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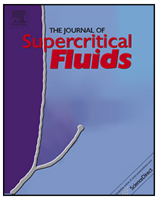

# High pressure vegetable tanning of sheepskins using supercritical carbon dioxide

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ABSTRACT

Leather is a porous material composed of a three-dimensional weave of collagen fiber bundles. The high pressure tanning (HPT) of sheepskins with valonea tannin in supercritical $CO_2$ was approached to investigate the diffusion process through the skin matrix. Uptake of vegetable tanning agent (VTA) was analyzed at 100 bar and 32 °C with varying tanning times (2–8 h). Shrinkage temperature ($T_s$) as thermal stability of the tanned collagen and filling coefficient (%) of pressurized vegetable tanning (PVT) were also analyzed. The best results were obtained at 8 h treatment yielding 83.77% of VTA uptake and a filling coefficient of 54.97%. PVT experiments showed a satisfactory conversion of the skins to leather in terms of the thermal stability. Scanning electron microscopy (SEM) of the tanned skins showed that high pressure did not alter the fiber structure and morphology negatively. The proposed technique has high potential to be deployed to industrial scale.

## 1. Introduction

Originally, leather production is governed by an eco-friendly industrial process, because slaughter house waste such as the hides/skins discarded as waste material, is processed into useful materials such as leather goods, footwear and garments. More than 210 million $m^2$ of leather are produced every year in over 2800 tanneries in the European Union. To produce this amount, about 7 million tons of skins are needed [1]. The average turnover is approximately 8 billion Euros [2].

Leather making involves operations like soaking (rehydration), liming, deliming, pickling, tanning, post-tanning and finishing processes [3,4]. During the leather making process, tanning is one of the most important operation, which improves the durability and practicability of leather products and prevent putrefaction, in which the tanning agents react with the collagen molecule, stabilizing the triple helical structure of collagen matrix; thereby the leather acquiring resistance toward chemical, thermal and microbiological degradation [5–7]. Collagen fibers consist of proteins and have different binding sites available. The used binding sites differ from the respective tanning agent [8]. The different binding sides are shown in Fig. 1.

Globally 90% of the leathers are tanned by basic chromium sulphates (BCS) result in 50–70% chromium uptake [9,10]. This poor uptake results in material wastage on one hand and ecological imbalances on the other. The international specification for the discharge of chromium in wastewater is in the range of 0.1–2 ppm [11]. Even a high-exhaust chrome tanning system does not provide such low concentration. Concerns have been expressed on the toxicity of chromium(III) [12,13]. Discussion exists regarding the possible conversion of chromium(III)–(VI) in certain soil conditions [14]. Moreover, the disposal of chromium containing solid wastes and sludge is posing major challenge [15]. On the whole, the popular chrome tanning method has come under the close scrutiny of the environmental authorities in the industrialized as well as developing countries due to increased awareness about environment and health. Hence, there is constant search for eco benign tanning materials and methods [3].

Tanning methods involving the use of vegetable tannins are regaining importance in the recent times [16]. Vegetable tannins are natural materials which have been considered as a suitable eco-friendly option to replace chromium. They have been used for conversion of animal hides/skins to leather for thousands of years. The vegetable tanning agents used for processing of different types of leathers are leached from woods of trees like quebracho, valonea and chestnut extract, fruits and fruits pods, leaves roots

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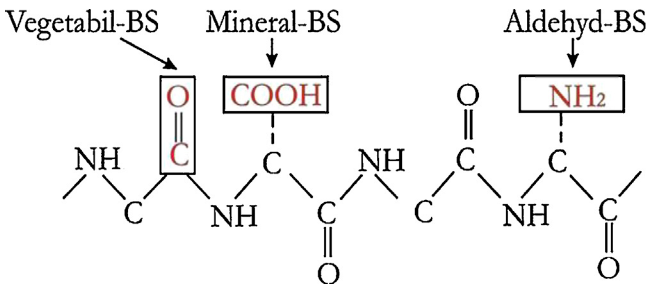

**Fig. 1.** Binding sides (BSs) of the collagen for the different tanning agents.

etc., which are water soluble, non-crystalline ingredients of plant matter. They possess distinct astringency. They have molecular weight range of 500–3000 Da [17], containing sufficient hydroxyls and other suitable groups (carboxyl) to form effectively strong complexes with protein and other macromolecules [18,19]. About 90% of the vegetable tannins produced in the world are applied in leather industry [20]. Tannins in the range of 350,000–400,000 ton are being used across the world for leather processing. The conventional vegetable tanning (CVT) system exhibits low exhaustion and long process time. A 60,000–80,000 ton of vegetable tannins are let out in 1,000,000–1,500,000 $m^3$ of spent vegetable tanning liquor in effluent. Hence, to overcome the problems associated with CVT process, it is necessary to device suitable strategies for improving the exhaustion and reducing the process time [3].

High pressure technology applications using supercritical $CO_2$ provide advantages as increasing the mass transfer, reducing the process time and lowering the costs [21]. This technology has also been applied for leather industry in several applications. Supercritical $CO_2$ has been employed in deliming [22], enzymatic unhairing [23] and degreasing [24] of leather as a new clean technology of leather making. It has been also used in chromium tanning process and provided great advantages for the rapid penetration of tanning agent, reducing the process time and waste load by increasing the float exhaustion [1,2]. This study aims to examine how float exhaustion changes by VTA uptake with different vegetable tanning time under pressure and how leather character as filling and thermal stability behaves by HPT using supercritical $CO_2$. Structural and morphological studies have also been carried out on the skins.

## 2. Materials and methods

### 2.1. Materials and chemicals

Commercial pickled Turkish domestic sheepskins with the thickness of 0.6 cm were used as the skin material. Valonea extract (68% tannin, Balaban Izmir Palamut Ltd., Co., Manisa, Turkey) was used as the vegetable tanning agent. Tanigan RFS as syntan, degreasing and surface active agents (Peltec AN 90) were supplied from "Lanxess Energizing Chemistry" (Leverkusen, Germany) and acidic enzymatic bating agent (Gemazym NAP) from "Gemsan Chemical Company", Turkey. Low-chromed ($Cr_2O_3 < 0.8\%$) hide powder used for the tannin content analyses in the tanning floats was purchased from "FILK" (Research Institute of Leather and Plastic Sheeting, Freiberg, Germany). Liquid $CO_2$ with 99.9% purity was used in all experiments.

### 2.2. Methods

#### 2.2.1. Experimental set up

The high pressure autoclave (Medimex 2543 Lengnau, Switzerland) has an internal volume of 1.5 L and is suitable for 200 bar and 300 °C. Using the shown equipment set up (Fig. 2), the piece of skin was put into the autoclave. Afterwards, the autoclave was closed and pressurized. The pressure build-up was done by a continuous working pump. $CO_2$ cooling system in front of the pump prevents cavitation. When the desired pressure was reached, the valves were closed. The autoclave was heated by two heating rods which were integrated in the casing of the autoclave. The substances in the autoclave were stirred for rapid phase equilibrium. $CO_2$ in the system was supplied from the 10 tons of storage tank. The employed gaseous $CO_2$ was recycled after processing and reused in the next process cycle.

#### 2.2.2. Pressurized vegetable tanning (PVT) processes using compressed $CO_2$

The basic idea of the new process was to carry out the tanning step under high pressure conditions. The skins were treated with VTA under the same conditions as applied in the conventional tanning; apart from that the whole system was set under gaseous $CO_2$. The $CO_2$ diffused into the solution and the skin, which was expected to swell the skin and widen the pores for the tannins. Depickled and syntan treated skins were used for the tanning processes. The recipe

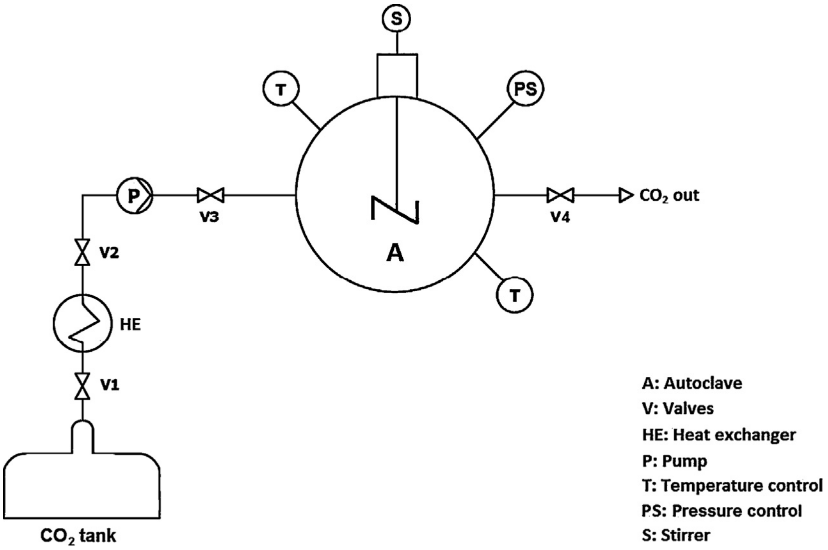

**Fig. 2.** Set up of the high pressure autoclave.