Is tanning indispensable for the conversion of rawhide to leather?

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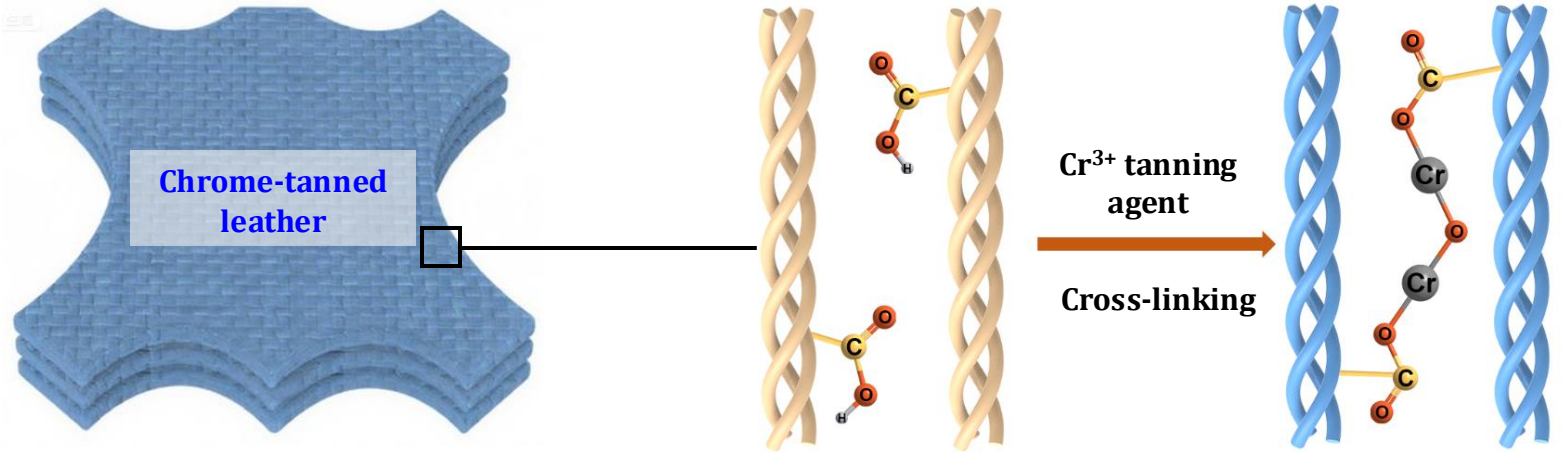
Main contents

The Classic Tanning Theory

In leather industry, tanning is considered to be the most important and indispensable step in converting rawhide into leather.

Based on the classic tanning theory, the cross-linking is a critical step for the conversion of rawhide to leather, which is believed to be indispensable for enhancing the thermal stability and dispersity of rawhide.



Tanning Effect	Enhanced thermal stability	Improved fiber disperstity

Trivalent chrome (Cr^{3+}) salt has been considered to be the most successfully tanning agent that relies on the coordination with collagen molecules to achieve the cross-linking of rawhide, eventually showing high thermal stability and excellent dispersibility.

The Classic Tanning Theory

Chrome-tanning → Chrome-containing discharges → ☐ Potential environmental pollution

Environmental concern raised from chrome-tanning

However, chrome tanning inevitably generates **chrome-containing discharges** during the tanning process, which **raises environmental concerns** that have to be resolved for realizing the sustainable development of leather industry.

Official Journal of the EU

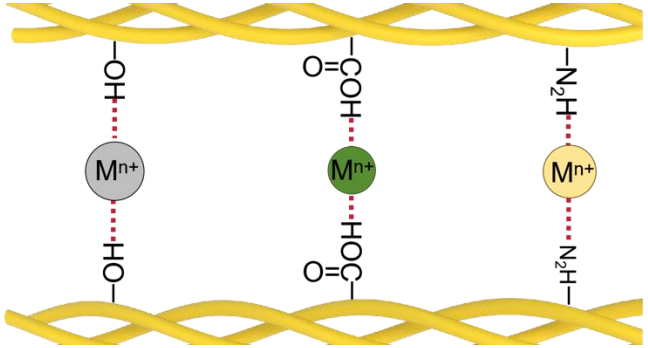
- **Germany** enacted the 2nd Amendment to the Food and Commodities Act, **baning the import of textiles and leather containing azo dyes**
- **EU** published Directive 2002/61/EC, which bans the import of **leather containing 22 types of azo dyes.**
- **EU** enacted the RoHS Directive, which restricts **Cr(VI)**, Pb, Cd, etc.
- **EU** Directive 2003/34/EC has come into force, **restricting 25 types of chemical substances.**
- **EU** Directive 2003/36/EC has come into force, **restricting 43 types of chemical substances.**
- **EU** has revised the RoHS Directive to further **expand its scope of control.**

The international community is imposing increasingly strict controls on such hazardous waste, which is specifically reflected in the fact that many countries are continuously raising the limit requirements for hazardous substances such as chromium in leather products by formulating technical standards based on environmental safety.

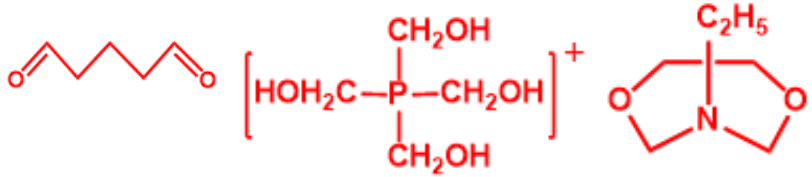
The Classic Tanning Theory

To address the challenging issue, tremendous investigations have been dedicated to developing chrome-free tanning techniques, including no-chrome metal tanning and organic tanning.

Non-chrome metal tanning



Organic tanning



Glutaraldehyde | Organic phosphine salt | Oxazolidine

Although these chrome-free tanning techniques eliminate the use of trivalent chrome (Cr^{3+}) salt, these techniques still follow the principle of classic cross-linking theory, which utilize non-chrome metals or organic compounds to cross-link the collagen in rawhide.

Chrome-free tanning

- Non-chrome metal tanning
- Organic tanning

■ **Nevertheless, all current chrome-free tanned leathers still fail to provide desired thermal stability and mechanical strength that are comparable to those of chrome-tanned leather, and these chromefree tanning process still involved the discharge of nonchrome metal or organic pollution.**

The Classic Tanning Theory

- These attempts of past several decades on non-chrome tanning promoted us to meditate on whether cross-linkage is a real necessity to accomplish the tanning of leather.

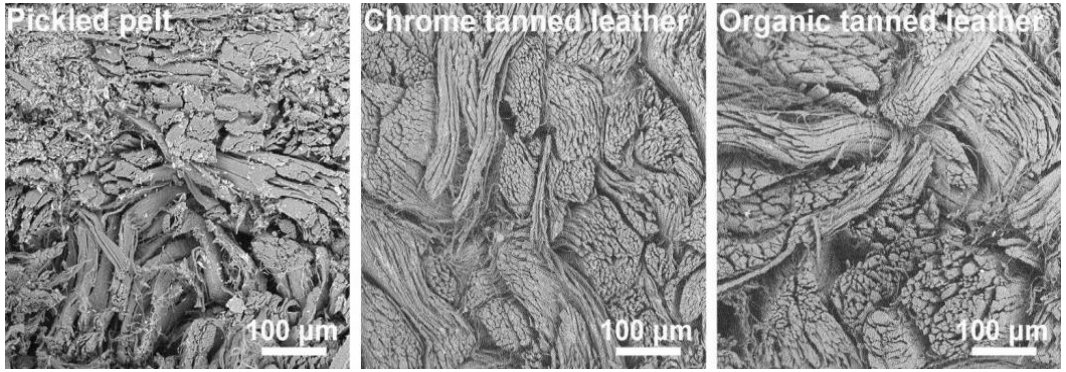
- If cross-linkage is not indispensable for the rawhide to convert to leather, a breakthrough of environmentally benign and sustainable leather manufacture is likely possible to achieve by a complete elimination of the use of tanning agent that is a necessity for a conventional cross-linking theory-based tanning process of leather making.

The Classic Tanning Theory

Decreased water content

Process stage	water content of collagen
Liming	~400
Deliming/bating	~320
Tanning	~160
Dewatering/shaving	~80
Drying	~45
Finished leather	~35

Improved Fiber dispersity

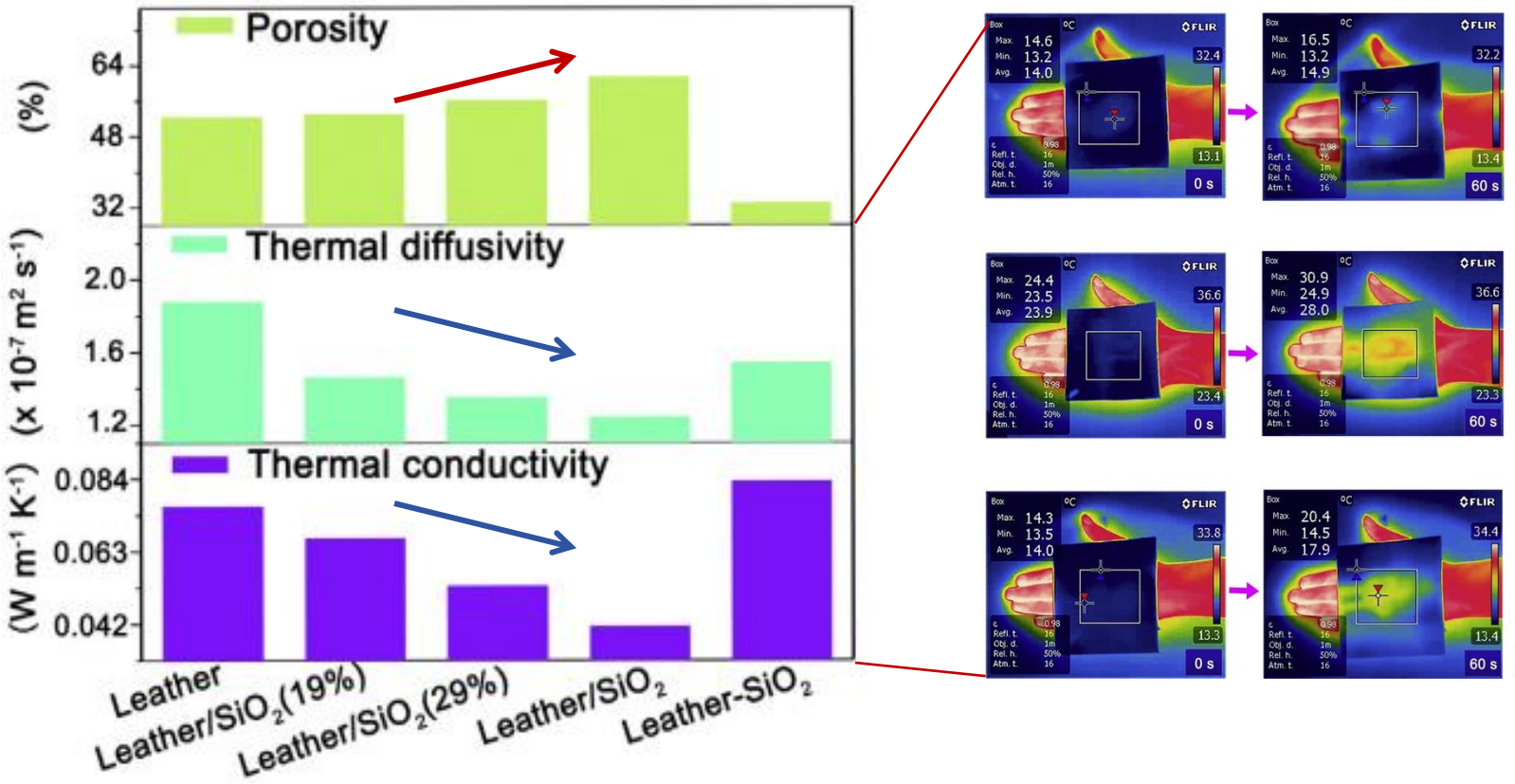


- The leather manufacture process begins with rawhide containing about 65% of water and ends with leather containing only about 15% of water.

- Moreover, the water absorption capacity of leather was found to substantially decrease as compared with that of rawhide.
- Along with the proceeding of the dehydration process, the collagen fibers also exhibit improved dispersity.

Therefore, the tanned leather obtained from tanning has a low water content and significantly improved fiber dispersity compared with the rawhide. The essence of tanning can be regarded as a controllable drying process of the rawhide.

The Controllable Drying Strategy



- On the other hand, the porosity of tanned leather was often found to significantly increase as compared with that of the rawhide, which is actually the consequence of dehydration of rawhide.

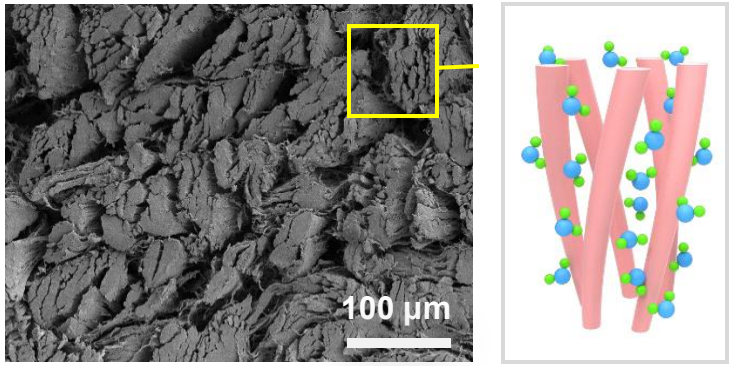
Wang, X., Tang, Y., Wang, Y., Ke, L., Ye, X., Huang, X., & Shi, B. (2019).. *Chemical Engineering Science*, *196*, 64-71.

The increased porosity contributes to the high thermal stability of the collagen-based material.

The Controllable Drying Strategy

If the necessity of rawhide converted to leather is not the formation of cross-linkage among collagen fibers but the regulation of water content in rawhide, the essence of leather making can be regarded as a controllable dehydration process of rawhide, which is accompanied with increased dispersity of collagen fibers in rawhide.

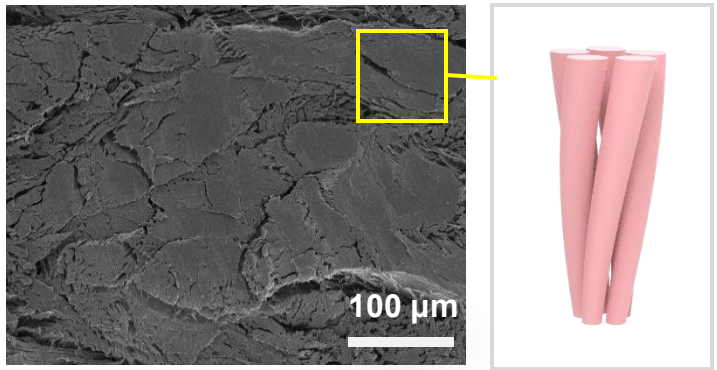
The rawhide



High fiber dispersity

Drying

Directly dried hide



Serious sticking of collagen fibers leads to low porosity

The collagen fibers in the rawhide will become sticky if directly dried. Based on this different viewpoint of leather making, polar organic solvent is more preferred alternative than chrome tanning to achieve more efficient controllable dehydration of rawhide.

The sticking problem of CFs is believed to be strategically resolved by controllable drying of the rawhides through polar organic solvent

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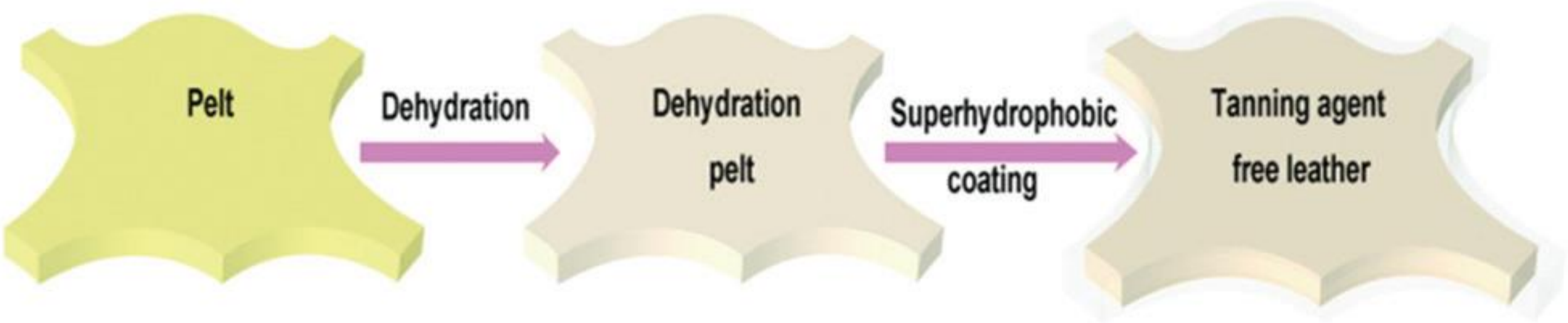
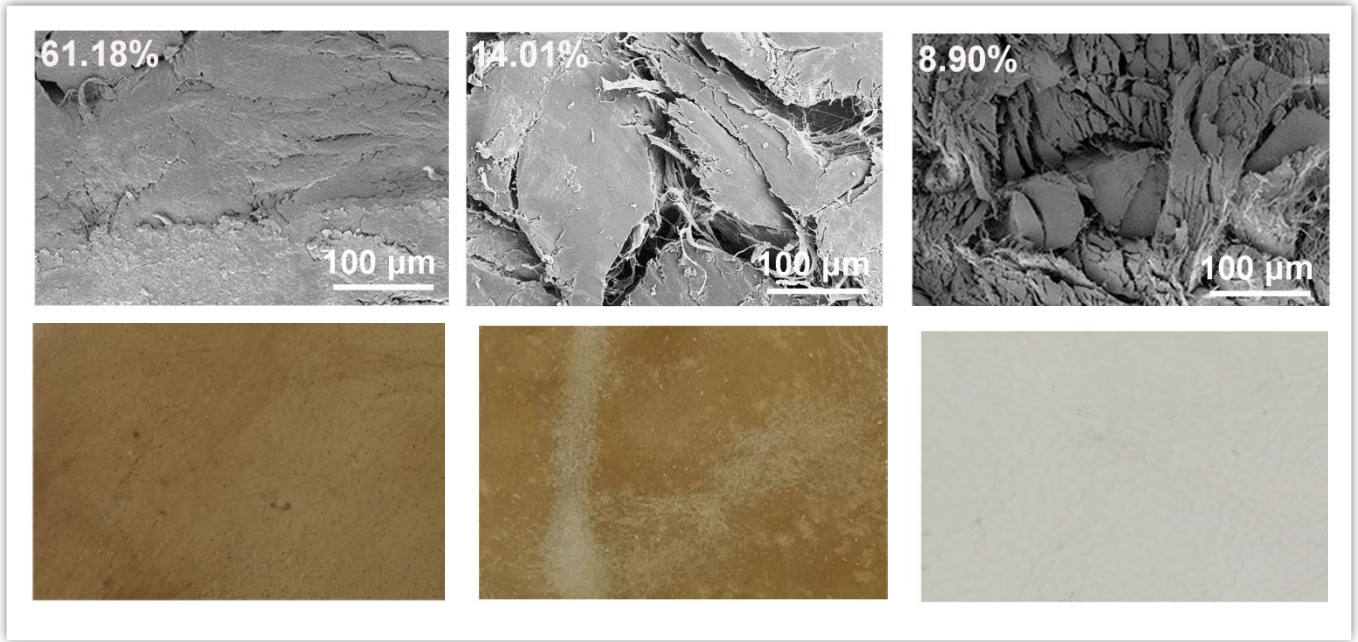
The Tanning-Free Leather



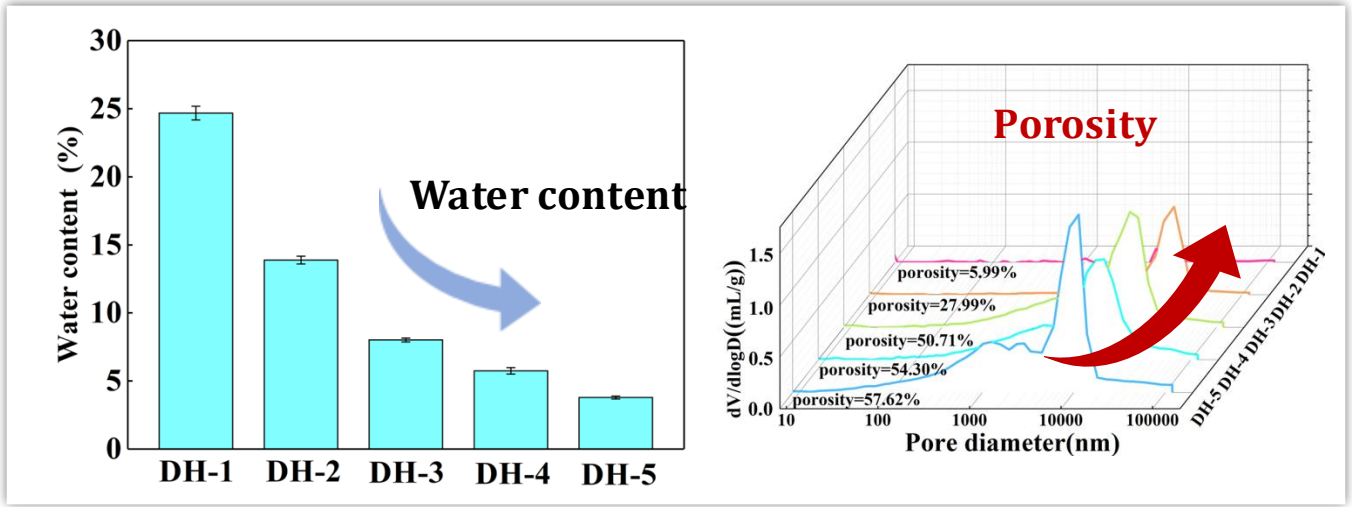
Based on the above considerations, we here demonstrated a conceptual new tanning agent free strategy by increasing the porosity and dispersity of collagen fibers via controlled dehydration with organic solvents, followed by the fixation of the resultant porous structure of the pelt through a superhydrophobic coating. Here, we employ ethanol as the dehydrating solvent.

The Tanning-Free Leather



- Ethanol could quickly displace most of the water in the rawhides under the osmotic exchange of ethanol in the float and water inside the rawhides, thus leading to the dramatic reduction of the water content of the rawhide.

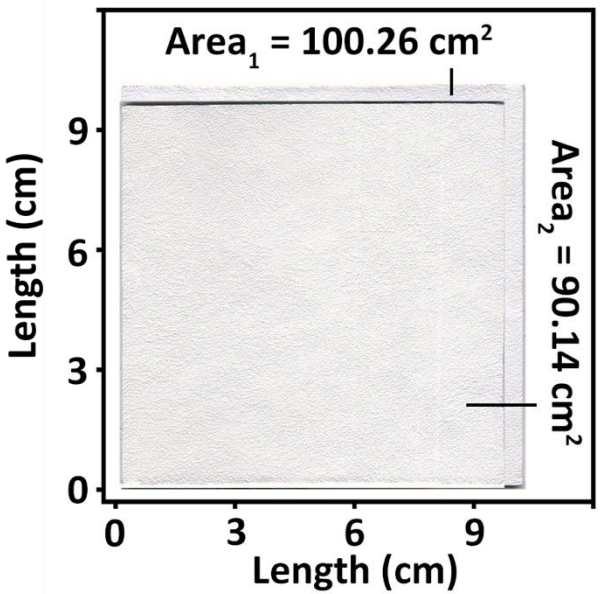
- The presence of water in rawhide serves as glue to adhere collagen fibers together and a high content of water leads to low porosity due to sufficient adhesion.



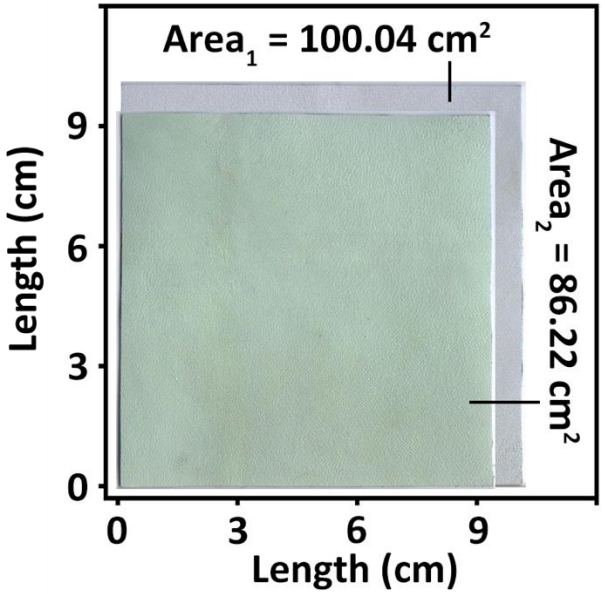
- Decreasing the water content in the rawhides allows the dispersity of collagen fibers, showing alleviated adhesion with an obvious increase in porosity. Hence, we believe that the water content of rawhides has critical influences on the porosity and the dispersity of collagen fibers.

The Tanning-Free Leather

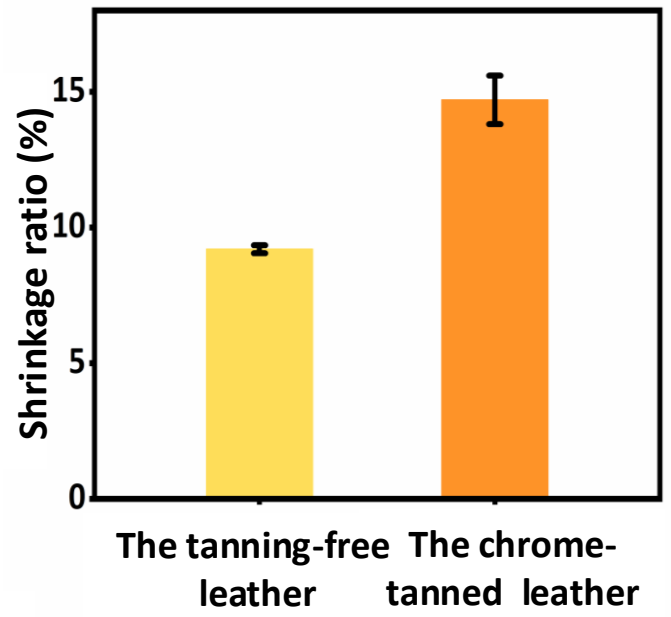
➢ **The area of controllable-dehydrated hide and chrome-tanned leather shrink after heat treatment at 150 °C for 30 min.**



The tanning-free leather



The chrome-tanned leather



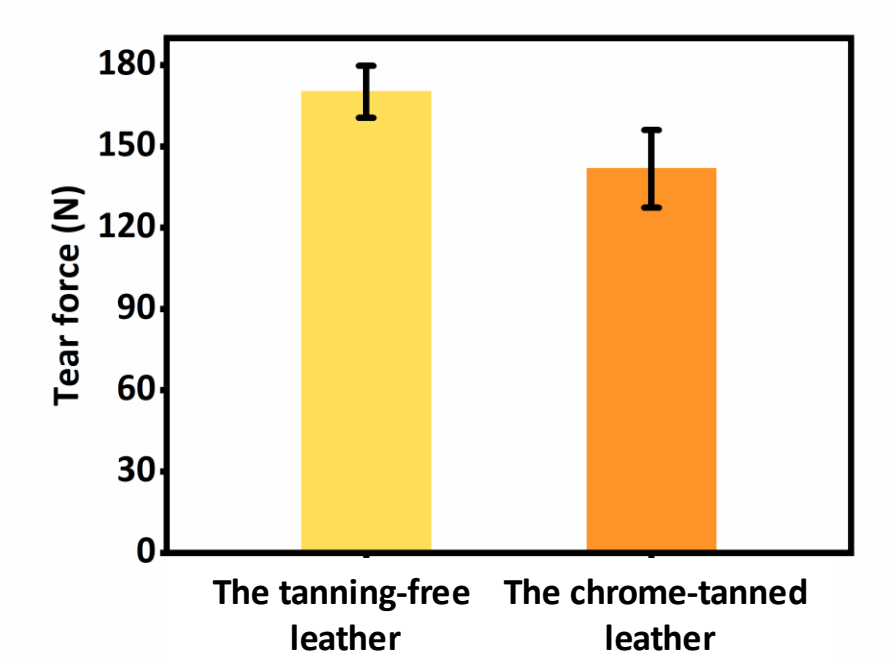
◆ **The shrinkage ratio of controllable-dehydrated hide was as low as 9.20%, while that of chrome-tanned leather was high up to 14.70%.**

Thermal stability is an important critical index for estimating the durability of leather in practical utilization. The obviously enhanced thermal stability of controllable-dehydrated hide indicates that the deep dehydration using ethanol media is capable of providing comparable and even better leather-like properties than the conventional chrome-tanned leather.

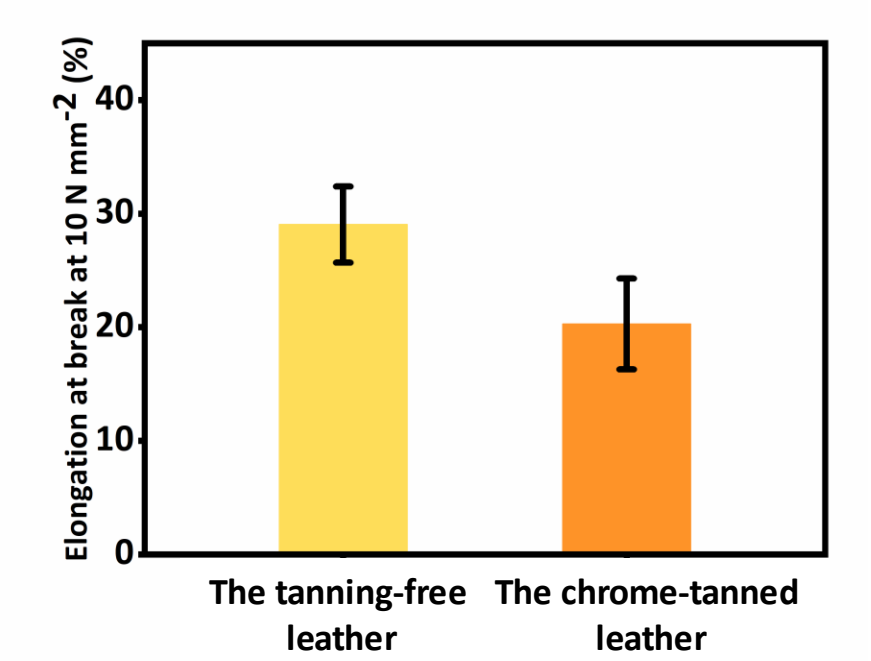
The Tanning-Free Leather

➢ **Mechanical properties of the tanning-free leather meet the criteria of leather standards**

Tear force

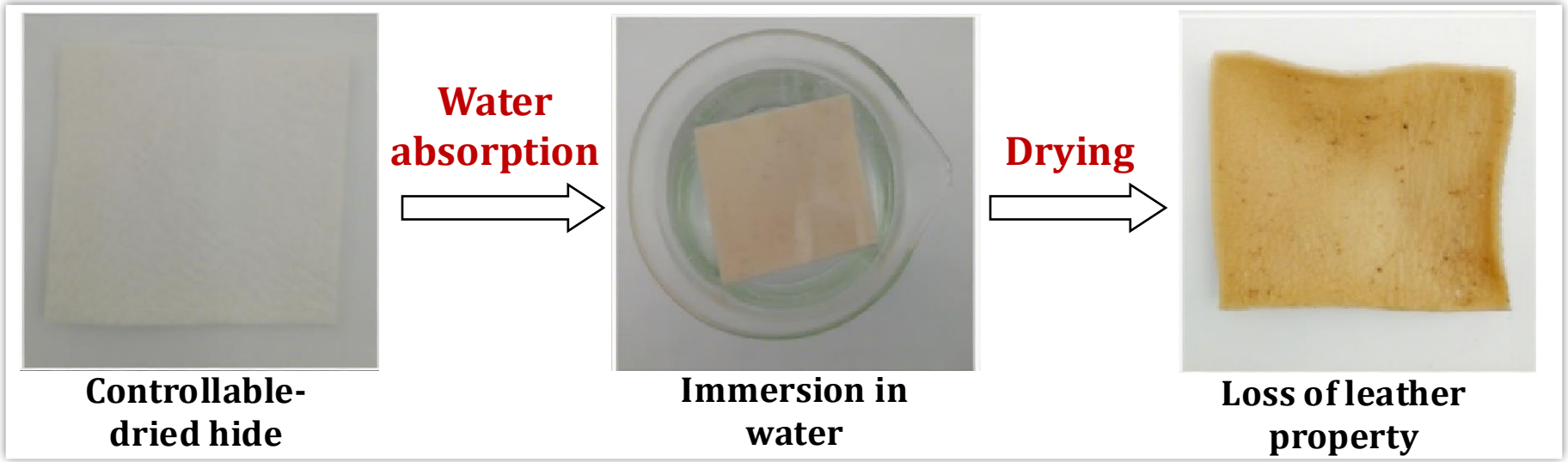


Elongation rate under specified load



Compared with the conventional chrome-tanned leather, the controllable-dehydrated hide exhibits superiority in mechanical properties of tear force and tensile strength when compared with the chrome-tanned leather.

The Tanning-Free Leather

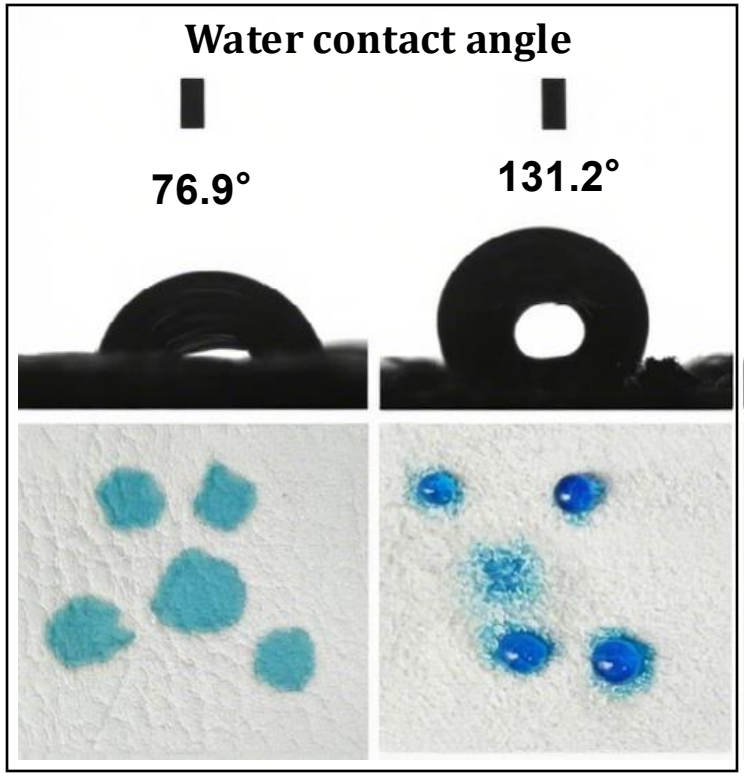


- The dehydration process endows rawhides with leather-like properties. Unfortunately, the dehydrated rawhides are easy to lose the leather-like properties due to their high tendency to re-absorb water.

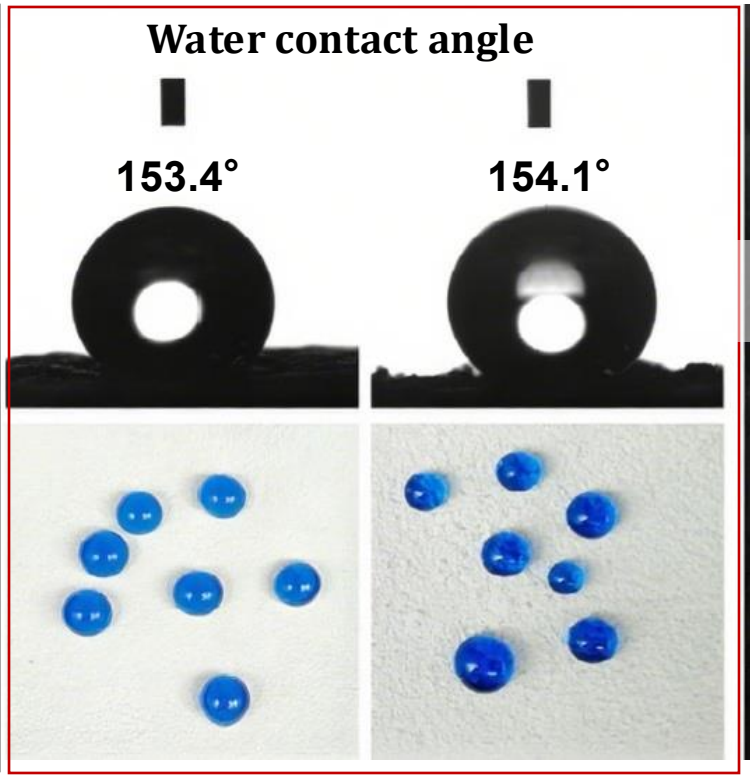
➢ Superhydrophobic treatment

- superhydrophobic coating is a straightforward and effective approach for the dehydrated rawhides to obtain long-term durable leather-like properties.

The Tanning-Free Leather



The controllable-dried hide



The superhydrophobic tanning-free leather

After being treated under the optimized conditions, the resultant tanning agent free leather exhibited outstanding water repelling properties, on which water droplets that were dyed with methyl blue appeared spherical on the grain surface and flesh surface of the as-treated dehydrated rawhides.

The water contact angles of water droplet on the grain surface and flesh surface of the decorated dehydrated rawhides are 153.4º and 154.1º, respectively, which further prove the superhydrophobicity of the as-prepared dehydrated rawhides.

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Summery

01 Controllable drying endows rawhide with high fiber dispersity during the drying process.

02 High fiber dispersity enhances the thermal stability of rawhide.

03 Cross-linking is not indispensable for the conversion of rawhide to leather, while the controllable drying is a promising alternative for eco-friendly leather making.

Acknowledgement

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- National Natural Science Foundation of China, National Key R&D Program, *etc.*
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Thanks for listening