A Method and Principle of Soft and Transparent Leather Manufacturing

by

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Abstract

For preparing a new kind of leather with transmittance and softness at the same time, glycerol was used to treat delimed and bleached split pelt. The softness, transmittance and mechanical properties were tested to evaluate the performance of soft and transparent leather (STL). FT-IR, SEM, XRD, DSC and TG were used to character the structure of STL and reveal the basic principle of STL manufacturing. The results showed that 25% glycerol based on limed pelt weight could make leather soft and transparent simultaneously. Pig pelt was more suitable for thin and transparent leather while cattle split was better for uniform and clear leather. Glycerol combined with collagen through multipoint hydrogen bonds, and the combination had slight positive effect on improving STL thermal stability. Fiber bundles of STL trended to disperse and collagen hierarchical structure including triple helix remained during transparent treatment. The soft and transparent leather could be a new choice for leather goods designers and might be a selectable substrate for high-performance electronic skin.

Introduction

Leather is a kind of natural polymer network mainly consisting of collagen matrix.[1] Generally, beamhouse, tanning, post tanning and finishing are chief sections for converting raw hides and skins into leather. In leather manufacturing, the raw hides and skins or leather are almost opaque at times, but it is translucent under certain processes such as liming and acid swelling. Leather is usually opaque no matter what kind of tanning method is used. However, some special kinds of skin or leather products are transparent, for example parchment,[2] drum skin and traditional Chinese shadow puppet.[3] Greasy skins (sheep skin, pig skin, monk skin and so on) with improper preservation would become semitransparent. Gelatin or collagen hydrolysate is transparent more or less after drying.[4-6]

Up to now, it has been impossible for leather to be transparent and soft at same time. Soft leather is opaque, and transparent leather or skin is nearly rigid and brittle. If leather could be soft and transparent simultaneously, it could be a new choice for designing new fashion leather goods, the transparent parts which are usually plastic now. Meanwhile, soft and transparent leather could be used for preparing electronic skins.[7]

As is well known, dried raw hides or skins look transparent but feel hard and the reason could be summarized as collagen fibers bond with each other when water is evaporated. In order to solve this problem, a lubricant material could be used to prevent collagen fibers bonding after drying, thus soft and transparent leather (STL) could be prepared. Polyol materials were used for solving the problems of water dehydration and crystallization in hydrogels.[8-10] Based on the properties of polyol materials, it could be inferred that they might be used as lubricants for STL manufacturing.

Up to now, there has been little research about transparent leather and the manufacturing method was missing. In this work, fully washed deliming pelt was treated with glycerol to prepare STL and the softness, transparency and mechanical properties were measured. In addition, FT-IR, SEM, XRD, DSC and TG were used for deducing the principle of STL manufacturing.

Experimental

Materials

Limed bovine hide split with thickness 2.0 mm and pig skin split with thickness 1.5 mm were bought from local tannery in Chengdu, Sichuan province, China. Glycerol and formic acid were provided by Chengdu Kelong Chemical Co. LTD. All chemicals used for preparing deliming pelt were industrial reagents, and the chemicals utilized for testing were commercially available of analytical grade.

Sample preparation

Soft and transparent leather preparation

Limed bovine hide split and pig skin split were trimmed and weighed at first, and then subjected to deliming, bleaching and transparent treatment to prepare STL in drum.[11, 12] The detail process of STL

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manufacturing is shown in Table I. The dosage of chemicals used in each process was based on the weight of limed pelt.

TM was an ammonium free deliming agent and DW was a nonionic degreasing agent from Sichuan Decision New Material Technology Co., Ltd. China.

The pelt without transparent treatment and toggling until dried directly was regard as Control Sample.

Testing methods

Transmittance measurement

The transmittance of both STL and Control Sample was measured by a WGT-S transmittance and haze tester (Jinan Saicheng Electronic Technology Co., Ltd, China) following the manufacturer's direction according to standard method.[13]

Mechanical properties measurement

Both STL and Control Sample were conditioned as the standard method before mechanical properties testing. The mechanical properties like tensile strength, elongation at break and tear strength were tested by AI-7000S tensile machine (GOTECH testing Machines Inc. China), and the softness was tested by measuring GJ9E1 apparatus for leather softness (GOTECH testing Machines Inc. China) following standard .[14]

FT-IR measurement

STL and Control Sample were tested by a Nicolet 10 FT-IR (Thermo Scientific Corporation, American) in the wavelength range from 500 to 4000cm^{-1} for 32 times.

Scanning electron microscope (SEM) observation

A JSM-7500F scanning electron microscope (Japan Electronic Co., Ltd., Japan) was used for producing leather cross section

Table I

STL manufacturing process

Process	Material	Dosage (%)	Temperature (°C)	Time (min)	Remark
Pre-deliming	water	150	30		
	TM	1			float pH about 9.5, drain
	DW	0.1		30	
Deliming	water	70	33		
	DW	0.2			
	ammonium sulphate	2.5		80	float pH 7.5-8.0, cross section colorless checked with phenolphthalein indicator, drain
Washing	water	300	25	10	twice
Bleaching	water	70	35		
	Sodium carbonate	0.5		10	float pH about 9.5
	hydrogen peroxide	2		20	float pH higher than 9.0
	hydrogen peroxide	2		60	drain
Washing	water	300	25	10	twice
Transparent treatment	water	60	25		
	glycerol	25		300	O/N
	formic acid	0.3		30	
	formic acid	0.3		60	
	formic acid	X		60	float pH 4.0-4.2
Toggling under 30-35°C until dried completely.					

images by operating the SEM at low vacuum with an accelerating voltage of 15 kV.

X-ray diffraction scanning (XRD) determination

The 20mm×20mm samples were tested by EMPYREANX-ray diffraction scanning meter (PANalytical B.V., Netherlands) with diffraction angle 2θ from 5° to 60° with a scanning rate of 2°/min at ambient temperature and humidity.

Thermal properties determination

The dried leathers were put into Aluminum crucibles and heated by a NETZSCH DSC 200 PC differential scanning calorimeter (Germany) with heating rate 5°C/min in a N_2 atmosphere (flow N_2: 100 mL/min). The range of temperature was from 25° to 250°C.

The dried samples were put into ceramic crucibles and heated by a NETZSCH TG 209 F1 thermal gravimetric analyzer (Germany) with heating rate 10°C/min in a N_2 atmosphere (flow N_2: 100 mL/min). The range of temperature was range from 40° to 800°C.

Results and Discussion

Performance of soft and transparent leather

After a huge number of trials, the dosage of glycerol in STL manufacturing process was optimized and 25% glycerol based on weight of liming pelt was selected. Less glycerol resulted in poor softness and transmittance, and more glycerol would make STL feel moist. The performance and images of pig STL are shown in Figure 1. The left two photos illustrate the STL is transparent and the right two photos show the STL is soft. It was clear that the

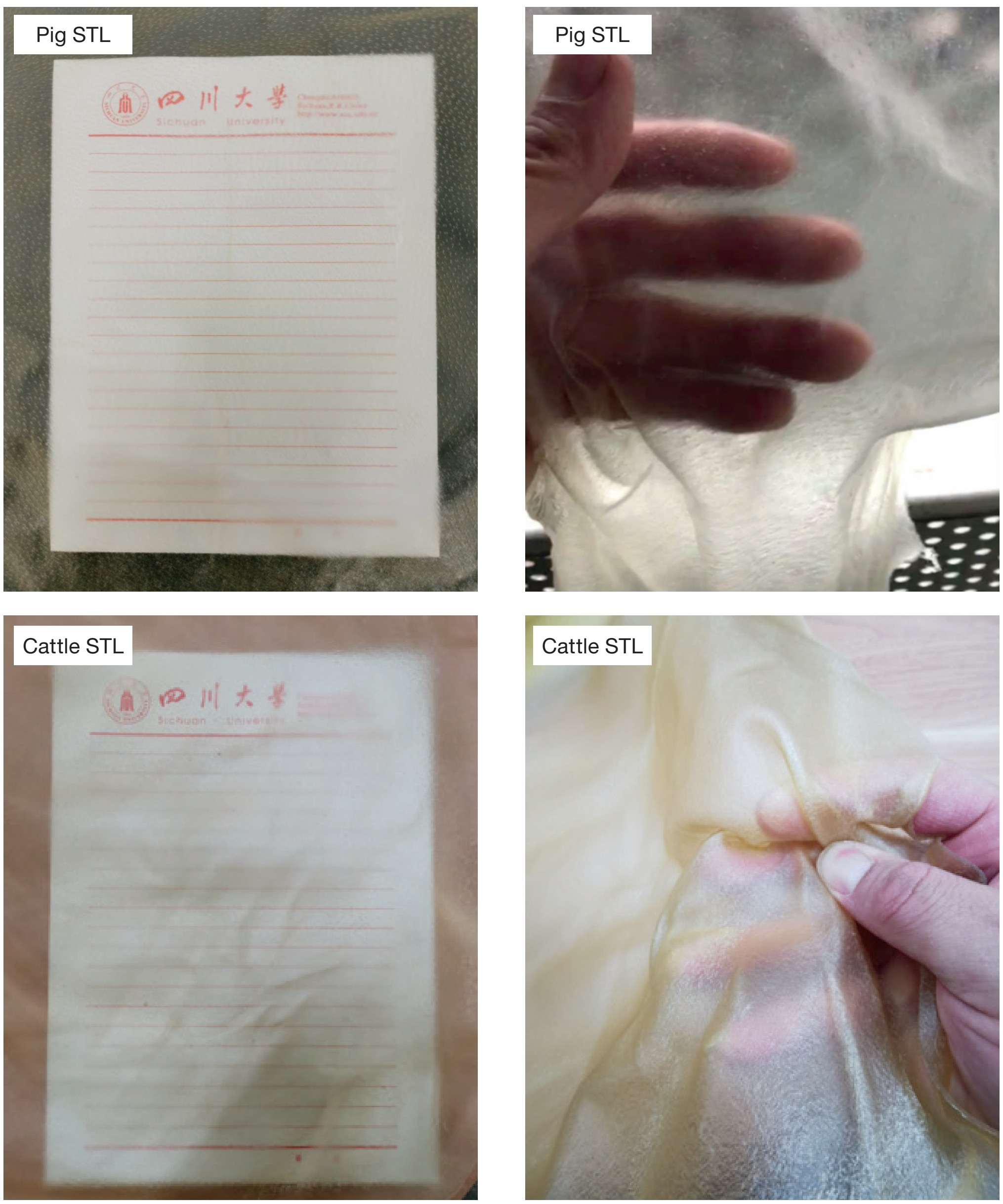

Figure 1. Performance and images of soft and transparent leather

Table II
mechanical properties of soft and transparent leather

Parameters	Cattle STL	Pig STL
Transmittance (%)	78.4	86.5
Softness (mm)	3.88	4.34
Thickness (mm)	0.885	0.442
Tensile strength (MPa)	33.62	25.91
Elongation at break (%)	22.17	23.86
Tear load (N)	20.58	17.57

leather was soft and transparent when glycerol was used to treat pig split pelt. The application of glycerol not only made leather soft but also improved the transmittance of leather. The STL was soft compared with dried pelt and transparent compared with conventional leather.

The mechanical properties of both cattle and pig STL were tested and the results are listed in Table II. As shown in Table II, the softness and transmittance of pig STL were better than cattle STL, but its tensile strength and tear load were slightly lower. As the fiber weaving of pig skin was tighter and denser than cattle hide, much thinner pig split could be obtained. Consequently, the thinner pig pelt might be more suitable for manufacturing soft and transparent leather. On the other hand, since cattle splits almost consist of pure collagen fiber and there was no hair follicles in cattle hides which prevent light scattering and refringence inner leather, the appearance of cattle STL had better uniformity and clarity. In short, the mechanical properties of pig and cattle STL were comparable, and pig pelt was more suitable for thin and transparent leather while cattle split was better for uniform and clear leather.

Structure of soft and transparent leather

Interaction between collagen and glycerol

The FT-IR images of pig STL and Control Sample were shown in Figure 2. It was obvious the absorption peak intensity around 3300 cm^{-1} was enhanced after glycerol treatment, indicating more hydrogen bonds formed between collagen and OH-groups of glycerol. In other words, the interaction between pelt and glycerol was mainly hydrogen bonds.

Figure 2 also illustrates that the collagen structure remained during transparent treatment. The absorption bands at around 1650 cm^{-1}, 1550 cm^{-1} and 1150 cm^{-1} were characteristic of collagen amide I band (stretching vibration of C=O coupled with hydrogen bonding), amide II band (bending vibration of N–H and stretching vibration of C–N) and amide III band (stretching vibration of C–O or C–N–C) respectively,[15] and they were the evidence of a collagen backbone. Moreover, no significant shift of the amide I band was observed, showing the triple helix structure of collagen was not impacted after transparent treatment.

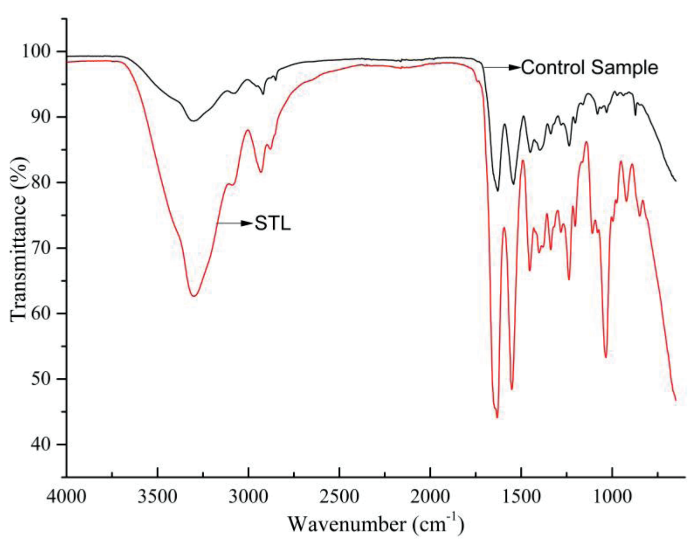

Figure 2. FT-IR images of pig STL and Control Sample

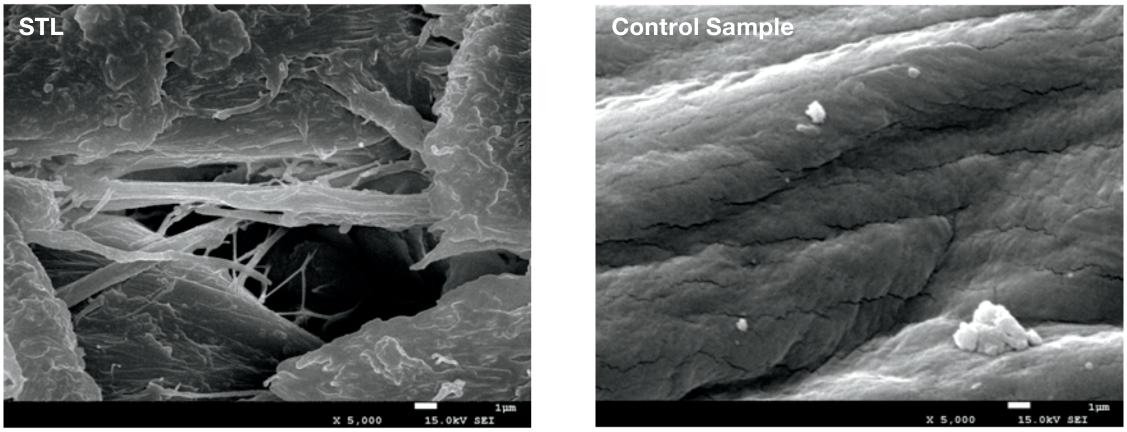

Figure 3. SEM images of pig STL and Control Sample

Histological structure of soft and transparent leather

In Figure 3, collagen fibers of STL appeared to be dispersed and while in the Control Sample they were adhesive. As glycerol was combined with collagen through multipoint hydrogen bonds, it could prevent fibers from adhering during the drying process and lubricate collagen fibers as water was removed. Thus, STL was soft macroscopically. The Control Sample was hard and brittle because there was no lubricant distribution between collagen fibers after evaporation of water during drying. However, the dispersion degree of fiber bundles and porosity of STL were poorer than any leather tanned by any representative tanning agent (chromium, vegetable tanning or aldehyde, etc) as tanning agents could open up the microfibrils, fibrils, elementary fibers and fiber bundles.[16] It could be inferred that the multipoint hydrogen bonds between collagen and glycerol were too weak to generate cross-linking effect.

Crystal structure of soft and transparent leather

Figure 4 indicated there were two peaks in both STL and Control Sample. The one was about 7°, representing the distance between molecular chains, and the other was around 21°, corresponding to diffuse scatter of collagen.[17] According to Bragg equation $2d\sin\theta=n\lambda$, larger 2θ meant the distance between collagen was shorter under same testing condition. A value of 2θ for the Control Sample about 7° was obviously higher than STL, indicating the collagen fibers adhere to each other without glycerol. Hence, the Control Sample was hard and brittle macroscopically. On the contrary, 2θ of Control Sample around 21° was obviously lower than STL, indicating the amorphous area of collagen fibers in STL was enlarged due to glycerol preventing the leather fibers shrink during drying.

Thermal stability of soft and transparent leather

According to DSC results illustrated in Figure 5, the thermal denaturation temperature of STL was much higher than Control Sample, which could match chrome tanned leather. Although glycerol had positive effect on improving thermal stability collagen to some extent,[18] this excellent denaturation temperature could not be attributed to tanning effect because the cross-linking

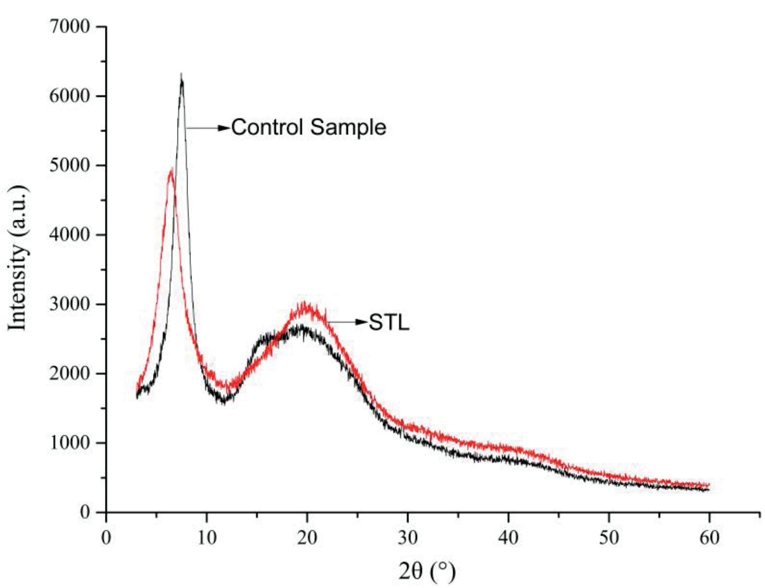

Figure 4. XRD images of pig STL and Control Sample

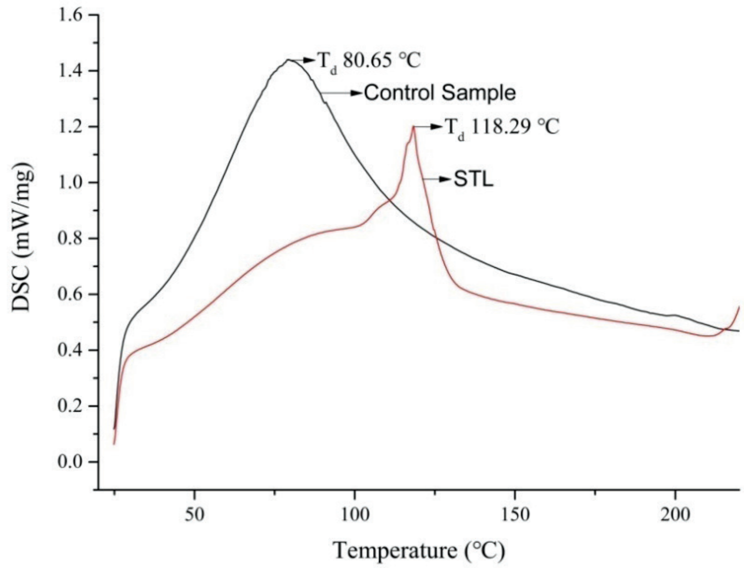

Figure 5. DSC results of pig STL and Control Sample

between collagen molecules could not be generated by glycerol. The reasonable interpretation might be that glycerol absorbed heat before collagen and then resulted in thermal denaturation delay. For Control Sample, collagen absorbed heat directly and the thermal denaturation occurred immediately.

The Thermogravimetric analysis results of pig STL and Control Sample are shown in Figure 6. It is obvious there are two peaks during STL thermal decomposition process; the first one is 237.28 °C which is the thermal decomposition of glycerol according to prior study,[19] and the second one is 314.70 °C. Only one maximum decomposition temperature (T_{max}) of Control Sample (310.07 °C) was observed during TG test. T_{max} near 310 °C was the temperature of collagen decomposition,[20] and the higher T_{max} STL might be the reason that the existence of glycerol could promote thermal stability of biomass.[21] Thermogravimetric analysis also proved that glycerol interacted with collagen successfully.

Mechanism of soft and transparent leather manufacturing

The mechanism of soft and transparent leather manufacturing could be summarized as follows. Glycerol combined with collagen through multipoint hydrogen bonds in the role of lubricant. Glycerol prevented collagen fiber bundles from adhering when water was almost completely removed after drying and resulted in soft and transparent leather. However, two questions about the relationship between leather structure and transmittance are still essentially unknown. First, why could glycerol make leather become transparent while the leather was opaque without glycerol? One possible reason could be inferred as: glycerol filled the air voids of leather and reduces the index of refraction; therefore the visible light could pass through easily with less scattering. Second, why was the leather tanned by any tanning agent opaque? One possible hypothesis was that collagen crystal structure was changed due to new chemical bonds generated during tanning. It would benefit the production of transparent leather with better performance and improved understanding of the tanning mechanism after answering the two questions and confirming the two preliminary speculations above.

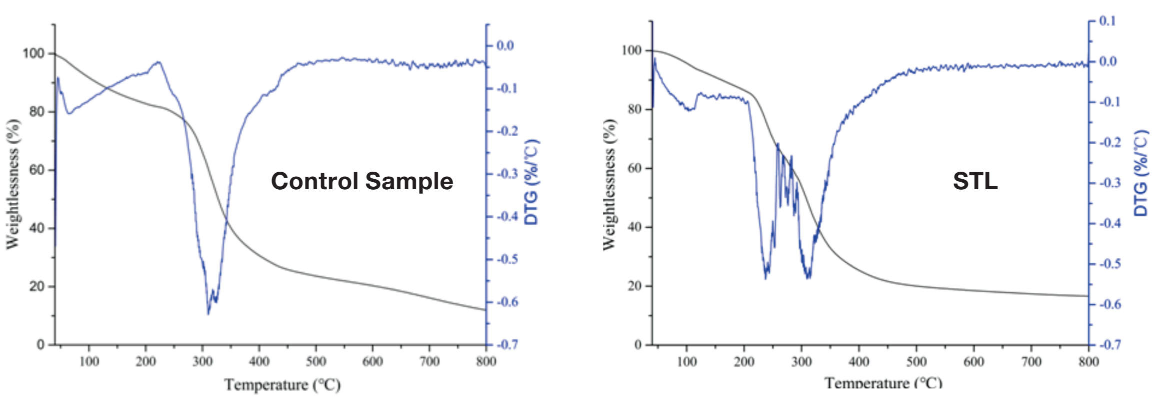

Figure 6. TG results of pig STL and Control Sample

Conclusions

Both cattle hide split and pig skin split could be used to prepare soft and transparent leather when 25% glycerol based on limed pelt weight was used for treating delimed and bleached split pelt. The leather was soft and transparent when compared with traditional leather which had incompatible softness and transmittance. Pig pelt was more suitable for thin and transparent leather while cattle split was beneficial to create uniform and clear leather. Glycerol combined with collagen through multipoint hydrogen bonds and the combination had slight positive effect on improving leather thermal stability. Fiber bundles of soft and transparent leather tended to be dispersed and the collagen hierarchical structure including triple helix preserved during transparent treatment. The soft and transparent leather could be a brand-new choice for leather goods designers and might be an optional strategy for high-performance electronic skin.

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