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Influence of crosslinking agents on the pore structure of skin

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Abstract

Analysis of pore structure of skin is important to understand process of diffusion and adsorption involved during any application of the skin matrix. In this study, the effect of thermal shrinkage on the pore structure of chromium and vegetable treated skin has been analyzed as these tanning agents are known to bring about thermal stability to the matrix. The changes brought about in the pore structure have been studied using mercury intrusion porosimetry and scanning electron microscopy. Response of the chromium treated and vegetable tanning treated skin structure to heat has been found to be quite different from each other. About 41% decrease in porosity is observed for chromium treated skin as against 97% decrease for the skin treated with vegetable tannins. This is primarily attributed to the basic nature of these materials and the nature of interaction of them towards skin.

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1. Introduction

An understanding of the internal pore structure of skin as a matrix has far reaching implications in both biological and industrial applications of the material. Skin, is an architectural marvel. Many of the unique properties of leather like visco-elasticity and breathability seem to stem from the pore structure and connectivity with their sizes ranging from 7 Å to 150 μ m of the skin [1]. Pore structure renders skin many unique properties. Insight into the pore structure of the skin matrix is required to understand mass and heat transport properties as well as fracture mechanism of material under flexural stress [2,3]. Several studies have been carried out on the water vapour adsorption and transmission of leather [4–6]. Pore structures of skin and leather have been investigated previously [7,8].

Characterization of porous space inside matrices can be approached using different methods including gas adsorption, vapour sorption, thermoporometry, mercury porosimetry and image analysis. Typically, the distribution of pore sizes is char-

0927-7765/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.colsurfb.2007.01.008 acterized by mercury intrusion porosimetry (MIP) and nitrogen adsorption [9]. The basic assumption in all these techniques is that the geometry of the pores is regular, that the pores are interconnected and that the size distribution is not affected by the loss of water in the pores upon drying. MIP is one of the few analytical techniques that uses data over a wide dynamic range ($0.003-10 \,\mu$ m) to investigate the porous structure of solid samples in a quantitative manner. This is widely used technique for the pore structure characteristics of many materials [10,11].

One of the characteristic features of skin is its dimensional change under heat. Skin undergoes length reduction at a characteristic temperature to a level of one third of its original dimension. Such shrinkage occurs at a characteristic temperature depending on the type and nature of skin [12]. Shrinkage temperature is considered an important parameter in leather making. Tanning, the process that converts raw hide/skin into leather, aims at bringing about thermal and enzymatic stability to the skin matrix [13,14]. The shrinkage temperature of skin is known to increase on tanning [15]. In our previous study on the shrinkage phenomenon of skin, the changes brought about in the porosity of the skin matrix as a result of thermal shrinkage has been reported [16]. The volume changes accompanying the removal of water from skin, expressed as partial fractions of

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Table 1	
The intrusion data summary for native, chrome treated, vegetable treated	and respective shrunken skin samples from the mercury porosimetry technique

Property	Native	Native shrunk	Chrome	Chrome shrunk	Vegetable	Vegetable shrunk
Total intrusion volume (mL/g)	0.2431	0.0446	0.4786	0.3280	0.5918	0.0145
Total surface area (m^2/g)	0.0986	1.7533	0.2430	0.6238	1.0602	0.0152
Median pore diameter (volume) (µm)	14.60	0.409	10.65	4.729	5.152	6.256
Bulk density at 0.10 psia (g/mL)	1.3646	2.0925	0.7580	1.1514	0.9919	1.3486
Total porosity (%)	33.17	9.33	16.34	9.5	31.35	0.85

volumes of solid, liquid and air has been studied using dilatometric technique [17]. A fundamental understanding of changes in shrinkage temperature on tanning in relation to pore size distribution is yet to be achieved. In the present work, an attempt has been made to unravel relationships, if any, between porosity of various tanned matrices in relation to increases in their shrinkage temperature using mercury intrusion porosimetry and scanning electron microscopy.



Fig. 1. Mercury intrusion volume to pore size curves for (a) native skin, (b) shrunk skin, (c) chrome treated, (d) chrome treated shrunk, (e) vegetable treated, and (f) vegetable treated shrunk.

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