is the primary structural element in the extracellular matrix in animal hides and skins, the heat resistance of leather against shrinkage was determined by the hydrothermal denaturation temperature (T_d) of collagen molecules.

However, such a commonly used indicator is based on heat transfer and lacks molecular level observations of collagen structural changes during denaturation, which is essential to understand the chromium–collagen reaction and for improving the sustainability of chrome tanning.

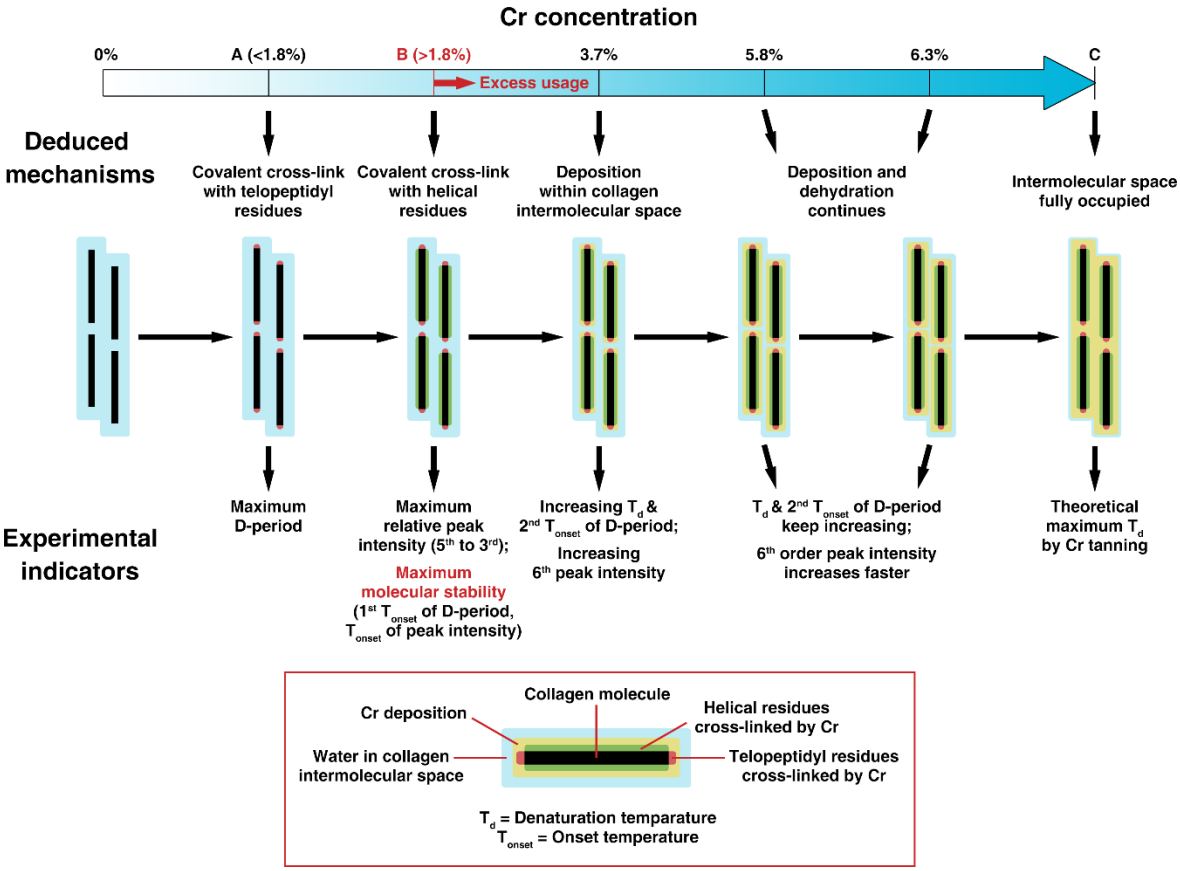

Fig. 1. Mechanistic model of the reaction between chromium and collagen at different concentrations, deduced from the molecular-level experimental indicators. © ACS Sustainable Chem. Eng. DOI: 10.1021/acssuschemeng.8b00954

The effect of chromium concentration in affecting the collagen structure in leather can be explained by a mechanistic model based on the observed molecular level indicators from SAXS measurements (Figure 1). At extremely low chrome concentration (A < 1.8%), chromium species form covalent bonds with telopeptidyl active sites causing the expansion of the axial staggering gaps, as indicated by the maximizing of the D-period.[7] At slightly higher chrome concentration (1.8% < B < 3.7%), chromium species covalently occupied the active sites in both the telopeptidyl and helical regions, resulting in the maximized relative intensity of the fifth and the third order peaks. The intramolecular stability of collagen thereby reaches its upper limit using chrome tanning, revealed by the unchanged first T_{onset} of D-period and peak intensity at 90 °C from our real-time SAXS denaturation experiment. Upon exhaustion of the active covalent sites, the relative intensity of the fifth and the third order peaks would be reduced, indicating the prevalence of non-covalent deposition. Meanwhile, the intensity of the sixth order peak starts to increase at a higher rate, confirming the dehydration effect due to chromium deposition and the displacement of water. The non-covalent interaction only contributes to the apparent denaturation temperature (T_d), which rests once the intermolecular space is fully occupied.[7]

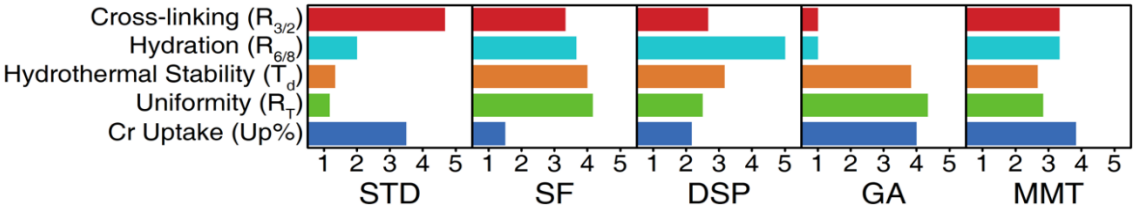

Fig. 2. Key aspects of the efficiency of chromium-collagen cross-linking through different pre-treating methods. © Int. J. Biol. Macromol. DOI: 10.1016/j.ijbiomac.2018.12.187.

The efficiency of chrome tanning can also be improved by using masking agents (Figure 2) such as monodentate complexing agent (sodium formate, SF), chelating agent (disodium phthalate, DSP), covalent cross-linker (glutaraldehyde, GA) and nanoclay (sodium montmorillonite, MMT).[9] By using a combination of SAXS and DSC studies we introduced a strategy to improve the efficiency of the cross-linking reaction at different concentrations of chromium sulphate by evaluating the performance of four common types of pre-treatments. The results suggest that SF, DSP and MMT affect the performance by decreasing chromium-collagen cross-linking and increasing hydration of the collagen molecule, denaturation temperature and uniformity of chrome. GA was found to initiates a decrease in both chromium-collagen cross-linking and hydration by covalently cross-linking with the collagen. The chrome uptake was observed to increase when using GA and MMT due to covalent cross-linking and adsorption, respectively. However, the uptake decreased due to the masking of SF and DSP that reduce chrome fixation.[9]

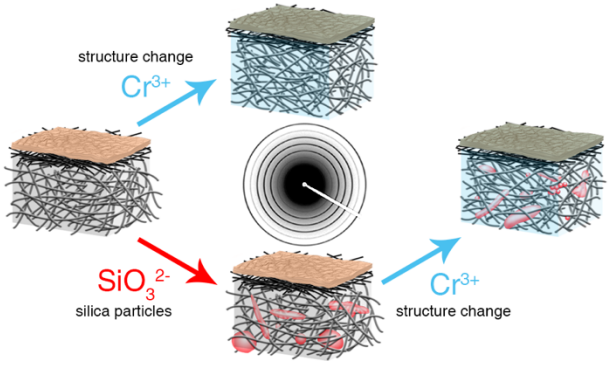

Fig. 3. Collagen structure changes during silicification with sodium silicate © RSC Adv. 10.1039/C7RA01160A

Benign inorganic materials can be used to fill the leather during the retanning process after cross-linking with low chrome offers.[5] For example, the electrostatic interactions between the positively charged amino groups in collagen with negatively charged silicate species lead to precipitation, forming coatings and aggregates of silica particles on the surface of the collagen fibrils (Figure 3). The introduction of silica into the leather matrix did not affect the axial periodicities of the collagen molecules, however an increase in collagen fibril diameter was observed during the main tanning step. From DSC studies, it was found that sodium silicate treated samples (So-Si) impart no effect on collagen stabilization in the absence of chrome. However, a pseudo-stabilization effect is observed in the So-Si + chrome samples possibly due to the inability of the collagen molecules to undergo conformational changes due to the silica coating on the collagen fibrils.[9]

3 Conclusions

Synchrotron based small-angle X-ray scattering (SAXS) technique is a powerful technique that has helped us understand the molecular-level changes in collagen structure during leather processing. The technique provides valuable information about collagen structure changes that could lead to more efficient use of chrome (or other tanning agents) in the leather industry.

Acknowledgements

S.P, Y.Z & G.H would like to thank the Ministry of Business, Innovation and Employment (MBIE) for providing funding through grant LSRX-1801. The research was undertaken on the SAXS/WAXS beamlines at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan, the Diamond Light Source in UK and the Australian Synchrotron in Australia.

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