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SYNERGISTIC EFFECT OF *Aloe barbadensis miller* AND CARRAGEENAN ON THE MECHANICAL PERFORMANCE OF LEATHER

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Abstract

This present study reports the effect of *Aloe barbadensis miller* and carrageenan on the physical properties of crusted leather. Tensile strength, tear strength, elongation at break and distensions for control samples at all processes of crusting operations were not significantly different from those of treated samples ($p=0.0972, 0.1324, 0.1565$ and 0.040741), respectively. The trend showed that values for treated samples were slightly smaller than those for control samples, although still within the standard recommended range for quality leather. The prospects of using the two eco benign products to improve the organoleptic (sensorial) characteristics of leather are valid. The study recommends the innovative application of the products to leather industry. More studies to determine the ideal volume fraction and particle sizes of carrageenan and *Aloe barbadensis miller* are needful. Better results can be obtained if appropriate wetting mechanism is adopted to lower contact angle and increase adhesion.

Keywords: *Aloe barbadensis*, tensile strength, tear strength, elongation at break.

1. Introduction

Persistent pressure on leather industry to improve leather quality within eco benign production technology that fosters additional functionalities has pushed the industry to adopt leather making technology that uses natural plant products. The plant products such as hazelnuts, thyme, olive shoots and walnut leaves, *Aloe barbadensis miller* and

carrageenan have been employed in leather processing at different stages either to replace a conventional chemical used or to accompany chemicals being used (Bayramoglu et al, 2008; Bayramoglu et al, 2012; Bitlisli et al, 2010; Contini et al, 2008; Li et al, 2009; Litke and Widdemer, 2003; Metreveli et al, 2006; Metreveli et al, 2010; Owlad et al, 2009; Pereira et al, 2007; Wang et al, 2009). Although these natural products impart additional functionalities such as excellent softness, antimicrobial, antifungal, antiviral and anti-inflammatory activities, however, their effect on the qualitative performance characteristics of the resulting leather has not been investigated (Bayramoglu et al, 2008; Bayramoglu et al, 2012; Bitlisli et al, 2010; Contini et al, 2008; Li et al, 2009; Litke and Widdemer, 2003; Metreveli et al, 2006; Metreveli et al, 2010; Owlad et al, 2009; Pereira et al, 2007; Wang et al, 2009). Therefore there is need to investigate the effect of these products on the quality performance characteristics of leather.

Phytochemistry researches have shown that *Aloe barbadensis miller* contains active constituents of sugars, lignin, vitamins, enzymes, minerals, saponins, salicylic acids and amino acids (Anitha, 2012; Ray et al, 2013). The sugars includes monosaccharides (glucose and fructose such as mannose-6-phosphate) and polysaccharides: (glucomannans/ polymannose such as glucomannans [β -(1, 4)-acetylated mannan]). Anthraquinones, which are phenolic compounds and mucopolysaccharides provide laxative effect, binds water content in their structure (Ishii et al, 1994; Surjushe et al,

2008). Carrageenan is a sea weed hydrocolloid polysaccharides, used as gelling agents, food thickener, stabilizing and emulsifying agent (Jayasinghe et al, 2016). Studies on incorporation of *Aloe barbadensis* miller into leather to improve its softness, cooling effect, antimicrobial, antibacterial, antiviral, antifungal effects are documented (Bitlisli et al, 2010; Litke and Widdemer, 2003). Litke and Widdemer (2003) have shown that incorporation of carrageenan into *Aloe barbadensis* miller improves its penetration into leather. Carrageenan molecules have a negative charge which enables them to react with positive salt ions or proteins in the collagens (Mchugh, 2003). They also have the ability to suspend particles to maintain relatively better distribution of particles within the leather (FMC Biopolymer, 2010; Litke and Widdemer, 2003). According to theories of filler reinforcement and adhesion, the interface formed by the incorporation of *Aloe barbadensis* miller-carrageenan in leather matrix determines the stress transfer capacity which, to a great extent, affects the physical properties of the final leather. The size of the particles also plays reasonable role in the distribution of the stress in the leather, hence affects the physical properties (Ervina et al, 2016; Hoshino et al, 2004; Hu et al, 2003; Song and Youn, 2005). Quite a number of studies have shown that when starch is combined with other graft copolymers and incorporated into leather, the strength properties improve remarkably (Liu et al, 2009; Lu et al, 2005; Lv et al, 2011; Xiaosheng et al, 2012).

Conversely, other studies have reported starch to be poor in both dimensional stability and mechanical properties, a reason why native starches are usually hydrolyzed before applied in various end products (Liu et al, 2009; Ozkan and Ozgunay, 2016). For these reasons, it is evident from this literature that incorporation of the *Aloe barbadensis* miller and carrageenan into leather matrix potentially modifies the hierarchical triple-helical structure which greatly impacts on the physical properties of the leather and hence its quality. To dispel all speculations therefore, this study investigated the effect of *Aloe barbadensis* miller mixed with carrageenan on the physical properties of leather during crusting operations; tanning, retanning and dyeing.

2. EXPERIMENTAL SECTION

2.1 Sample preparation

Freshly flayed bovine hide, commercially procured from Dagoreti slaughter house, was processed to chrome tanning stage using conventional procedure as describe in Nalyanya et al. (2016). The wet blue was cut into two identical pieces along the backline as shown in figure 1.

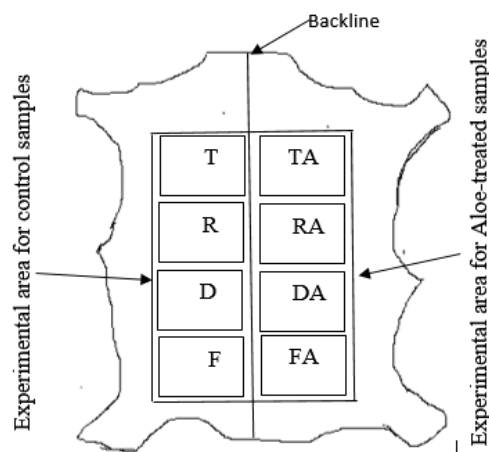


Figure 1: Representation of sample preparation for control and samples treated with additives.

Part labelled T and TA were cut out. The remaining part proceeded to retanning stage using chromium Sulphate in a drum. Before this stage, the wet blue was wetted in water, basified using sodium bicarbonate and then neutralized using ammonium bicarbonate. Antimould of 1% and 2 % sodium formate were also added during neutralization stage to prevent bacterial growth and adjust the pH to 6.5, respectively. Retannage was carried out using 150 % water at 45 oC and 6 % retannages agent (chromium Sulphate) in a drum running moderately slow for 45 minutes.

After penetration check, 1.5 % formic was added to fix the crust. The crust was then drained, washed and toggled overnight prior to dyeing. Parts labelled R and RA were cut off and the remaining underwent dyeing. To prepare the crust for dyeing, piece was basified using ammonium bicarbonate to adjust the pH to 6.5. Dyeing involved 100 % water at 50 OC and 2 % of black dye added through the axle as the drum runs. The crust was then fixed using formic acid before it was drained, washed and toggled overnight. The parts labelled D and DA were cut off and the remaining crust was then fatliquored. Then 100 % of water at 50 OC and 2 % fat liquor was run in a drum for 45 minutes. After fixing, the fatliquored crust was drained, washed in 200 % water, and toggled

overnight. The part labelled F and FA were cut out.

2.2 *Aloe barbadensis* Miller and carrageenan preparation and impregnation

By weight of the crust, 6% of both *Aloe barbadensis* Miller powder and carrageenan powder, were reconstituted with 100 parts of water at 37 °C. The pH of the gel formed was measured to be 5.5. The parts labelled TA, RA, DA and FA, one a time, were run in a drum with 100 % water at 37 °C. The prepared solutions of *Aloe barbadensis* miller and carrageenan was introduced into the drum via the axle. One at a time, the drum was run at 20 rpm for one hour. After one hour, the penetration of the gel was checked against the control samples. Well penetrated crusts assumed yellow-brown color.

2.3 Sampling, sampling location and sample conditioning

The specimens for physical tests were kept in a standard atmosphere of temperature 25 ±2 °C and Relative Humidity of 65 % ± 2 % for at least 48 hours according to ISO 2419: 2012. Sampling was done in accordance with the standard ISO 2418 (2005). In this procedure, the samples are cut within butt and around the backline to avoid the rapidly changing composition and high degree of anisotropy areas. For tensile strength, tear strength, percentage elongation and flexing endurance, eight (8) samples were cut; 4 sampled parallel while 4 sampled perpendicular to the backline as shown in figure 1.

2.4 Determination of Physical properties

Determination of physical properties of leather is vital these properties determine the quality of technological operations in the leather applications (Kosar et al, 2014). Tensile strength (also known as ultimate tensile strength) is the capacity of a material or structure to withstand loads tending to elongate it. Tensile strength determines the maximum tensile stress/tension that the leather can sustain without fracture (Liu et al, 2015). Quantitatively, this can be expressed as the force required to rupture a material specimen of unit cross sectional area. In leather, this strength is thus the combined breaking strength of all the fibers which are taking part to fight against the applied load. For most leather end uses or applications, this strength must be adequate; the acceptable minimum tensile

strength for chrome tanned is 20 MPa (Liu et al, 2015). Elongation refers to the ability of a material to lengthen/stretch when stress is applied to it and represents the maximum extent the material can stretch without breaking. In leather, this is an important quality parameter to be considered, especially when choosing garment leathers, because a low elongation value results in easy tear while a high elongation value causes leather goods to become deformed very quickly or even loose usability (Ork et al, 2014). Good quality leathers should have a percentage elongation of at least 40 % (Roig et al, 2012).

For tensile strength and elongation, eight dumbbell-shaped (dog-bone shaped) test pieces (four from each principal direction) were cut from the crusts using special steel press knife in template according to ISO 3376: 2002 as described in Nalyanya et al (2015). The thickness of each specimen was measured at three points along its length in accordance with ISO 2589 using micrometer screw gauge. The mean of the three thickness measurements was taken as the thickness of the specimen. These tests were carried out using an Instron machine 1011. The jaws of the machine were set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the jaws lie along the mid line. The machine was run until the specimen was broken cross-head speed of 100 mm/min. The tensile strength and the elongation were recorded on the Instron screen in N/mm² and mm, respectively at room temperature according to ISO 3376: 2012. The highest load reached was taken as the breaking load. The tensile strength and percentage elongation were calculated as shown in equation 1 and 2, respectively.

$$\text{Tensile strength} = \frac{\text{Maximum breaking force (N)}}{\text{Cross-section area (mm}^2\text{)}} \quad (1)$$

Then the cross sectional area of the specimen was calculated by multiplying its width by its thickness in mm.

$$\text{Percentage Elongation at break (\%)} = \frac{\text{Elongation (mm)}}{\text{Original free length (mm)}} \times 100\% \quad (2)$$

Baumann tear strength (also known as slit tear resistance) is a measure of how well a material can withstand the effects of tearing. It specifically measures a material's resistance to the growth of any cuts when under tension, measured in N/mm (Nalyanya et al, 2015). In the leather fracture behavior, deformation and

crack growth, this strength measures the resistance to the formation of a tear (tear initiation) and its corresponding expansion or growth (tear propagation within the structure). The least recommended tear strength for chrome-tanned shoe upper side leathers is 40 N/mm. In this test, rectangular specimens of dimensions 50 mm by 25 mm wide were cut by use of a press knife (template machine) in parallel and perpendicular at each position according to ISO 3377: 2002. This strength was determined as described in Nalyanya et al (2015).

Shrinkage temperature is the temperature at which the leather starts to shrink in water or over a heating media (Millikan, 2001). This property is used to characterize the thermal stability of leather. It provides information about the degree of tanning, because the better the crosslinking reactions between the collagen fibres and the tannins, the higher the shrinkage temperature (Heidemann, 1993). Good quality leather should have a minimum shrinkage temperature of 75 °C. In this study, the shrinkage temperature was measured using SATRA STD 114 test apparatus according to the official method (ISO 3380:2002). Strips of leather of dimensions 75 mm by 20 mm were cut from the crusts. Holes were punched at the ends of the leather to allow the specimen to be held vertically in the test chamber filled with water and a small weight was attached to the lower end. The position of the lower end was indicated by an adjustable marker outside the tube to help judge when the shrinkage occurs. The apparatus was then closed and water heated at a rate of 2 °C/min by applying the external heat source to the boiler components. The temperature at which the leather started to shrink was taken as the shrinkage temperature. The strips were placed on a water-grooved microscope slide.

Grain distension at grain crack and burst is a physical property for testing quality of leathers intended to indicate the grain resistance to cracking during top lasting of the shoe uppers. The threshold recommended values for grain crack and grain burst for upper leathers is 6.5 mm and 7.0 mm, respectively. In this study, the ball burst test was measured using a Lastometer according to the official method (ISO 3379:1976). In this method, a disc shaped specimen of the leather is firmly held with the grain side up between the clamping rings, with the spherical tip of the steel rod just

touching the flesh surface. The specimen is moved downward against the rod, distending the grain of the leather immediately above the rod, while the surface is watched for incipient cracking and bursting. The force and distention values at the point at which the grain side of the leather cracks and bursts is observed and the force and distention values are recorded.

Bally flex or flexing endurance is an indication of the finishing resistance to crack and crease when repeatedly flexed, emulating the flexing of the actual use of the shoe. It's a very good indication of the ability of leather grain to withstand lasting operation during shoe making without cracks. Flexing endurance of the prepared leather crust was measured using SATRA STM 701 Bally flexometer according to the official method (ISO 5402:2002). Samples of dimensions 70 mm x 45 mm were cut. Two ends of the specimen were folded and fixed to the jaws of the instrument in such a manner that the grain side remain outside with fold on the specimen. The bottom edge of the upper clamp was adjusted in a horizontal position clamp the leather, grain to grain, the machine was started (100 flexes min⁻¹) which causes a running folds in the leather passing through an angle of 22.5. The motor was switched on when one clamp remains fixed and the other move backward and forwards causing folds in the specimen to run along it. The leather was thus flexed in the folded condition. The leather samples were subjected to pre-determined 100,500, 1,000, 5,000, 10,000, 20,000, 50,000 flexes/cycles and it was observed periodically for any signs of crack on the grain surface of the leather. Results were definite by observing tendency of cracking with the help of an illuminated lens (10x magnification).

2.5 Statistical Analysis of Data

The results were evaluated statistically by using One-Way ANOVA, descriptive statistical and represented as mean for four independent measurements. Comparison of means of control samples and samples treated with the additives was analyzed and differences were considered as significant when $p < 0.05$.

3.0 RESULTS AND DISCUSSION

The values of tensile strength, tear strength, elongation at break and distensions are shown in table 1. Every value reported is an average of eight values from specimens tested; 4 specimens sampled in parallel to the backline

and 4 in perpendicular to the backline. The value of the properties tested for both control

and treated samples qualified the minimum recommended standards of leather for all applications.

Table 1: averages of physical properties of both crust matrices and their composites

	T	TA	R	RA	D	DA	F	FA
Tensile strength (MPa or N/mm²)	20.66 ± 0.54	19.05 ± 0.52	23.24 ± 1.41	20.10 ± 0.37	20.99 ± 1.47	16.82 ± 0.60	18.60 ± 1.15	18.28 ± 1.1
Tear strength (N/mm)	89.81 ± 4.22	94.88 ± 6.55	104.64± 6.42	79.88 ± 6.89	82.49+1 7.99	67.77 ± 4.48	86.94 ±11.29	78.99 ± 2.49
Percentage elongation	56.57 ± 5.07	45.58 ± 1.38	48.088± 3.11	41.44 ± 0.76	52.05 ± 5.26	43.16 ± 0.86	68.42 ± 4.45	57.72 ± 1.65
Distension at grain crack (mm)	8.26 ± 0.42	10.49 ± 2.57	13.09 ± 0.22	9.37 ± 1.43	13.77 ± 0.96	11.85 ± 0.31	17.66 ± 0.06	12.39 ± 2.35
Distension at grain burst (mm)	9.19 ± 0.67	12.75 ± 2.92	16.40 + 0.23	10.44 ± 1.82	16.38 ± 0.48	16.19 ± 1.04	17.77 ± 0.03	13.81 ± 2.32
Shrinkage Temp (°C)	108	108	117	116	118	114	115	114
Flexual endurance	Over 50,000	Over 50,000	Over 50,000	Over 50,000	Over 50,000	Over 50,000	Over 100k	Over 100k

Comparatively, the tensile strength, tear strength, elongation at break and distensions for control samples at all stages of post tanning stages were not significantly different from those samples treated with *Aloe barbadensis* miller and carrageenan (p= 0.0972, 0.1324, 0.1565 and 0.040741), respectively. The general trend showed that the values for control samples were slightly higher than values for samples treated with *Aloe barbadensis* miller and carrageenan. Both increase and decrease in physical properties upon incorporation of *Aloe barbadensis* miller and carrageenan in leather were expected. Authors in this study discussed the concurrent mechanisms of *Aloe barbadensis* miller and carrageenan that increase and those that decrease the strength properties of leather. The functional components in *Aloe barbadensis* miller and carrageenan (starch) such as hydroxyl (-OH), amine groups (-NH₃), carboxylate (-COOH), ester and ethers potentially form hydrogen bonds within themselves and with collagen in the leather (Bitlisli et al, 2010; Surjushe et al, 2008). This behavior mimics cross linking action in leather's collagen. Significant bond formation by this crosslinking action elevates the strength of the biopolymer matrix especially when the starch (carrageenan) is oxidized and reduced since this increases the available hydroxyl groups and hence stronger bonding (Liu et al, 2009). On the other hand, incorporation of starch in leather gave rise to a leather that exhibits good separation characteristics of the

fibre bundles (Xiaosheng et al, 2012). Mechanically, separation of fibre bundles creates regions of weakness, where the propagation/distribution of stress within the structure is hindered. This leads to congestion of stress in one region hence breaking/failure at lower applied forces of deformation. Poor stress distribution weakens the structure of the leather and hence decrease the physical properties. Similarly, *Aloe barbadensis* miller and carrageenan contain water loving (hydrophilic) functions such as hydroxyl (-OH), amine groups (-NH₃) from amino acids, carboxylate (-COOH), esters and ethers. There's therefore a tendency to absorb moisture (water) from the surrounding and retaining them in the leather crust matrix, causing leather to be humectant (Aggary et al, 2005; Bitlisli et al, 2010; Hamman, 2008; Millikan, 2001). The moisture interacts with collagen to alter the structure at the fibrillar scale including an increase in D-spacing (d-periodicity) of collagen (Budrueac et al, 2003; Huang and Meek, 1999; Komanowsky, 1990; Rich and Crick, 1961). Increase in d-spacing is a reflection of the expansion of fibrillar and disruption of the hydrogen bonds that provide the structural integrity to the molecular backbone. This can explain the decrease of the physical properties of leather treated with *Aloe barbadensis miller* and carrageenan-treated leather. The decrease in physical properties was also discussed using the theory of reinforcement and the theory of adhesion. From the two theories, the interface



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formed between the leather matrix and the *Aloe barbadensis miller*-carrageenan mixture is responsible for stress transfer within the structure and hence across the entire sample via frictional shear forces resulting from the interface slippage (Hu et al, 2003). The stress transfer capacity is determined by the particle distribution and their interaction (adhesion) with the leather matrix. The agglomeration of *Aloe barbadensis miller* and its poor dispersibility limits load/stress transfer, which initiates cracks and areas of weakness where plastic deformation/ breaking takes place at minimal stress (Ervina et al, 2016; Litke and Widdemer, 2003; Hoshino et al, 2004). The size of the particles of *Aloe barbadensis miller* and carrageenan may have contributed to their non-uniform distribution within the leather matrix and poor interaction with the leather matrix. Non-uniform distribution of the particles leads to uneven distribution of stress concentration; the regions of high internal stress concentration create defects within the leather matrix and hence the break/failure takes place lower load/force (Basil-Jones et al, 2012; Wells et al, 2017). Poor adhesion is analogous to cracks and voids which make deformation to propagate easily and lowers interfacial stress transfer capacity which consequently reduces the strength of the leather (Ervina et al, 2016; Song and Youn, 2005; Zhang et al, 2005). From the Patent by Litke and Widdemer (2003), *Aloe barbadensis miller* lubricates leather matrix, reducing friction. Using crack blunting mechanism, a partially lubricated fibre structure enables the network to efficiently distribute the applied load, hence a stronger leather. From the results, it's apparent that there was over lubrication which may arise from higher volume fraction. Over lubricated fibres result to a structure that disentangles easily to a lower coefficient of sliding friction between the fibres. The resultant leather has lower energy of rupture and hence the strength properties of the final leather decrease. We therefore gathered that more mechanisms of the *Aloe barbadensis miller* and carrageenan worked out to decrease the physical properties of the final leather as compared to those that increase the strength. The authors therefore proposed that both mechanisms worked competitively and concurrently to give a net decrease in the physical properties.

The samples treated with *Aloe barbadensis miller* and carrageenan samples were softer, tight and more full than their corresponding

control samples. These results agree with previous studies using *Aloe barbadensis miller* on leather by Litke and Widdemer (2003) and Bitlisli *et al.* (2010). They observed that *Aloe barbadensis miller*-treated leathers had decreased compression and decompression energy which implied increase in. Similarly, studies on starch and leather showed an improved softness, fullness, selective filling property, uniformity, tightness, thickness and shrinkage temperature (Liu et al, 2009; Lu et al, 2005; Lv et al, 2011; Xiaosheng et al, 2012). The softness may have been induced by the oily nature and moisturizing effect of the *Aloe barbadensis miller* (Litke and Widdemer, 2003).

CONCLUSION

Tensile strength, tear strength, elongation at break and distensions for control samples at all stages of post tanning stages were not significantly different from those samples treated with *Aloe barbadensis miller* and carrageenan ($p= 0.0972, 0.1324, 0.1565$ and 0.040741), respectively. The general trend showed that the values for control samples were slightly higher than values for samples treated with *Aloe barbadensis miller* and carrageenan. Therefore, the entry of the *Aloe barbadensis miller* and carrageenan particles is in the interstices between the collagen fibres with minimal effect on the physical strength. The value of the properties tested for both control and treated samples qualified the minimum recommended standards of leather for all applications. The increase and decrease in physical properties upon incorporation of *Aloe barbadensis miller* and carrageenan in leather were expected and the two competed with each other with a net decrease in the strength properties. Since the decrease was insignificant, the study found the prospects of using the two natural products to improve the organoleptic properties (sensorial characteristics) of chrome tanned leathers. Since both *Aloe barbadensis miller* gel and carrageenan are biodegradables to some extent, and their net effect on the physical properties was insignificantly small, the innovative application of these two components can be adopted by the leather industry. This is alongside other benefits to human health and significantly better sensorial characteristics. The study suggests more vigorous research into ideal volume fraction/factor loadings, and particle sizes of carrageenan and *Aloe barbadensis miller* to be used. The *Aloe*

barbadensis miller and carrageenan can be activated by sulphuric acids for better wetting to lower contact before being used to increase adhesion.

CONFLICT OF INTEREST

The authors declare that no conflict of interest exists regarding the submission of this manuscript for exclusive publication.

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REFERENCES

- Agarry, OO, Olaleye, MT and Bello-Michael, CO., 2005. Comparative antimicrobial activities of Aloe vera gel and leaf. *Afric. J Biotechnol.* 4, 1413-1414.
- Anitha, T., 2012. Medicinal plants used in skin protection. *Asian J Pharmaceut Clin Res.* 5 (3), 35-38.
- Basil-Jones, M.M., Edmonds, R.L., Norris, G.E., Haverkamp, R.G., 2012. Collagen fibril alignment and deformation during tensile strain of leather: A small-angle X-Ray scattering study. *J. Agric. Food Chem.* 60 (5), 1201-1208.
- Bayramoglu, E.E., Korgan, A., Kalender D., Gulumser, G., Okcu, B., Kilic, E., 2008. Elimination of free formaldehyde in leather by *Vinca rosea* and *Camellia sinensis* extracts. *JALCA.* 103 (3), 119-123.
- Bayramoglu, E.E., Onem, E., Yorgancioglu, A., 2012. Reduction of Hexavalent Chromium Formation in Leather with Various Natural Products (*Coridothymus capitatus*, *Olea europaea*, *Corylus avellana*, and *Juglans regia*). *Ekoloji.* 21 (84), 114-120.
- Bitlisli, BO, Yasa, I, Aslan, A, Cadirci, BH and Basaran, B., 2010. Physical and antimicrobial characteristics of *Aloe vera* treated split suede leather. *JALCA.* 105, 34-40.
- Budrugaec, P., Trandafir, V and Albu, M.G., 2003. The Effect of the Hydration Degree on the Hydrothermal and Thermo-Oxidative Stability of Some Collagenous Matrices. *Journal of Thermal Analysis and Calorimetry.* 72, 581-585
- Contini, M., Baccelloni, S., Massantini, R., Anelli, G., 2008. Extraction of natural antioxidants from hazelnut (*Corylus avellana* L.) shell and skin wastes by long maceration at room temperature. *Food Chemistry,* 110 (3), 659-669.
- Ervina, J., Mariati, M., Hamdan, S., 2016. Effect of Filler Loading on the Tensile Properties of Multi-walled Carbon Nanotube and Graphene Nano powder filled Epoxy Composites. *Procedia Chemistry.* 19, 897 - 905.
- FMC BioPolymer. 2010. Carrageenan.
- Hamman, J.H., 2008. Composition and Applications of Aloe vera Leaf Gel. *Molecules.* 13, 1599-1616.
- Heidemann, E., 1993. *Fundamentals of Leather Manufacturing*, Eduard Roether KG, Darmstadt, London.
- Hoshino, A., Fujioka, K., Oku, T., Nakamura, S., Suga, M., Yamaguchi, Y., Suzuki, K., Yasuhara, M., 2004. Quantum dots targeted to be the assigned to the organelle in living cells. *Microbiology and immunology.* 48, 985-994.
- Hu, Y., Jang, I., Sinnott, SB., 2003. Modification of carbon nanotube-polystyrene matrix composites through polyatomic-ion beam deposition: predictions from molecular dynamics simulations. *Composites Science and Technology.* 63, 1663 -1669.
- Huang, Y. F., Meek, K.M., 1999. Swelling studies on the cornea and sclera: the effects of pH and ionic strength. *Biophys. J.* 77, 1655-1665
- Ishii, Y., Tanizawa, H., Takino, Y., 1994. Studies of aloe V: Mechanism of cathartic effect. *Biol Pharm Bull.* 17, 651-3.
- Jayasinghe, P.S., Pahalawattarachchi, V., Ranaweera, K.K.D.S., 2016. Effect of extraction methods on the yield and physiochemical properties of polysaccharides extracted from sea weed available in Sri Lanka. *Poultry, Fisheries and Wildlife Sciences,* 4 (1), 1-6, Case Report.
- Kozar, O., Mokrousova, O., Wozniak, B., 2014. Deformation characteristics of leather for shoe upper, filled with natural minerals. *J. Chem. Eng.* 8, 47-53.
- Li, K., Chen, H., Wang, Y., Shan, Z., Yang, J., Brutto, P., 2009. A salt-free pickling regime for hides and skins using oxazolidine. *Journal of Cleaner Production.* 17, 1603-1606

- Litke, K.S., Widdemer, J.D., 2003. *Aloe vera* Processed Leather and Leather Gloves, Garments, Shoes and Sandals made from *Aloe vera* processed Leather and a process for making *Aloe vera* processed Leather, Patent Application Publication (10) Pub. No.: US 2003/0217416A1.
- Liu, C.K., Latona, N.P., Taylor, M., Eble, C., Aldema-RaMos, M.L., 2015. Characterization of mechanical properties of leather with airborne Ultrasonics. JALCA. 110, 88-93.
- Liu, G., Lv, S., Ma, Y., 2009. Synthesis and Leather-tanning Properties of a Starch-polyacrylamide Graft Copolymer by Means of HRP, <http://www.aqtic.org.ar/congresos/china2009/download/2-4/2-122>. Pdf
- Lu, S., Liang, G., Ren, H., Wang, J., Yang, Q., 2005. Synthesis and application of graft copolymer retannage of degraded starch and vinyl monomers. Journal of the Society of Leather Technologies and Chemists. 89(2), 63-66.
- Lv, S., Gong, R., Duan, J., Ma, Y., Gao, R., 2011. Preparation and Properties of Graft Copolymer of Phenols and Starch with HRP Catalysis. Advanced Materials Research. 201, 2825-2828.
- Komanowsky, M., 1991. Thermal stability of hide and leather at different moisture contents. JALCA. 86, 269-279.
- McHugh, D. J., 2003. Ch. 7 Carrageenan. In A guide to the seaweed industry: FAO fisheries technical paper 441. Food and agriculture organization of the United Nations, Rome.
- Metreveli, N., Namicheishvili, L., Jariashvili, K., Mrevlishvili, G., Sionkowska, A., 2006. Mechanisms of the Influence of UV Irradiation on Collagen and Collagen-Ascorbic Acid Solutions. International Journal of Photoenergy. 2006, 1-4.
- Metreveli, N.O., Namicheishvili, L.O., Jariashvili, K., Svintradze, D.V., Dgebuadze, M., Chikvaidze, E.D., Skopinska, J., Sionkowska, A., 2010. UV-Vis and FT-IR Spectra of Ultraviolet irradiated collagen in the presence of antioxidant ascorbic acid. J Ecotoxicol and Envir Saf. 73,448-455.
- Millikan, L.E., 2001. Cosmetology cosmetic cosmeceutical definitions and regulations clinics in dermatology. 19(4), 371-374.
- Nalyanya, K.M., Rop, R.K., Onyuka, Migunde, P.O., Ngumbu, R.G., 2016. Thermal and mechanical analysis of pickled and tanned cowhide: Effect of solar radiations. J Appl Polym Science. 133, DOI: 10.1002/app.43208.
- Nalyanya, K.M., Rop, R.K., Onyuka, A., Migunde, A., Kamau, J., 2015. Tensile properties of Kenyan Indigenous Boran bovine. Internat J of Sc and Res. 4 (3), 2149-2154.
- Ork, N., Ozgunay, H., Mutlu, M.M., Ondogan, Z., 2014. Comparative Determination of Physical and Fastness Properties of Garment Leathers Tanned with Various Tanning Materials for Leather Skirt Production. Tekstil ve Konfeksiyon. 24(4), 413-418.
- Owlad, M., Aroua, M.K., Daud, W.A.W., Baroutian, S., 2009. Removal of hexavalent chromium-contaminated water and waste water: A review. Water Air Soil Pollut. 200, 59-77.
- Ozkan, C.K., Ozgunay, H., 2016. Usage of Starch in Leather Making, ICAMS 2016 – 6th International Conference on Advanced Materials and Systems.
- Pereira, J.A., Oliveira, I., Sousa, A., Valentao, P., Andrade, P.B., Ferreira, I.C.F.R., Ferreres, F., Bento, A., Seabra, R., Estevinho, L., 2007. Walnut (*Juglans regia* L.) leaves: Phenolic compounds, antibacterial activity and antioxidant potential of different cultivars. Food and Chemical Toxicology. 45 (11), 2287-2295.
- Ray, A., Gupta, S.D., Ghosh, S., 2013. Isolation and characterization of potent bioactive fraction with antioxidant and UV absorbing activity from *Aloe barbadensis* M. gel. J. Plant Biochem. Biotechnol. 22(4), 483-487.
- Rich, A., Crick, F.H.C., (1961). The Molecular Structure of Collagen. J. Mol. Biol., 3, 483-506.
- Roig, M., Segarra, V., Bertazzo, M., Martínez, M.A., Ferrer, J., Raspi, C., 2012. Chrome-free leather, tanned with oxazolidine. Journal of aqeic. 63(4), 101-111.
- Sizeland, K.H., Wells, H.C., Kelly, S.J.R., Edmonds, R.L., Kirby, N.M., Hawley, A., Mudie, S.T., Ryan, T.M., Haverkamp, R.G., 2017. The influence of water, lanolin, urea, proline, paraffin and fatliquor on collagen D-spacing in leather. Journal of Royal Society of Chemistry Advances. 7, 40658.
- Song, Y.S., Youn, J.R., 2005. Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites. Carbon. 43, 1378-1385.
- Surjushe, A., Vasani, R., Saple, D.G., 2008. Aloe Vera: A Short Review. [Indian J Dermatol](http://www.IndianJ Dermatol). 53(4), 163-166 DOI: [10.4103/0019-5154.44785](https://doi.org/10.4103/0019-5154.44785)
- Wang, F., Chen, G., Fang, Z.Q., 2009. Study on synergistic effect of surface sizing starch and synthesized agent. Paper science and Technology. 128 (6), 56-60.
- Wells, H.C., Sizeland, K.H., Kelly, S.J.R., Kirby, N., Hawley, A., Mudie, S., Haverkamp, R.G., 2017.

Collagen fibril intermolecular spacing changes with 2-propanol: A mechanism for tissue stiffness, ACS Biomaterials science and Engineering. DOI:10.102/acs.biomaterials.7b00418.

Xiaosheng, D., Hui, C., Rui, D., Zhihua, S., 2012. Preparation and Application of Denatured Starches. Journal of the Society of Leather Technologies and Chemists. 96, 189-194.

Zhang, J., Jiang, D.D., Wang, D., Wilkie, C.A., 2005. Polymer Advance Technology. 16, 800.