THE EFFECT OF HEATING TIME ON THE THERMAL STABILITY OF CHROME-TANNED LEATHER

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Received: 30.11.2022 Accepted: 13.02.2023 https://doi.org/10.24264/lfj.23.1.3

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ABSTRACT. Chrome tanning is an essential process to convert raw animal skin into leather, in which collagen, as the main structure of leather, is stabilized against degradation through cross-linking using chromium, consisting of two steps: penetration and basicity. However, the uptake of chrome in leather still needs to be improved. The purpose of this study was to find the best heating time in the chrome tanning process by thermal analysis. Pickled sheepskin was used as raw material for the chromium tanning process. The samples were varied into four categories: heated at the penetration stage of the tanning process (Initial Heating), heated at the basification stage of the tanning process (Final Heating), and heated both at the penetration and basification stage (Continuous Heating). In this study, the thermal stability of wet blue leather was evaluated by shrinkage temperature behavior (Ts), thermogravimetry analysis (TGA/DTG), and differential scanning calorimetry (DSC). The tanning efficiency was measured by Cr_2O_3 content. The results demonstrated that wet blue samples heated continuously shows better thermal characteristics. In conclusion, the results can be used for finding the best possible technique for the leather tanning process using chrome salts to gain thermal stability.
KEY WORDS: chrome tanning, leather, thermal stability

INFLUENȚA TIMPULUI DE ÎNCĂLZIRE ASUPRA STABILITĂȚII TERMICE A PIELII TĂBĂCITE ÎN CROM

REZUMAT. Tăbăcirea în crom este un proces esențial pentru transformarea pielii brute în piele finită, în care colagenul, ca structură principală a pielii, este stabilizat împotriva degradării prin reticulare folosind crom, constând în două etape: pătrunderea tanantului și bazificare. Cu toate acestea, absorbția cromului în piele are nevoie de îmbunătățire. Scopul acestui studiu a fost de a găsi cel mai bun timp de încălzire în procesul de tăbăcire în crom prin analiza termică. S-a folosit piele de oaie piclată ca materie primă pentru procesul de tăbăcire în crom. Probele au fost împărțite în patru categorii: încălzite în stadiul de pătrundere a tanantului (încălzire inițială), încălzite în stadiul de bazificare al procesului de tăbăcire (încălzire finală) și încălzite atât în stadiul de pătrundere a tanantului, cât și în cel de bazificare (încălzire continuă). În acest studiu, stabilitatea termică a pielii wet blue a fost evaluată prin temperatura de contracție (Ts), analiza termogravimetrică (TGA/DTG) și calorimetria de scanare diferențială (DSC). Eficiența tăbăcirii a fost măsurată prin conținutul de Cr_2O_3. Rezultatele au demonstrat că probele de piele wet blue încălzite continuu prezintă caracteristici termice mai bune. În concluzie, rezultatele pot fi folosite pentru găsirea celei mai bune tehnici posibile pentru procesul de tăbăcire a pielii folosind săruri de crom pentru o stabilitate termică mai mare.
CUVINTE CHEIE: tăbăcire în crom, piele, stabilitate termică

L'EFFET DU TEMPS DE CHAUFFAGE SUR LA STABILITÉ THERMIQUE DU CUIR TANNÉ AU CHROME

RÉSUMÉ. Le tannage au chrome est un processus essentiel pour convertir la peau animale brute en cuir, dans lequel le collagène, en tant que structure principale du cuir, est stabilisé contre la dégradation par réticulation à l'aide de chrome, composé de deux étapes : pénétration et basicité. Cependant, l'absorption du chrome dans le cuir doit encore être améliorée. Le but de cette étude a été de trouver le meilleur temps de chauffage dans le procédé de tannage au chrome par l'analyse thermique. La peau de mouton picklée a été utilisée comme matière première pour le processus de tannage au chrome. Les échantillons ont été répartis en quatre catégories : chauffés à l'étape de pénétration du processus de tannage (chauffage initial), chauffés à l'étape de basification du processus de tannage (chauffage final) et chauffés à la fois à l'étape de pénétration et de basification (chauffage continu). Dans cette étude, la stabilité thermique du cuir wet blue a été évaluée par la température de rétrait (Ts), l'analyse thermogravimétrique (TGA/DTG) et la calorimétrie différentielle à balayage (DSC). L'efficacité du tannage a été mesurée par la teneur en Cr_2O_3. Les résultats ont démontré que les échantillons de cuir wet blue chauffés en continu présentent de meilleures caractéristiques thermiques. En conclusion, les résultats peuvent être utilisés pour trouver la meilleure technique possible pour le processus de tannage du cuir en utilisant des sels de chrome pour une plus grande stabilité thermique.
MOTS CLÉS : tannage au chrome, cuir, stabilité thermique

INTRODUCTION

Leather is the first biomaterial humans ever made and has continuously been produced until now. The characteristic of leather as the raw material used for a wide variety of products is still irreplaceable. Nowadays, 80-90% of leather is produced by the chrome tanning process using trivalent chromium (Cr^{3+}) salt as the tanning agent [1, 2].

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The chrome-tanned leather has excellent organoleptic properties, versatile applicability, and hydrothermal stability compared with other-tanned leather [3]. Thus, the chrome tanning process is still the most popular and widely preferred system in leather tanning industries.

Chrome tanning is an essential process to convert raw animal skin into leather, in which collagen, as the main structure of leather, is stabilized against degradation through cross-linking using chromium consists of two steps: penetration and basicity. In the first step, basic chrome sulfate will penetrate the collagen matrix. Then, the chromium and the carboxyl collagen will form inter and intra-molecular cross-links through the basicity step [1]. However, the uptake of chrome in leather is only 40-70% [2, 4], and as a consequence, 30% of chrome is discharged into tannery effluent resulting in environmental stress and severe health effects on humans because chromium (Cr^{3+}) might potentially transform into hexavalent chromium (Cr^{6+}).

Poor chromium uptake can cause parallel problems: low quality of tanned leather produced, high level of toxicity in the environment, and resulted in increased amount of production costs [5]. Thus, research in the area of chromium tanning still focuses on a cleaner tanning process by increasing chrome uptake [1, 5]. However, a more efficient tanning process needs to be achieved to increase chromium uptake without adding more chromium which might harm the environment and cause higher costs. Temperature is an additional driving force in the tanning process that can affect the diffusion rate [6] and the reaction rate of basification [6]. However, the appropriate heating time still needs to be explored to achieve better chromium uptake.

One of the most significant changes caused by the tanning process is the increase in thermal stability using various methods [7]. Thermal analysis is a helpful group of analytical techniques to measure the property of leather as a function of temperature. Remembering that collagen is the primary structural element in the extracellular matrix of animal skin, one of the methods to measure the quality of tanned leather is its thermal resistance against shrinkage, which indicates the amount of chromium reacted with the collagen carboxyl leather [1]. The more chromium can be fixed to the collagen carboxyl group, the higher the thermal stability. Unfortunately, such an indicator still lacks the molecular level observation of collagen in the tanning process [4]. Thermogravimetry Analysis (TG/DTG) and Differential Scanning Calorimetry (DSC) are the most used methods to characterize collagen-based material. Therefore, investigation of the thermal behavior of wet blue leather with different heating stages using TG/DTG and DSC will drive a new strategy in the tanning process.

MATERIAL AND METHODS

Samples Preparation

Pickled sheepskins have been selected for this experiment since it is the raw material in the worldwide garment industry, and there is still severe research about sheep leather's thermal properties. Pickled sheepskins were obtained from skin suppliers in Yogyakarta, Indonesia. Then, the skin was cut approximately into 10 x 10 cm samples from the same lateral positions of the sheepskin following the line of the backbone of the sheep, assuming that the samples have similar thicknesses and properties. Meanwhile, chemical stores in the same region acquired NaCl, H2O, basic chromium sulfate (BCS), HCOONa, and $NaHCO_3$. BCS used in this study was Chromosal® chrome tanning salt from

Lanxess contained approximately 26% of Cr_2O_3 content and 33% basicity [8].

Chromium Tanning Procedure

The chrome tanning was conducted in a 1000 mL glass beaker covered with aluminum foil to prevent loss of liquid caused by heating. It was kept in the water bath to maintain the temperature. The samples were varied into four categories: heated at the penetration stage of the tanning process (Initial Heating), heated at the basification stage of the tanning process (Final Heating), and heated both at the penetration and basification stage (Continuous Heating). The control experiment was performed by tanning the sheepskin at room temperature (Without Heating). The temperature was heated as soon as the beaker was placed in the water bath until the targeted temperature was achieved at 40 ± 2 °C.

Table 1: Chrome tanning recipes

Stage	Chemicals	Quantity (%)	Duration (min)	Remarks
Penetration	BCS	3	30	Penetration was checked
	BCS	3	30	
	HCOONa	1	30	
		0.375	15	
Basification	$NaHCO_3$	0.375	15	pH = 4
		0.375	15	
		0.375	15	
	-	-	90	Stirred and then drained
Horse up	-	-		Overnight

The percentage of chemicals and water in this experiment was calculated based on the weight of the pickled sheepskin. Before tanning, the samples were stirred with 100% of water and 8% of NaCl for 10 minutes (pH = 3). This step was conducted in the beaker glass at room temperature. Then, the samples were added with chemicals based on the tanning recipes from Schroepfer & Meyer [9] and Mengistie *et al*. [1] with slight modifications, as seen in Table 1. Before the addition, HCOONa and $NaHCO_3$ were diluted 1:10 with water. After horsing up, each wet blue leather sample was stored in a plastic bag for analysis.

Tanning Efficiency

The tanning efficiency in this study will be measured by the content of Cr_2O_3 in the wet blue leather. The samples were analyzed for the Cr_2O_3 content using titration [10]. Samples were ground and weighed into a conical flask. 10 mL of nitric acid was added and let stand for 2 minutes. Then, 15 mL of sulfuric/perchloric acid mixture and a few antibumping grains were added. A funnel was placed in the flask's neck and brought to a boil on a wire gauze over a moderate flame. When the reaction mixture began to become orange, the flame was reduced. After the color has completely changed, it was heated for at least 2 minutes. Then, it was left for 5 minutes until cool and diluted to 200 ml. It was boiled l for 10 minutes to remove chlorine and let it cool. Next, 5 mL of orthophosphoric acid was added to cover up any iron.

The obtained solution was added to the potassium iodide solution and left in the dark. After that, 0,1 mol/L sodium thiosulfate solution was titrated until the solution was either light green or blue using 5 mL of starch indicator solution that was added at the end of the process. The amount of chrome oxide can be calculated by equation (1).

$$w_{Cr} = \frac{V1x0.00253x100xF}{m_0} \quad (1)$$

where w_{Cr} is the percentage by mass on dry matter of Cr_2O_3, $V1$ is the volume of 0.1 mol/L of thiosulfate solution (mL), m_0 means the

weight of the samples (g), and F is the correct factor to 0% volatile matter that was calculated by equation (2). w_w is the content of volatile matter (%).

$$F = \frac{100}{100 - w_w} \quad (2)$$

Shrinkage Temperature

Each sample was cut into three rectangular shapes with a size of (50±2) x (3±2) mm. The shrinkage temperature test was conducted using a digital shrinkage temperature tester with the ISO 3380 [11] method. One end of the sample was attached to a fixed holder and the other was attached to a movable hook. Next, the threads, pulleys, and mass were adjusted so that the sample was attached to the load pressure. Water : glycerine (75:25) was placed in a beaker glass and heated at the rate of temperature 2 °C/minute ± 0,2 °C/minute. The digital panel will show the temperature when the sample shrinkage at 150 µm. The average of three pieces of samples is the shrinkage temperature.

Thermogravimetry (TG) and Derivative Thermogravimetry (DTG)

TG/DTG curves were obtained in a temperature range of 30-550 °C, utilizing STA 200 RV Thermal Analyzer under a nitrogen atmosphere (100 mL/min) with a heating rate of 5 °C/min. An Aluminum sample pan containing a mass of around 7-9 mg was used in the analysis. Data were analyzed by Origin software.

Differential Scanning Calorimetry (DSC)

DSC curves were obtained at the temperature range of 30-550 °C, utilizing the software STA 200 RV Thermal Analyzer under nitrogen atmosphere (5 °C/min heating rate) with an aluminum pan containing sample mass around 7-9 mg as a reference. Also for DSC, data were analyzed by Origin Software.

RESULTS AND DISCUSSION

Tanning Efficiency

The efficiency of chromium tanning in this study is depicted with the Cr_2O_3 content of wet blue leather. The effect of heating on Cr_2O_3 uptake is shown in Fig. 1. Leather that is tanned without heating neither at the penetration nor the basification stage shows the lowest content of Cr_2O_3. Meanwhile, leather with continuous heating has uptake more Cr_2O_3 than others. The reaction between chrome and collagen increases when the temperature rises [6]. The optimal uptake of Cr_2O_3 appears at the longest heating time, starting from the beginning of the penetration stage until the end of the basification stage.

Temperature is one of the factors that affect the reaction between chromium and collagen because it can influence viscosity, equilibrium composition, and chromium polymerization. Then, heating can increase acid-base dissociation in the chromium complexes aqua ligands [12]. However, a study by Bickley *et al*. [13] found that the diffusion of chromium in the collagen matrix will only increase when the temperature is lower than 50 °C. When chrome was fixed at a temperature of more than 60 °C chrome content will be high but the chrome precipitation on the surface of the leather will be uneven. The results are in accordance with this study since the leather tanning process was heated at the temperature of 40 °C. The chrome uptake of heated samples shows higher Cr_2O_3 content than those without heated samples.

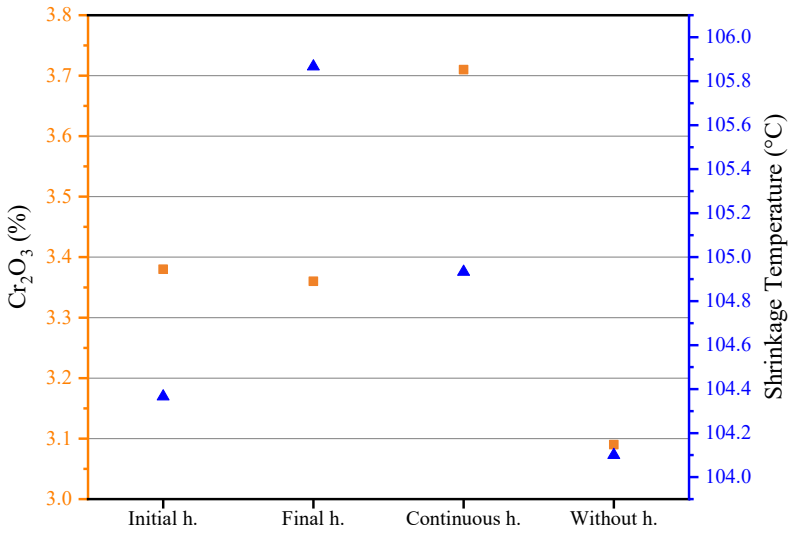


Figure 1. Cr_2O_3 content and shrinkage temperature of different heating times

Shrinkage Temperature Behaviour

The success of a leather tanning process is generally indicated by the shrinkage temperature (Ts), the temperature at which a sudden and irreversible shrinkage occurs when it is heated gradually in the aqueous solution [14]. The result of this study is expressed in Fig. 1 that the unheated sample shows the lowest Ts as the Cr_2O_3 content. However, Final heating samples show the highest Ts with lower Cr_2O_3 uptake and Continuous heating samples show the highest content of Cr_2O_3 with lower Ts. Those results are consistent with the study conducted by Mengistie *et al*. [1] that compared with lower temperature, heating at 40 °C in the tanning process could result in higher Ts but the chrome uptake was lower. In contrast, higher Ts normally means higher Cr_2O_3 content because chrome fixation on collagen is increased [6].

It might be caused by the nature of collagen changing early in the process as a result of increased temperatures [1]. Shrinking is the process to break and unravel the hydrogen bonding in the triple helices besides entailing the chrome-collagen bonds [6]. Thus, the higher temperature might shrink the collagen before it fully tanned which allows the pores less open for chrome to get to the reaction site [1]. According to Esteban *et al*. [14], determining shrinkage temperature involves a series of processes starting with the first shrinkage when the individual fiber is noticed, other fibers follow the shrinking fiber to shrink, and most fibers shrink at the same time. The initial temperature when most fibers simultaneously shrink is the Ts. This process is still followed by the fibers experiencing concurrent shrinking, the last individual fibers shrinking, and finally, the fibers ultimately shrinking.

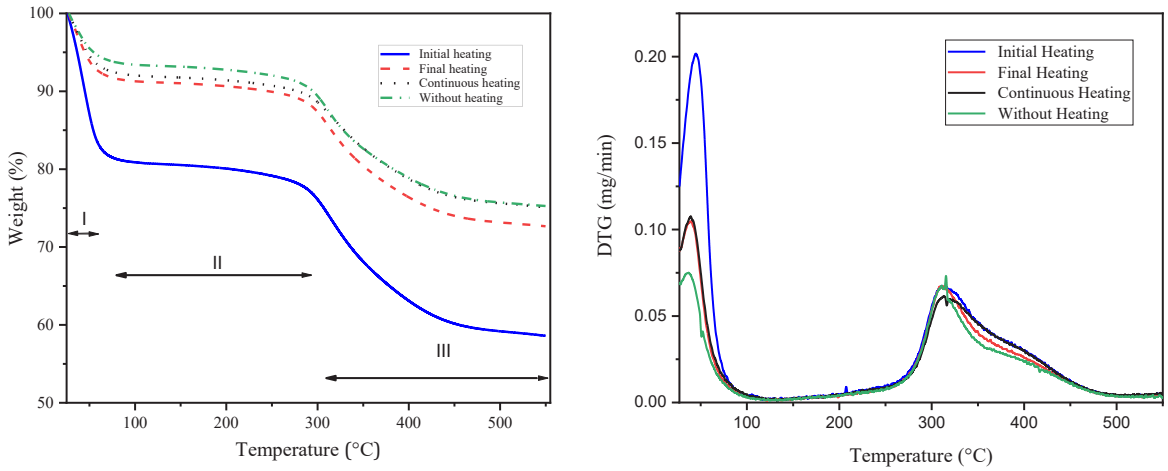
TG and DTG Analysis

Thermogravimetry analysis is a widely used method for analyzing material decomposition and thermal stability by measuring mass change as a function of temperature in scanning mode or time in isothermal mode [15]. Fig 2a and b present the TG and DTG curves of the wet blue samples with different heating times. The thermogravimetric curve shows that all samples have three decomposition stages. The first stages happened at a temperature of about 26.744-60.03 °C (Table 1) which mainly indicates the loss of water, volatile compounds

with low molecular weight [16], and trapped gasses [17].

At the first stage of decomposition, the Initial Heating sample lost a higher percentage of mass (18.85%) than those of other samples. As explained by Gil *et al*. [18] that at the temperature up to 100 °C, leather focused on the loss of water presented in minor weight loss in the TGA curve, it is expected that the Initial Heating sample has a higher amount of water than the other samples. The initial heating sample only heated at the penetration stage and then decreased temperature at the beginning of the basification stage. When it is heated, more water-containing chromium diffuses in the collagen fiber. Then the temperature at the basicity is decreased which might cause less chrome to react with collagen carboxyl and result in a higher weight loss percentage at the third stage.

At the same stage, the Without Heating samples lost a lower percentage of mass (6.252%), as described in Table 2. Meanwhile, The Final Heating and Continuous Heating show similar weight loss results at the first stage of decomposition, and both are higher than those Without Heating. It can be assumed that heating can increase the water penetration into the collagen matrix. The second stage occurred between 56.873-291.361 °C (Fig. 2b). In this stage, the chemisorbed water and low molecular weight molecules are responsible for mass loss [17]. As described in Table 2, the loss of weight for all samples shows a similar percentage and they show relatively small degradation at this stage. This might be due to the adsorbed or unstructured water being evaporated at about 100 °C and the collagen has just started to decompose at about 200 °C [19].



(a) (b)

Figure 2. TG (a) and DTG (b) curves of wet blue samples

From Fig. 2a, it is found that the last stage goes from 284.029-549.913 °C. This stage is characterized by the most significant amount of weight loss and detected as peak and shoulder at the DTG curves (Fig. 2b). Most total volatiles are decomposed in this stage, including collagenous materials as the main component of leather. Moreover, the shoulder at a temperature of 330-440 °C appears more separated which might be due to collagen's varying degree of crosslinks. Mostly, at this range of temperatures, the carbonaceous components are decomposed [16]. Moreover, the scission of the hydroxyl groups happened at a temperature of around 300 °C [19]. From Table 1, the onset temperature of Continuous Heating is higher followed by a lower percentage of weight loss than those of others.

This result is consistent with the results of the Cr_2O_3 content explained in Fig. 1. This result is also found in stages one and two. It shows that penetrating and basifying at a higher temperature in the chrome tanning process can delay the leather fibers' decomposition and improve thermal stability [20].

Table 2: TG data of the wet blue leather at the different decomposition stages

Parameter	Initial Heating	Final Heating	Continuous Heating	Without Heating
Stage 1				
Onset Temperature (°C)	26.744	27.303	27.413	27.594
End temperature (°C)	58.635	58.496	60.03	56.873
Weight loss (%)	18.854	8.297	7.84	6.252
Stage 2				
Onset temperature (°C)	58.635	58.496	60.03	56.873
End temperature	281.276	288.119	291.361	286.686
Weight loss (%)	2.065	2.207	2.045	2.199
Stage 3				
Onset Temperature (°C)	284.029	288.119	291.361	286.686
End temperature (°C)	549.760	549.913	549.879	549.878
Weight loss (%)	20.482	16.829	15.015	16.285

The DTG peaks can be attributed to the thermal degradation of collagen leather (Fig. 2b). The peaks start at about 100 °C and end at about 550 °C for all wet blue samples with different heating times. The DTG curves show that the thermal decomposition of all the samples starts at the same temperature. However, the shoulder at about 380 °C appears more separated from the peak at 330 °C. The heating treatment seems to have the most influence on the fractions of leather disintegrating at the temperature of 330-440 °C. Many polymer decompositions took place at this range of temperature [19], and most organic components are decomposed.

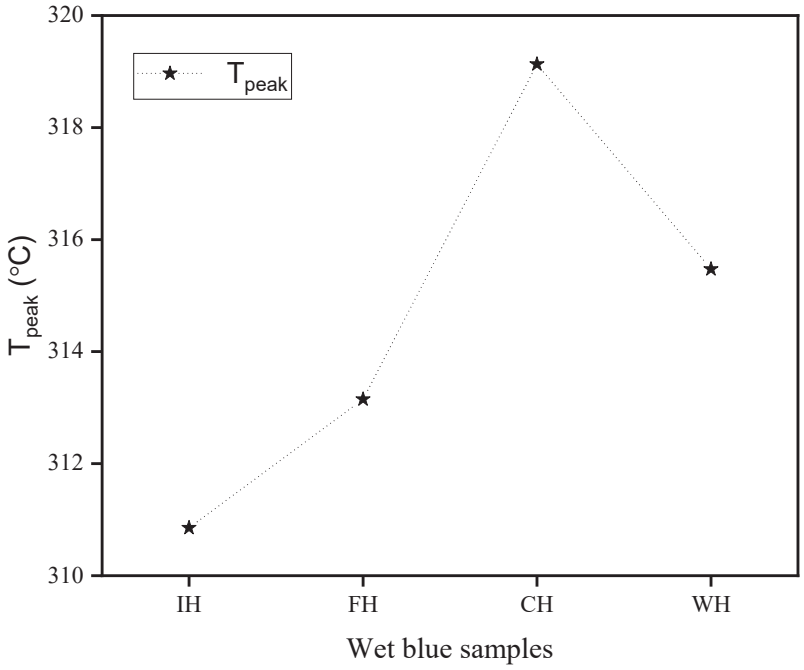


Figure 3. The temperature of the maximum decomposition rate (T_{peak})

The thermal stability of the samples in this study can be characterized by the temperature of the maximum rate of mass loss (T_{peak}). As shown in Fig. 3, all of the samples show T_{peak} at the range of temperature 310-320 °C. The peak of the Continuous Heating sample is significantly lower than that of other heating treatment samples but shows a higher T_{peak} in the DTG curve (Fig. 3). This result is consistent with the previous analysis that heating continuously from the beginning until the end of the chrome tanning process increases the chrome – collagen coordinate covalent bonds. At the diffusion stage, heating could help the chromium to penetrate into the collagen matrix and at the basification stage, heating could accelerate the reaction rate of collagen carboxyl and chromium. Amino acid carboxyl groups might dissociate during molecular thermal motion and release H^+ because heating could decrease the pH of the amino acid chromium complex solution. By increasing the temperature, the dissociated carboxyl group of the amino acid may penetrate the inner part of the complex and coordinate with the chromium ion, resulting in a smaller amount of dissociated amino acid and a larger number of dissociated amino acid carboxyl groups in the solution [21].

DSC Evidence of The Thermal Denaturation in Leather

The broader the peak of DSC thermogram indicates that the diffusion of the tanning agent across the thickness of the sheepskin is caused by the uneven crosslinking [22].

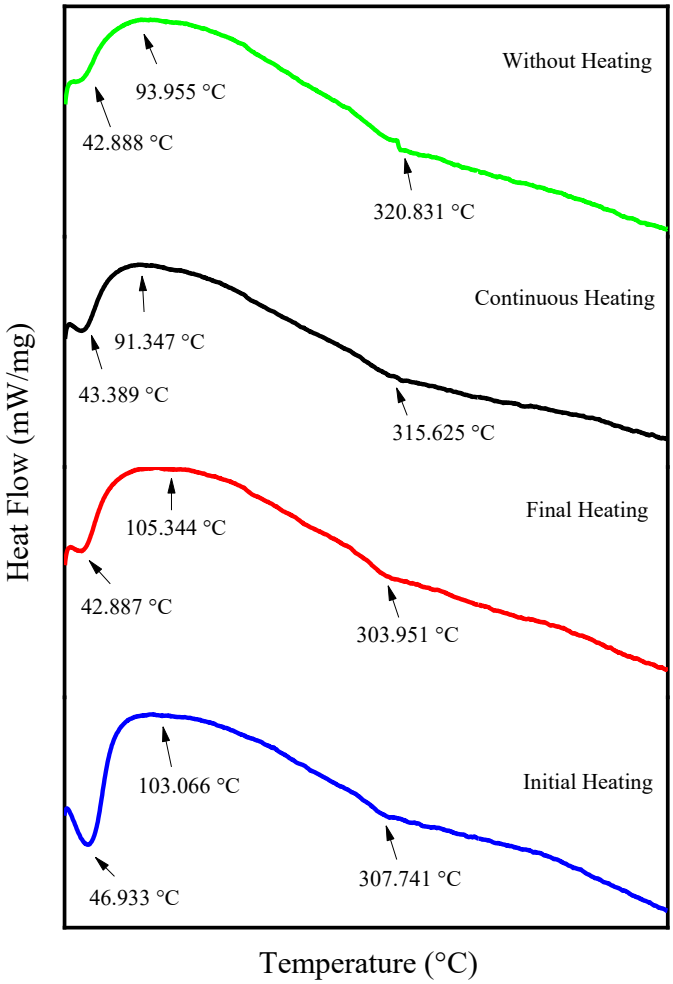


Figure 4. DSC Thermogram of wet blue samples

The overlay DSC thermogram of the wet blue samples is presented in Fig. 4. It can be seen that the samples show similar trends indicating that the collagen leather used has the same characteristic. There are three peaks observed from the thermograms as presented in Fig. 4. The first peaks are endothermic peaks in the range of temperature of 42.887-46.993 °C, the second peaks were at 91.347-105.344 °C, and the last peaks at 303.951-320.831 °C. The first ones indicate loose water and pore water evaporation of wet blue leathers [23]. It can be observed as the glass transition (Tg) temperature which manifests as a subtle shift in the slope of the thermogram [24]. From Fig. 4 all of the samples in the experiment show a similar Tg unless the Initial Heating (46.933 °C). According to Jeyapalina *et al*. [25] tanning agents are a plasticizer in the leather tanning process. It is possible that chrome salts will work by inserting themselves between the chains of the polymer and therefore changing the forces that are keeping the chains together. As a result, Tg, as a viscoelastic transition is depressed. Thus, Tg of more stable leather is lower than that of unstable leather.

At a higher temperature, the collagen gains enough energy to rearrange its microstructure as presented in the second peaks of DSC thermograms. These peaks can be observed as crystallization temperature (Tc). Quite unexpectedly that the Tc of Continuous Heating show is lower than those of other samples. This might be due to the effect of moisture content to support collagen–chrome crosslinking [9, 25]. This result is consistent with the TG results (Fig. 2a) that at the second stage of the decomposition, the excess water is still degraded. Besides, the curves are broader than other curves as an indication of how abrupt the temperature transition was and the uneven distributions of the collagen population with different thermal stability [22].

When the temperature is higher than 200 °C (third peaks) the collagen might be concluded as melting temperature (Tm) [26]. Tm is the temperature where the crystalline zone in the amorphous matrix is melted. Compared with others, Tm Without Heating presents multiple peaks in accordance with the DTG analysis (Fig. 2b) that at the temperature of about 300 °C samples experienced a major weight loss. Meanwhile, Continuous Heating exhibits a smaller melting peak than other samples. This might be due to a higher degree of crosslinking that affect the Tm of wet blue leather.

CONCLUSIONS

In this study, an experimental investigation was carried out to predict the thermal behavior of wet blue leather tanned with different heating times, namely Initial Heating, Final Heating, Continuous Heating, and Without Heating. Differential Scanning Calorimetry and Thermogravimetry analysis combined with Shrinkage Temperature and Cr_2O_3 content was used in this study to observe the effect of heating time on the thermal stability of leather. The obtained results can be used for finding the best possible technique for the leather tanning process using chrome salts to gain thermal stability.

Acknowledgements

We are grateful to the Doctoral Dissertation Research Program of the Ministry of Research, Technology, and Higher Education for the financial support with contract number 089/E5/PG.02.00.PT/2022; 1924/UN1/DITLIT/Dit-Lit/PT.01.03/2022 and to the Center of Standardization and Services for Leather, Rubber, and Plastics Industry. Ministry of Industry for the laboratory facilities.

REFERENCES

1. Mengistie, E., Smets, I., van Gerven, T., Ultrasound Assisted Chrome Tanning: Towards a Clean Leather Production Technology, *Ultrason Sonochem*, **2016**, 32, 204–212, https://doi.org/10.1016/j.ultsonch.2016.03.002.
2. Sathish, M., Dhathathreyan, A., Rao, J.R., Ultraefficient Tanning Process: Role of Mass Transfer Efficiency and Sorption Kinetics of Cr (III) in Leather Processing, *ACS Sustain Chem Eng*, **2019**, 7, 3875–3882, https://doi.org/10.1021/acssuschemeng.8b04876.
3. Wang, L., Han, W., Yu, Y., Zhou, J., Zhang, W., Shi, B., Thermodynamic Investigation on Chrome and Aluminum Tanning, *J Am Leather Chem Assoc*, **2017**, 112, 360–366.
4. Zhang, Y., Mansel, B.W., Naffa, R., Cheong, S., Yao, Y., Holmes, G., Chen, H.L., Prabakar, S., Revealing Molecular Level Indicators of Collagen Stability: Minimizing Chrome Usage in Leather Processing, *ACS Sustain Chem Eng*, **2018**, 6, 7096–7104, https://doi.org/10.1021/acssuschemeng.8b00954.
5. Zhu, R., Yang, C., Li, K., Yu, R., Liu, G., Peng, B., A Smart High Chrome Exhaustion and Chrome-Less Tanning System Based on Chromium (III)-Loaded Nanoparticles for Cleaner Leather Processing, *J Clean Prod*, **2020**, 277, 123278, https://doi.org/10.1016/j.jclepro.2020.123278.
6. Covington, A.D., *Tanning Chemistry: The Science of Leather*, Royal Society of Chemistry: Cambridge, **2009**.
7. Carşote, C., Badea, E., Miu, L., della Gatta, G., Study of the Effect of Tannins and Animal Species on the Thermal Stability of Vegetable Leather by Differential Scanning Calorimetry, *J Therm Anal Calorim*, **2016**, 124, 1255–1266, https://doi.org/10.1007/s10973-016-5344-7.
8. Lanxess, Chromosal B.
9. Schroepfer, M., Meyer, M., DSC Investigation of Bovine Hide Collagen at Varying Degrees of Crosslinking and Humidities, *Int J Biol Macromol*, **2017**, 103, 120–128, https://doi.org/10.1016/j.ijbiomac.2017.04.124.
10. BSN SNI ISO 5398-1: 2013: Kulit - Penentuan Kimiawi Kadar Krom Oksida - Bagian 1 : Kuantifikasi Dengan Cara Titrasi; Jakarta, **2013** (in Indonesia).
11. ISO 3380:2015 - Leather - Physical and Mechanical Tests - Determination of Shrinkage Temperature up to 100 °C (IULTCS/IUP 16); 3rd edition, International Organization for Standardization: Switzerland, **2015**.
12. Sreeram, K.J., Ramasami, T., Sustaining Tanning Process through Conservation, Recovery and Better Utilization of Chromium Related Papers Sustaining Tanning Process through Conservation, Recovery and Better Utilization of Chromium, *Resour Conserv Recycl*, **2002**, 38, 185–212, https://doi.org/10.1016/S0921-3449(02)00151-9.
13. Bickley, J.C., Lee, H., Whitton, J.B., Comparison between Conventional Chrome Tannage and Heated Low Float Tannage, *J Soc Leather Technol Chem*, **1967**, 51, 385–397.

14. Esteban, B., Baquero, G., Cuadros, R., Morera, J.M., Proposal and Application of a New Method to Determine Leather Shrinkage Temperature, *Thermochim Acta*, **2021**, 698, https://doi.org/10.1016/j.tca.2021.178880.

15. Bañón, E., García, A.N., Marcilla, A., Thermogravimetric Analysis and Py-GC/MS for Discrimination of Leather from Different Animal Species and Tanning Processes, *J Anal Appl Pyrolysis*, **2021**, 159, https://doi.org/10.1016/j.jaap.2021.105244.

16. Liu, J., Luo, L., Zhang, Z., Hu, Y., Wang, F., Li, X., Tang, K., A Combined Kinetic Study on the Pyrolysis of Chrome Shavings by Thermogravimetry, *Carbon Resour Convers*, **2020**, 3, 156–163, https://doi.org/10.1016/j.crcon.2020.11.003.

17. Saadatkhah, N., Carillo Garcia, A., Ackermann, S., Leclerc, P., Latifi, M., Samih, S., Patience, G.S., Chaouki, J., Experimental Methods in Chemical Engineering: Thermogravimetric Analysis—TGA, *Can J Chem Eng*, **2020**, 98, 34–43, https://doi.org/10.1002/cjce.23673.

18. Gil, R.R., Girón, R.P., Lozano, M.S., Ruiz, B., Fuente, E., Pyrolysis of Biocollagenic Wastes of Vegetable Tanning. Optimization and Kinetic Study, *J Anal Appl Pyrolysis*, **2012**, 98, 129–136, https://doi.org/10.1016/j.jaap.2012.08.010.

19. Sebestyén, Z. Czégény, Z. Badea, E. Carsote, C. Şendrea, C., Barta-Rajnai, E., Bozi, J., Miu, L., Jakab, E., Thermal Characterization of New, Artificially Aged and Historical Leather and Parchment, *J Anal Appl Pyrolysis*, **2015**, 115, 419–427, https://doi.org/10.1016/j.jaap.2015.08.022.

20. Yang, L., Liu, Y., Wu, Y., Deng, L., Liu, W., Ma, C., Li, L., Thermal Degradation Kinetics of Leather Fibers Treated with Fire-Retardant Melamine Resin, *J Therm Anal Calorim*, **2016**, 123, 413–420, https://doi.org/10.1007/s10973-015-4873-9.

21. Wang, S., Chen, W., Yang, L., Zhang, J., Effect of Microwave Irradiation on the Solution of Amino Acid Chromium Complexes, *Leather and Footwear Journal*, **2020**, 20, 43–50, https://doi.org/10.24264/lfj.20.1.5.

22. Tang, H.R., Covington, A.D., Hancock, R.A., Use of DSC to Detect the Heterogeneity of Hydrothermal Stability in the Polyphenol-Treated Collagen Matrix, *J Agric Food Chem*, **2003**, 51, 6652–6656, https://doi.org/10.1021/jf034380u.

23. Balasubramanian, V., Velappan, B., Vijayan, S.K., Jabamani, H., Nagarajan, V., Victor, J.S., Ranganath, S.P., Badiger, M. V. Chinnaraj, V.K., Chellappa, M., Studies on the Use of Sodium Polyacrylate (SPA) for Low-Salt Animal Skin Preservation, *Environ Sci Pollut Res*, **2019**, 27100, https://doi.org/10.1007/s11356-019-05871-y.

24. Leyva-Porras, C., Cruz-Alcantar, P., Espinosa-Solís, V., Martínez-Guerra, E., Piñón-Balderrama, C.I., Martínez, I.C., Saavedra-Leos, M.Z., Application of Differential Scanning Calorimetry (DSC) and Modulated Differential Scanning Calorimetry (MDSC) in Food and Drug Industries, *Polymers (Basel)*, **2020**, 12, https://doi.org/10.3390/polym12010005.

25. Jeyapalina, S., Attenburrow, G.E., Covington, A.D., Dynamic Mechanical

Thermal Analysis (DMTA) of Leather Part 1: Effect of Tanning Agent on the Glass Transition Temperature of Collagen, *J Soc Leather Technol Chem*, **2007**, 91, 236–242.

26. Cucos, A., Budrugeac, P., Mitrea, S., Hajdu, C., The Influence of Sodium Chloride on the Melting Temperature of Collagen Crystalline Region in Parchments, *J Therm Anal Calorim*, **2013**, 111, 467–473, https://doi.org/10.1007/s10973-012-2453-9.