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Chrome Uptake and Thermal Stability of Wet Blue Leather Tanned by Static and Rotating Drum

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Article

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ABSTRACT

Leather tanning can be done by soaking the skin in pits or rotating in tannery drums. Technical soaking of rotate movement and static soaking affects the skin microstructure matrix. This study aims to compare the quality of wet blue leather tanned by static soaking in a vessel and rotating in a tannery drum, particularly in terms of chrome uptake and thermal stability. The penetration time in the soaking experiment varied from 8, 16, 24, 32, 40, 48, and 56 hours. Meanwhile, the control was processed in a small-scale tannery drum with two hours of penetration time. Then, each sample was subjected to basification using HCOONa and $NaHCO_3$. The results showed that all samples increased in weight and thickness after tanning. After penetration, wet blue leather tanned in a tannery drum performed better blue-green colour evenness compared with the soaked ones. Tannery drum leather also showed better chromium uptake, shrinkage temperature, and thermal stability. When the drum rotates, the pickled pelt gets mechanical action, such as being stretched, bent, and slammed, helping the collagen fibre open and the chromium penetrates deeper and faster. This study revealed that darker wet blue leather indicates higher thermal stability and chromium uptake.

KEYWORDS

tanning, leather, soaking, mechanical action

INTRODUCTION

Currently, enterprises involved in selling clothing are gaining significant popularity [1]. Leather is one of the sought-after materials for apparel because of its versatility, durability, and timeless appeal. During prehistoric times, the importance of skin as raw material for clothes cannot be overstated since the discovery of animal skinning in the sands of Lower Austria in the 10th century AD [2]. Raw animal skin can easily be damaged by microorganisms [3]. Tanning has been characterized as the initial endeavour in human manufacture by transforming it into leather products, such as clothing, footwear, bookbinding, etc [4]. Vegetable tanning is a traditional technique employed in tanning, wherein the untreated animal skin is submerged in tanning solutions consisting of locally sourced plant matter rich in tannins. Another method to produce leather was kneading the raw animal skin with alum paste or oil. This manufacture is called tawing [2]. Subsequently, in 1858, the tanning effect of chromium salt was discovered by Friedrich Knapp, and until 1884 the chromium compounds were initially employed as tanning agents for commercial manufacturing of leather [5]. Nowadays, chromium compound is by far the most widely used of all the tanning agents in the production of leather [6].

The modern leather tanning process consists of numerous steps, from rehydrating to finishing [2]. Special attention is paid to the tanning step, where the chromium compound is added to the pelt so the Cr^{3+} can interact with the collagen's carboxyl groups to form a stable collagen-chromium complex [6]. Chrome tanning consists of two main stages: penetration and basification. The first stage allows the carboxyl group of the pickled pelt (pH value 2.5 - 3) to be protonated and penetrated by the chrome tanning agent. The pH value then increased to 3.8 - 4.2 in the fixation stage to create crosslinking of collagen fibres by enhancing the formation of strong coordination bonds between the deprotonated carboxyl group and Cr^{3+} ions [7,8]. Chrome-tanned leather has high thermal stability and better performance but generates excessive chrome discharge in wastewater. Over 40,000 tons of basic chromium sulfate are released globally by the leather industry during tanning every year due to low chrome uptake in pelt [9].

Since the early 20th century, the push for industrialization has made rotary drums have played a crucial role in the entire tanning process compared with tanning in pits. A rotary tanning drum is a cylindrical object that undergoes rotational motion around its axis. The transition from the traditional practice of soaking hides in pits to the utilization of rotary drums for chrome tanning exemplifies the leather industry's overarching trends toward mechanization and enhanced productivity [10]. Meanwhile, the traditional process of static soaking hides in pits facilitated a gradual and thorough penetration of chrome. Thus, tanning in a static process could produce high-quality leather, and a long period is needed to finish the process [11].

Moreover, a prolonged soak of pelt in a chrome solution will fully saturate the pelt. No more chrome solution can be absorbed so that the maximum chrome tanning agent can penetrate the pelt. Penetration and fixation stages could determine the chrome uptake and thermal stability of the resulting wet blue leather [8]. Therefore, this paper carried out the comparison of chrome tanning in static soak and the usual tanning process using a rotary drum in terms of chrome uptake and thermal stability in wet blue leather.

EXPERIMENTAL

Materials

This research focused on raw lamb skins (under 12-month-old sheep) because they are the source of tanned leather for clothing worldwide [12]. Eight sheets of lamb skin used in this experiment were obtained from local skin collectors in Yogyakarta, Indonesia. Chemical used in this experiment were Na_2CO_3, wetting agent (Teepol), degreasing agent (Dephan B, Clariant, Swiss), Na_2S, $Ca(OH)_2$, $(NH_4)_2SO_4$, H_2O_2, dan bating agent (Oropon OO, TFL, Jerman), salt, HCOOH, H_2SO_4, antifungal, basic chromium sulfate (Chromosal®, Lanxess, India), HCOONa, and $NaHCO_3$.

Methods

This research method started with processing raw lamb skin into pickled pelt (Figure 1). All the samples used in this process were rotated in a bigger rotary drum. After that, the pickled pelt was tanned with basic chromium sulfate using two methods: soaking in a vessel and rotating in a rotary tanning drum. Chromium tanning consists of two steps, the first is penetration and ends with basification [13]. The penetration time for static soaking varied from 8, 16, 24, 32, 40, 48, and 56 hours. Meanwhile, penetration in a rotary tanning drum (RD) was conducted in two hours as formulated by Lyu, et al. [14].

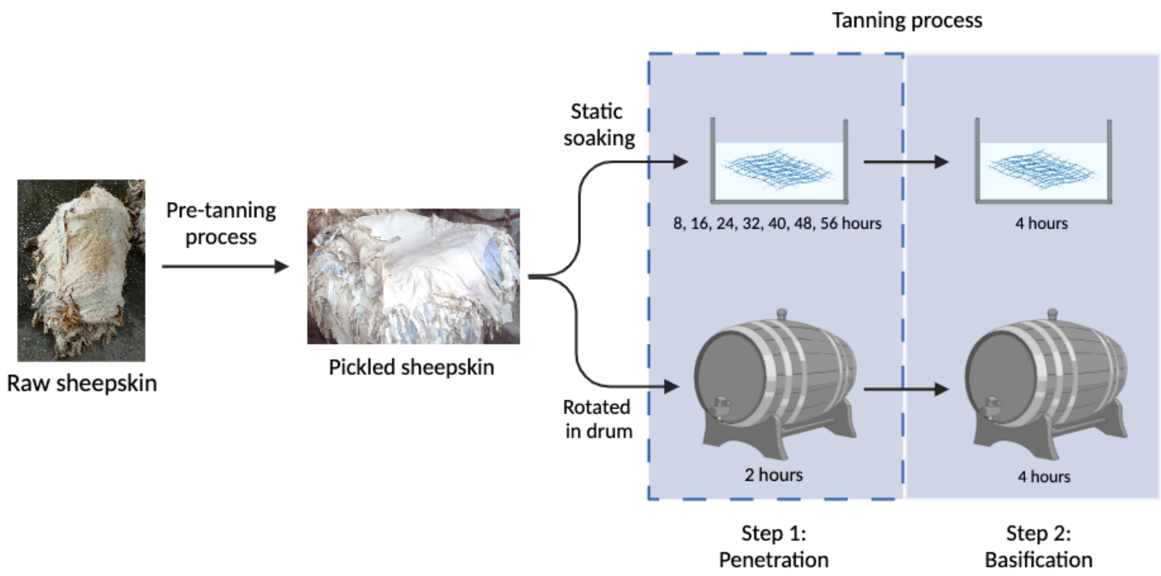

Figure 1. Research method in conducting soaking

Pre-tanning Process

Pre-tanning consists of several processes of converting raw lamb skin into pickled pelt with 2.5 - 3 pH values to prepare for the addition of the tanning agent. The recipe used to make pickled lamb skin can be seen in Table 1 [14,15]. Raw lamb skins were weighed before rehydration to calculate the chemicals used before fleshing. After the fleshing operation, the skins were weighed again for free subcutaneous connective tissue and meat residue skin weight. All percentages of chemicals after the fleshing operation were calculated based on fleshed lamb skin.

Table 1. Pre-tanning recipe of the research

Operation	Chemicals	Offer (%)	Time (min)	Remarks
Rehydration	Water	100	30	
	Na_2CO_3	0.2		pH = 8
	Wetting agent	0.2		
Degreasing	Water	100	30	pH = 8
	Degreasing agent	0.3		
Unhairing and liming 1	Water	60	30	
	Na2S	1.25		pH = 12 - 13
	$Ca(OH)_2$	0.5		
Unhairing and liming 2	Na_2S		60	Stops 30 min and runs 60 min
	$Ca(OH)_2$			
Water addition	Water	100	Overnight	
Fleshing				pH = 12 - 13
Deliming	Water	100	30	pH = 8
	$(NH_4)_2SO_4$	2		
Degreasing	Water	100	30	pH = 8
	H_2O_2	0.2		
	Degreasing agent	0.2	30	pH = 8
Bating	H_2SO_4	0.4	45	pH = 5
	Acid bating agent	0.2	60	pH = 5
Pickling	Water	80	10	pH = 5
	Salt	8		
	HCOOH	0.5	60	pH = 4
	Antifungal	0.04		
	H_2SO_4	1	3 x 15	pH = 2,5 - 3

Chrome Tanning

Subsequently, each lamb skin was cut into four parts, extracted from corresponding lateral places along the lamb's backbone as a representation of the whole skin [16]. It was assumed that these samples possessed comparable thicknesses and qualities. A preliminary study was observed for the penetration under 8 hours. It showed that the wet blue leather colour was a pale blue, and the basic chrome sulfate did not penetrate well in the middle of the pickled skin based on penetration tests using scissors. Thus, the minimum time of this study was 8 hours. Pickling solution was taken from the pickling step as much as 1% of the cut sample weight. Each sample and the pickling solution were placed in vessels right after the Chromosal B was added. During penetration, the skin is pressed lightly with a container filled with water to ensure all skin parts are submerged in the solution. The percentage of the chrome and bases for the control samples were the same in the experiment. Still, the penetration time was only two hours, according to the recipe mentioned by previous studies [3, 4]. Next, the pH was adjusted to 3.8 - 4.2 with HCOONa and $NaHCO_3$, as described in Table 2. This operation was conducted for an hour. After the pH was achieved, the basification time was set up for three hours for all the samples. All experimental samples for soaking treatment were carried out without stirring, except at the beginning of adding chemicals, light stirring was carried out by hand within ±1 minute so that the solutions and chemicals were homogeneous. Lastly, the skins were piled up and aged for about 12 hours.

Table 2. Recipe of the tanning operation

Operation	Chemicals	Offer (%)	Time (min)
Penetration	Pickling solution	100	X
	Chromosal B	6	
Basification	HCOONa	0.5	15
	$NaHCO_3$	0.5	15
	$NaHCO_3$	0.5	15
	$NaHCO_3$	0.5	15
	-	-	+ 3 hours

Determination of Thickness and Weight Increase

The thickness of wet blue leather samples was measured with a leather thickness gauge in three different spots to get a more accurate measurement [12]. The average of the pickled skin and wet blue leather thickness was used in this study. The thickness increase rate (TIR) was calculated according to the equation (1) where (TWB) was the thickness of wet blue leather as the final thickness and TP was the thickness of pickled skin as the initial thickness [17].

$$TIR\ (\%) = \frac{TWB - TP}{TP}\ x\ 100 \tag{1}$$

It is assumed that the heavier the skin, the more chromium solution is absorbed into the skin. Thus, the weight change of the lamb pickled skin and wet blue leather were analyzed. Equation (2) shows the percentage of the weight increase where WWB was the final weight of wet blue and WP was the weight of pickled skin before tanning.

$$Weight\ increase\ (\%) = \frac{WWB - WP}{WP}\ x\ 100 \tag{2}$$

Determination Chromium Uptake

During the tanning process, part of the chromium oxide is fixed into the hide, and the other part remains in the bath as wastewater. The residual of total chromium in the wastewater was determined by flame atomic absorption spectrometry (AAS). The chrome uptake of wet blue leather was calculated using equation (3) [8].

$$Cr\ uptake\ (\%) = \frac{Added\ Cr - Cr\ in\ wastewater}{Added\ Cr}\ x100 \tag{3}$$

Shrinkage Temperature Test

The specimens were partitioned into three rectangular configurations, each with dimensions of (50 ± 2) x (3 ± 2) mm. The experimental procedure consisted of conducting the shrinkage temperature test utilizing a digital shrinkage temperature tester, following the ISO 3380 standard [18]. One extremity of the specimen was affixed to a stationary holder, while the other was affixed to a mobile hook. Subsequently, the threads, pulleys, and mass were appropriately modified to enable the attachment of the sample to the load pressure. A mixture of water and glycerine at a ratio of 75:25 was introduced into a glass beaker and subjected to heating at a controlled pace of 2 °C per minute with a tolerance of ±0.2 °C per minute. The temperature will be displayed on the digital panel when the sample experiences shrinkage of 150 µm. The shrinkage temperature is determined by calculating the average of three sample pieces.

Evaluation of Thermal stability

After ageing, the wet blue leather samples were added into aluminium pans and sealed. Differential scanning calorimetry (DSC) was carried out with a DSC-60 in the range from 25-30 °C with a scanning rate of 10 °C per minute under a nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Determination of Thickness and Weight Incerase

Table 3 shows the colour change of the samples after penetration. Samples soaked for 8 - 24 showed more uneven colour than samples soaked for more than 24 hours which means shorter soaking time tends to ununiformed blue-green colour. When soaked in the chromium solution, the pickled lamb skins were folded so that the whole skin could be immersed. It can cause some areas to become darker and others to become lighter. The longer it soaks, the more likely the pale area will turn more blue-green. Meanwhile, penetrating leather by rotating the drum resulted in an even blue-green colour.

Table 3. Percentage of thickness increase and colour uniformity after penetration

Penetration time	Colour uniformity after penetration	Thickness increase (%)
8	Uneven colour	46.34
16	Uneven colour	59.46
24	Uneven colour	41.03
32	Less uneven colour	50.00
40	Less uneven colour	75.68
48	Uneven colour	60.53
56	Less uneven colour	46.34
RD	Even colour	53.33

After tanning, The thickness rate indicated the filling properties of chromium penetrated the collagen matrix [19]. The percentage of thickness increase in this experiment ranges from 41.03% (24 hours) to 75.68% (40 hours) (Table 3). The higher the thickness increases, the higher the chromium solution diffused into the collagen matrix. The final weight of this determination was carried out after 12 hours of ageing. The weight increase was calculated based on the initial weight and illustrated in Figure 2. It is shown that the weight increase of S24 was higher (39.49%) than that of other samples, including the rotated dum sample. The lowest weight increase was 48 hours of soaking (2.17%). The weight change value between 16 hours of soaking and 40 hours of soaking was almost the same. This result indicated that chromium solution could penetrate the collagen matrix of the pelt. Thickness and weight increase could serve as evidence to demonstrate that the lamb skin collagen can be penetrated by chromium solution.

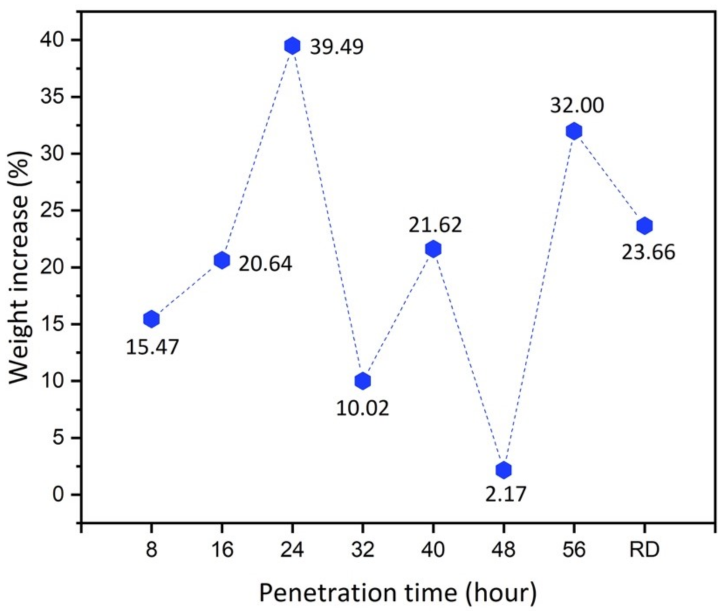

Figure 2. The weight increase results after the tanning operation

As a result of this study, wet blue leather showed different colours, as illustrated in Figure 3. The colour measurement was conducted after 12 hours of ageing. Leather after tanning contains a blue chrome tanning agent (Chromium (III) oxide), which gives it a bluish colour. The colour of wet blue samples ranges from greyish-light blue to dark blue. For 8 hours of penetration by static soaking, the resulting wet blue leather was paler than other samples.

Meanwhile, other static-soaked wet blue samples showed almost similar light blue colours. Unlike the static-soaked wet blue, leather tanned in the rotary tanning drum has a darker blue colour. According to Jian-Xun et al., the colour of chromium-tanned leather is affected by the amount of chromium fixed on the collagen fibre [20]. The darker the colour, the higher the content of chromium.

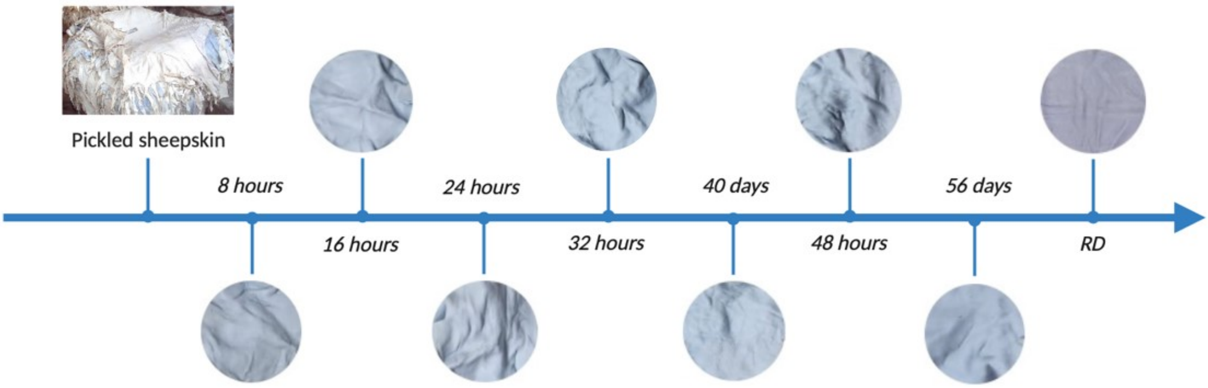

Figure 3. Colour differences of the wet blue leather

Chromium Uptake

The chromium uptake of different soaking times and rotated samples are shown in Figure 4. Wet blue leather processed in the rotary tanning drum showed higher Cr uptake (93%) compared with soaked samples. The sample soaked in chromium solution for 32 hours (28.59%) showed the lowest (42.91%). Penetration for 48 hours (72.69%) showed higher chromium uptake than other soaked samples. It has demonstrated that tanning in a rotary drum could improve chromium uptake in leathers.

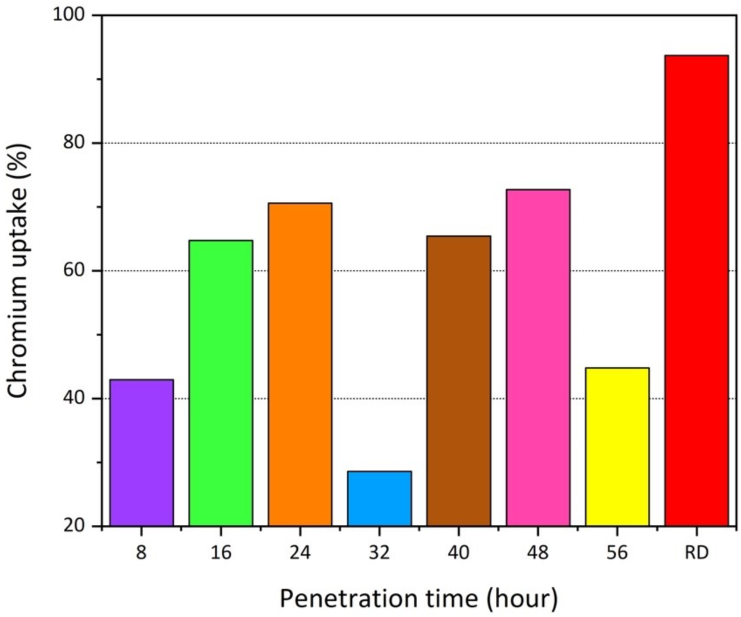

Figure 4. Chromium uptake of the wet blue leather

According to Figure 4, higher penetration time has no significant effect in increasing chromium uptake in leather. Diverse chrome uptake content in leather soaked in chromium solution might be caused by uneven chromium absorbed in the collagen matrix. Leather tanned in a rotary tanning drum might have a more even distribution of chromium facilitated by continuous movement and agitation of the pelt resulting in more consistent penetration. The tanning process in a rotational drum facilitates thorough mixing, enabling chromium to enter more deeply into the lamb skin [21].

Shrinkage Temperature

The chrome tanning method is used in tanneries because it is easy to use, has good mechanical qualities, and has a high shrinkage temperature [19]. Shrinkage temperature is one of the most important parameters to evaluate the tanning effect [7]. The average shrinkage temperature of vertical and horizontal samples near the backbone was taken as each sample's shrinkage temperature (Ts). The results displayed in Figure 5 reveal that tanning in a rotary tanning drum produces significantly higher Ts (111.45 °C) than that in a vessel. As can be seen in the figure, Ts of leather soaked for 24 hours was the lowest (88.15 °C). Chromium tanning in static soaking can only reach 100.45 °C (32 hours) of shrinkage temperature and the Ts of the wet blue leathers were lower for more than 32 hours of penetration. These results indicate that a longer penetration time could not increase Ts of wet blue leather. Particle motion and mixture in a rotating drum might allow the chromium tanning agent to penetrate better into fibrous material [22].

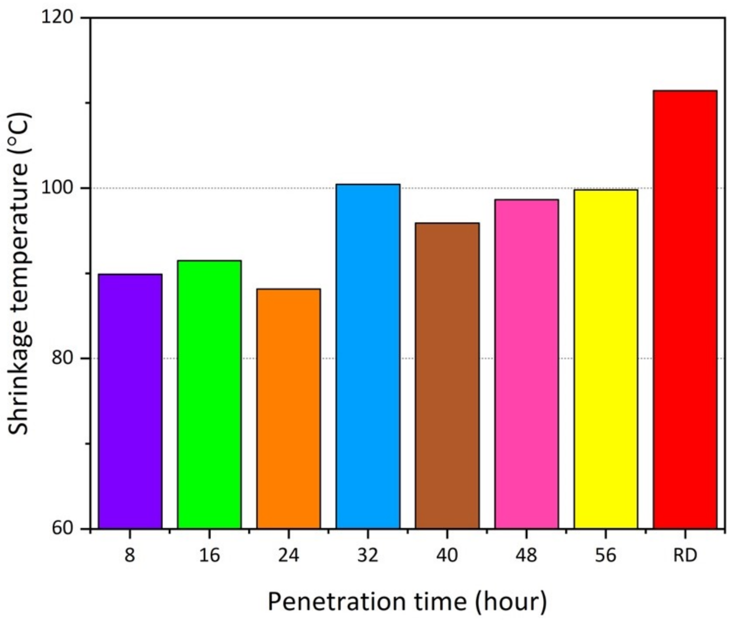

Figure 5. Shrinkage temperature of the experiment

Thermal Stability

The determination of the thermal stability of crosslinked collagen can be analyzed by differential scanning calorimetry (DSC) curve. The onset temperature was used for the final evaluation in this study because it is the beginning of the denaturation (Td) and describes the collagen denaturation temperature more accurately [23]. Td represents the temperature at which the collagen triple helix in the wet blue leather transitioned from its structured triple helix form to a random coil form. The samples used for DSC analysis were wet blue leathers soaked for 8, 32, and 56 hours, and RD. Those samples represented a short, middle, and long time of soaking and drumming wet blue leather respectively (RD). Figure 6 shows the DSC thermograms of wet blue leather. Generally, the results of the DSC analysis were in line with the shrinkage temperature. Leather tanned in a rotating drum resulted in higher Ts and denaturation Td than those of with static soaking. Leather penetrated for 32 and 56 hours has similar Td (99.48 and 99.93 °C). Meanwhile, Td of leather soaked in a shorter time (8 hours) produced a slightly higher Td (101.78 °C) than longer penetration time samples. Eight hours of penetration showed a broader DSC peak. It suggests that the endothermic event of collagen denaturation occurring in a wide range of temperatures can be attributed to an uneven distribution of chromium throughout the collagen matrix [24].

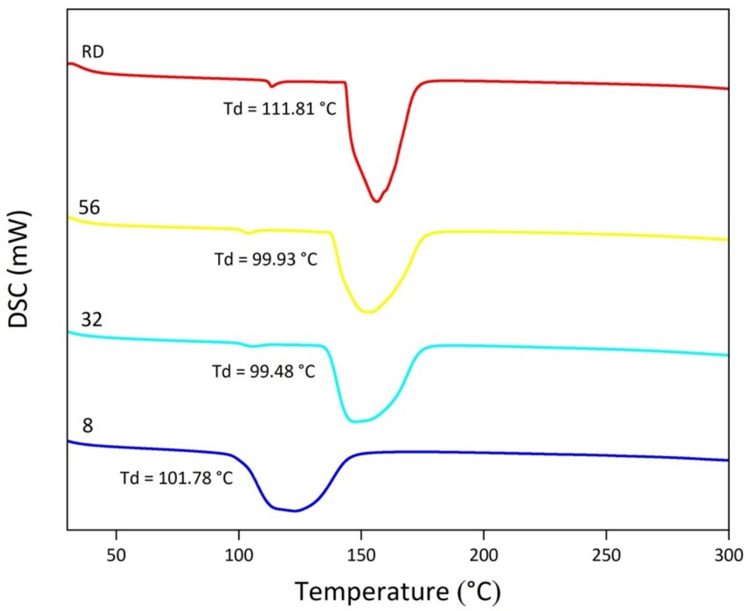

Figure 6. DSC thermogram results

Several mechanical activities occur during the leather tanning process in a rotational drum, including stretching, flexing, agitating, and mixing [25]. When the drum rotates, the pickled pelt gets stretched, bent, and slammed helping the collagen fibre to open and the chromium could penetrate deeper and faster (Figure 9). The pelts also underwent compression as they came into contact with the inside wall of the drum. The mechanical action also helps chromium fixed to the leather at the basification step.

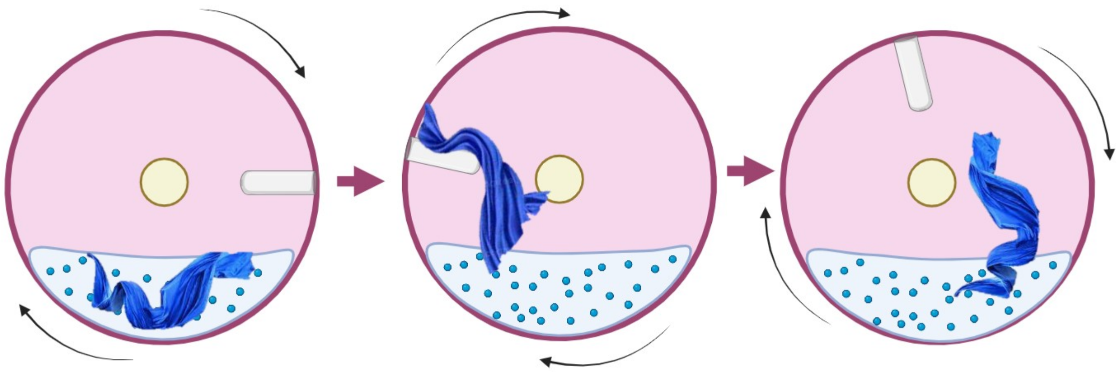

Figure 9. Mechanical action in the rotary tanning drum

CONCLUSION

Leather tanning by a static soak in vessels could form chromium-collagen crosslinking eliminating the need for financial investment in the procurement or rental of tannery drums, water usage, and energy consumption. Meanwhile, tanning leather in a rotary drum resulted in better wet blue leather in terms of chromium uptake, shrinkage temperature, colour uniformity, and thermal stability. A prolonged soak of pelt in a chrome solution for more than two days could not reach maximum chromium uptake. Based on the results, it also can be summarized that wet blue leather with a darker blue colour represents higher thermal stability. The transition from the traditional practice of soaking hides in vessels to using rotary tanning drums exemplifies the leather industry's overarching trajectory towards mechanization and enhanced efficiency. Although both processes possess their own merits, the rotating drum technique is more suited to meet the requirements of modern industrial-scale leather production.

Author contribution

Conceptualization – Kusumastuti Y, Griyanitasari G, Erwanto Y; methodology - Kusumastuti Y, Griyanitasari G, Erwanto Y, Wagiman; formal analysis - Griyanitasari G, Erwanto Y, Fitriyanto NA, Pertiwiningrum A; investigation - Griyanitasari G, Fitriyanto NA, Pertiwiningrum A, Abidin MZ; writing original draft preparation - Griyanitasari G, Erwanto Y; writing review and editing - Griyanitasari G, Erwanto Y, Fitriyanto NA, Pertiwiningrum A, Wagiman, Abidin MZ, Kusumastuti Y; supervision – Erwanto Y, Pertiwiningrum A, Fitriyanto NA. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

This research has no competing interest.

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