Insight into the Correlations Between Fiber Dispersion and Physical Properties of Chrome Tanned Leather

by
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Abstract

The correlations between fiber dispersion and physical properties of chrome tanned leather were investigated to provide new insights into improving leather quality and designing tanning agents and tannages. Wet blues were prepared by tanning pickled pelts with different amounts of chrome powder, and their pore structures in the range of 5.48 nm–120 μm were measured using a mercury intrusion porosimetry (MIP). The porosity and total pore area of wet blue increased with increasing amount of chrome powder from 2% to 8%. These MIP data combined with the images observed using a field emission scanning electron microscopy and a scanning transmission electron microscopy–energy dispersive spectroscopy indicated that chrome tanning agent opened up the microfibrils, fibrils, elementary fibers and fiber bundles of wet blue. The sufficient fiber dispersion of wet blue was attributed to the fact that chrome tanning agent penetrated into the microfibrils and fixed collagen fibers from microfibril level to fiber bundle level. The wet blues were then fatliquored to prepare crust leathers. The tensile strength, tear strength, elongation at break, softness, fullness and water vapor permeability of the leathers improved with increasing chrome powder. These results implied that there is a positive correlation between fiber dispersion and physical properties of chrome tanned leather.

Introduction

Leather products are popular goods due to their high mechanical strength, unique organoleptic properties, excellent water vapor permeability and so on.[1] Modern leather processing mainly involves beamhouse, tanning and post-tanning processes.[2] The beamhouse process removes unwanted components from raw hides/skins and opens up their collagen fibers to facilitate the penetration of tanning agents.[3–5] The tanning process converts putrescible raw hides/skins into durable leathers by crosslinking collagen fibers with tanning agents.[6–9] During this process, adhered fibers of pelts are turned into a stably dispersed state.[8] The post-tanning process improves the organoleptic and mechanical properties of leathers with various retanning agents, dyes and fatliquors.[10,11] The usage of these agents also changes the dispersion of collagen fibers.[2] Generally, the fiber dispersion of leather is affected by almost all processes. Tanners have believed that the properties of leather are closely related to its fiber dispersion. However, the correlation between fiber dispersion and physical properties of leather remains unclear.

Leather is a fibrous material with hierarchical structure, which from primary level to high level is woven by tropocollagens, microfibrils, fibrils, elementary fibers and fiber bundles.[12–15] The tanning process greatly influences the microstructure of collagen fibers, and the effect of tanning agents on the fiber dispersion at high level (elementary fibers and fiber bundles) has been observed by scanning electron microscopy (SEM) and biological microscopy. [3,6–8,15–18] However, minimal attention has been paid to the change in fiber dispersion at primary level (tropocollagens, microfibrils and fibrils), because it is difficult to observe the fiber dispersion at this level by common technologies.[3,4] Previous studies showed that the microstructure of fabrics affects their macroscopic properties. Niu et al. reported that the increased orientation of fiber molecular structure improves the tensile strength and elongation of wool fiber, compared with parent wool fiber.[19] Hence, the fiber dispersion of leather at primary level may significantly affect the macroscopic properties of leather. We previously verified that the mercury intrusion porosimetry (MIP) can measure the pore structure of leather in a wide range to quantify its fiber dispersion from primary level to high level with high accuracy.[20] Thus, we planned to investigate the change in fiber dispersion at primary level during tanning process by using MIP.

This study aimed to assess the correlation between fiber dispersion and physical properties of chrome tanned leather and to give some suggestions for improving leather quality and developing novel tanning agents and tannages. Wet blue with different fiber dispersion degrees were prepared by tanning pickled pelts with different amounts of chrome powder. Field emission scanning electron microscopy (FESEM), scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDS) and MIP were used to analyze the fiber dispersion of these wet blue from primary

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level to high level. After fatliquoring, the physical properties of the crust leathers, including tensile strength, tear strength, elongation at break, softness, fullness and water vapor permeability were determined, so that the correlation between fiber dispersion and physical properties of leather can be analyzed.

Experimental

Materials

Pickled cattle pelts were purchased from Ruixing Leather Co., Ltd. (Haining, China). Chrome powder (24% Cr_2O_3, 33% basicity) was supplied by Minfeng Chemical Co., Ltd. (Chongqing, China). The other reagents used for leather processing were of commercial grade. The chemicals utilized for analyses of leathers were of analytical grade.

Preparation of Wet Blue and Crust Leathers

To obtain wet blue, four pieces of pickled cattle pelts cut from back region were tanned by 2%, 4%, 6% and 8% of chrome powder, respectively, as shown in Table I. The wet blue were then rewetted, neutralized and fatliquored following the post-tanning processes shown in Table I to prepare crust leathers. The wet blue and crust leathers tanned by 2%, 4%, 6% and 8% of chrome power were recorded as Cr-2, Cr-4, Cr-6 and Cr-8, respectively.

Morphological Observation

The pickled pelt and wet blue samples were collected and lyophilized by freeze dryer (LGJ-30F, XinYi, China). Next, the cross sections of these samples were observed by FESEM (Nova Nanosem 450, FEI, USA). Besides, the lyophilized samples were embedded in epoxy resin and then sliced into 100 nm thickness using a freezing microtome (UC7, Leica, Germany). The thin slices were placed on copper fabricates for imaging at 200 kV by STEM (JEM 2100F, JEOL, Japan), and for surface elemental analysis by EDS (X-Max^N 80T, Oxford, UK). The cross sections of crust leather samples were observed by SEM (Phenom Pro, Phenom-world, Netherlands).

Measurement of Pore Structure

The pickled pelt and wet blue samples were lyophilized, and the crust leather samples were dried at 45 °C for 48 h. Then, the pore structures of the pickled pelt, wet blue and crust leather samples were measured using a mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics, USA) as described by He et al.[20]

Determination of Chrome Content

A total of 0.1 g dried wet blue sample was digested with the mixture of nitric acid (10 mL) and H_2O_2 solution (5 mL, 30wt%) with a microwave digestion instrument (Multiwave PRO, Anton Paar,

Table I

Tanning and post-tanning processes

Process	Chemicals	Amount[a] (%)	Temperature (°C)	Time (min)	Remarks
Pickling	Water	100	22		
	Sodium chloride	7		10	
	Formic acid	0.3		30	pH=2.9
Tanning	Chrome powder	X	22	180	X=2, 4, 6, 8
	Sodium formate	1	22	30	
	Sodium bicarbonate	(0.1-0.3)×n		15×n+30	pH =3.8
	Water	100	40	180	
Next day, run 30 min. Horsing up and wringing. Wet blue sampling.					
Rewetting	Water	400	35		
	Degreasing agent	0.3		60	
Washing	Water	400	35	10	
Neutralizing	Water	200	35	30	
	Sodium formate	2			
	Sodium bicarbonate	1.2		10+60	pH=6.2
Washing	Water	400	40	10	
Fatliquoring	Water	200	50		
	Compound fatliquor	6			
	Surface fatliquor	3			
	Synthetic fatliqour	1		60	
	Formic acid	0.6		30	pH=3.8
Washing	Water	400	25	3×10 min	
Horsing up, drying and staking. Crust leather sampling.					

[a] The percentage of chemicals was based on the double weight of pickled pelt.

Austria). The digestion solution was properly diluted to 50 mL to determine the chrome content by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 8000DV, PerkinElmer, USA). The chrome content of wet blue was calculated as follows:

$$\text{Chrome content} = (c \times 0.05)/(m \times 1000) \times 100\%$$

Where c is the chrome concentration measured by ICP-AES (mg/L), 0.05 is the volume of diluted digestion solution (L), and m is the mass of the dried sample (g).

Determination of Physical Properties of Crust Leather

The dried crust leather samples were conditioned at 20 °C and 65% relative humidity for 48 h in accordance with IUP 3 method, and then sampled to determine physical properties. The tensile strength, tear strength and elongation at break of the samples were measured according to the IUP 6 and IUP 8 methods using a tensile tester (AI-7000SN, Gotech, China). The softness of the samples was measured using a standard leather softness tester (GT-303, Gotech, China) following the IUP 36 method. The fullness of sample was evaluated by compressed and resilient thicknesses using the method described by Penget al.[21] The water vapor permeability was measured using a GT-7005-E instrument (Gotech, China) following the IUP 15 method.

Results and Discussion

Fiber Dispersion of Wet Blue

As mentioned earlier, the aim of this study was to assess the correlation between fiber dispersion and physical properties of chrome tanned leather. Therefore, wet blue with different fiber dispersion were first prepared by tanning pickled pelts using different amounts of chrome powder varying from 2% to 8%. The fiber dispersion of pickled pelt and wet blue was observed by FESEM at different magnifications. The low magnification FESEM images in Figure 1 show that the fiber bundles (Φ 20–200 μm)[12] of the pickled pelt were adhesive, while those of the wet blue were highly dispersed. Moreover, the degrees of fiber dispersion of wet blue increased with increasing chrome content. Here, the chrome content of wet blue increased from 1.05% to 2.27% when the amount of chrome powder rose from 2% to 8%. This suggested that high chrome content of wet blue favored the crosslinking and fixation collagen fibers. It is worth noting that the degrees of fiber dispersion increased slightly when the amount of chrome powder exceeded 6%, because the carboxyl on collagen that can react with chrome is limited.

The high magnification FESEM images in Figure 2 show the fiber dispersion of the pickled pelt and wet blue at primary level. The chrome tanning process increased the dispersion of fibrils and the clearness of collagen D–period. This implied that the chrome tanning agent penetrated into the fibrils. The STEM images in Figures 3(a) and 3(d) show that alternately arranged light banding (~0.6 D gap) and dark banding (~0.4 D overlap) were observed in

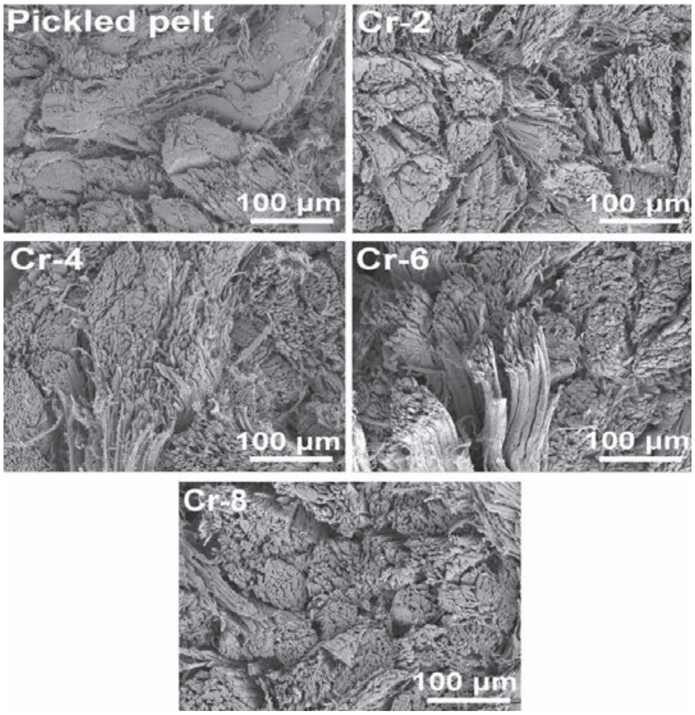

Figure 1. Low magnification FESEM images of cross sections of pickled pelt and wet blue.

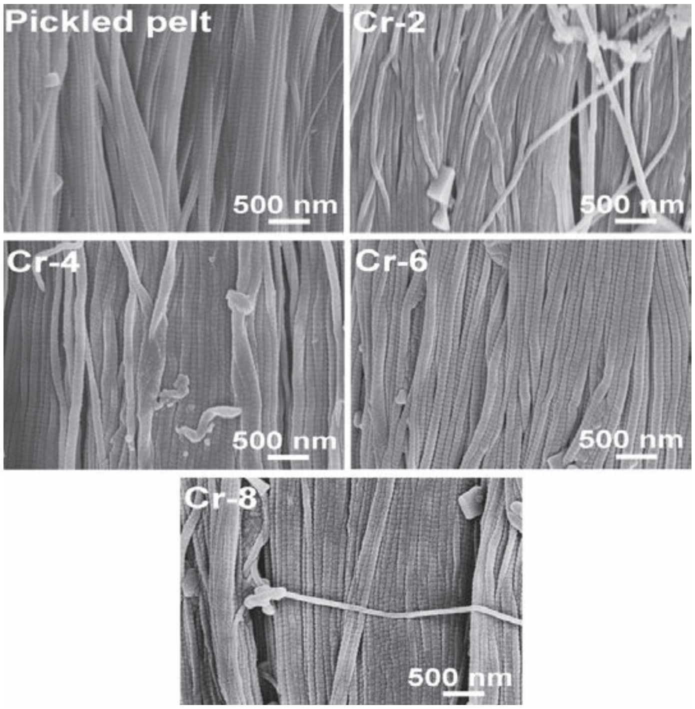

Figure 2. High magnification FESEM images of cross sections of pickled pelt and wet blue.

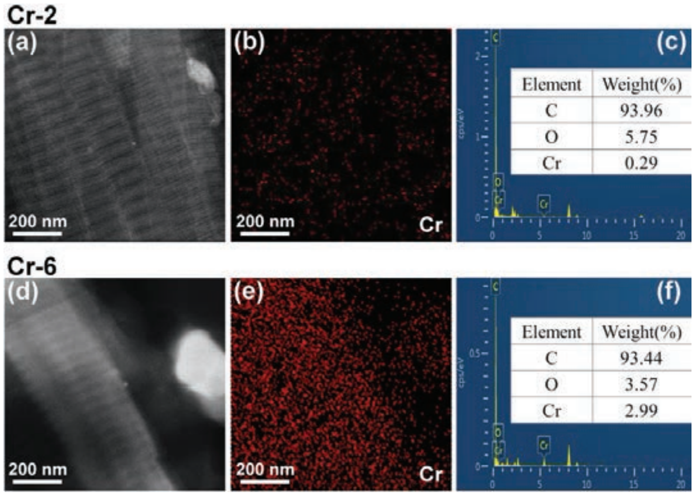

Figure 3. STEM and EDS mapping images of wet blue tanned by 2% chrome powder (a-c) and 6% chrome powder (d-f).

Table II

Effect of amount of chrome powder on pore structure of wet blue.

Wet blue	Average pore diameter (nm)	Porosity (%)	Total pore area (m^2/g)
Pickled pelt	1955.79	49.73	1.449
Cr-2	1691.38	50.25	2.212
Cr-4	1130.14	50.90	2.998
Cr-6	841.36	56.79	4.066
Cr-8	806.04	57.80	4.418

fibrils. The characteristic D-period structure was approximately 65 nm, which was close to the value reported in literature.[22] The wet blue had uniform distribution of chrome within the fibrils (Figures 3(b) and 3(e)), which also indicated that the chrome tanning agent could penetrate into the fibrils. By comparing Figures 3(c) and 3(f), it was found that higher content of chrome in the fibrils led to better fiber dispersion at fibril level.

In our previous work, we demonstrated that the dispersion of collagen fibers can be evaluated by its pore structure with MIP.[20] Table II lists the pore structure properties of pickled pelt and wet blue. The pickled pelt had the largest average pore diameter but the lowest porosity and total pore area. As for the wet blue, the average pore diameter decreased while the porosity and total pore area increased with increasing chrome powder. These results suggested that better fiber dispersion of wet blue was obtained with higher amount of chrome powder.

The pore size distribution was categorized using a theoretical model to further evaluate the fiber dispersion of pickled pelt and wet blue. The pore sizes of microfibrils, fibrils, elementary fibers and fiber bundles are smaller than 12 nm, 100 nm, 1000–3,000 nm and larger than 3000 nm, respectively.[23] Figure 4 shows that the pores in pickled pelt mainly ranged from 3000 nm to 50000 nm, whereas nearly none of them ranged from 5.48 nm to100 nm. These findings combined with the low magnification FESEM images (Figure 1) indicated that the fiber dispersion of pickled pelt was mainly concentrated at the fiber bundle level. After chrome tanning, the distribution of pore size in the range of 5.48–3000 nm increased from 26.91% to higher than 50%. Moreover, the pores in the range of 5.48–100 nm increased with increasing chrome powder. These results implied that a large number of pores at the microfibril, fibril and elementary fiber levels were formed by chrome tanning.

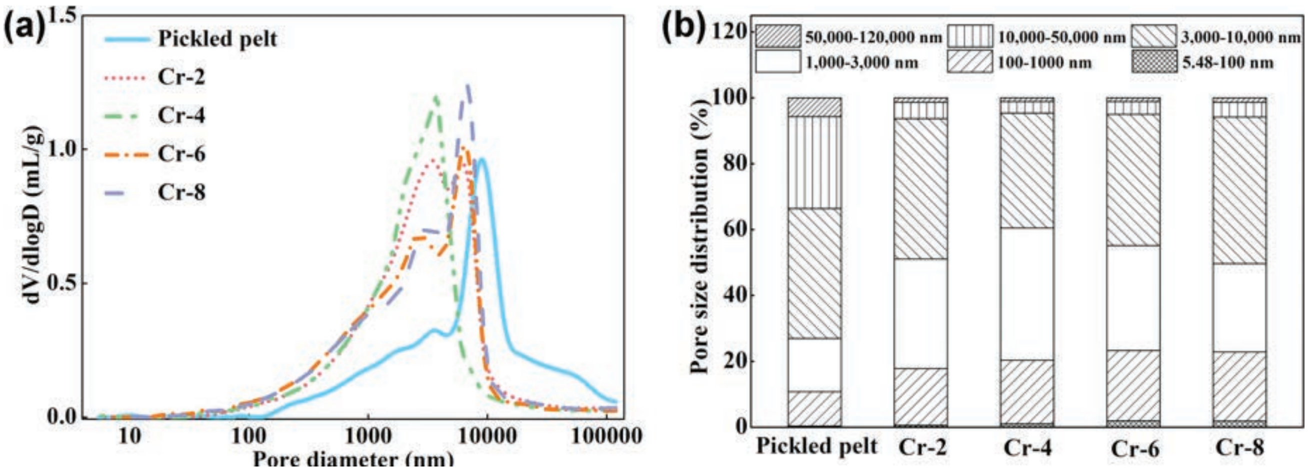

Figure 4. Effect of amount of chrome powder on pore size distribution of wet blue.

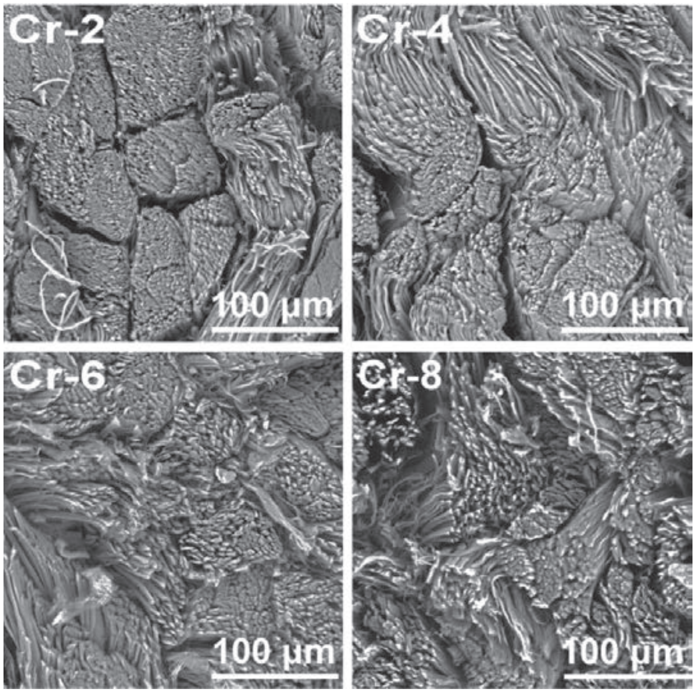

Figure 5. SEM images of cross sections of crust leathers.

Table III

Effect of amount of chrome powder on pore structure of crust leather.

Crust leather	Average pore diameter (nm)	Porosity (%)	Total pore area (m2/g)
Cr-2	1937.52	44.56	1.373
Cr-4	1442.02	44.81	1.744
Cr-6	1176.50	45.41	1.821
Cr-8	829.76	47.66	2.770

In summary, the results of FESEM, STEM–EDS and MIP confirmed that leathers with different fiber dispersion were obtained by tanning pickled pelts using different amounts of chrome tanning agent. Chrome tanning process plays an important role in the fiber dispersion of leather from primary level to high level because of deep penetration of chrome tanning agent.

Fiber Dispersion of Crust Leather

The wet blue samples were then fatliquored to prepare crust leathers, which can be determined for physical properties of leather. Because fatliquors would affect the dispersion of collagen fibers,[2] the fiber dispersion of crust leathers was analyzed by SEM and MIP. As shown in Figure 5, the degrees of fiber dispersion of crust leathers increased with increasing chrome powder, which was consistent with the trend of fiber dispersion of wet blue (Figure 1). The pore structure parameters and pore size distribution of crust leathers were listed in Table III and Figure 6, respectively. The average pore diameters of crust leathers were larger, and their porosities and total pore areas were lower than those of wet blue (Table II). Especially, the crust leathers had almost no pores in the range of 5.48-100 nm. These results implied that fatliquors penetrated crust leathers from primary level to high level, wrapping the collagen fibers. Nevertheless, the trend of crust leather pore structure with increasing chrome powder was consistent with that of wet blue. These results indicated that the fatliquoring process almost preserved the fiber dispersion of leather obtained from the chrome tanning process, although it resulted in a slight decrease in the porosity of leather. As a result, the crust leathers also had different fiber dispersion depending on the amount of chrome powder in tanning process.

Physical Properties of Crust Leather

Table IV and Figure 7 present the physical properties of crust leathers, including mechanical properties (tensile strength, tear strength and elongation at break), organoleptic properties (softness and fullness), and hygienic property (water vapor permeability). The data in Table IV show that the tensile strength, tear strength and elongation at

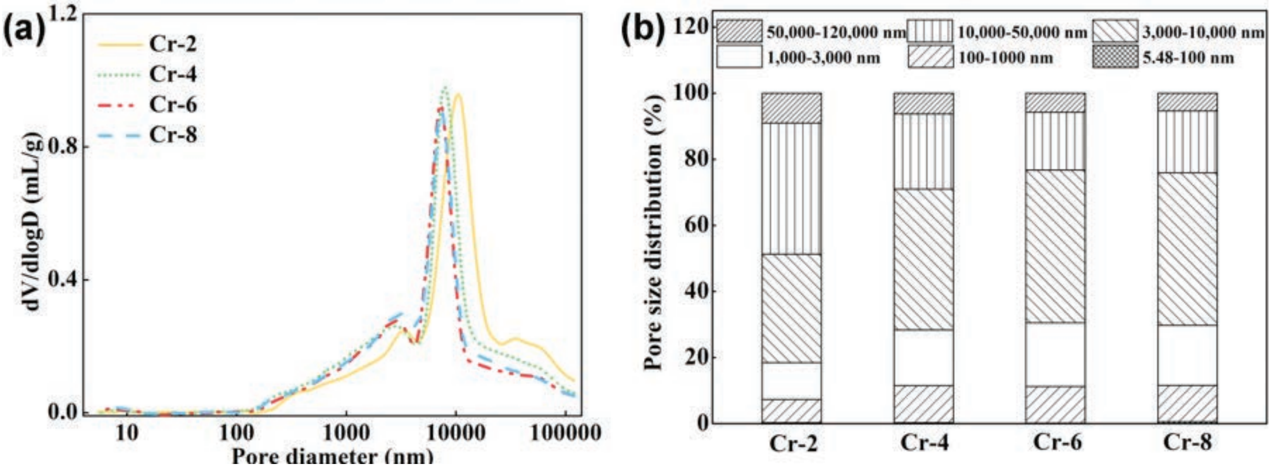

Figure 6. Effect of amount of chrome powder on pore size distribution of crust leather.

break of crust leathers increased with increasing chrome powder. However, these mechanical properties did not remarkably improve after the amount of chrome powder exceeded 6%. As mentioned previously, the fiber dispersion of wet blue and crust leather increased with increasing amount of chrome powder, particularly in the range of 2%-6%. Hence, the mechanical properties of leather were positively correlated with its fiber dispersion. This should be due to the fact that the crosslinking among collagen fibers caused by chrome tanning agent is helpful to improve both the mechanical properties and the porosity of leather. [6,24,25] The softness of crust leather increased from 7.14 mm to 8.21 mm (Figures 7(a)) when the amount of chrome powder rose from 2% to 8%. The compressed and resilient thicknesses of crust leather gradually increased with increasing chrome powder (Figures 7(b) and 7(c)), and the Cr-6 and Cr-8 crust leathers had the highest and similar compressed and resilient thicknesses. These data indicated that the fullness of crust leather was improved with increasing chrome powder. The above phenomena suggested that the organoleptic properties of leather were also positively correlated with its fiber dispersion because the pore structure of leather is the key factor to the compressibility of leather.[21,26] Figure 7(d) shows that the water vapor permeability increased from 8.88 mg/cm^2×h to 10.89 mg/cm^2×h when the amount of chrome powder rose from 2% to 8%. This is because more chrome powder resulted in higher porosity of leather, which could make more water molecules pass through the leather from high humidity environment to low humidity environment.[27,28] In summary, high physical properties of crust leather were accompanied by and even depended on its good fiber dispersion.

Table IV

Mechanical properties of crust leathers.

Crust leather	Tensile strength (N/mm2)	Tear strength (N/mm)	Elongation at break (%)
Cr-2	22.84±0.68	96.94±0.53	47.21±5.55
Cr-4	24.86±1.63	97.27±1.17	53.21±4.87
Cr-6	25.24±0.58	117.82±3.12	55.50±1.15
Cr-8	23.29±2.04	110.28±4.11	64.32±2.87

Conclusion

Chrome tanning process endowed leather with high fiber dispersion at different levels because chrome tanning agent could penetrate into elementary fibers, fibrils and microfibrils to fix collagen fibers. The crust leather with higher fiber dispersion presented better physical properties, indicating that the fiber dispersion is an important factor producing leathers with excellent physical properties. These results may provide a new insight into tanning performance and developing novel tanning agents and tannages.

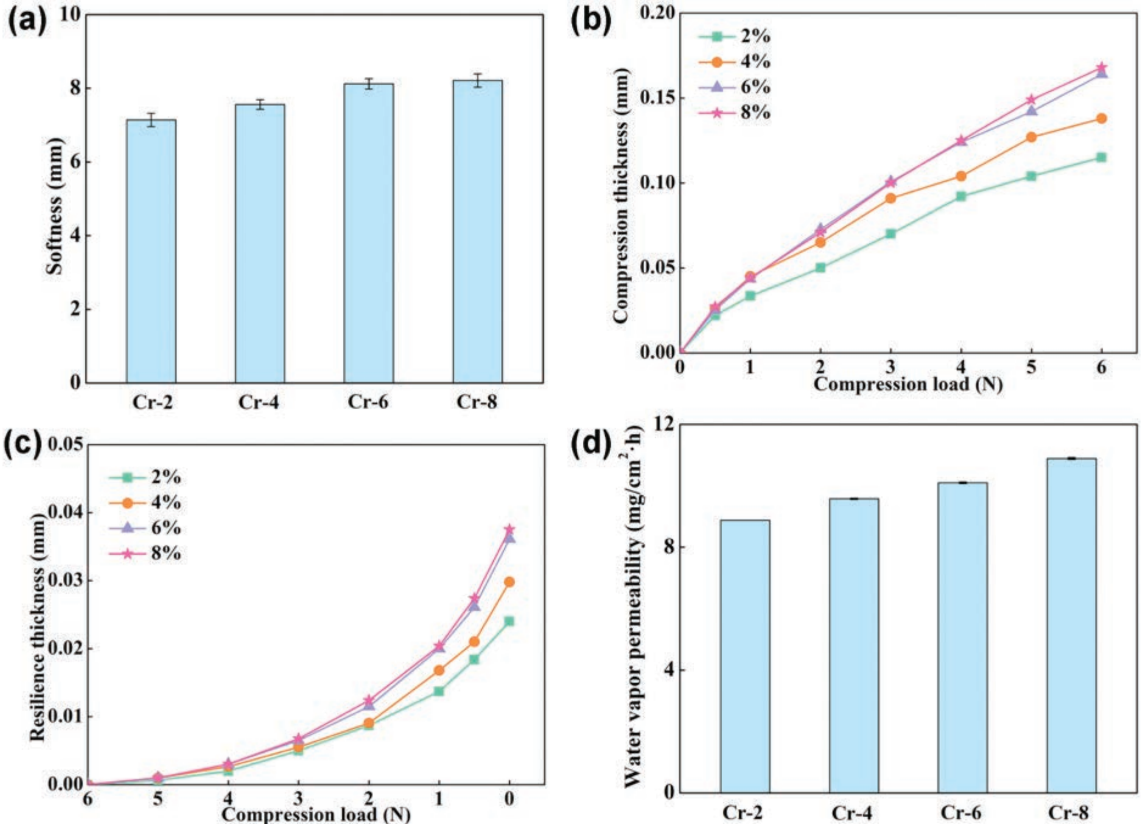

Figure 7.Effects of amount of chrome powder on properties of crust leathers: (a) softness, (b) compression performance, (c) resilience performance and (d) water vapor permeability.

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