Majalah Kulit, Karet dan Plastik, 33(2), 99-107, 2017
©Author(s); https://doi.org/10.20543/mkkp.v33i2.3139

Influence of some mechanical finishing processes on manufactured leather properties

Ahmed Ibrahim Nasr

Department of Wool Production and Technology, Animal and Poultry Production Division,
Desert Research Center, El Matareya, Cairo, Egypt.
E-mail: ainasr@drc.gov.eg

Received: 15 July 2017 Revised: 25 September 2017 Accepted: 29 September 2017

ABSTRACT

The objective of this study is to investigate the influence of using some mechanical finishing processes on final properties of produced leather types. Nappa, nubuck, pigmented and corrected grain leather types were produced by applying some of the following operations: hang drying, vacuum drying, molissa staking, drum milling, buffing, spraying and/or embossing surface with extreme pressure. Hydrophobic-hydrophilic status, scanning electron micrographs, organoleptic and mechanical properties were determined on all finished leather types. Results showed that water behavior was hydrophobic for nappa leathers, while it was hydrophilic with the rest of produced leather types. Buffing surface in nubuck leather increases the water absorption and water vapor permeability, while the opposite was found when applying external coat layer in pigmented and corrected grain leathers. Applying vacuum drying in nappa leathers increases surface smoothness and surface water contact angle while decreases tensile and tearing strengths. These results elucidate that all studied leather types are suitable for manufacturing purposes except nubuck leather which is not recommended for footwear uppers manufacturing due to its high water absorption. The present study emphasized that while mechanical finishing processes could have profound effects on leathers surface behavior, they must be adequate to the requirements and properties of the end products.

Keywords: finishing, hydrophilic, hydrophobic, leather, surface, tanning.

INTRODUCTION

Leathers are the final material produced from tanning skins or hides of animals such as cattle, sheep, goats, and camels (UNIDO, 2010). It also exists as an independent industry due to the unique properties of the leather and its wide usages such as footwear, upholstery, gloves, garments, cases, and other purposes (Fathima *et al*., 2012).

The processing of skins or hides into leather is a very complicated procedure that comprises a specific combination of various chemical and mechanical processes (Liu *et al*., 2007). The smooth side of the leather is called the grained side, which is the original outer surface for the skin of the animal, and has the structural characteristics of the particular animal (Covington, 2009). Once skins or hides are finished the tanning process, surface defects appear as a major factor affecting their aesthetic appearance, the amount of usable area and thus their value. Therefore, there are very few leathers which do not have natural surface imperfections that require corrections to the grain (Georgieva *et al*., 2003).

The leather surface can undergo several finishing processes for a variety of looks, textures and touch, which include two main processes; mechanical operations and applying a surface coat. A wide range of mechanical operations is carried out to improve the appearance of leather, while applying a surface coat provides a protection from contaminants, modify the color and disguise defects. The most surface finishing methods used in tanneries are buffing, dry milling, and embossing for the mechanical operations in addition to spray and transfer coatings for the applying a surface coat (Dutta, 2008).

After applying finishing processes, different leather types are produced according to which of these operations are applied. Nappa, nubuck, pigmented and corrected grain leathers considered to be the most produced leather types from tanneries to achieve different manufacturing purposes (BASF, 2007). Results of previous research revealed some answers for the separate effect of some finishing operations such as vacuum, toggle-drying, milling and coating on leather properties (Liu, 2001; Liu *et al*., 2007; 2011). But the collective effect for applying some of these finishing processes to produce a specific type of leather is not studied. Therefore, the objective of this study is to investigate the collective influence of using some of finishing processes together on the final properties of produced leather. Additionally, the study aims to investigate physical and organoleptic properties of main leather types; nappa, nubuck, pigmented and corrected grain leathers.

MATERIALS AND METHODS

Sixteen half sides of camel wet-blue were used in this study to finish it with different mechanical processes and produce four different leather types; nappa, nubuck, pigmented and corrected grain. Thus, the replications of each leather type were four camel wet-blue sides. All tanning processes were done in El-Shafei sons' tannery, Alexandria, Egypt. All wet-blues were mechanically shaved and post-tanning steps were done as illustrated in Table 1. After post-tanning, each leather type was produced by applying some of mechanical finishing processes as shown in Table 2.

Leather Testing

Finished leather specimens were taken from the four leather types to determine water hydrophobic-hydrophilic status, mechanical and organoleptic properties. Also, scanning electron micrographs were captured.

Hydrophobic-Hydrophilic Status

According to Serenko *et al.* (2014), the water contact angle Θ and changes in the water droplet contour were determined by analysis of video images of droplet spreading and absorption obtained with Panasonic Lumix FZ2500 digital camera. Images were analyzed using video play software form Adobe Photoshop version 20150529.r.88. The size of the droplet contour was calculated by averaging at least 5 diameters measured on the image of a droplet or a wet spot on the leather surface obtained by video recording of the process with camera located perpendicular to the material surface. The relative droplet contour was determined as a ratio of the current value to the initial size which calculated by extrapolating the initial section of kinetic dependence of contour to the time equaling zero.

Table 1. Executed recipe for post-tanning wet-blue to produce different leather types.

Step	Description		Time (min.)	Remarks
	%	Added		
Washing	100	Water 40 ºC	20	Drain float
	1	Soap		
Re-chrome	100	Water	60	Overnight then drain float
	4	Chrome (33% basicity)		
Fixation	1	$NaHCO_3$	60	
Washing	100	Water	10	Drain float
Naturalization	100	Water	60	To adjust pH= 5.5
	2	$NaHCO_3$		
Washing	100	Water	10	Drain float
Re-tanning & Dyeing	100	Water	90	Check dye penetration before next step
	2	Mimosa extract		
	2	Quebracho extract		
	3	Dyestuff powder		
Fatliquoring	150	Water	90	
	8	Lanoline, sulphited fish oil and waterproof fatliquors		
	0.2	Soap		
Fixation	1	Formic acid	30	pH = 4
	1	Formic acid	60	
Washing	100	Water	10	Out & overnight as horse up then sammying.

Table 2. The mechanical finishing processes for studied leather types.

Type	Description	Mechanical finishing processes
Nappa	Aniline leather with full natural grain surface.	-Vacuum drying for 10 min at 60 ºC and 0.8 bar. -Hang drying overnight. -Molissa staking machine at a medium setting twice at a rate of 1.5 meters/min
Nubuck	Leather grain is textured to have a similar nap surface.	-Hang drying overnight. -Milling for 4 hours in a high speed drum. -Buffing surface lightly.
Pigmented	Leather with protected grain surface by applying a pigment resin layer.	-Hang drying overnight. -Molissa staking machine at a medium setting twice at a rate of 1.5 meters/min -Light spraying, 50 ml/m^2, with polyurethane resin perpendicular to the surface from 20 cm above it. -Hang drying overnight.
Corrected grain	Leather with an artificial grain applies to its surface.	-Hang drying overnight. -Abrading surface strongly. -Coating surface with base coat of cross-linking for protein binders and then an artificial grain. -Embossing surface with extreme pressure (12 bar) for 5 sec.

Scanning Electron Microscopy (SEM)

The leather specimens (1 cm^2) were cut from official sampling position according to ASTM-D2813 (ASTM, 2014), subjected to sputter coating with gold ions and evaluated using a JEOL JSM-5300 electron microscope to obtain the micrographs for the cross section, surface, and flesh sides.

Leather Mechanical Properties

Qualitative and operational properties of the finished leather were assessed according to indices of physico-mechanical investigation of the finished leather (ASTM, 2014). A testing machine (Benchtop Tinius Olsen 5KN Tester) was used to determine tensile strength, elongation, and split tear strength. Flex resistance test was done on a flex tester machine rotating at 100 cycles/min. Each specimen size was measured 45 x 90 mm and the test was done up to 20000 cycles. Water absorption (WAb) after 2 and 24 hrs was measured using Kubelka apparatus, whereas water vapor permeability (WVP) was measured using Herfeld apparatus.

Leather Organoleptic Properties

All finished leathers were assessed for softness, grain smoothness, grain tightness, fullness, and general appearance by standard tangible evaluation technique (Kasmudjiastuti & Murti, 2017). Five experienced tanners rated the leathers in a scale of 1-10 points for each functional property (higher points indicate a superior property). The average of the five tanners was recorded for each sample.

Statistical Analysis

Data were analyzed using GLM procedure of SAS (2008) to evaluate the differences among produced leathers. The following model was used in the analysis:

$$Y_{ij} = \mu + T_i + e_{ij}$$

Where Y_{ij} is the observation taken on finished leather, μ is overall mean, T_i is a fixed effect of leather types (1 = nappa, 2 = nubuck, 3 = pigmented and 4 = corrected grain) and e_{ij} is the random error assumed to be normally distributed with mean = 0 and variance = σ^2e.

RESULTS AND DISCUSSION

Scanning electron micrographs of different types of leathers are illustrated in Figures (1-4). Cross section, surface and flesh sides were depicted for each leather type. In nappa leather specimen, the surface structure is homogenous, smooth and contains many hair pores with an

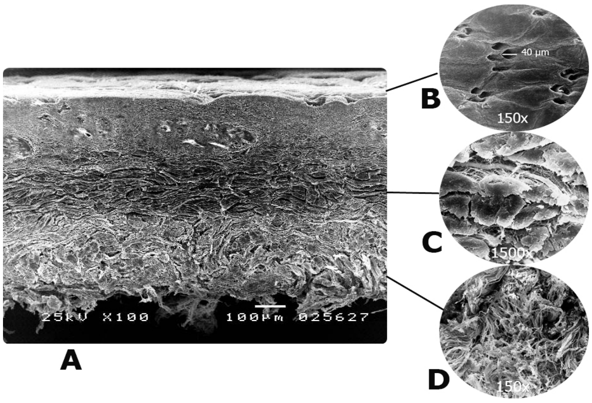

Figure 1. Scanning electron micrographs of nappa leather: (A) vertical image of cross section (100X), (B) transverse image of surface (150X), (C) vertical image of reticular layer (1500X), and (D) transverse image of flesh side (150X).

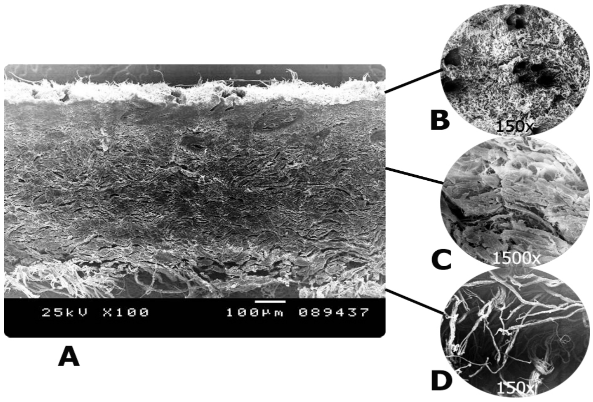

Figure 2. Scanning electron micrographs of nubuck leather: (A) vertical image of cross section (100X), (B) transverse image of surface (150X), (C) vertical image of reticular layer (1500X), and (D) transverse image of flesh side (150X).

average diameter of 40 µm (Figure 1B). Due to the abrasive treatment of surface in nubuck leather, the smooth, hair pores, even areas and thinned (residual) nap cover were observed (Figure 2B). However, pigmented and corrected grain leathers showed different surface structure, which were non-porous homogenous due to the addition of the surface layer (Figures 3C and 4B). The surface layer of pigmented leathers tended to be coarser than corrected grain leather's surface due to the changes in the methods of applying surface layer. In pigmented leathers, surface layer was added by spray polyurethane resin as a thin layer mask of combined drops without any compress treatment which increased surface roughness (Figure 3B), whereas in corrected grain leather embossing surface with extreme pressure caused an increase in smoothness.

Perhaps the different surface morphology of leather types will cause the changes in the behavior of water droplet on the leather surfaces and the water contact angle Θ. Figures (5, 6, and 7) show the behavior of water droplet during contact time of 10 min.

The important point when studying water droplet behavior on material's surface is that angle 90º is the distinguishing degree between hydrophobic and hydrophilic behavior of water with the surface material. The angle is always

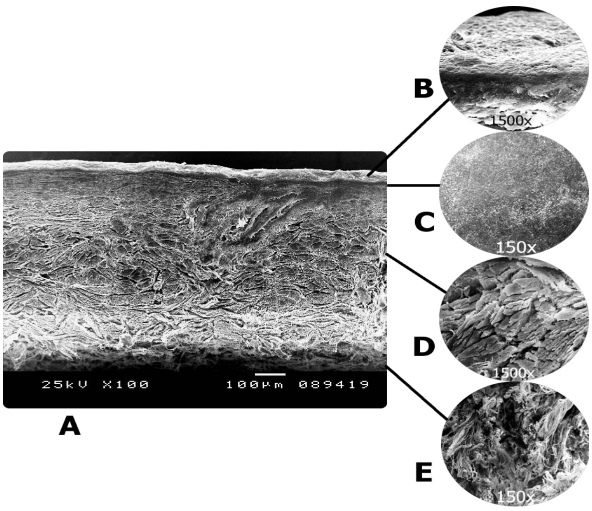

Figure 3. Scanning electron micrographs of pigmented leather: (A) vertical image of cross section (100X), (B) transverse image of surface (1500X), (C) transverse image of surface (150X), (D) vertical image of reticular layer (1500X), and (E) transverse image of flesh side (150X).

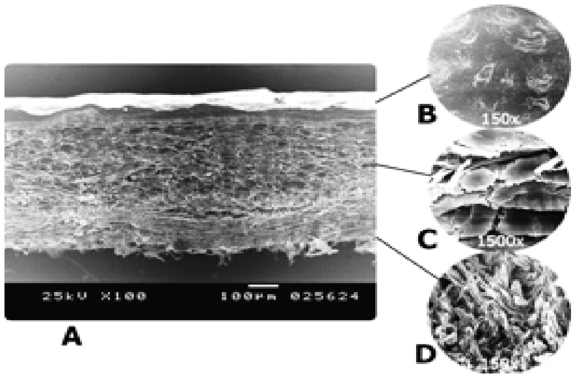

Figure 4. Scanning electron micrographs of corrected grain leather: (A) vertical image of cross section (100X), (B) transverse image of surface (150X), (C) vertical image of reticular layer (1500X), and (D) transverse image of flesh side (150X).

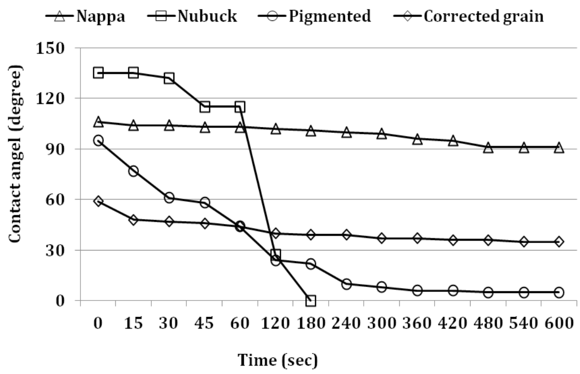

Figure 5. The changes in water contact angles on the surface of different leather types by contact time.

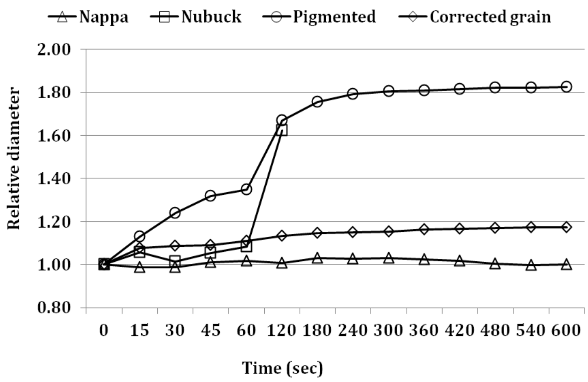

Figure 6. The changes of the relative droplet water diameter on surface of different leather types by contact time.

greater than 90º in hydrophobic surfaces, while hydrophilic surfaces always have contact angles less than 90º (Yuan & Lee, 2013; Serenko *et al.*, 2014).

Although the contact angle decreases by increasing contact time, nappa leathers were always hydrophobic water unlike other leather types. The reduction rate of contact angle in nappa and corrected grain leathers were dramatically slow during the contact time. Additionally, the contact angle did not reach 0º, which reflect impermeability of leather's surface (Figure 7). On the other hand, although pigmented leathers did not absorb water droplets, the behavior was different from nappa and corrected grain leathers. The reduction rate of contact angle in pigmented leathers was quick for the first four minutes, thereafter the rate was slowly decreased similar

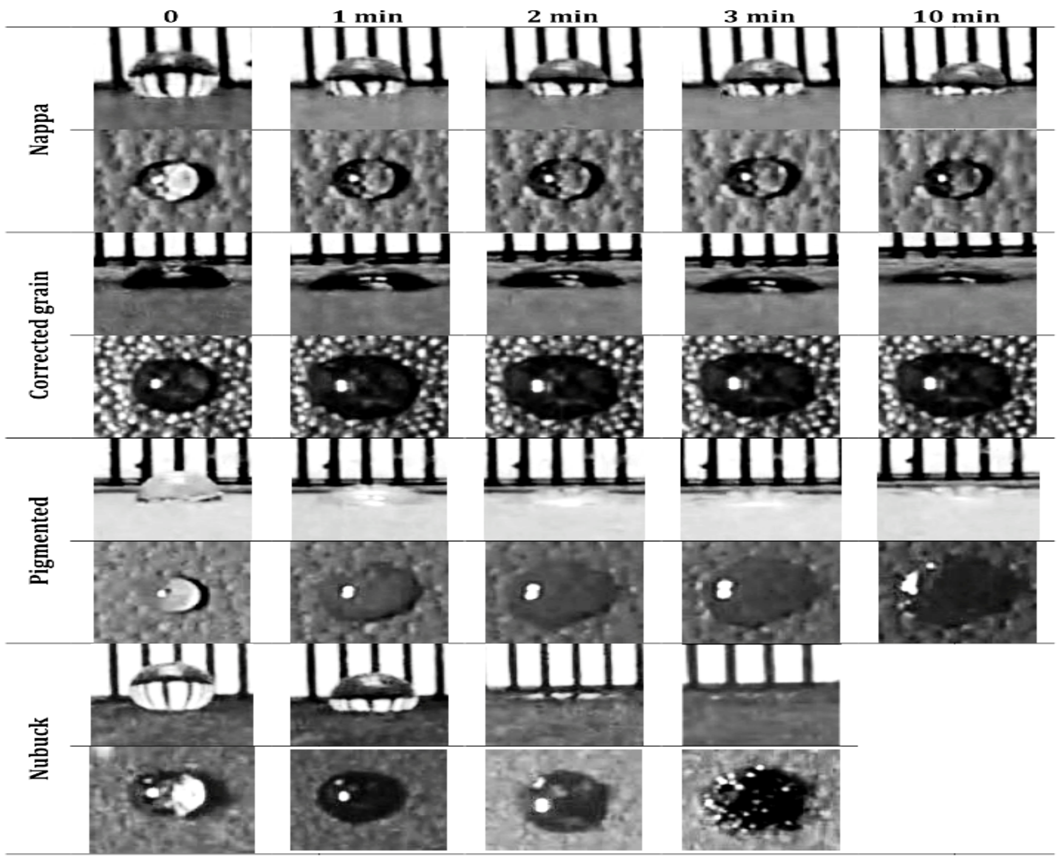

Figure 7. Horizontal and vertical views for changing behavior of water droplet on the surface of different leather types during 10 minutes.

to that observed in nappa and corrected grain leathers. Regarding nubuck leathers for the first two minutes, the contact angle started with a highest contact angle and a slow rate of decreasing contact angle, there after a sharp decline in contact angle was observed within the third minute until the water droplet was completely absorbed.

Figure 6 shows the changes in relative water droplet diameter on surface of different leather types by contact time, while Figure 7 shows the changes in horizontal and vertical views of water droplet. In nappa and nubuck leathers, when contact time increases, the increase in water droplet diameter is accompanied by a reduction in water droplet size. The illustration for this behavior due to the absorption of water droplet from surface into leather's layers (Figure 7). On the other hand, pigmented and corrected grain leathers showed an increase in water droplet diameter along with water droplet size which might due to the horizontal kinetic of water droplet on the surface as a spread without any absorption inside leathers, which are more clear in water droplet pictures of pigmented leather (Figure 7). Also, pigmented leather was the highest in relative diameter value whereas nappa and corrected grain leathers exhibited similar values. This could be due to the surface tension of polyurethane resin when sprayed on surface without any mechanical embossing of the surface as described previously, which enhances the positive relation between roughness and surface wetting (Moita & Moreira, 2003; Yuan & Lee, 2013).

Consequently, it can be inferred that leather is a water absorbent material but chemical and mechanical treatments of leather's surface might change its water absorption behavior. Addition of waterproof fatliquor and vacuum drying in nappa leathers increases surface smoothness as well as water droplet contact angle and thus partially decreases water absorption across leather surface without prevent it completely (Jankauskaitė *et al.*, 2012). However, addition of external thin waterproof layer on surface of both pigmented and corrected grain leathers prevents water absorption across surface completely (Serenko *et al.*, 2014) but it produces hydrophilic leathers as a result of an increase in surface roughness. In nubuck leathers, although it was treated with a waterproof fatliquor, a quick spreading and absorbing of water droplet through surface was enhanced as a result of microstructure of velvety nap which, in turn, increases the contact area with water droplets than untreated surface in nappa leather (Serenko *et al.*, 2014).

Organoleptic and Mechanical Properties of Leathers

Organoleptic and mechanical properties of different leather types are shown in Tables 3

Table 3. Organoleptic properties of different leather types.

Item	Unit	ASTM	Nappa	Nubuck	Pigmented	Corrected grain	SEM	Sig
Thickness	mm	D1813	1.69[b]	1.67[b]	1.73[a]	1.58[c]	0.01	**
Tensile strength	kg/cm^2	D2209	290.68[b]	276.02[b]	295.95[b]	329.29[a]	5.00	**
Tearing strength	kg/cm	D4704	69.23[b]	69.67[b]	73.37[b]	86.94[a]	1.39	**
Elongation	%	D2211	51.87[b]	68.36[a]	54.11[b]	48.19[c]	1.10	**
Water Abs 2hrs	%	D6015	95.13[c]	123.24[a]	108.45[b]	91.57[c]	3.30	**
Water Abs 24hrs	%	D6015	103.31[c]	136.31[a]	119.96[b]	104.38[c]	3.58	**
WVP	mg/cm^2/h	D5052	4.82[b]	5.43[a]	1.45[c]	1.41[c]	0.48	**
Color fastness	Degree	D5053	Good	Fair	Good	Good	--	--
Flex resistance after 20000 flex	--	D6182	No damage	No damage	Thin cracks in top finish coat	Cracks into base coats	--	--

[a,b,c] Means in the same row having different superscripts are significantly different (P<0.05).
SEM: standard error of mean
Sig: significance ** P<0.01

Table 4. Physical properties of different leather types.

Item	Nappa	Nubuck	Pigmented	Corrected grain
Fullness	8	8	7.6	8
Grain tightness	1.6	0	2.4	3.2
Grain smoothness	8.8	0	6.4	7.4
Softness	7.6	9.2	7.2	5.8
General appearance	8.6	8.8	6.8	7.6

and 4. The properties of each leather type can be illustrated as follows:

Nappa Leather

Nappa leather was exposed to vacuum drying and molissa staking in finishing. Vacuum drying enhances grain smoothness. Thus, it may negatively affect collagen fiber strength (Liu, 2001), whereas molissa staking was less effective than drum milling (Liu *et al.*, 2007). Consequently, collagen fiber bundles were intermediate in compactness and separation due to weak effects of vacuum and mollissa machine. In addition, flesh side showed less nap or lint effects than other leather types (Figure 1). These effects produced nappa leather with high general appearance, grain smoothness and good softness values. Moreover, its mechanical properties were in an acceptable range for footwear leather properties (UNIDO, 1994; BASF, 2007) because it is distinguished with good values of strengths, elongation, flex resistance, color fastness and low value of water absorption.

Nubuck Leather

Mechanical abrasion of surface in nubuck leathers increases the surface contact area which could be the reason for significant (P<0.01) increasing water absorption and water vapor permeability across the surface (Serenko *et al.*, 2014). Furthermore, velvety nap surface reduced the colorfastness degree of nubuck leather.

On the other hand, mechanical milling of nubuck leathers increases collagen fibers bundle separation and increases nap or lint on flesh side as shown in Figure 2, which may facilitate water and/or water vapor permeability through leather's layers (Liu *et al.*, 2007). In addition, it increased the values of softness property and elongation (P<0.01). With respect to strengths, tensile and tearing strength values did not differ significantly among nubuck, nappa and pigmented leathers. Therefore, nubuck leather was distinguished by its softness, grain tightness and smoothness compared with other leather types.

Pigmented Leather

Pigmented leather showed separated fiber bundles similar to that of nappa leather but tended to be lower in compactness due to the lack of vacuum drying effect (Figure 3). Although no significant difference was observed in elongation and strength values of pigmented leather compared to those of nappa leather, it was markedly higher. This could be also due to the lack of vacuum drying effect (Liu *et al.*, 2011). Applying a thin coated layer on the surface increased the grain tightness but decreased grain smoothness, which led to decrease the general appearance. In contrast, addition of a thin waterproof layer decreased water vapor permeability and thus it would be acceptable for footwear industry similar to nappa leather.

Corrected Grain Leather

Corrected grain leather showed the highest (P<0.01) strength values and the lowest (P<0.01) elongation, water absorption, water vapor permeability and flex resistance. The explanation of this trend might due to apply the base coat and artificial grain in finishing operations. The base coat enhances the cross-linking for protein binders which increase strengths (Wakaso, 2014), whereas the artificial grain is a waterproof layer which decreases water vapor permeability.

Embossing surface with extreme pressure affected compactness of leather's layers as shown in Figure 4. Consequently, the leather thickness decreased significantly (P<0.01) and collagen fiber bundles were more compacted and less separated. Although mechanical properties of leather were enhanced, the organoleptic properties were diminished. Grain tightness, flex resistance and softness results led to a decrease in general appearance property.

Evaluating Different Leather Types For Manufacturing

Recommended quality requirements of different leather types were introduced (UNIDO, 1994; BASF, 2007). From the previous data for different leather types, all leather types were in acceptable range for different leather manufacturing uses except for water vapor permeability particularly for footwear upper leather, which tended to be higher than the maximum range.

Although all mechanical properties of nubuck leathers were in the acceptable range of different leather manufacturing, using nubuck leather for making external parts of footwear upper is not recommended due to its high water absorption. This is in accordance with previous reports of Serenko *et al.* (2014). Therefore, nappa leather can be considered the highest quality type due to its water hydrophobic behavior, good appearance and mechanical properties, whereas both pigmented and corrected grain leathers tended to be of lower quality which might due to their water hydrophilic behavior, the low general appearance and flex resistance. Nevertheless, applying some mechanical finishing processes on leathers is necessary to improve their final quality according to their grade and manufacturing purpose as described previously by Nasr (2015).

CONCLUSIONS

The present study indicated that mechanical finishing processes could have profound effects on leather's surface behavior against water, organoleptic and mechanical properties. Vacuum drying while increases surface smoothness and the contact angle of water droplet, it decreases leather strengths than normal dry hanging without thermal treatment. Moreover, milling leathers in high speed drum enhances the leather softness better than using molissa staking machine due to increasing the separation among collagen fiber bundles. Using extreme pressure in embossing surface decreases leather thickness and increases collagen fiber compactness. Buffing leather surface slightly changes the surface behavior against water and enhances general appearance. The study emphasized that using finishing treatments to produce particular types of leathers must be adequate to the requirements and properties of the end products.

ACKNOWLEDGEMENT

Author would like to thank Eng. Mohamed El-Shafei, director of El-Shafei's sons tannery, Alexandria, Egypt for his help and support in the practical part of this study.

REFERENCES

ASTM. (2014). *Books of standards Vol.15.04*. USA: American Society for Testing and Materials.

BASF. (2007). *Pocket book for leather technologist* (4th ed.). 67056 Ludwigshafen, Germany: Badische Anilin- und Soda-Fabrik.

Covington, A.D. (2009). *Tanning chemistry: The science of leather*. Cambrige, UK: RSC publishing.

Dutta, S. (2008). *An introduction to the principles of leather manufacture* (4th ed.). India: Indian Leather Techno Association.

Fathima, N., Rao, R. & Nair, B. (2012). Tannery solid waste to treat toxic liquid wastes: A new holistic paradigm. *Environmental Engineering Science, 29*(6), 363-372, https://doi.org/10.1089/ees.2010.0445.

Georgieva, L., Krastev, K. & Angelov, N. (2003). Identification of surface leather defects. *International Conference on Computer Systems and Technologies*, Sofia, Bulgaria.

Jankauskaitė, V., Jiyembetova, I., Gulbinienė, A., Širvaitytė, J., Beleška, K., & Urbelis, V. (2012). Comparable evaluation of leather waterproofing behaviour upon hide quality. I. Influence of retanning and fatliquoring agents on leather structure and properties. *Materials Science, 18*(2), 150-157, https://doi.org/10.5755/j01.ms.18.2.1918.

Kasmudjiastuti, E. & Murti, R.S. (2017). The effects of finish type on permeability and organoleptic properties of python (*Python reticulatus*) skin finished leather. *Majalah Kulit, Karet, dan Plastik, 33*(1), 19-28, https://doi.org/10.20543/mkkp.v33i1.1575.

Liu, C.K. (2001). Effects of vacuum drying variables on the mechanical properties of leather. *JALCA, 96*, 243-254.

Liu, C. K., Nicholas, P. L. & DiMaio, G. C. P. (2007). Milling effects on mechanical behaviors of leather. *JALCA, 102,* 191-197.

Liu, C. K., Latona, N. P. & Lee, J. (2011). Drying leather with vacuum and toggling sequentially, *JALCA, 106*, 76-82.

Moita, A. S. H. & Moreira, A. L. N. (2003). Influence of surface properties on the dynamic behavior of impacting droplets. *9th ICLASS Conference*, Sorrento, Italy.

Nasr, A.I. (2015). Evaluation of egyptian camel hides for leathers manufacturing. *World Applied Sciences Journal, 33*(8)*,* 1329-1333.

SAS (2008). *SAS/STAT 9.2 User's guide*(2nd ed.). Cary, NC: SAS Institute Inc.

Serenko, O., Nizamova, Z., Kalinin, M., Ostrovsky, Y., Polukhina, L., & Muzafarov, A. (2014). Effect of the morphology of leather surface on the hydrophobic hydrophilic properties, *Advances in Materials Physics and Chemistry, 4*, 13-19, https://doi.org/10.4236/ampc.2014.42003.

UNIDO. (1994). *Acceptable quality standards in the leather and footwear industry*. Vienna: United Nations Industrial Development Organization.

UNIDO. (2010). *Future trends in the world leather and leather products industry and trade*. Vienna: United Nations Industrial Development Organization.

Wakaso, M. (2014). *Studies on effect of different pigment and binder combinations on surface property of finished leather* (Thesis). Addis Ababa University, Addis Ababa, Ethiopia.

Yuan, Y. & Lee, T. R. (2013). *Contact angle and wetting properties, in Surface Science Techniques*. Berlin, Germany: Springer-Verlag Berlin Heidelberg.