

Surface Charge and Isoelectric Point of Leather: A Novel Determination Method and its Application in Leather Making*

by

Ya-nan Wang,¹ Wanli Huang,¹ Hongshou Zhang,¹ Ling Tian,¹ Jianfei Zhou^{1,2**} and Bi Shi^{1,2}

¹National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China

²Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, China

Abstract

Surface charge and isoelectric point (pI) of leather play an important role in leather making processes. However, a proper method for the determination of surface charge and pI of leather is unavailable nowadays due to the complexity of leather structure and property, especially for the burgeoning chrome-free tanned leathers. Therefore, it is necessary to develop a quantitative determination method. In this study, a novel method for determining zeta potential (to characterize the surface charge of leather) of solid-state leather was established using a zeta potential analyzer based on the principle of streaming potential. Test conditions including suspension concentration, sample grain size, temperature and conductivity were optimized. Then the pI (the pH value at the zero point of zeta potential) of a variety of chrome-free tanned leathers, such as mineral, vegetable, organic and combination tanned leather, were obtained by this zeta potential method. Moreover, we managed to monitor the pI and surface charge state of zirconium tanned leather during post-tanning processes using this method. As a result, application of this precise and rapid determination method enables us to reasonably regulate the pI and surface charge of chrome-free leather so as to effectively improve tanning and post-tanning performances.

Introduction

Leather is one type of natural polymer matrix in three dimensions woven by collagen fibers. Collagen, the main component of leather, is a typical amphoteric polyelectrolyte. The amino groups in the side chains of basic amino acid residues (e.g. lysine and arginine) and carboxyl groups on the side chains of acidic amino acid residues (glutamic acid and aspartic acid) of collagen can bind/release H⁺ and be ionized in aqueous solution. This makes the fiber surface of leather positively/negatively charged. pH plays as an important control for surface charge of

leather.¹ The pH at which the total number of positive charges and negative charges present in leather are equal is commonly referred to as isoelectric point (pI). In leather processing, skin collagen binds/crosslinks with various leather chemicals, such as tanning agents and post-tanning agents, which leads to the consumption of acidic/basic groups on the side chains of collagen. On the other hand, the bound chemicals themselves are charged as well. So, the pI of leather depends on the charge characteristics of both collagen and chemicals. Moreover, it will be constantly changed during leather processing.

Surface charge and pI of leather have an important effect on leather processing as they influence the penetration, distribution and fixation of chemicals in leather matrix. However, methods for determining pI of leather are seldom reported due to the complexity of leather matrix structure, both physically and chemically. The test object of the existing methods is generally collagen solution,²⁻⁴ where the real pI of leather matrix is unable to be characterized. Although there were reports concerning the pI of chrome leather powder,⁵⁻⁷ they still have limitations on universality, accuracy or operability. As for the surface charge of leather, only a qualitative method has been reported where a dyestuff solution was used as charge indicator of leather.⁸ Therefore, it is necessary to develop a precise and rapid method to determine the surface charge and pI of leather, especially when tanners are returning their attention to the development of chrome-free tannage and various chrome-free tanned leathers are springing up. In fact, the existing post-tanning processes are designed and conducted according to the surface charge characteristic of chrome tanned leather (pI approx. 7), mostly by experience. During post-tanning processes, the electro-positivity of chrome tanned leather increases gradually with decreasing pH (from 6.5 to 3.8), leading to the enhancement of fixation of post-tanning agents (mostly anionic chemicals) in leather.⁹⁻¹⁰ However, it may not work in the case of chrome-free tanned leather as its pI is probably much lower than that of chrome tanned leather.

*Part of this work was presented at the XXXIII IULTCS Congress, November 2015, Brazil.

**Corresponding author email address: zhouamao2004@126.com

Manuscript received March 6, 2017, accepted for publication April 18, 2017.

Zeta potential is the electric potential in the interfacial double layer at the location of the slipping plane relative to a point in the bulk fluid away from the interface. It can be used for quantification of the magnitude of surface charge of solid or colloid. For instance, a method for determining zeta potential of pulp has been widely used in paper industry.¹¹⁻¹² In consideration of the similarity of structures between paper fiber and leather collagen fiber, zeta potential of solid-state leather could also be determined by borrowing the method from paper industry. In addition, the pI of leather was found to be the pH value at the zero point of zeta potential. In this study, various test conditions such as suspension concentration, grain size of leather sample, temperature and conductivity were optimized. Then the pI values of numerous chrome-free single and combination tanned leathers as well as chrome tanned leather were determined using this method. Furthermore, the relationship between surface charge state of leather in post-tanning processes and uptake of post-tanning chemicals was investigated.

Experimental

Preparation of Leather Samples

Leather samples used for the determination of zeta potential and pI were prepared as below. Pickled cattle pelt was used as raw material, and a variety of tanning processes were carried out conventionally, as listed in Table I. The chemicals used in leather processing were of commercial grade. After horsing-up, the tanned leathers were cut into pieces (2 cm × 2 cm), washed with 400% water for 10 minutes three times. Then they were dried in drying oven at 45°C for 24 h. The dried leather pieces were ground into fibers and particles (diameter less than 4 mm) using a cutting mill (SM 100, Retsch, Germany) and then sealed for determination.

Procedures for Zeta Potential and pI

Determination of Leather Sample

Leather sample was dispersed in a certain amount of water to form suspension, and then was vibrated at 150 rpm in water bath

Table I
Tanning trials.

Tanning process	Tanning agents ^a	Final pH	Temperature
Chrome tanning	6% chrome powder (Cr ₂ O ₃ 1.5%, basicity 33%)	4.0	25°C at first 40°C at last
Aluminium tanning	19.5% Al ₂ (SO ₄) ₃ ·18H ₂ O (Al ₂ O ₃ 3%)	4.0	25°C at first 40°C at last
Zirconium tanning	11.5% Zr(SO ₄) ₂ (ZrO ₂ 4%)	3.6	25°C at first 40°C at last
Vegetable tanning	20% mimosa (tannin content 72.5%)	4.2	25°C
Synton tanning	15% phenolic condensate (solid content 45%)	4.2	25°C
Glutaraldehyde tanning	6% glutaraldehyde solution (glutaraldehyde content 50%)	7.5	25°C at first 40°C at last
F-90 tanning	10% F-90 tanning agent	4.5	30°C
TWT tanning	8% TWT tanning agent (solid content 50%)	8.0	25°C at first 40°C at last
Vegetable-glutaraldehyde combination tanning	10%~20% mimosa and 1%~4% modified glutaraldehyde	4.0	25°C at first 40°C at last
Zirconium-HOS tanning	8.7% Zr(SO ₄) ₂ (ZrO ₂ 3%) and 2.4% HOS ^b	3.8	25°C at first 40°C at last

^a – The dosages of chemicals were based on weight of limed pelt.

^b – HOS is a type of highly oxidized starch used as ligand for zirconium tanning.¹³

with a set temperature for 30 min in order to fully soak the sample and equilibrate the pH. Then the zeta potential of leather sample was determined by a zeta potential analyzer (Mütek™ SZP-10, BTG, Germany) suitable for solid samples (shown in Figure 1). The suspension was sucked and sampled into the measuring cell of the analyzer by vacuum for 50~80 s. A leather plug was formed, and a filtrate was recovered through a screen (mesh size 308 μm). After a settling time for stabilizing the plug (40~50 s), a set pressure variation of -0.2 bar to -0.4 bar was applied. An oscillating flow of liquid through the plug was generated. The sheared off counterions induced a streaming potential that was measured by electrodes. Zeta potential was calculated by streaming potential, conductivity and pressure difference using Helmholtz-Smoluchowski equation and given by the instrument.

As for the determination of pI, we first determined the zeta potential of leather sample, and subsequently measured the pH of the suspension. Then 5 mL of 0.1 mol/L HCl solution or NaOH solution was added each time to form a pH gradient of the suspension. It should be noted that either acid or alkali was added into one sample. The determination of zeta potential as well as pH was repeated. A pH-zeta potential curve was plotted, and the pH value at the zero point of zeta potential was considered the pI of leather.

Effect of Suspension Concentration on Zeta Potential of Leather

A certain amount of chrome tanned leather sample (2, 3, 5, 10 and 15 g) was dispersed in 400 mL of water to form suspension,

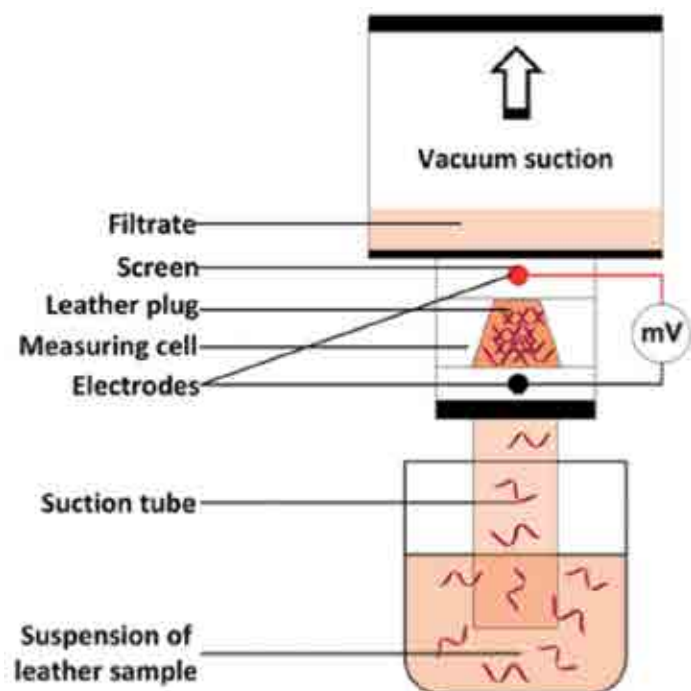


Figure 1. Schematic diagram of zeta potential analyzer.

where the concentration of suspension was 5, 7.5, 12.5, 25 and 37.5 g/L, respectively. Zeta potential of each sample was determined according to the procedures described above. Similar experiment was also conducted using F-90 tanned leather sample.

Effect of Sample Fiber Particle Size on pI of Leather

Chrome tanned leather was ground into fibers and particles smaller than 4.0 mm by a cutting mill and sieved into three fractions (2.0~4.0 mm, 1.0~2.0 mm and <1.0 mm) using a vibratory sieve shaker (AS200 digit, Retsch, Germany). Then the zeta potential and pI of each fraction was determined according to the procedures described above.

Effect of Temperature on pI of Leather

Chrome tanned leather and vegetable tanned leather were used in this experiment. The suspension of each leather sample was vibrated in water bath at different temperatures (30, 40, 50 and 60°C) for 30 min, and then zeta potential and pI were determined under the same temperature.

Effect of Conductivity on pI of Leather

Chrome tanned leather was used in this experiment. The original conductivity of the suspension was 0.14 mS/cm. In addition, the conductivity of other three groups was adjusted to 3, 5 and 7 mS/cm, respectively, using 1 mol/L NaCl solution. Then the zeta potential and pI of each group was determined.

pI Determination of Leather Tanned by a Single Tanning Agent

Eight types of leather tanned by a single tanning agent (shown in Table I) as well as pickled pelt were used for the determination of pI. The determination conditions optimized in the previous subsections were employed.

pI determination of Combination Tanned Leather

Vegetable-glutaraldehyde (Veg-Ald) combination tanned leather was made according to the traditional processes.¹⁴ The effect of tannin dosage on the pI of leather was investigated by first using 10%, 15% and 20% mimosa tannin, respectively, combined with 3% modified glutaraldehyde. Moreover, the effect of aldehyde dosage on the pI of leather was also investigated by first using 15% mimosa tannin, combined with 1%, 2%, 3% and 4% modified glutaraldehyde, respectively.

pI Determination of Leather from Post-tanning Processes

Zr-HOS tanned leather, a kind of novel chrome-free leather tanned by zirconium sulfate and starch-based ligand HOS (shown in Table I, containing a great number of coordinating groups such as hydroxyl, carboxyl and carbonyl), was used as raw material for this trial. Traditional chrome tanned leather was also used for comparison. They were treated separately according to the same post-tanning recipe. After wringing and

shaving to thickness of 1.1 mm, the leather was rewetted with non-ionic surfactant, neutralized to pH 6.5 by sodium bicarbonate and then washed thoroughly. Then retanning was conducted using 10% retanning agents (3% acrylic resin, 2% syntan and 5% mimosa tannin) and 2% dyestuff for 90 min. Formic acid was added at the end of retanning to adjust the float pH to 4.0. Subsequently, the leather was fatliquored in 150% fresh water with 15% fatliquoring agent for 60 min and fixed by formic acid to pH 3.8. After tanning, neutralizing, retanning and fatliquoring processes, leather samples were collected respectively for the determination of pI. Meanwhile, Total Organic Carbon (TOC) concentrations of retanning floats before and after processing were measured by TOC analyzer (vario TOC, Elementar, Germany). Similar analysis was also performed on fatliquoring process. The uptake rate of retanning/fatliquoring chemicals was calculated according to the TOC values.

Results and Discussion

Optimization of Conditions for Determining Zeta Potential and pI of Leather

Zeta potential as well as pI of leather was determined using a zeta potential analyzer which can be applied to solid samples, and various parameters were optimized. The effect of suspension concentration on zeta potential was investigated at first. It was observed during determination that leather plug became denser with increasing suspension concentration, which led to the decrease of shearing force of fluid and then the decrease of streaming potential. From Helmholtz-Smoluchowski equation, we know that zeta potential is in proportion to streaming potential, so the zeta potential of leather was reduced gradually as the concentration of suspension was increased (shown in Figure 2). In addition, leather plug was difficult to form when the suspension concentration was less than 25 g/L, suggesting that the accuracy of determination would be affected. Therefore, the suspension concentration was set to be 25 g/L (10 g leather sample mixing with 400 mL water) in the subsequent determination.

Furthermore, the effects of sample fiber particle size, temperature and conductivity on the pI of leather were investigated. Figure 3 shows that smaller sample fiber particle size resulted in lower pI of chrome tanned leather. But generally, fiber particle size had little impact on zeta potential and pI of leather. It should be noted that sample with fiber particle size over 4.0 mm was unable to form a plug for determining zeta potential. In terms of plug formation, fiber particle size of 2.0~4.0 mm was suitable for soft leather (e.g. aldehyde tanned leather), and fiber particle size of 1.0~2.0 mm was recommended for hard leather (e.g. zirconium tanned leather).

From Figure 4 we can see that pI values of chrome tanned leather and vegetable tanned leather were almost not affected by

temperature. In consideration of the adequate soaking of sample and efficient equilibrium of pH, 30°C was used for the vibration of suspension before determination.

The effect of conductivity on zeta potential and pI of chrome tanned leather is shown in Figure 5. The absolute values of zeta potential declined remarkably as the conductivity of the suspension was increased. This should be due to the fact that the interfacial double layer was compressed with the increased ion strength of the suspension, leading to the reduction of streaming potential and thus also the zeta potential. This means that if the surface charges of different leather samples are to be determined for comparison, the conductivity of the suspensions is expected to be identical. Thus, sufficient washing of leather samples before determination is recommended. However, pI of leather was hardly influenced by conductivity, as it only depended on the zwitterionic structure of leather being tested.

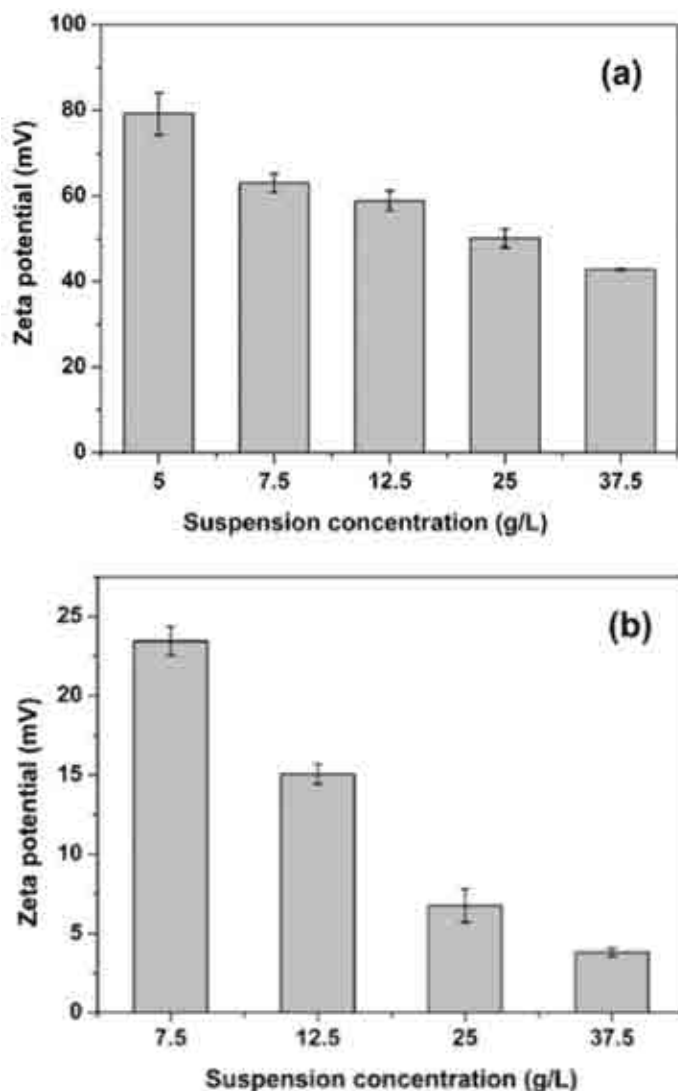


Figure 2. Effect of suspension concentration on zeta potential of (a) chrome tanned leather and (b) F-90 tanned leather.

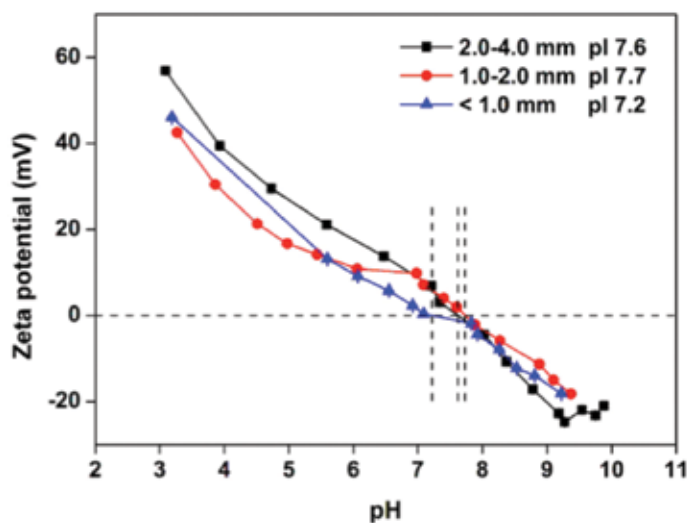


Figure 3. Effect of fiber particle size on pI of chrome tanned leather.

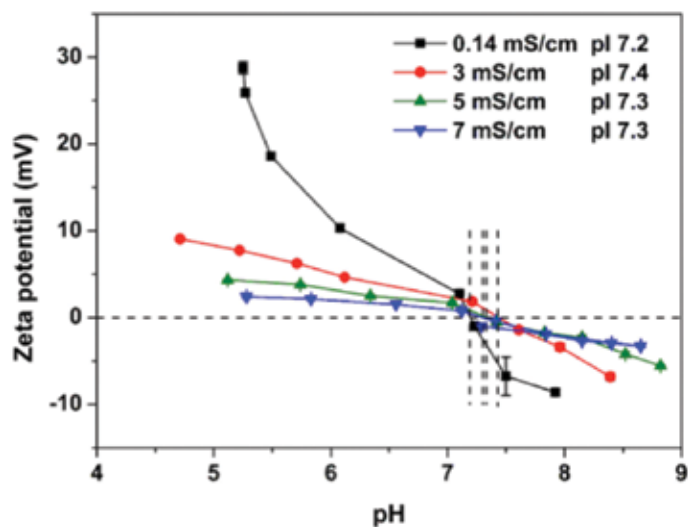


Figure 5. Effect of conductivity on pI of chrome tanned leather.

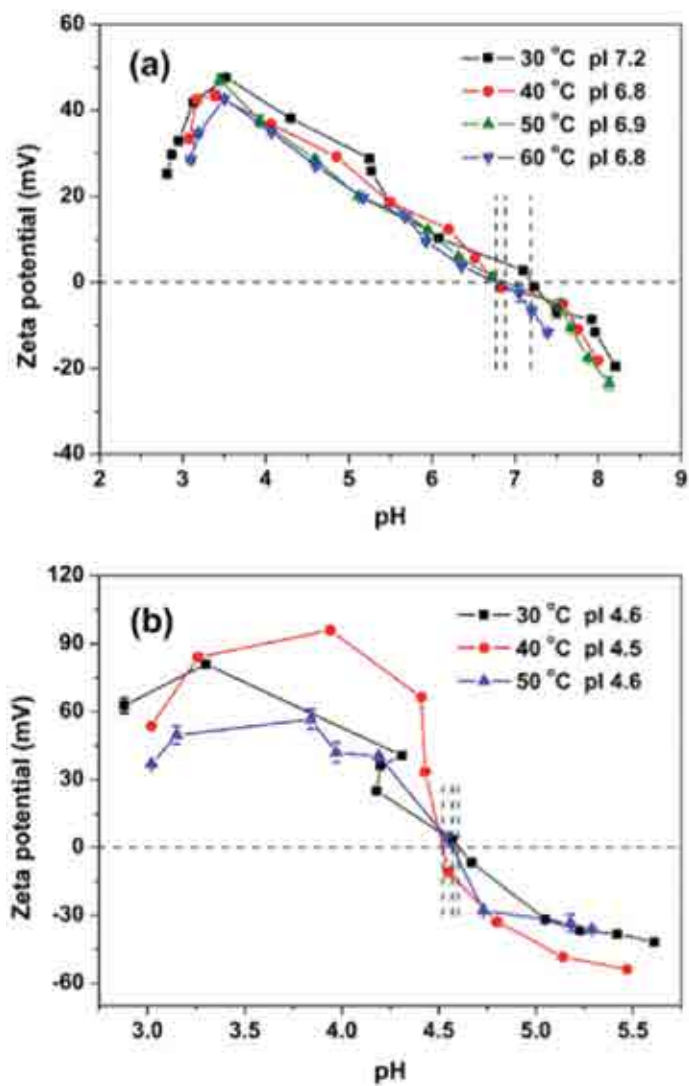


Figure 4. Effect of temperature on pI of (a) chrome tanned leather and (b) vegetable tanned leather.

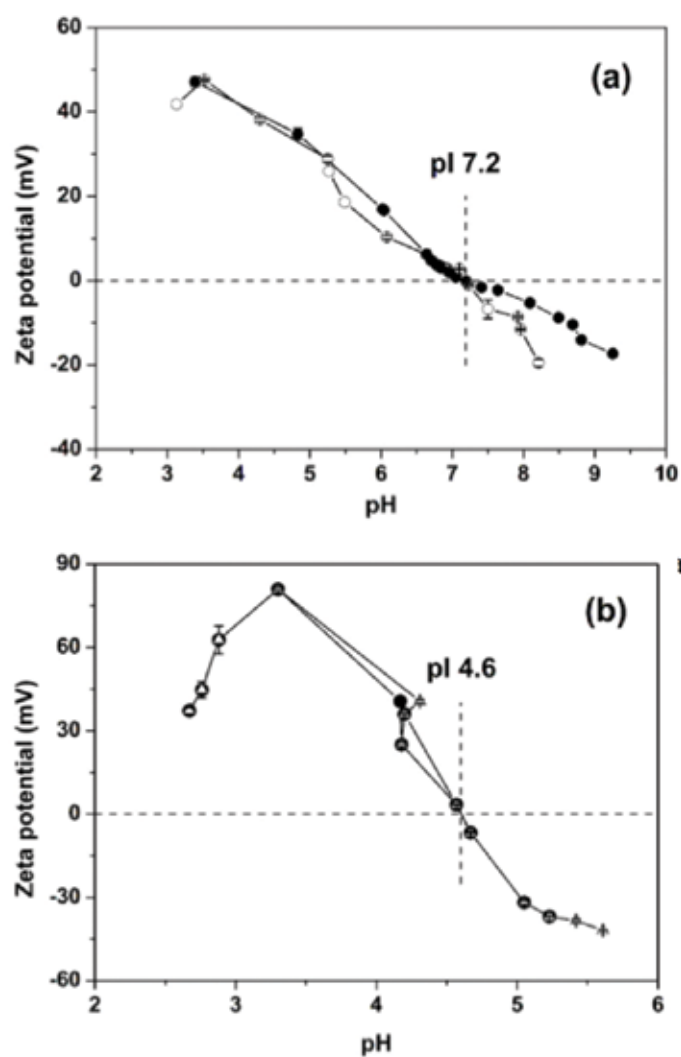


Figure 6. pI of (a) chrome tanned leather and (b) vegetable tanned leather.

In summary, the optimized conditions for determining zeta potential and pI of leather were as below. 10 g of leather sample (grain size 1.0~4.0 mm) was dispersed in 400 mL of water to form a 25 g/L suspension. The suspension was vibrated at 150 rpm in 30°C water bath for 30 min. Then zeta potential was determined by the zeta potential analyzer in 3 min, and pI, i.e. the pH value at the zero point of zeta potential, was read from the pH-zeta potential curve. Figure 6 illustrate that the same pI values were obtained under the optimized conditions in two experiments for both chrome tanned leather and vegetable tanned leather, indicating good repeatability of the determination method.

Application of the Determination Method in Leather Making

As we know, zeta potential of solid/colloid surface is changed by adjusting the pH of suspension/solution, and the pH value at the zero point of zeta potential is regarded as the pI of the solid/colloid. Based on this principle, a method for determining pI of solid-state leather has been established as described above. Pickled cow pelt (used as raw material for tanning) and various types of tanned leather were used for pI determination. Table II shows that the pI of pickled pelt was 5.4, which was close to the value measured by SDBS adsorption method and much lower

than that of bovine hide collagen (approx. 7~8¹⁵). This should be due to the deamidation of asparagine and glutamine residues and the hydrolysis of peptide bond in collagen during the whole beamhouse processes. As expected in chrome tanning process, positively charged chrome complexes were introduced and mainly bound with carboxyl groups of collagen, which resulted in the significant increase of pI (7.2). The pI of aluminium tanned leather (7.6) was also higher than that of pickled pelt based on an analogous tanning mechanism to chrome tanning. Interestingly, the pI of zirconium tanned leather was determined to be 8.3, which was higher than those of the other two mineral tanned leathers, although its tanning mechanism was previously regarded as a theory¹⁶⁻¹⁷ that zirconium could coexist as cationic, neutral and anionic species, and react with both amino group and carboxyl group of collagen during tanning process. In addition, there are some differences in the pI values of aluminium and zirconium tanned leathers between our results and other reports, including the ones measured by SDBS adsorption method that we established previously.⁷ This may be explained by the differences in the types and amounts of tanning agents as well as tanning conditions. Anyway, the zeta potential method is supposed to be reliable in terms of its test object, accuracy and repeatability.

Table II
pI of tanned leather.

Sample	pI		
	Zeta potential method	SDBS adsorption method ⁷	Reports in the literature
Pickled pelt	5.4	5.8~5.9	—
Chrome tanned leather	7.2	7.7~7.9	6.7 ¹ / 6.9 ⁹ / 6.5~7.5 ¹⁰
Aluminium tanned leather	7.6	8.5~8.6	7.2 ¹
Zirconium tanned leather	8.3	7.3~7.4	7.5 ¹
Vegetable tanned leather	4.6	—	4.0 ¹ / 3.4 ⁹
Syntan tanned leather	4.2	—	—
Glutaraldehyde tanned leather	4.8	5.1~5.2	2.0 ¹
F-90 tanned leather	4.5	—	—
TWT tanned leather	5.0	5.8~5.9	—

Tanning with vegetable tannin or syntan would introduce anionic compounds into leather and give leather lower pI values (shown in Table II) than those of pickled pelt and mineral tanned leathers. Similar phenomenon was found in the pI values of other organic (glutaraldehyde, F-90 and TWT) tanned leathers, where amino groups in the side chains of collagen were consumed through covalent crosslink by these tanning agents, leading to the decline of pI. Amphoteric tanning agent TWT introduced extra amino groups into leather¹⁸⁻²⁰ and resulted in higher pI than the other organic tanned leathers. It is worth noting that relatively low pI of conventional organic tanned leather may lead to poor uptake and fixation of post-tanning agents that are mostly anionic chemicals.

Until now, there have been a few reports concerning the pI of leather tanned by a single agent.⁶⁻⁷ However, the situation about the combination tanned leather is more complicated. Fortunately, our method is universal to all kinds of leather in terms of its mechanism. Taking classical Veg-Ald combination tanned leather as an example, the effect of tanning agent dosage on pI of combination tanned leather are shown in Figure 7. The pI of leather was found to be decreased with increasing dosage of mimosa tannin or modified glutaraldehyde. Moreover, the pI values of Veg-Ald combination tanned leathers were all lower than that of single vegetable tanned leather. The mechanism of Veg-Ald combination tanning has turned out to be that condensed tannin penetrates into hide and reacts with oxygen or nitrogen atoms of collagen through hydrogen bond at first, and

then aldehyde forms covalent crosslinkage between amino groups of collagen side chain and A rings of tannin.²¹⁻²² Therefore, the reduction of pI resulted from both the introduction of anionic tannin extract and the consumption of collagen amino groups.

Surface charge state of tanned leather plays an essential role in post-tanning processes, as it strongly affects the penetration and fixation of chemicals in leather, and thus influences the physical and organoleptic properties of crust leather. Using our determination method, the zeta potential and pI of a novel chrome-free leather (Zr-HOS tanned leather) during post-tanning processes were monitored, and chrome tanned leather sample was used for comparison. The results in Figure 8 indicate that the pI of Zr-HOS tanned leather (6.5) was close to that of chrome tanned leather (7.3), implying a good potential of the leather in post-tanning performance. After neutralizing to pH 6.5, Zr-HOS tanned leather was electrically neutral as its pI was

exactly 6.5, suggesting that the subsequent anionic retanning agents and dyestuff could easily penetrate into the leather fiber network rather than fixing on the surface layer. However, chrome tanned leather was weakly positive (pI 7.7) after neutralizing, which may have a detrimental effect on the uniform distribution of retanning chemicals in leather. The results in Figure 9 also indicate that the uptake rate of retanning chemicals in Zr-HOS tanned leather was higher than that in chrome tanned leather. What's more interesting is that Zr-HOS tanned leather was still electropositive after retanning (pH 4.0, pI 4.7) although it had bound with a great quantity of retanning chemicals. That is why the uptake rate of fatliquoring agents in Zr-HOS tanned leather was also higher than that in chrome tanned leather (Figure 9). Uptake of these anionic post-tanning chemicals in large numbers finally resulted in the gradual reduction of pI.

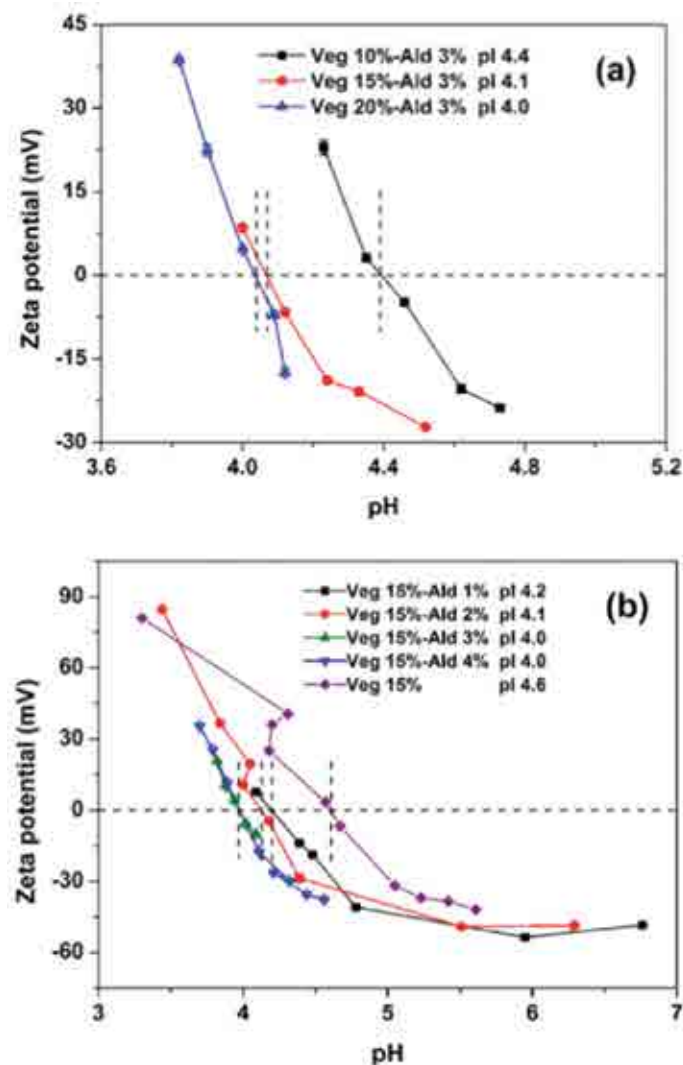


Figure 7. Effects of dosages of (a) mimosa tannin and (b) modified glutaraldehyde on pI of Veg-Ald combination tanned leather.

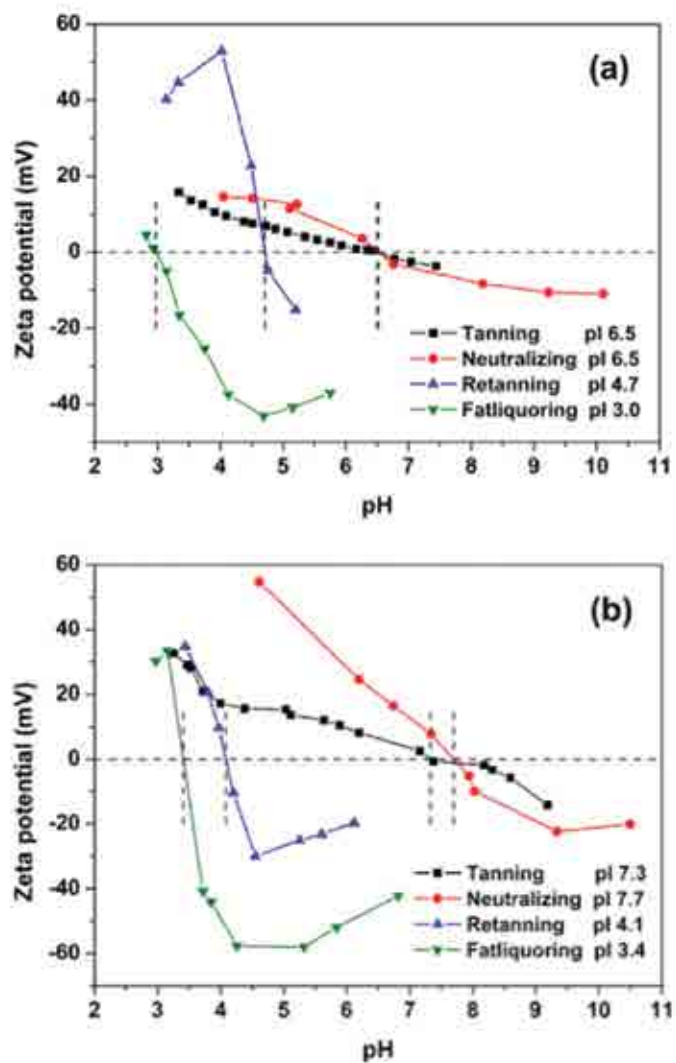


Figure 8. pI of (a) Zr-HOS tanned leather and (b) chrome tanned leather from various post-tanning processes.

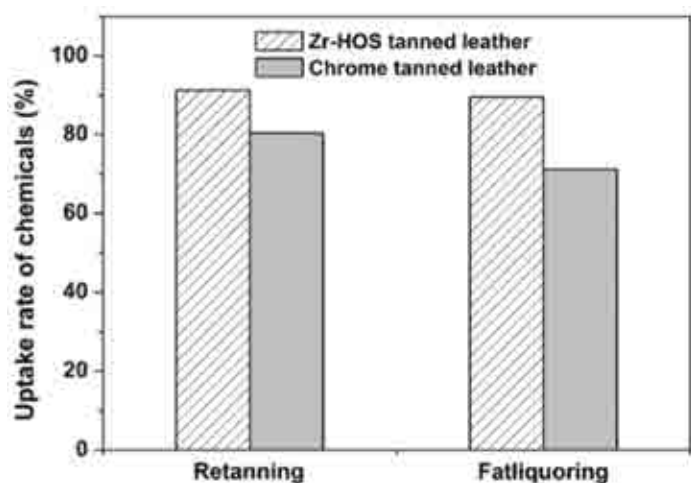


Figure 9. Uptake of post-tanning chemicals in leather.

Conclusion

A novel method for determining surface charge and pI of leather has been established based on zeta potential determination. It can be applied to scientific research and online monitoring of leather manufacture due to its universality, repeatability and rapidity. The pI values presented in this study were in accordance with classical tanning mechanisms. The determination of zeta potential and pI of tanned leather provides a scientific guide for the adjustment of charge state of leather (especially the emerging chrome-free leather) and the effective fixation of post-tanning chemicals with leather. Furthermore, it could be a complement to explore the mechanism and application of newly developed chrome-free tanning methods.

Acknowledgement

This project is financially supported by the National Natural Science Foundation of China (21506129, 21476149).

References

- Guthrie-Strachan, J., Flowers, K.; Protein and leather charge. *World Leather* **18**, 19-23, 2005.
- Higberger, J. H.; The isoelectric point of collagen. *J. Am. Chem. Soc.* **61**, 2302-2303, 1939.
- Heidemann, E., Schmidt, A.; The charge structure of collagen and leather. London: The 24th IULTCS Congress, Sep. 11-14, 1997.
- Cheng, H. M., Wang, L., Wang, R., et al.; The use of zeta potential measurement for determining isoelectric points of collagen and its degradations. *Leather Science and Engineering* **16**, 40-43, 2006.
- Gustavson, K. H.; The isoelectric points of chromium collagen compounds. *JALCA* **47**, 425-437, 1952.
- Nakamura, M., Inatsugi, T.; Isoelectric point and zeta potential of tanned leather. *Japanese Journal of Zootechnical Science* **61**, 22-29, 1990.
- Sun, Q. Y., Wang, Y. N., Liao, X. P., et al.; SDBS adsorption method: a new method for determination of isoelectric point of skin and leather. *China Leather* **42**, 9-13, 2013.
- Pocket book for the leather technologist, 4th ed., BASF, 276, 2003.
- Heidemann, E.; Fundamentals of leather manufacture, Eduard Roether KG, 335-336, 1993.
- Covington, A. D.; Tanning chemistry: The science of leather, The Royal Society of Chemistry, 356-359, 2011.
- Cadena, E. M., Garcia, J., Vidal, T., et al.; Determination of zeta potential and cationic demand in ECF and TCF bleached pulp from eucalyptus and flax. Influence of measuring conditions. *Cellulose* **16**, 491-500, 2009.
- Vishtal, A. G., Rousu, P., Hultholm, T., et al.; Drainage and retention enhancement of a wheat straw pulp containing furnish using microparticle retention aids. *BioResources* **6**, 791-806, 2011.
- Yu, Y., Wang, Y. N., Ding, W., et al.; Preparation of highly-oxidized starch using hydrogen peroxide and its application as a novel ligand for zirconium tanning of leather. In press.
- Covington, A. D., Shi, B.; High stability organic tanning using plant polyphenols. Part 1. The interactions between vegetable tannins and aldehydic crosslinkers. *J. Soc. Leather Technol. Chem.* **82**, 64-71, 1998.
- Covington, A. D.; Tanning chemistry: The science of leather, The Royal Society of Chemistry, 9, 2011.
- Guo, J. L., Huang, X., Wu, C., et al.; The further investigation of tanning mechanisms of typical tannages by ultraviolet-visible and near infrared diffused reflectance spectrophotometry, *JALCA* **106**, 226-231, 2011.
- Cao, S., Zeng, Y. H., Cheng, B. Z., et al.; Effect of pH on Al/Zr-binding sites between collagen fibers in tanning process. *JALCA* **111**, 242-249, 2016.
- Shi, B., Li, J., Wang, Y. N., et al.; A novel wet white technology based on an amphoteric organic tanning agent. Taipei: 9th AICLST Congress, Nov. 12-14, 2012.
- Wu, C., Zhang, W. H., Liao, X. P., et al.; Transposition of chrome tanning in leather making. *JALCA* **109**, 176-183, 2014.
- Ding, W., Cheng, Y. H., Wang, Y. N., et al.; Chrome-reduced combination tanning for cleaner dyed sheep fur processing. *JALCA* **110**, 363-371, 2015.
- Lu, Z. B., Liao, X. P., Shi, B.; The reaction of vegetable tannin-aldehyde-collagen: A further understanding of vegetable tannin-aldehyde combination tannage. *J. Soc. Leather Technol. Chem.* **87**, 173-178, 2003.
- Lu, Z. B., Liao, X. P., Zhang, W. H., et al.; Mechanism of vegetable tannin-aldehyde combination tannage. *JALCA* **100**, 432-437, 2005.