

Thermal stability of shoe upper leather: Comparison of chestnut and quebracho as vegetable tanning agent

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Abstract. Thermal stability is one of the most important factors in the leather tanning process and mainly affected by the tannin type used to tan the hides. Vegetable-tanned leather for shoe upper is a material that could be used and preserved for a long time. However, it makes leather easily degraded because of temperature and time. Additionally, one of the stages in shoe making process is the heating process to stick the upper leather into midsole material. Therefore, this study aims to compare the effect of different tanning agents, chestnut and quebracho, on the thermal stability of shoe upper leather. Measured were degree of tannage and thermal stability, using shrinkage temperature, thermogravimetric analysis and differential scanning microscopy. The morphology of leathers tanned with chestnut and quebracho in different concentration were also observed. The shrinkage temperature of leather tanned with chestnut was lower than that of quebracho-tanned leathers. Leathers tanned with 20 and 25% of chestnut showed higher degree of tannage than the ones tanned with quebracho. Thermogravimetric analysis (heating rate of 10 °C min⁻¹; gas flow of 60 ml min⁻¹) showed that the maximum weight loss rate decreased with the increase in the concentration of chestnut or quebracho. The differential scanning calorimetry results showed that quebracho-tanned leather had a higher heat resistance than chestnut-tanned one. The presence of vegetable tanning agent improved the thermal stability of leather. Furthermore, it was shown that leather tanned with 20% and 25% of chestnut resulted in almost equal thermal stability. Quebracho calf leather was more resistant against heat than chestnut calf leather.

1. Introduction

Vegetable tanning is an ancient method of leather tanning. It is still in use, even as its popularity has declined and it has been largely replaced by chrome tanning, and more than 90% leather production in the world are using chrome as tanning agent [1] because of its simple technology application and the reliability of the tanning procedures [2]. Vegetable tanning agent is still used in the leather tanning industry because of its advantages, such as the fullness [3], compatibility with human skin, and its cleaner tanning process waste. Leather-making process consists of three parts: beamhouse operation, tanning, and finishing. Vegetable tanning agents are used in the tanning process [4] to stabilize the raw material into stable materials.

Upper shoes leather usually made of leather tanned with chromium. Chromium-tanned leather has higher collagen stability but has negative effect for the environment. Vegetable tanning is an alternative method for cleaner production of shoe upper leather. Even though vegetable tanned leather is more difficult to biodegrade than chrome tanned leather [3], it is material that would be used and preserved



for a long time, which makes leather being easily degraded because temperature and time [5]. Besides, one of the stages in shoe making process is the heating process to stick the upper leather into midsole material. Thus, it is necessary to measure the thermal stability of vegetable tanned shoe upper leather.

Thermal analysis is a useful method to evaluate the thermal stability and behavior, degradation temperature, and thermal decomposition [6]. When the leather is degraded, its physical and chemical properties will decrease. In the leather tanning process, the increased of thermal stability is one of the most important changes [7]. Shrinkage temperature is the most common way to measure hydrothermal stability of leather and as a cook proof at once. Shrinkage temperature of leather is the temperature at which a leather shrinks when heated in water at $2\text{ }^{\circ}\text{C min}^{-1}$ and it is commonly related to degree of tannage [7, 8]. Another way to measure thermal stability of leather is using thermogravimetric analysis [1, 6, 7, 9, 10]. This technique is possible to calculate the thermal stabilities and kinetic decomposition of vegetable tanned leather. Kinetic analysis is a new interesting topic of research because of its importance in thermal analysis and its role in decomposition reaction mechanism [5]. Differential Scanning calorimetry is also one of the technique to measure leather thermal stability [11].

Thermal stability mainly depends on the tannin type used to tan the skin [7]. The most common vegetable tanning agents are mimosa, quebracho [4], chestnut, tara, haraz, and genipin. Beside mimosa, quebracho and chestnut are vegetable tanning agents that easy to obtained and have high tannin content. Vegetable tannins are classified into condensed tannins and hydrolyzable tannin based on its structure and chemical behavior [12]. Tannin in chestnut belongs to hydrolyzable tannin, while tannin in quebracho is condensed tannin [13].

Thermal stability of leather is a new research concern, so that there are still few studies about it. A study by Carsote *et al.* [7] concluded that using micro-DSC, it was known that quebracho tanned calf leather displayed the highest resistance against deterioration than chestnut. There are also still a few study concerning thermal stability of leather, such as study conducted by Yang *et al.* [6] that used thermogravimetric analysis to measure thermal stability of fire retardant leather; Bañón *et al.* [1] that conducted study about thermal stability of leather treated with NaOH, using thermogravimetric analysis; Sanchez-Olivares *et al.* [10] who studied the effect of sodium montmorillonite on the thermal properties of leather. Based on those previous research, there were yet study concerning the thermal properties of quebracho-and-chestnut-tanned calf leather using thermogravimetric analysis and shrinkage temperature. Therefore, this study aims to compare the effect of different tanning agents, chestnut and quebracho, on the thermal stability of calf leather.

2. Experimental

2.1. Materials

Quebracho and chestnut were obtained from chemical suppliers in Yogyakarta, Indonesia. This experiment used cow pickled-hides from Magetan, East Java, Indonesia. Tanning chemicals used in this experiment are alum, NaCl, wetting agent, bating agent, sodium formate, sodium bicarbonate, relugan GT50, basyantan DLX-N, vegetable fatliquor, white syntan, oxalic acid, novaltan PF, neutralising syntan, ipertan 502, retigan R7, levelling agent, dyestuff, synthetic fatliquor, anti-mold, and formic acid.

2.2. Leather tanning procedure

Table 1. Sample identification.

Vegetable tanning agent	Quantity (%)	Sample identification
Chestnut	20	Cx
	25	Cy
Quebracho	20	Qx
	25	Qy

In this study, the quantity of quebracho and chestnut were used to tan calf hides to make upholstery leather and the quantity was varied (Table 1). At the tanning step of the leather tanning procedure, the tanning agent was varied into quebracho and chestnut. The quantity of each was differentiated for 20% and 25%. Other steps but tanning in the leather tanning procedure were controlled.

Table 2. Leather tanning procedure.

Process	%	Materials	Time (min)
Wetting back	200	Water	30
	20	NaCl	
	0,5	Wetting agent	60
	2	Bating agent	
Depickling	100	Water	
	10	NaCl	10
	1	Sodium formate	
	0,5	Sodium bicarbonate	30
Pre-tanning	2	Relugan GT 50	
	1	Basyntan DLX-N	30
	2	Vegetable fatliquor	
Tanning	20;25	Quebracho/chestnut	
	9	Alum	180
Basification	0,75	Sodium bicarbonate	3x15 + 30
	1	White syntan	30
Washing	400	Water	2x10
Bleaching	200	Water	
	1	Oxalic acid	30
	0,5	Wetting agent	30
Neutralising	100	Water	
	2	Novaltán PF	45
	2	Neutralising syntan	30
	1	Sodium formate	30
	0,50	Sodium bicarbonate	3 x 20 + 30
Retanning	100	Water (40 °C)	
	2	Basyntan DLX-N	45
	3	Ipertan 502	30
	2	Dysiamin (RR7)	60
Dyeing	100	Water (50 °C)	
	1	Levelling agent	10
	2	Havana dyestuff	60
Fatliquoring	50	Water (50 °C)	60
	3	Vegetable fatliquor	
	3	Synthetic fatliquor	
	2	Taural ICN	
	1	Tannit LSW	30
	0,05	Anti-mold	
Finishing	1,5	Formic acid	3 x 10+ 30

This research used calf pickled pelts as raw material. First, the pelts were soaked in a rotating drum with water, NaCl, soaking agent and run for 30 min, then bated for 60 min. In order to raise the pH of the pelts, depickling process was conducted to achieve the pelts' pH at 5-5.5. Depickling process were done by adding sodium formate and sodium bicarbonate for 30 min. Prior to tanning, the pelts were pre-

tanned with Relugan GT50, Basyntan DLX-N and Leathernol BLM for 30 min. Tanning process were based on Table 1 in using vegetable tanning agent.

The experiment used Quebracho and Chestnut, as the vegetable tanning agent with different weight concentration. The concentration of the vegetable tanning agent were 20% (m/m) and 25% (m/m), while alum used in the experiment were 9% (m/m). The vegetable tanning agent were combined with alum and run for 180 min. Following to that sodium bicarbonate were added to reach the pH of pelts at 6-6.5. The wetblue leather, as a result, were then aging and shaving. The shaved-wetblue leather were ready to be processed further for post-tanning as in Table 2.

3. Results and discussion

3.1. Shrinkage temperature

The shrinkage temperature of leathers was determined using Shrinkage Temperature Tester. The T_s is the temperature when the sample shrinks 150 μm . Shrinkage temperature (T_s) of leather tanned with chestnut and quebracho are given in Figure 1 to observe the different hydrothermal stability. The average T_s of finished leathers were higher than semi crust leather for both leather with chestnut and quebracho. T_s of semi crust leathers were obtained after tanning process, while T_s of semi crust leathers were after the finishing process. It was clearly observed that after retanning process, there were some chemicals added to the leather, such as leveling agent, dyestuff, fat liquors, anti-mold, acid, and finishing materials. In the fatliquoring process, fatliquors were added to prevent the collagen fiber resticking when it is dry [13]. During drying, the water was removed and the diameter collagen fibrile shrunk.

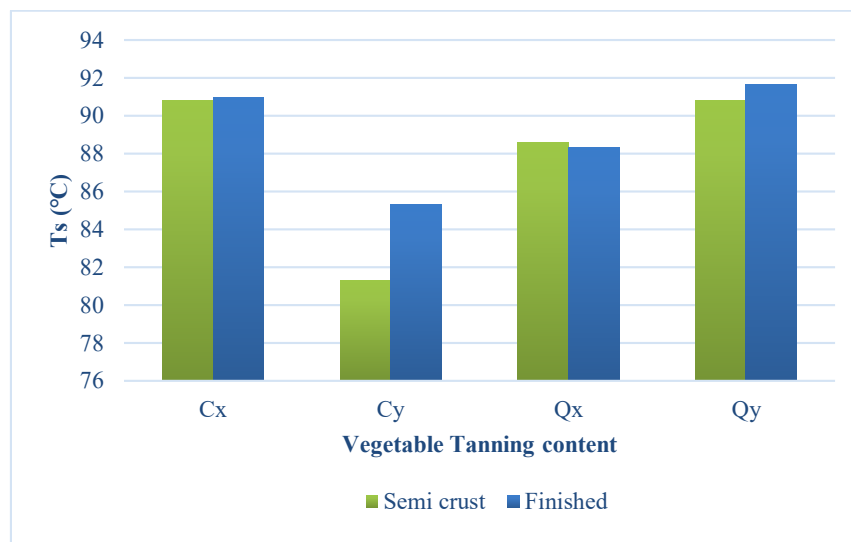


Figure 1. Shrinkage temperature of leather tanned with different vegetable tanning agent.

Shrinkage temperature is used as an indicator to measure the effectiveness of tanning process, while thermal stability gives information about the stability of collagen to heat but it does not reveal other information related to the performance of material [14]. Compared with quebracho, in general, chestnut delivered lower T_s of leather, both for semi crust and finished (Figure 1).

3.2. Degree of tannage

From the Figure 1, it can be inferred that leathers tanned with chestnut have higher tannin bound than leather tanned with quebracho. Leathers tanned with 25% of chestnut (22.4%) have higher tannin bound than 20% of chestnut (21.41%), while leathers tanned with 25% of quebracho (16.97%) have lower tannin bound than 20% of chestnut (21.19%).

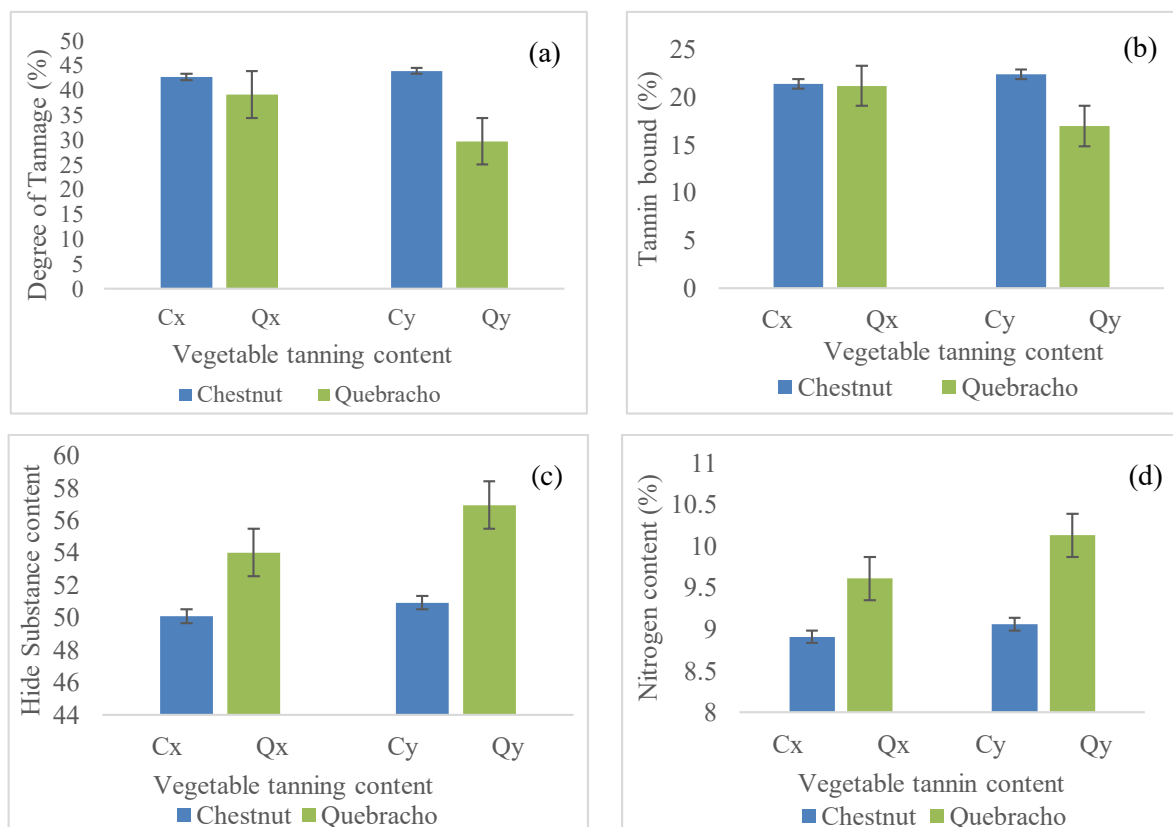


Figure 2. Degree of tannage (a); tannin bound (b); hide substance content (c); and nitrogen content (d) of leather tanned with different vegetable tanning agent.

The degree of tannage of chestnut tanned leathers was higher than quebracho tanned leather, both for 20% and 25%. The use of 20% of chestnut to tan the leathers (42.75%) showed lower degree of tannage than 25% of chestnut (43.99%), while the use of 20% of quebracho to tan the leathers (39.22%) showed higher degree of tannage than 25% of quebracho (29.8%) (Figure 2). These results were in line with the result of the tannin bound test. The higher content of vegetable tanning agent, the higher the percentage of tannin bound. Chestnut-tanned leather showed lower degree of tannage and tannin bound than quebracho-tanned leather.

Different with the Figure 2(a) and 2(b), Figure 2(c) and 2(d) shows contrary results. Hide substance content of leather tanned with 20% of chestnut (50.07) was slightly lower than leathers tanned with 25% of chestnut (50.92). Hide substance of leather tanned with 20% of quebracho (54.01) was lower than that of 25% of quebracho (56.93). Nitrogen content for each 20% of chestnut (8.91%) and 20% of quebracho (9.61%) was lower than that of 25% of each chestnut (50.92%) and quebracho (56.93%). A previous research conducted by Kasmudjiastuti *et al.* [15] reported that high content of nitrogen in the leather displays the incomplete bating process (removal non collagen protein in the leather tanning process) that inhibit the penetration of vegetable tanning agent into the collagen fiber.

3.3. Thermogravimetric analysis

Samples were analyzed using thermogravimetric to measure the effect of percentage of different vegetable tanning agent on thermal decomposition. The thermogravimetric tests of finished calf leather were carried out in Shimadzu DTG 60 at heating rates of 10 °C min⁻¹ under air atmosphere with 60 ml min⁻¹ gas flow. Samples were placed in an alumina pans.

Figure 3 shows the DTG curves from each one of six samples of leathers tanned with chestnut and quebracho with different concentrations. All of the samples were degraded through three stages (Figure 3). The first stage was the initial stage between 28 and 120 °C. In this stage, for chestnut and quebracho, leather tanned with 20% of vegetable tanning agent resulted in higher residue than that of 25%. The initial stage is an endothermic phase [16] when moisture and small molecules in the leather were evaporated [15, 16].

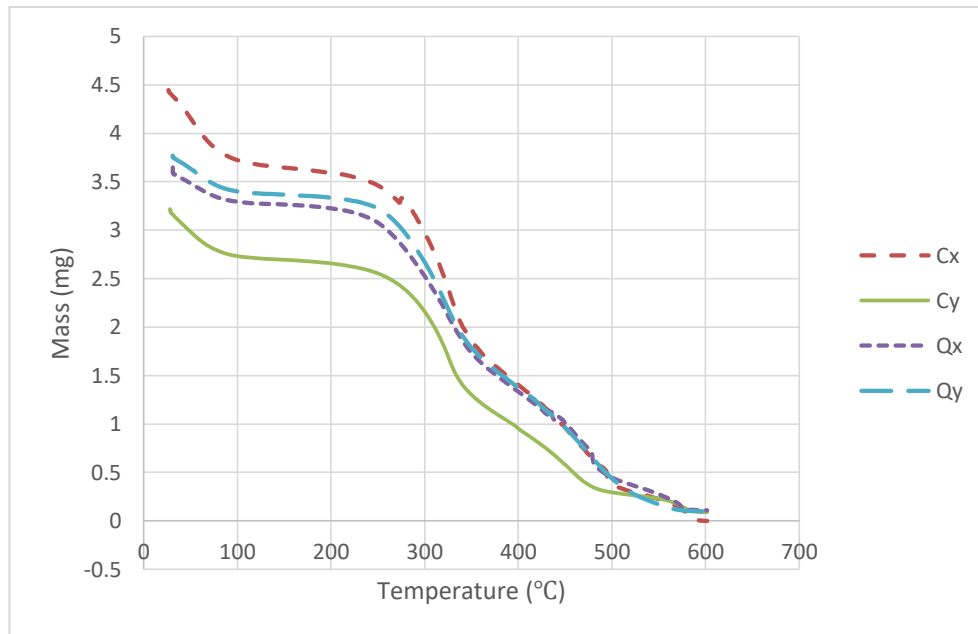


Figure 3. TG curves of leather samples.

The main phase happened in two stages: at the temperature between 205 – 509 °C and 552 – 594 °C. Those stages are more complex than the stage before. The mass loss at this stage was because of decomposition of collagen. T_{max} reflects the thermal stability of collagen of leather [7], the higher residue at the T_{max} the more stable is the collagen. From the Table 3, 20% of chestnut showed better thermal stability leather than 25% of chestnut at the initial stage. In contrast, at the first and second stages, leather with 25% of chestnut showed higher thermal stability than leather with 20% of quebracho. A previous study of Carçote, *et al.* [7] reported that the loss of water at the initial stage could affect cross-linking which increase the thermal stability because the interfibrillar water content of leather leads to thermal stability. Water molecules have been displaced by the tannin molecules when it filled the empty area of collagen at the tanning process to stabilize the collagen within leather [19].

At the second stage (Table 3), the higher content of vegetable tanning agent used the higher residue at the maximum degradation. It is clearly observed that 25% of vegetable tanning agent resulted in better leather residue than those of 20%. The second and third phase are exothermal process. Pyrolytic decomposition and thermo-oxidation were happened at these stages [20]. Due to the presence of disordered regions and the well-defined sequences of amino acid residues, leather is both crystalline and amorphous material that could show thermal properties [14]. This last phase indicates the melting crystalline area of leather or the evaporation of residual strongly bond water and continued conformational changes of super helix of collagen [16].

At 600 °C, the higher content of chestnut, the higher the residue. On the other hand, the final residue of quebracho tanned leather is almost equal (Table 4). The higher content of both chestnut and quebracho can inhibit the decomposition of the leather and therefore improve the leather thermal stability.

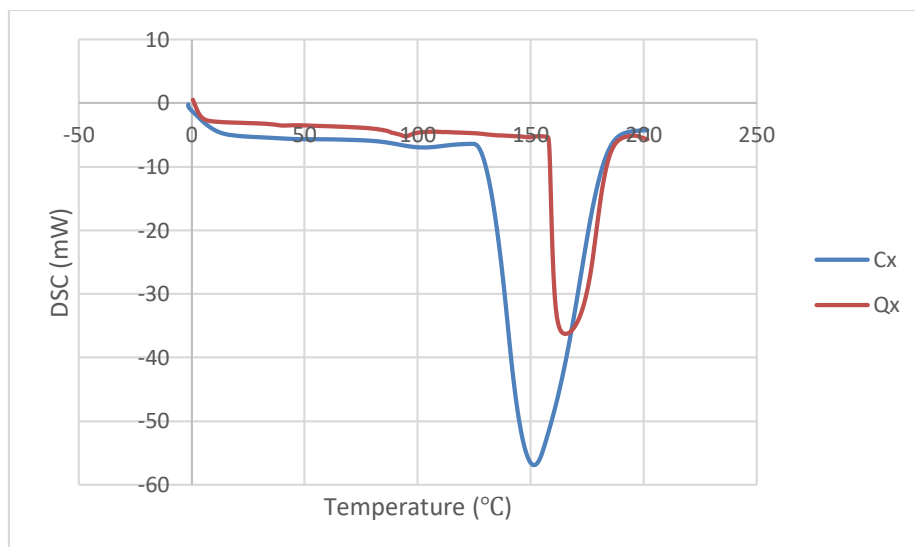
Table 3. Different decomposition stages of the samples.

Samples	Index	Initial stage	Stage 1	Stage 2
Cx	Temperature (°C)	28.80 – 120.71	214.336 – 376.91	552.54-593.80
	Residue at Tmax (%)	92.26	52.82	1.01
Cy	Temperature	29.37 – 108.03	205.25 – 508.63	546.61 – 593.64
	Residue at Tmax (%)	90.65	55.82	3.93
Qx	Temperature	33.90 – 96.04	215.90 – 371.26	567.25 – 578.31
	Residue at Tmax (%)	89.19	82.38	3.91
Qy	Temperature	32.57 – 107.58	218.41 – 528.61	540.32 – 583.46
	Residue at Tmax (%)	88.46	57.08	4.16

Table 4. Residue of the samples at 600 °C.

Samples	Residue at 600 °C (%)
Cx	0
Cy	3.93
Qx	2.75
Qy	2.36

3.4. Differential scanning calorimetry

**Figure 4.** DSC curves of leather tanned with 20% of chestnut and quebracho, respectively.

Due to the efficiency of vegetable tanning agent, DSC was operated under the nitrogen atmosphere and 15 ml/minute flow rate, the samples were analyzed. It was conducted to determine the phase transition and denaturation temperature. DSC curves (Figure 4) showed that leather tanned with 20% of chestnut have and quebracho respectively have two endothermic processes. The maximum peak value of the endothermic phase was the denaturation temperature. From Figure 4, at the first process, chestnut tanned

leather showed higher denaturation temperature (102.72 °C) than that of chestnut (94.64 °C). Meanwhile, at the primary process, the denaturation temperature of chestnut tanned leather (151.45 °C) was lower than quebracho tanned leather (165.47 °C). This results parallel with the TGA results, where the first process was the phase when the water in the leather was totally lost, and the second process was the decomposition of the materials [14, 9].

The DSC results were also in line with the conventional shrinkage temperature value, both for semi crust and finished leather. The decomposition temperature of samples from DSC method was slightly different with the shrinkage temperature (the deviation range is 6-12 °C). The higher the hydrothermal stability of leather, the higher the bond strength of the collagen [13]. From the Figure 4, all of the curves are narrow. Narrow and symmetric DSC curve indicate that the population of collagen molecules are grouped [7].

Tannin in quebracho belongs to condensed tannin, while chestnut is hydrolyzable tannin. Condensed tannins consist of polymeric flavonoids, while hydrolyzable tannins are gallotannins and ellagitannins [7]. Content of gallic acid in the hydrolyzable tannin was considered as the most obviously structural difference to condensed tannins, so that it also regarded as the important factor for the formation and stabilization of tannin-metal complexes [21].

3.5. Scanning electron microscopy

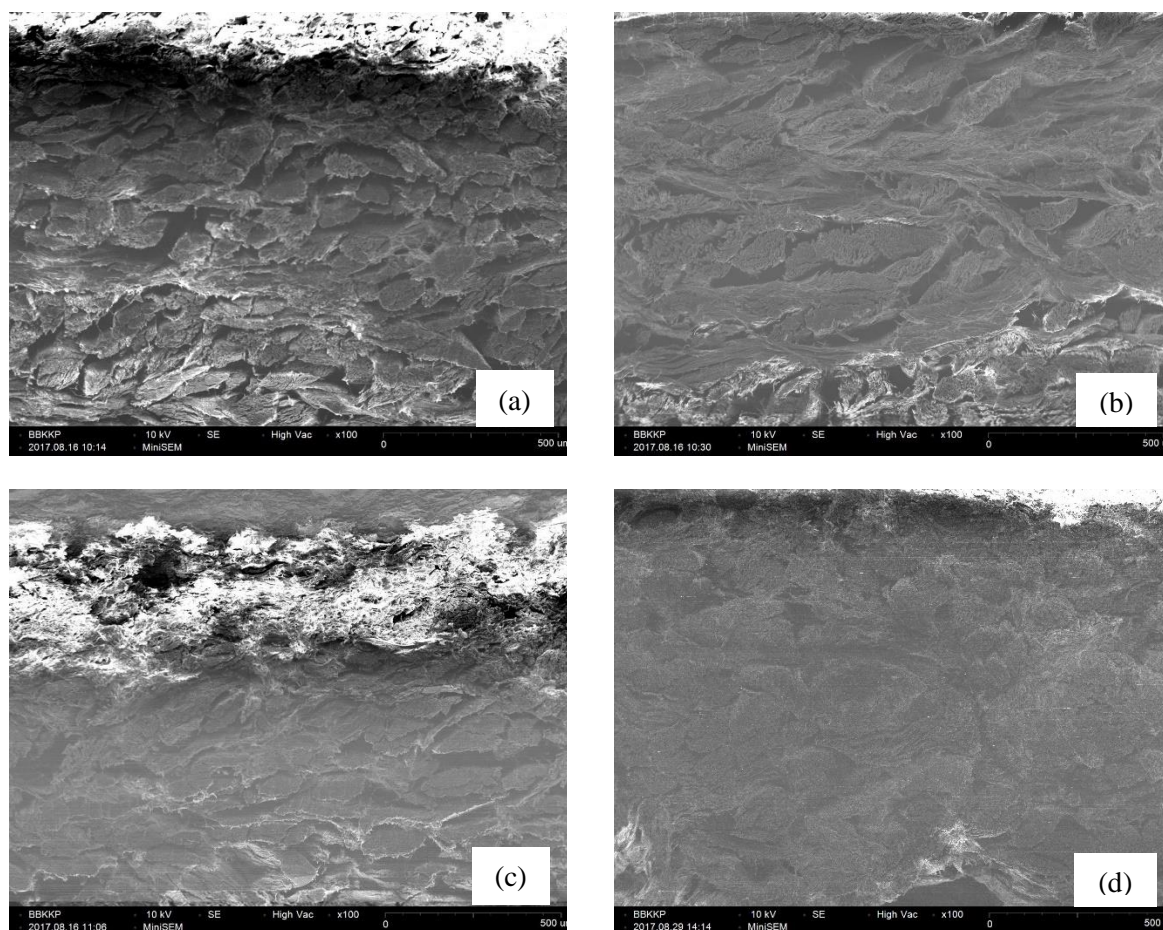


Figure 5. Leather morphology by SEM of samples:(a) leather tanned with 20% chestnut; (b) 25% of chestnut; (c) 20% of quebracho; and (d) 25% of quebracho.

Scanning Electron Microscopy SEC type SNE 3200 M was used to analyze samples at an accelerating voltage of 5 kV. The morphology of cross-section leather samples was investigated using SEM at 100X magnification are shown in Figure 5. There are no major differences in the leather morphology between 20 and 25% of chestnut, while leather tanned with 25% were tighter, bulkier, and plumper than that of 20%.

4. Conclusion

In the present work, the thermal stability of leather tanned with different tanning agent have been studied using shrinkage temperature, chemical properties, thermogravimetric analysis, DSC, and SEM. The presence of vegetable tanning agent improved the thermal stability of leather. Furthermore, it was shown that leather tanned with 20% and 25% of chestnut resulted in almost equal thermal stability. Quebracho calf leather was more resistance against heat than chestnut calf leather.

Acknowledgment

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