Supplementary information

A Salt-free Pickling and Chrome-free Tanning Technology: Sustainable Approach for Cleaner Leather Manufacturing

Xinhua Liu [a, b, c*], Youyou Wang [a, b], Xuechuan Wang [c], Tengfei Han [a, b], Wanni Wang [a, b], Huie Jiang [a, b*]

[a] College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science & Technology, Wei Yang District, Xi'an 710021, Shaanxi, China

[b] National Demonstration Center for Experimental Light Chemistry Engineering Education, Shaanxi University of Science & Technology, Weiyang District, Xi'an 710021, Shaanxi, China

[c] Institute of Biomass & Functional Materials, Shaanxi University of Science & Technology, Weiyang District, Xi'an 710021, Shaanxi, China

[*]Corresponding Author:

Dr. Xinhua Liu, E-mail address: liuxinhua@sust.edu.cn

Dr. Huie Jang, E-mail address: jianghuie@sust.edu.cn

Process of making leather

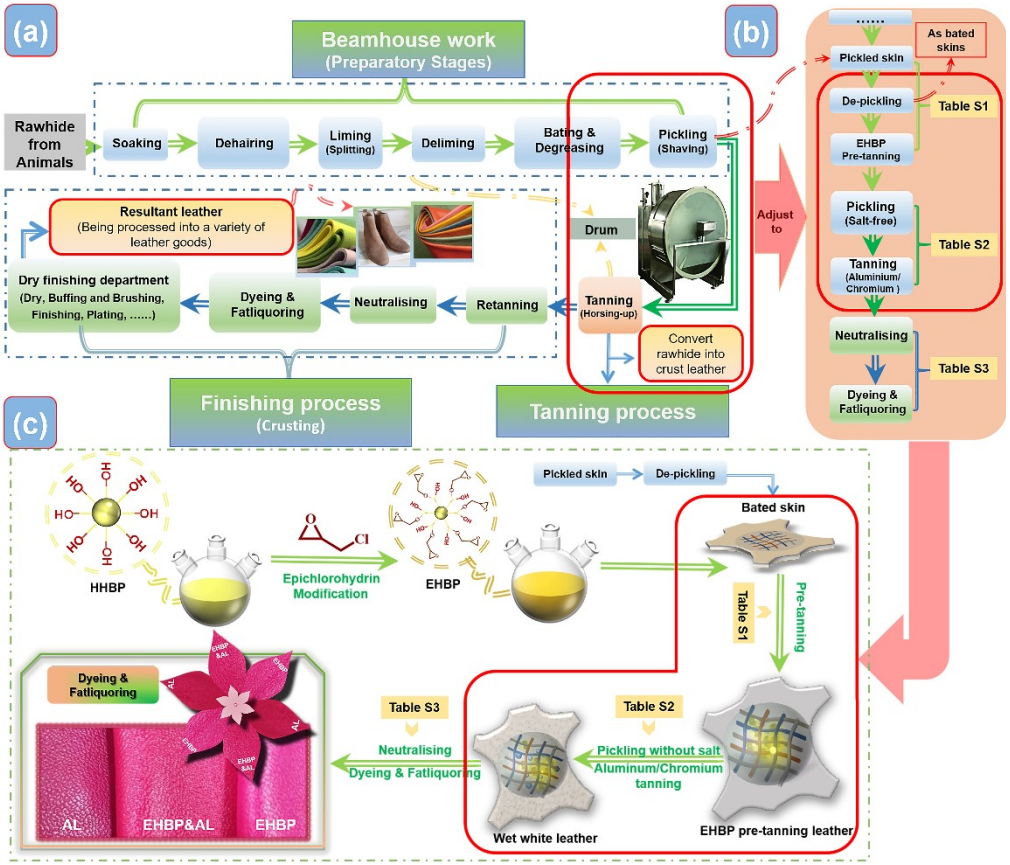

Fig.S1 Major processing sketch of conventional leather making (a), and the adjusted process (circle the part in the red box) (b) and specific flow diagram (c) involved in this research (Tables S1-S3 is the process recipe involved in this paper, which details are presented below.)

Leather is made from a variety of animal skins through multiple processes (**Fig. S1a**), and can be used to make leather products such as garment, footwear and so on to meet human needs[1, 2]. Fig. S1a introduces the mainly conventional process of leather making, which includes three main processes: preparatory stages, tanning process of leather, finishing (crusting), and then the finishing processes can also be divided into wet finishing process and dry

finishing process. Pickling is after the process of bating and degreasing, which is usually the last step in the preparatory stage followed by tanning process, such as chrome tanning. Usually, dyeing and fatliquoring are in the stage of wet finishing department after the process of tanning, retanning and neutralizing. In this paper, a salt-free pickling and aluminium tanning technology based EHBP was tried (Fig. S1b, c), which Tables S1-S3 are the specific process recipe presented below. The bated skin obtained by conventional process is used as the raw material for follow-up processing, but the bated skin is not resistant to storage and is difficult to get it commercially., so sheep pickled skin is de-pickling at first, and then to be used as bated skin for subsequent processing.

Application of EHBP as salt-free pickling auxiliaries

The specific implementation process for EHBP pre-tanned leather was shown in Table S1.

Table S1

Pre-tanning processes.

Process	Chemicals	Offer/%	T/°C	t/min	Remarks
De-pickling	Water	250	25	20*5	Check pH, until the pH is 7.5±, continue the mechanical action for 40 minutes, and then wash twice, drain.
	Salt	10			
	$NaHCO_3$	a			
Pretreatment	Water	150	25	120	Mechanical action.
	Hexamethylenetetramine	1			

Proceed on Table S1

Pre-tanning	SDS	1	25	4-5	Check pH.
	EHBP	X			
Basification	Sodium bicarbonate/ Sodium carbonate	b	30	20×3	Slowly adjust the pH of the bath liquid to 8.5± and stop mechanical action then stayed overnight.

Note: ①The values of X for EHBP are 6%, 7%, 8%, 9% and 10% respectively.

②The squeezed sheep pickled skin is weighed 200% as the basis for the dosage

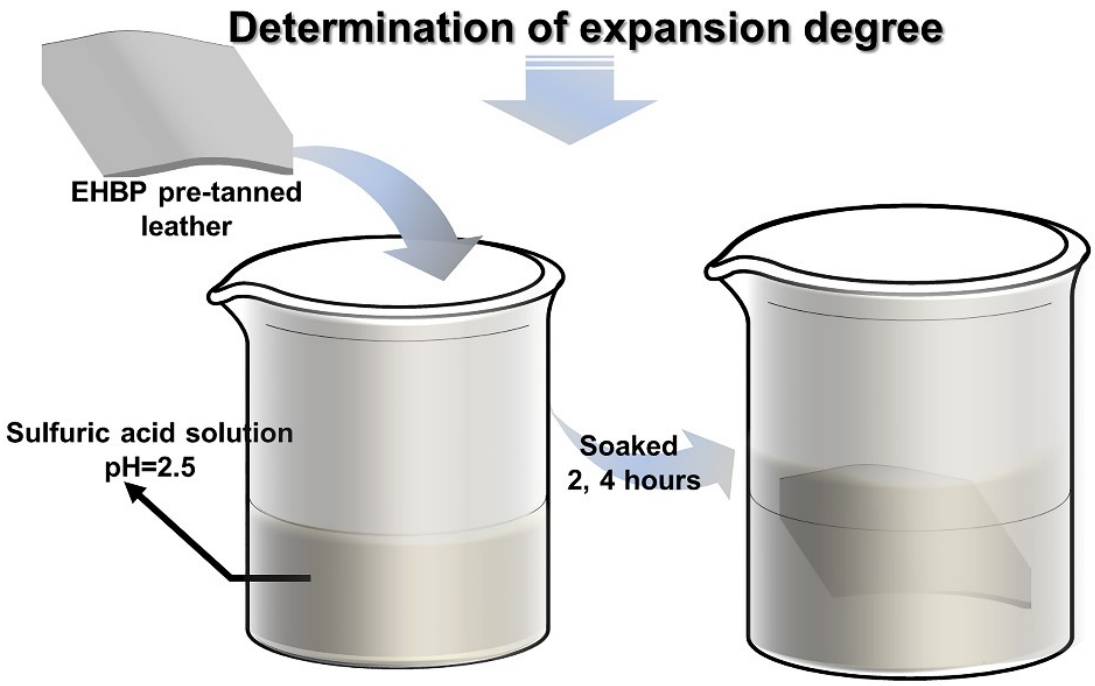

Fig. S2 Schematic diagram for testing the expansion degree of EHBP pre-tanned leather with different dosage.

Pickling and aluminum/chromium tanning of EHBP pre-tanned leather

The specific implementation process for pickling and aluminum/chromium tanning of EHBP pre-tanned leather was shown in Table S2.

Table S2

Tanning processes.

Process	Chemicals	Offer/%	T/°C	t/min	Remarks
Pickling	Water	100	25	150～180	Dilute 10 times and cool to room temperature added in four times at an interval of 30 min. Check pH, then stay overnight.
	Salt	0			
	H_2SO_4	1.2～1.8			
	CH_3COOH	0.5～0.8			
Tanning	Aluminum/Chromium tanning agent	Y	25	240～300	Check pH.
Basification	Sodium bicarbonate	b	35	20×4	Slowly adjust the pH of the bath liquid to 3.8～4.2 and stop mechanical action then stayed overnight.

Note: ①The values of Y for aluminum tanning agent are 5%, 6%, 7% and 8% respectively.

② The values of Y for chromium tanning agent is 6%.

③The squeezed sheep pickled skin is weighed 200% as the basis for the dosage.

Fatliquoring and dyeing process of different treated leather

The specific implementation process for fatliquoring and dyeing of different tanned leather to investigate its compatibility with anionic leather chemicals was shown in **Table S3.**

Fatliquoring and dyeing processes.

Process	Chemicals	Offer/%	T/°C	t/min	Remarks
Raw materials	EHBP tanned leather, EHBP & AL 6% combined tanning leather, conventional aluminum tanned leather				
Degreasing	Water	200	40	60	Drain water.
	Degreasing agent (DESOTAN DN)	1.0			
Washing	Water	300	37	10	Washing twice; Drain water.
Neutralization	Water	100	37	40	Check pH; Adjust pH to 5.5.
	Sodium formate/ Formic acid	c			
	Sodium bicarbonate	d		3×15+20	
Fatliquoring	Water	150	45	40	Adjust pH to 3.5. Drain and wash twice.
	Anionic fatliquor (LQ-5)	17			
	Formic acid	e			
Neutralize again to adjust the pH of green leather to 5.5±. Washing and draining.					
Dyeing	Dye (TRUPOCOR RED BB)	1.2	45	40	Adjust pH to 3.5. Drain and wash twice. Out of the drum and dry.
	Water	150			
	Formic acid	f		2×15+20	

Note: The squeezed sheep pickled skin is weighed 200% as the basis for the dosage.

Optimization of dosage of EHBP in salt-free pickling

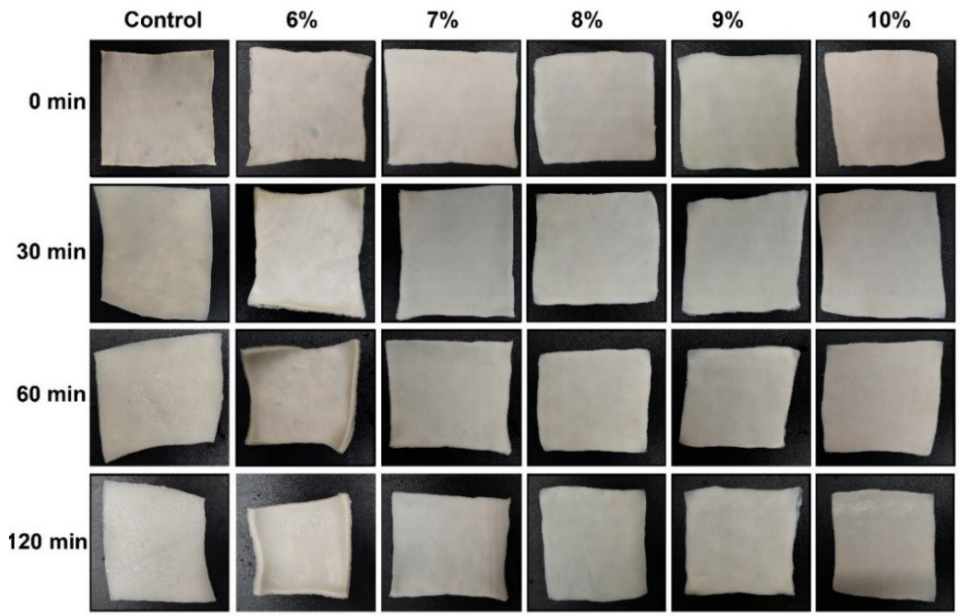

Fig. S3 Photos of crust leather treated with different dosages of EHBP after pickling at different times

Physical mechanical properties

Table S4. Physical mechanical characteristics of different treated leather

Type	EHBP	EHBP&5%AL	EHBP&6%AL	EHBP&7%AL	EHBP&8%AL	8%AL
Thickening rate (%)	60.67	60.98	67.79	67.57	64.47	63.4
Softness (mm)	5.37±0.50	5.04±0.45	5.31±0.45	4.78±0.63	5.11±0.84	5.28±0.42
Tensile strength (MPa)	8.59±1.24	9.41±1.22	11.68±2.31	10.39±1.53	9.53±0.95	9.38±1.27
Tear strength (N/mm)	23.06±2.36	25.41±3.56	27.45±2.73	24.24±4.47	21.80±2.44	21.36±2.58
Elongation at break (%)	78.79±10.04	79.17±12.59	95.78±8.43	93.86±10.47	84.14±5.47	85.40±7.11

EHBP pre-tanned and chromium tanned leather

After the implementation of pre-tanning with EHBP and salt-free pickling, it can not only choose aluminum tanning, but also other chrome-free metal tanning agents, or chrome tanning to obtain different styles of crust leather. For instance, replace aluminium tanning agent with 6% chromium tanning agent, and other processes are similar to **Table S1** and **Table S2** to obtain EHBP & chromium tanning leather. Then, the hydrothermal stability, physical and mechanical properties of the EHBP & 6% chromium tanned leather, including T_s, tensile strength, elongation at break, tear strength, thickness and softness were characterized and results were shown in **Fig. S4**. Furthermore, the grain of EHBP & 6% chromium treated leather was characterized by ultra-depth-of-field three-dimensional microscopy, and the degree of fiber dispersion was explored by Field emission scanning electron microscope, as well as the EDX was used to analyze the composition and distribution of elements, which presented in **Fig. S5**.

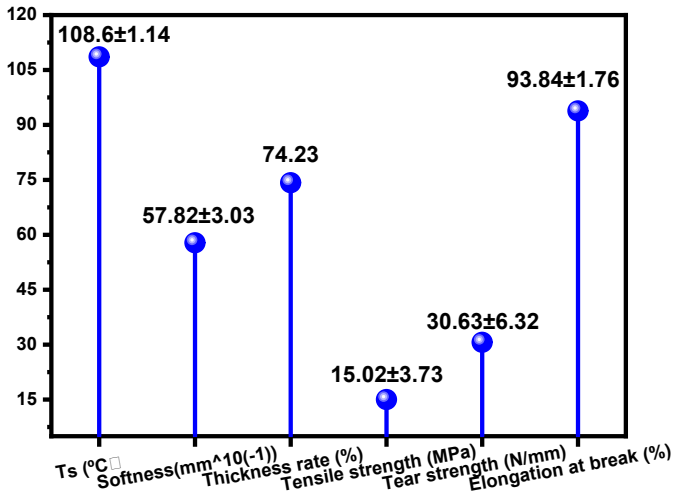

Fig.S4 The T_s value, physical and mechanical properties of the EHBP & 6% chromium tanned leather.

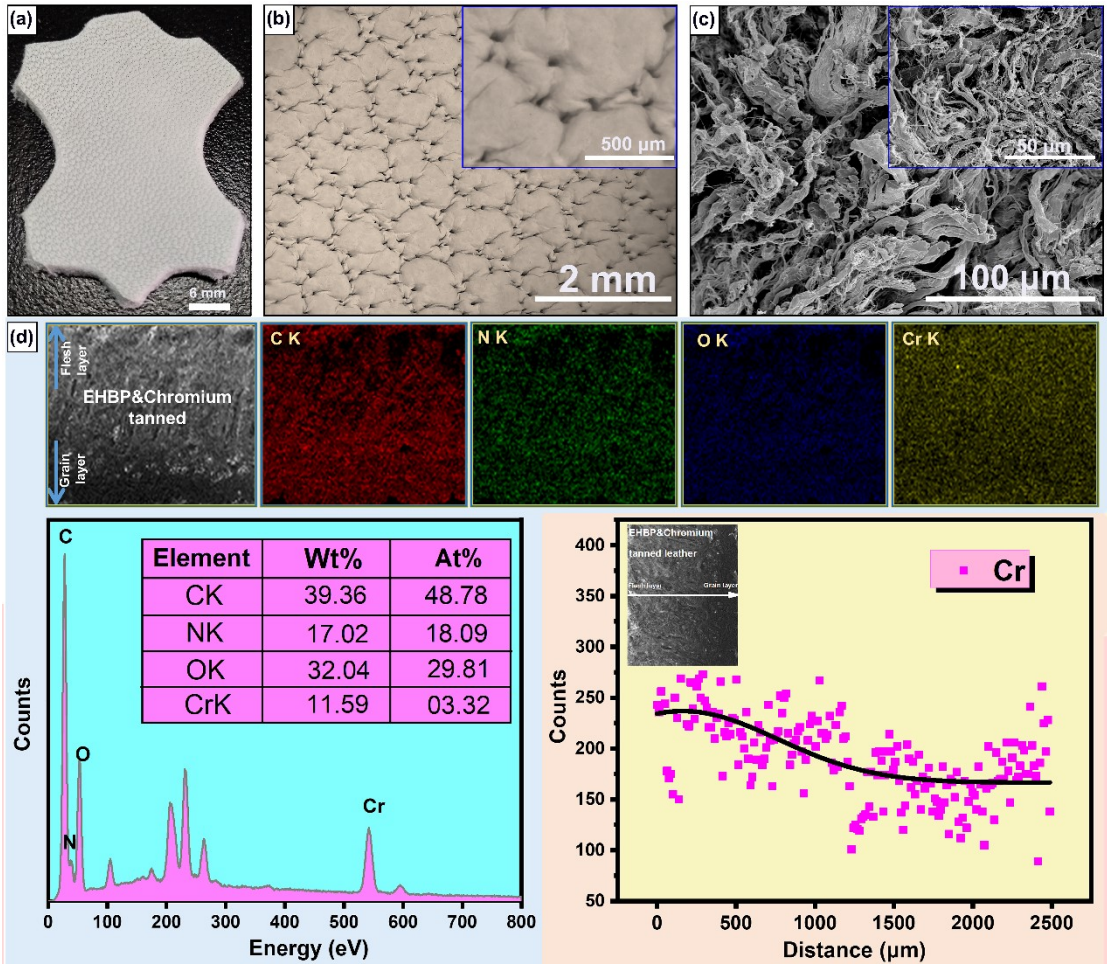

Fig. S5 Optical photos (a), super depth-of-field three-dimensional microscopic grain images (b), SEM images of longitudinal section (c) and the corresponding EDX mappings (d) of EHBP & 6% chromium tanned leather.

As demonstrate as **Fig. S4**, the hydrothermal stability was significantly improved of the EHBP & chromium tanned leather, and the T_s reached 108.6°C. The thickening rate is more than 70% (**Fig. S5**), surpassing that of EHBP & AL tanned leather. Furthermore, the physical and mechanical properties are also quite well. Compared with EHBP & AL tanned leather, the overall performance

of EHBP & chromium tanned leather be superior, which due to the excellent performance of chromium tanning, although it will bring chromium pollution, it is indeed beyond the reach of most current tannage[3]. Fortunately, the implementation of pre-tanning with EHBP and salt-free pickling can eliminate the widespread neutral salt pollution in leather industry and realize less-chrome tanning.

Water-vapour permeability of different treated leather

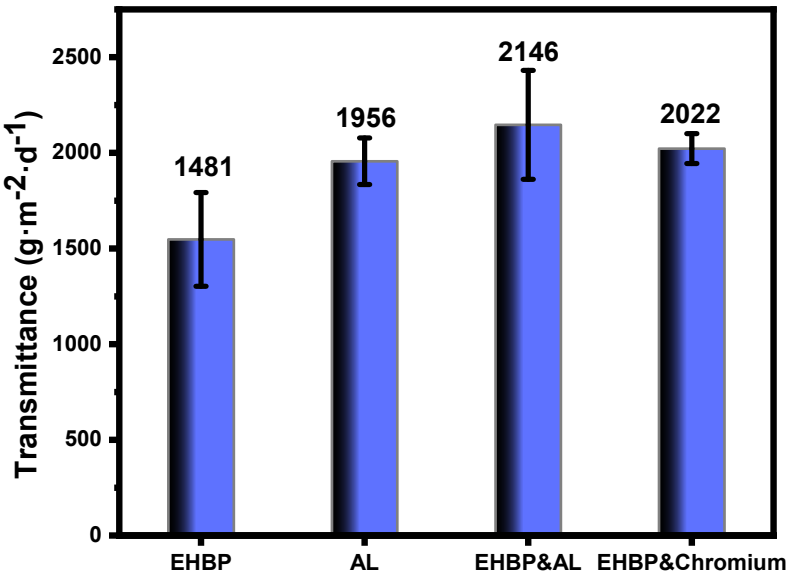

Fig. S6 The water-vapour permeability of different treated leather

Water vapor permeability is an important index of the hygienic performance of leather, just because the natural leather possesses this performance to expel the sweat from the wearer's body and keep comfortable wearing experience, which is beyond all synthetic materials nowadays. The water-vapor permeability of different treated leather was characterized by static method[4],

and the result was shown in **Fig. S6**. As described as **Fig. S6**, the combined tanned leather showed better water vapor permeability, of which, the aluminum combined tanned leather was slightly higher than the chromium combined tanned leather, while the EHBP pre-tanned leather manifested the worst performance, which was mainly contributed to the dispersion of collagen fibers.

References

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