



Quality properties of leather produced in water and supercritical fluid (SCF) media

Ersin Onem^{a,b,*}

^a Department of Leather Engineering, Faculty of Engineering, Ege University, 35100 Bornova, Izmir, Turkey

^b Fraunhofer Institute UMSICHT, Osterfelder Str. 3, 46047 Oberhausen, Germany

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ABSTRACT

Supercritical fluid (SCF) technology is defined as green processing system and used in the industrial applications. This study aims to search the quality properties of leather produced in water and SCF media. Supercritical carbon dioxide (scCO₂) was used as SCF. Tanning process was carried out by valonea tannin as natural tanning agent with different process time from 2 h to 8 h. After tanning in SCF, the skins were processed with conventional methods in water media and finished. Another group of the skins were just conventionally produced. ScCO₂ tanned and finished leathers were compared with the leathers which completely processed in conventional ways as control group. Light fastness, tensile strength, tear load and stitch tear resistance analyses for the quality control of the products were carried out. Thermal stability characterization of the leathers were also done by differential scanning calorimetry (DSC) and mechanical shrinkage tests. The results showed that 2 h and 4 h of SCF-CO₂ tanning applications were insufficient in terms of the physical properties expected, but 6 h and 8 h tanned leathers were in a good quality.

1. Introduction

Leather manufacturing involves operations like soaking (rehydration), dehairing, liming, deliming, degreasing, pickling, tanning, post-tanning and finishing processes. Tanning process comprises the conversion of putrefiable skins/hides to a nonputrescible and durable materials [1,2]. Globally 90% of the leathers tanned by basic chromium sulphates (BCS) result in 50–70% chromium uptake in conventional tanning (CT) [3]. This poor uptake in CT results in material wastage on one hand and ecological imbalances on the other. The international specification for the discharge of chromium in waste water is in the range of 0.1–2 ppm [4]. Concerns have been expressed on the toxicity of chromium(III) [5,6]. Discussion exists regarding the possible conversion of chromium(III) to chromium(VI) in certain soil conditions [7]. Moreover, the disposal of chromium containing solid wastes and sludge is posing major challenge [8]. 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 human health. Hence, there is constant search for eco-benign tanning materials and green processing technologies. Tanning methods involving the use of vegetable tannins and other natural materials [9,10] are regaining importance in recent times for sustainability in the industry [2,11].

Vegetable tanned leather is very much appreciated and demanded due to its versatility. It is the main material of a wide range of artefacts and adapted to very diverse functional needs such as footwear, book-bindings, saddles, harness, liquid vessels, cases and caskets coverings or seating furniture and carriages upholstery. Beyond its utilitarian function, it is also used as support material for artistic and decorative paintings, wall hangings and screen coverings. Different ornamental techniques such as dyeing, painting, gilding, moulding, tooling, embroidering, cutting-out, scorching or sewing, have been often incorporated transforming vegetable tanned leather into a noble, luxurious and valuable material [12].

Vegetable tannins in the range of 350,000–400,000 tons are being used across the world for leather processing. The conventional vegetable tanning (CVT) system exhibits low exhaustion and long process time [11]. 60,000–80,000 tons of vegetable tannins are let out in 1,000,000–1,500,000 m³ of spent vegetable tanning liquor in effluent. Hence, to overcome the problems associated with CVT process, it is necessary to devise the suitable and sustainable strategies [2].

High pressure technology applications using scCO₂ provide advantages as increasing the mass transfer, reducing the process time and lowering the costs [13]. This technology has also been applied for leather industry in several applications. ScCO₂ has been employed in deliming [14], enzymatic unhairing [15] and degreasing [16] of leather

* Corresponding author at: Department of Leather Engineering, Faculty of Engineering, Ege University, 35100 Bornova, Izmir, Turkey.
E-mail address: ersin.onem@ege.edu.tr.

Table 1
Depickle process recipe of sheepskins.

Process	(%)	Substances	Temp. (°C)	Time	Remarks
Depickle	200	Water	30	30 min	7 Bé
	1.5	HCOONa		30 min	
	4	Degreasing agent		30 min	
	1	Enzymatic bating agent		1 h	
	0.8	NaHCO ₃		3 × 30 min	
Washing x 3	150	Water	30		pH = 4.5
	0.5	Surface active agent		15 min	

as a new clean technologies. The most important application of this technology was on tanning process as an alternative carrier medium for the industry. Renner et al. [17,18] used this innovative technology in chromium tanning and provided great advantages. They reduced the tanning time from 12 h to 3 h and achieved zero waste water with 100% float exhaustion in the industrial scale equipment. Using CO₂ 14 million liters of sewage water in the tanning process, 270 million liters of sewage water to produce the tanning agents, 160,000 tons of chrome and 500,000 tons of salt could be saved [17,18]. Onem et al. [11] also put forward the basic and successful results for vegetable tanning in a short process time by high pressure CO₂ equipment. The obtained results for high pressure vegetable tanning conducted in the lab-scale without any mechanical effect under only a stirrer was highly promising. On the other hand, no literature was reported how leather's final quality changes by this innovative technology up to now.

Tanning is one of the most important operations, which improves the durability and physical properties of leather products, in which the tanning agents react with the collagen molecule, stabilizing the triple helical structure of collagen matrix [19–21]. It's well known that the physical and quality characteristics of leathers are mainly defined by tanning operation. Nowadays, producers introduce more qualified products with high performance properties into the market owing to the increased customer satisfaction [22]. Thus, tanning has come into prominence in leather manufacturing by contributing to the physical properties to meet the customers' expectations. It defines the final performance and quality of the products required by end users [23]. In this framework, this study aimed to research the important physical properties of leather indicating the quality of final products tanned as vegetable under pressure in water and SCF carrier media with different process times, and to put forward the outputs of this new tanning technology on the leather quality.

2. Materials and methods

2.1. Skin and tanning agent materials

Commercial pickled Turkish domestic sheepskins with the thickness of 0.6 cm were used as the skin material. Valonea tannin (Balaban Izmir Palamut Ltd. Co., Manisa, Turkey) was used as the vegetable tanning agent. Degreasing and surface active agents were supplied from "Lanxess Energizing Chemistry" (Leverkusen, Germany) and acidic enzymatic bating agent from "Gemsan Chemical Company", Turkey.

2.2. Carbon dioxide

CO₂ employed in processes has been accumulated as byproduct in processes of ammonia production so that it has not to be counted as "emitted CO₂". It is of 99.9% purity. It is non-flammable, relatively inert, non-carcinogenic, non-mutagenic, shows a very low toxicity.

2.3. Vegetable tanning process in SCF media

Depickle process including degreasing and enzymatic bating

applications of the skins as pre-tanning operations was given in Table 1 before the tanning description.

The basic idea of the new process was to carry out the tanning step under the pressure of CO₂. The skins were treated with valonea tannin and in the same conditions as in the conventional tanning; apart from that the whole system is set under CO₂ pressure. After depickle process, tanning operations were applied at pH = 4.5. The skins were tanned in water supported by CO₂ as supercritical fluid during 2 h to 8 h. Pressure was ensured with CO₂ at 100 bar and temperature was adjusted to 32 °C which are over the critical points of CO₂. The skins as control group were tanned by CVT just in water during 8 h as in the tanneries. Fig. 1 shows the schematic set up of the supercritical CO₂ system.

CO₂ in the system was supplied from the 10 tons of storage tank. By compressing CO₂ the CO₂ shows solubility of liquids and penetration of gases and exhibits excellent mass transfer properties. CO₂ is able to penetrate into the structures, to change material properties and enables the transport of other substances into or out of the structures. The employed gaseous CO₂ can be recycled after processings and reused in the next process cycle.

After the tanning step, the skins which are SCF and CVT tanned were processed with the same recipe (Table 2), and final products were obtained.

2.4. Physical tests of the final products

Final products were subjected to the tests of tensile strength, tear load and stitch tear resistance. Shimadzu AG-IS brand tensile testing device was used for all tests. For the tests, the measurement of the thickness of the samples was performed in accordance with EN ISO 2589 [24], tensile strength with EN ISO 3376 [25], tear load with EN ISO 3377-2 [26] and measurement of stitch tear resistance with EN ISO 23910 [27]. Light fastness analyses were performed by using ATLAS-XENOTEST ALPHA+ test instrument and according to ISO 105-B02 standard test method [28]. Blue wool test references (1 to 8) were evaluated to the scale (according to grade 4 – contrast between the exposed and the unexposed portions of the specimen), then grey scale was used for evaluation of the color changing on the leathers against UV application of an artificial light source representative of natural daylight (Xenon arc fading lamp).

The shrinkage temperature (T_s , °C), indicator of hydrothermal stability of the products, was measured by Theis leather shrinkage meter. The temperature at which the collagenous fiber shrinks to one third of its original length was noted as the shrinkage temperature of the fiber [29]. Differential scanning calorimetric analyses to identify thermal transition of the leathers were performed on Shimadzu DSC-60 Plus apparatus. The samples typically weighing 3–5 mg in dry state were placed in aluminum pans having three small holes and heated from room temperature to 250 °C at a heating rate of 10 °C min⁻¹, under nitrogen flow (20 mL min⁻¹; nitrogen purity of 99.999%). The reference had a similar empty crucible. All the physical analyses were done in triplicate.

2.5. Statistical analysis

The results were statistically evaluated by using One-Way ANOVA and descriptive statistical test at SPSS 15.0 statistical software package for the determination of standard deviations of the averages. All data were represented as mean for three independent measurements.

3. Results and discussions

Getting high float exhaustions in a short process time, reducing the wastes and saving the costs by using supercritical fluid system are one point, but another point is whether high pressure application affects the final leather quality or not. Onem et al. [11] and Renner et al. [17,18] obtained good results with SCF-CO₂ system on tanning process, but

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