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郑州大学
ZHENGZHOU UNIVERSITY

Influence of high temperature and humidity on the leather tanned with betel nut extract

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Overview

- 1) Various factors affecting leather
- 2) Materials and methods
- 3) Results and discussion

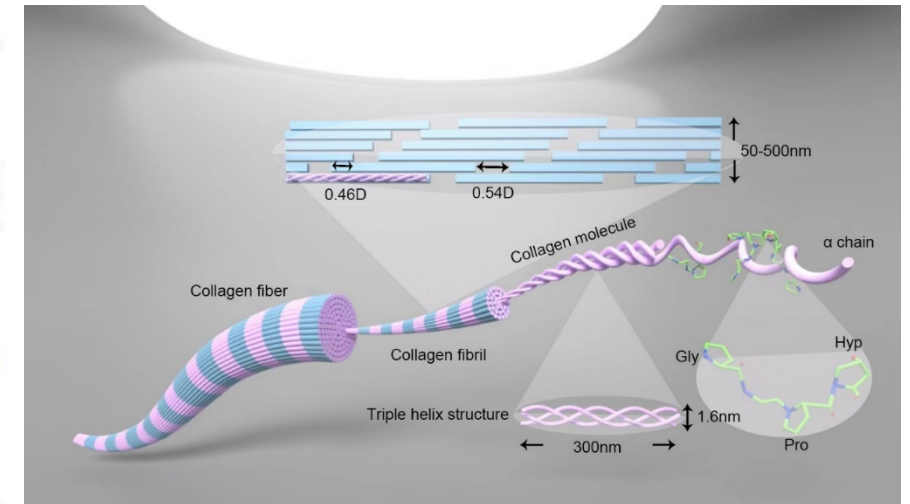
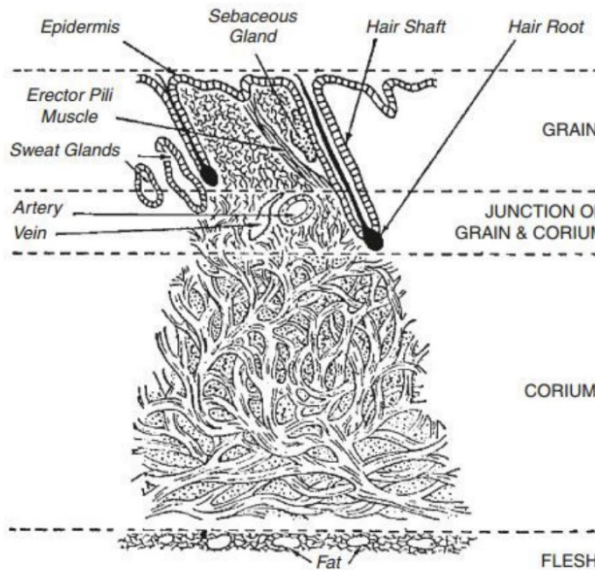


1 Introduction – An illustration of Leather



Images from Internet

Leather is ubiquitous and consists mainly of collagen derived from animal hides.



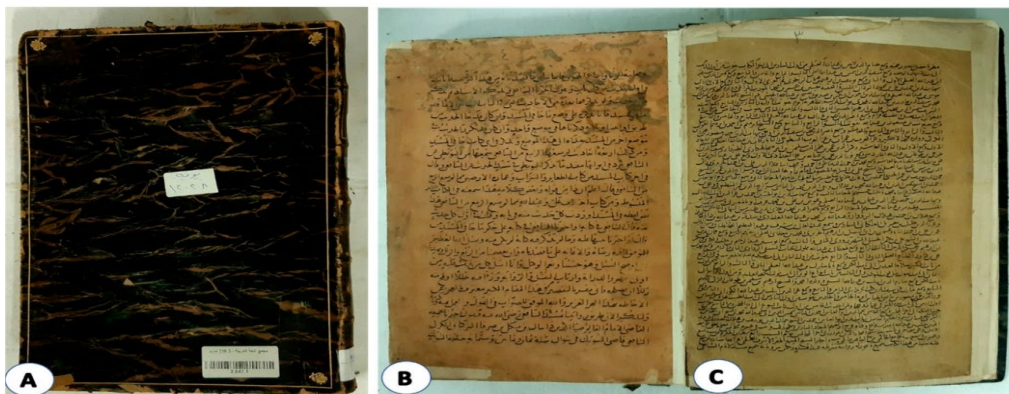
Qijue Chen et al., *Collagen and Leather*, 2023, 5(1): 20

Kite, M., & Thomson, R. (Eds.). (2005). *Conservation of Leather and Related Materials* (1st ed.). Routledge

Various factors affecting Leather

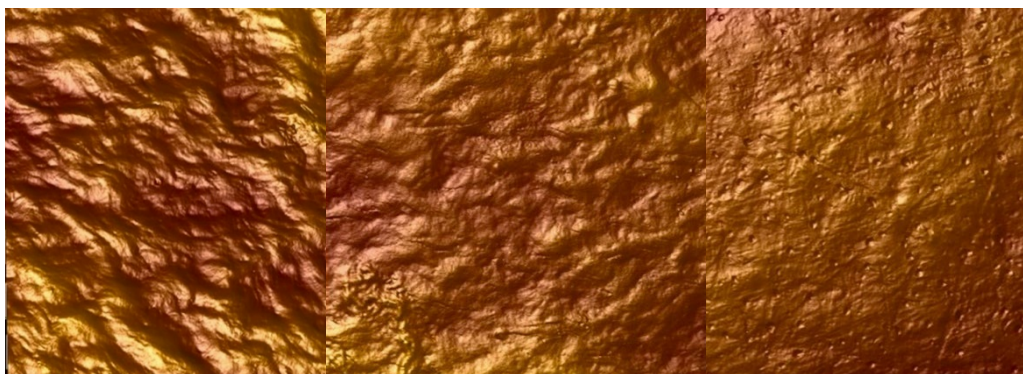
Leather is prone to deterioration in diverse environmental conditions.

Microorganisms



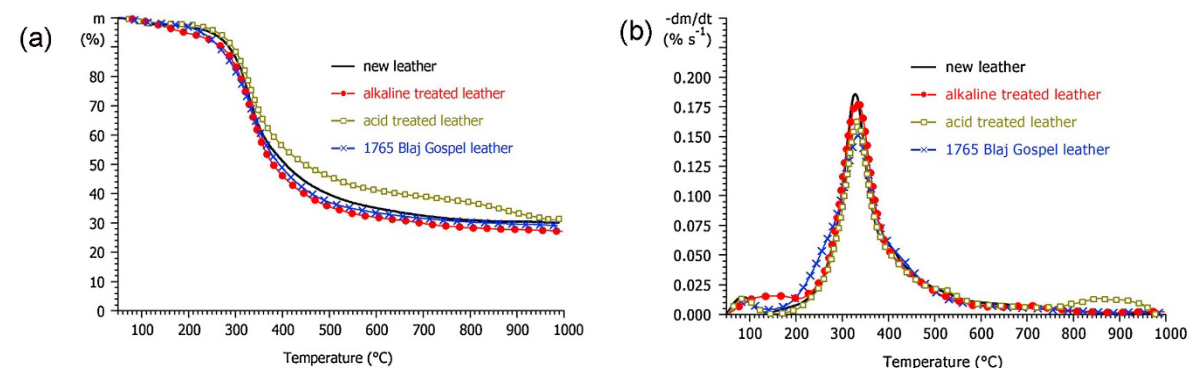
Gomaa Abdel-Maksoud et al., *Life*, 2022, 12, 1821

Light



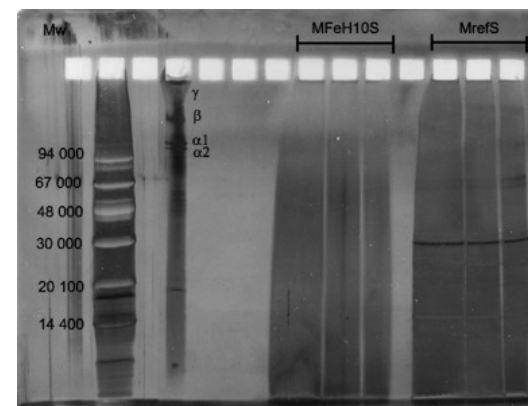
Katarzyna Adamiak et al., *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2022, 282, 121652

Acid and alkaline



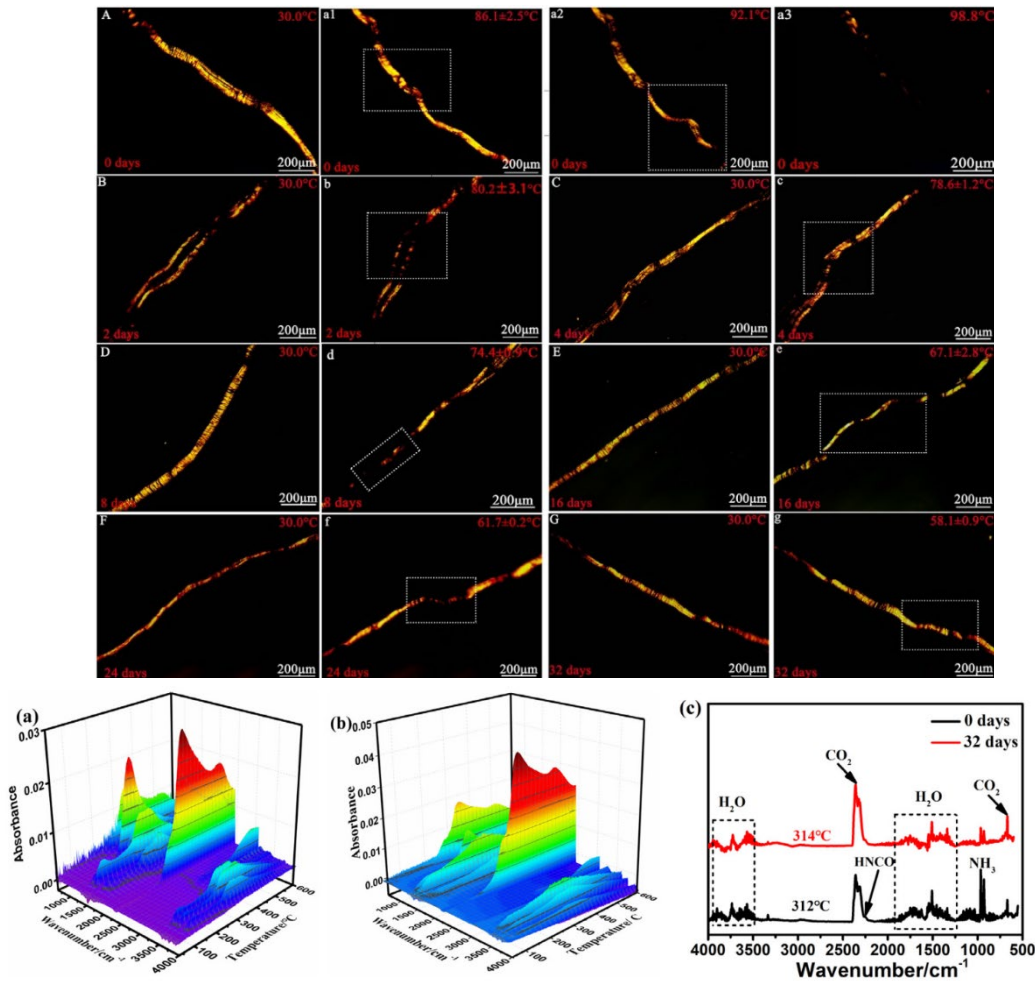
Zoltán Sebestyén et al., *Journal of Analytical and Applied Pyrolysis*, 2015, 115, 419-427

Metal cations



Martina Ohlídalová et al., *Journal of Cultural Heritage*, 2017, 24, 86-92

Synergistic effect of temperature and humidity



Yadi Hu., *Journal of Cultural Heritage*, 2022, 53, 118-126

High temperature and humidity?



Simulated aged leather for what?

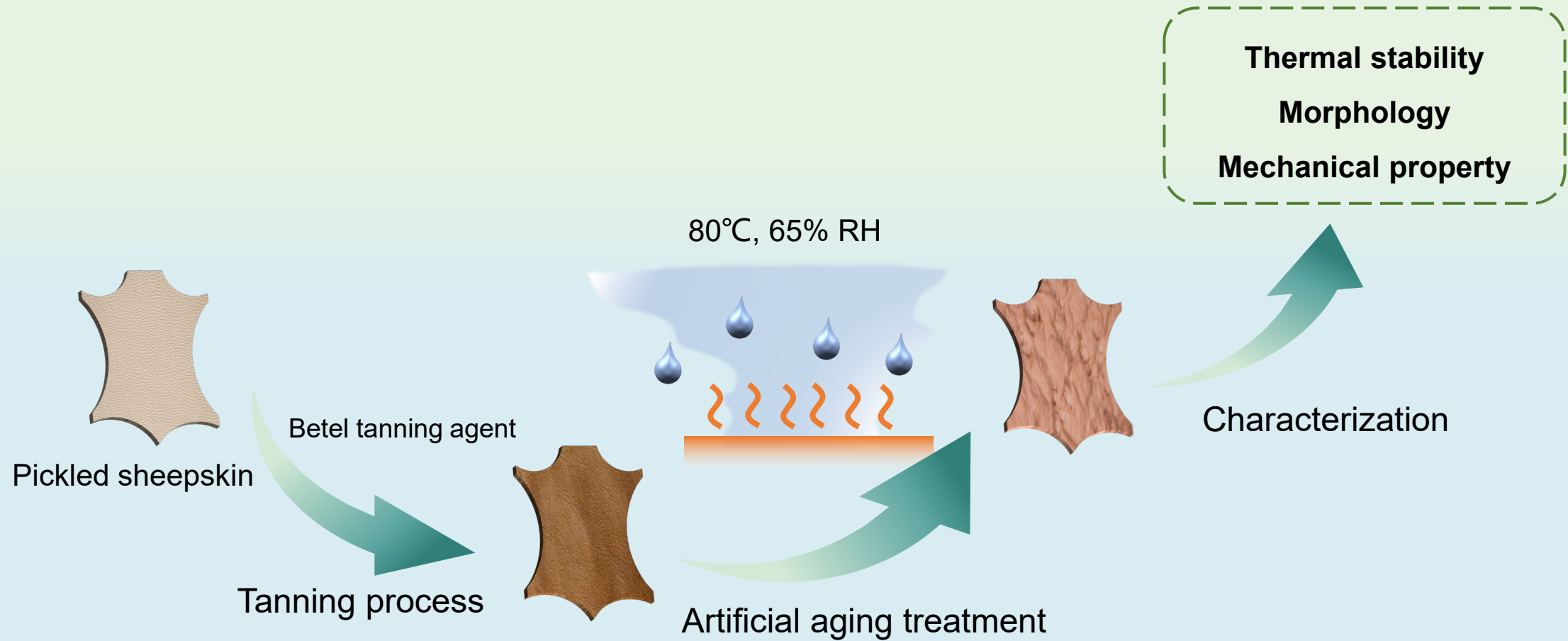


Preservation for historical leather heritages



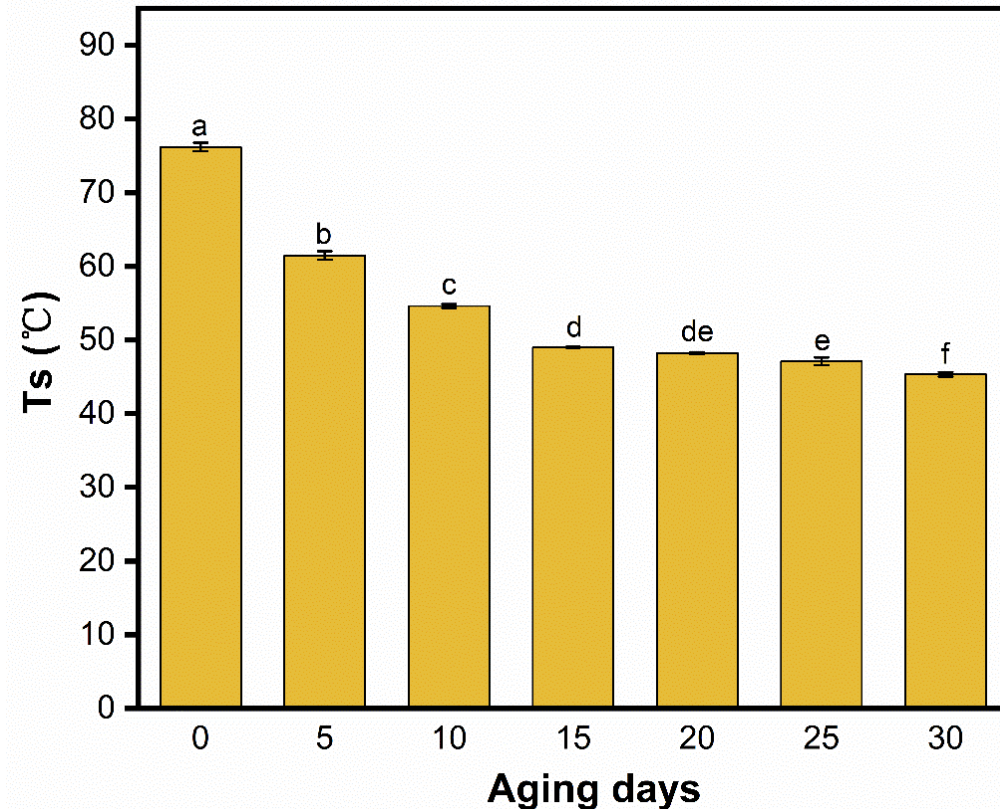
Image of sliced leather armor from Turpan Museum, Xinjiang, China

2 Materials and methods



3 Results and discussion

Shrinkage temperature (T_s)



Continuously decreasing T_s meant reduced durability of leather

Fig. 1 T_s of the Betel-tanned leather after aging at 80 °C and 65% RH for 0, 5, 10, 15, 20, 25, and 30 days. Different letters mean significance in the same group.

Table 1. The thermal degradation characteristics of betel-tanned samples during aging period.

Aging time (day)	T _{peak2} (°C)	DTG _{max} (%/min)	Final residue at 600 °C (%)
0	312	4.41	33.81
5	318	5.22	34.55
10	317	5.29	35.64
15	318	5.14	35.99
20	317	4.95	37.36
25	318	4.87	38.23
30	308	5.06	40.16

- Water loss
- Rapid thermal pyrolysis
- Carbonization
- Similar decomposition tendency
- Char reconstruction

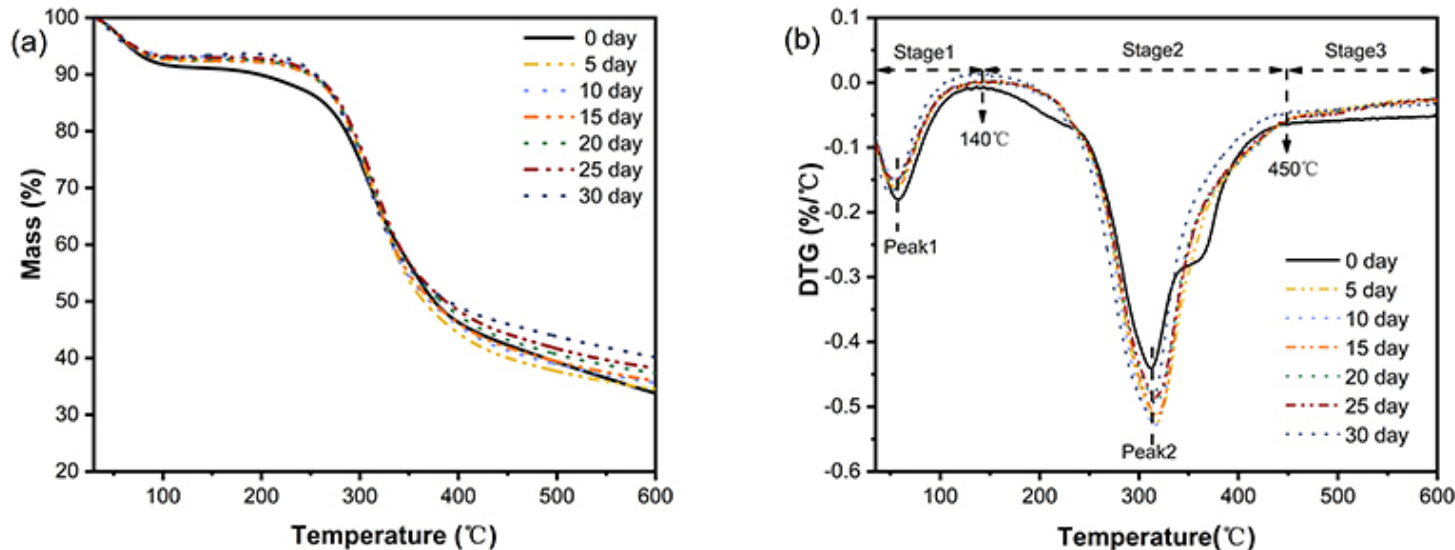


Fig. 2 TG/DTG curves of Betel-tanned leather samples during different aging period (a and b).

Color change

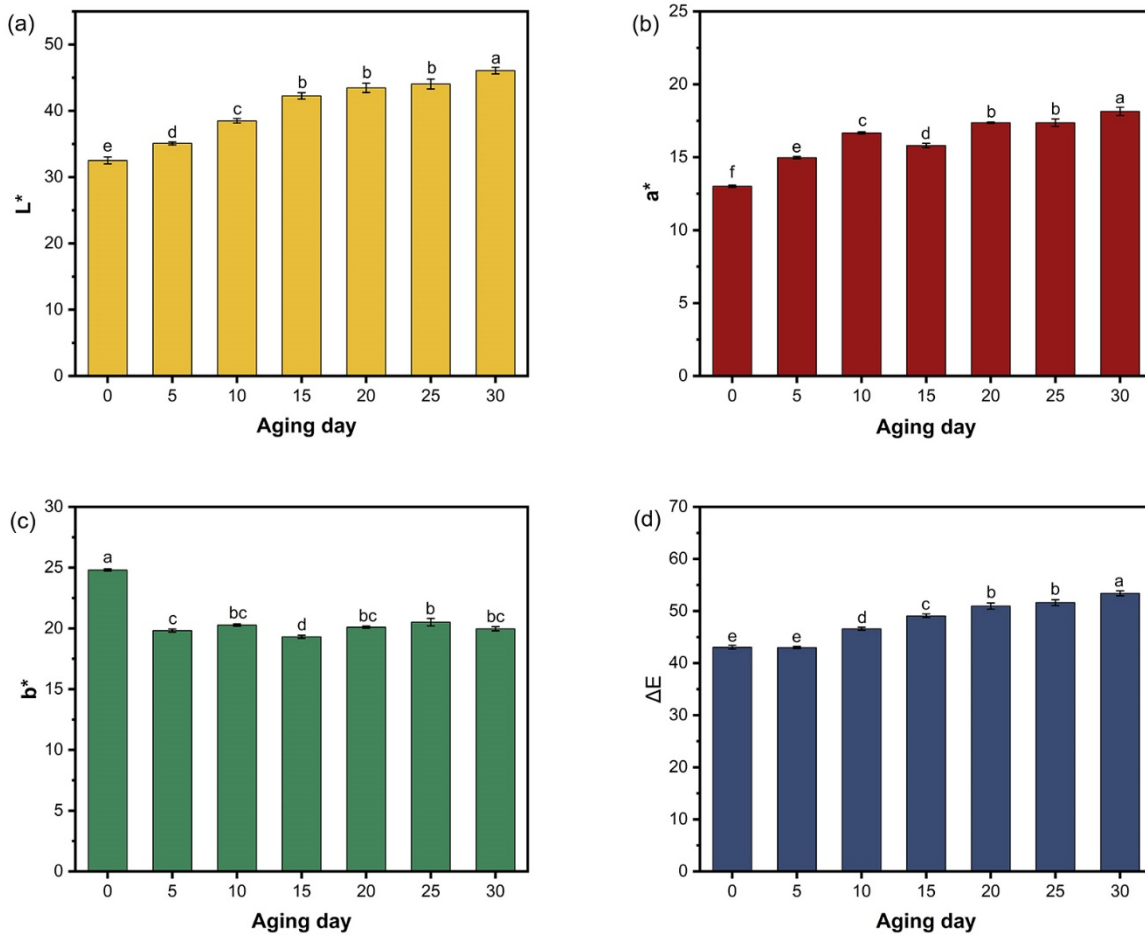


Fig. 3 The changes in (a) brightness (L^*), (b–c) chromaticity (a^* , b^*) and (d) color difference (ΔE^*) of leather tanned with betel tanning agent during different aging periods. Different letters mean significance in the same group.

Table 2. Color difference of betel-tanned leather after aging at 80 °C and 65% RH among different days.

Aging time (day)	ΔL^*	Δa^*	Δb^*	ΔE^*
0	-32.53 ± 0.52	13.02 ± 0.07	24.81 ± 0.09	43.06 ± 0.35
5	-35.10 ± 0.23	14.97 ± 0.08	19.82 ± 0.13	43.00 ± 0.21
10	-38.50 ± 0.34	16.67 ± 0.07	20.28 ± 0.09	46.60 ± 0.29
15	-42.26 ± 0.48	15.81 ± 0.15	19.31 ± 0.13	49.08 ± 0.35
20	-43.48 ± 0.71	17.37 ± 0.05	20.11 ± 0.08	50.96 ± 0.59
25	-44.05 ± 0.75	17.37 ± 0.26	20.51 ± 0.31	51.62 ± 0.57
30	-46.68 ± 0.50	18.14 ± 0.29	19.97 ± 0.17	53.40 ± 0.47

Leather darkened and changed to a vermillion hue

Surface morphology

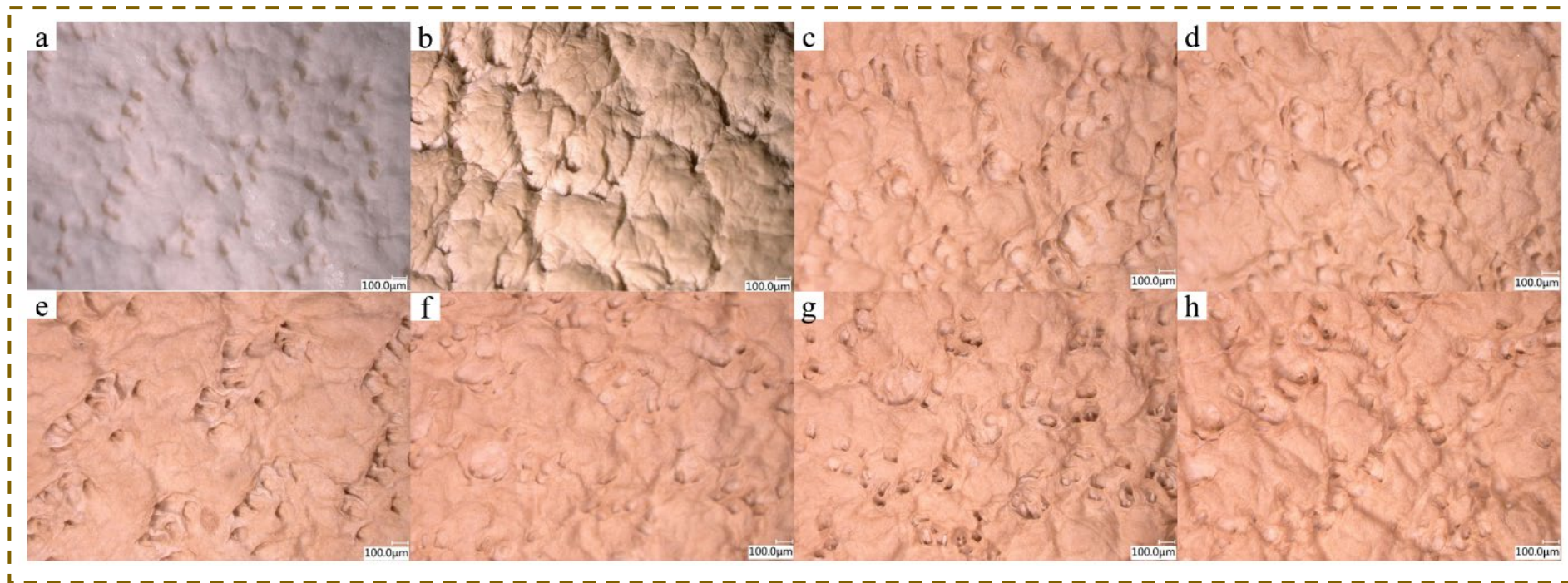


Fig. 4 Optical super depth-of-field microscope images of (a) pickled sheepskin and (b-h) betel-tanned leather samples aging for 0, 5, 10, 15, 20, 25, 30 days, respectively.

- Increased sizeable hole structure on leather surface by time
- Leather shrank with uneven grain surface

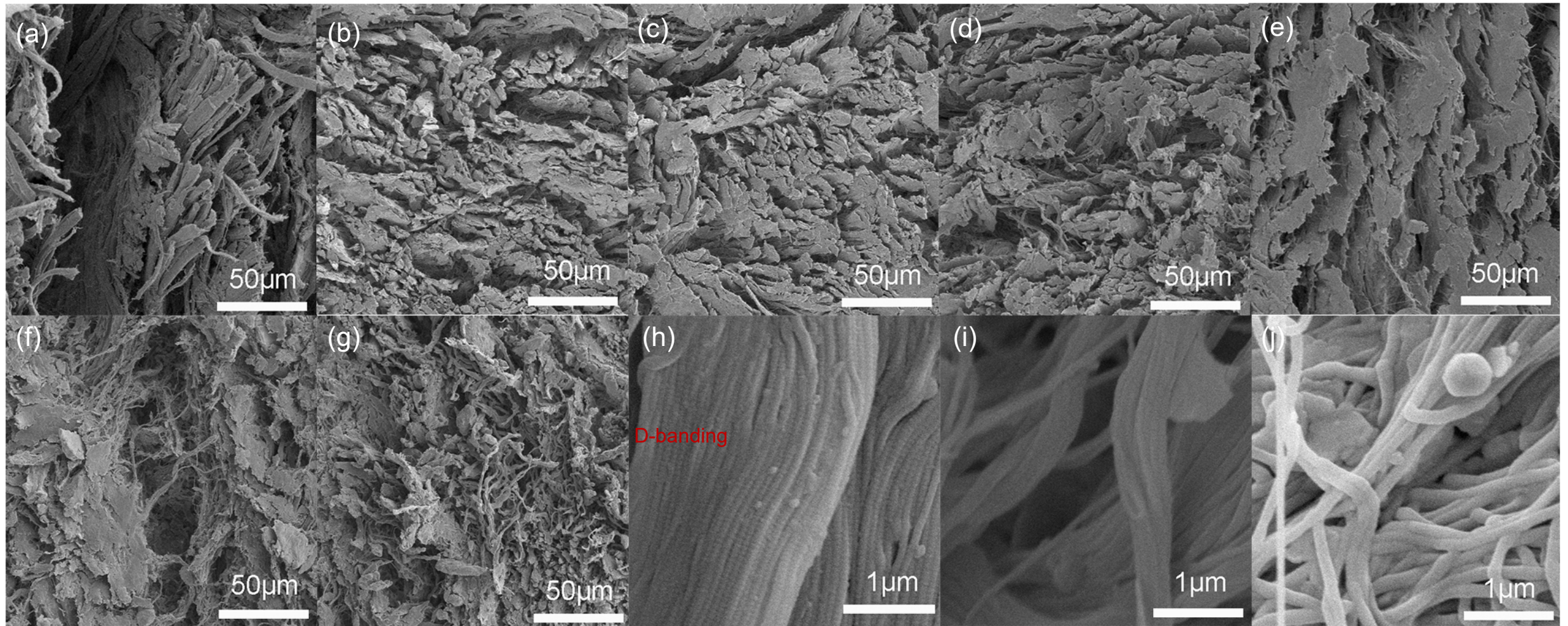


Fig. 5 Cross-sectional SEM images of betel-tanned samples after aging at 80 °C and 65% RH for (a, h): 0 day, (b): 5 days, (c): 10 days, (d, i): 15 days, (e): 20 days, (f): 25 days, and (g, j): 30 days.

- Narrowed gap between thinner collagen fiber bundles
- Diminished D-banding period
- Destroyed orientation of collagen fibers
- Disordered collagen fibers

Table 3. Characterization peaks of betel-tanned leather under different aging period.

Characterization absorption peaks	Wavenumber(cm^{-1})		
	Unaged leather	Aged leather (15days)	Aged leather (30days)
Amide A	3326	3294	3289
Amide B	3091	3084	3081
Amide I	1663	1661	1660
Amide II	1544	1537	1536
Amide III	1238	1236	1237

Table 4. Absorbance ratio of the characteristic peak of amide III band to the characteristic peak at 1453 cm^{-1}

Unaged leather	Aged leather (15days)	Aged leather (30days)
0.95	0.95	0.89

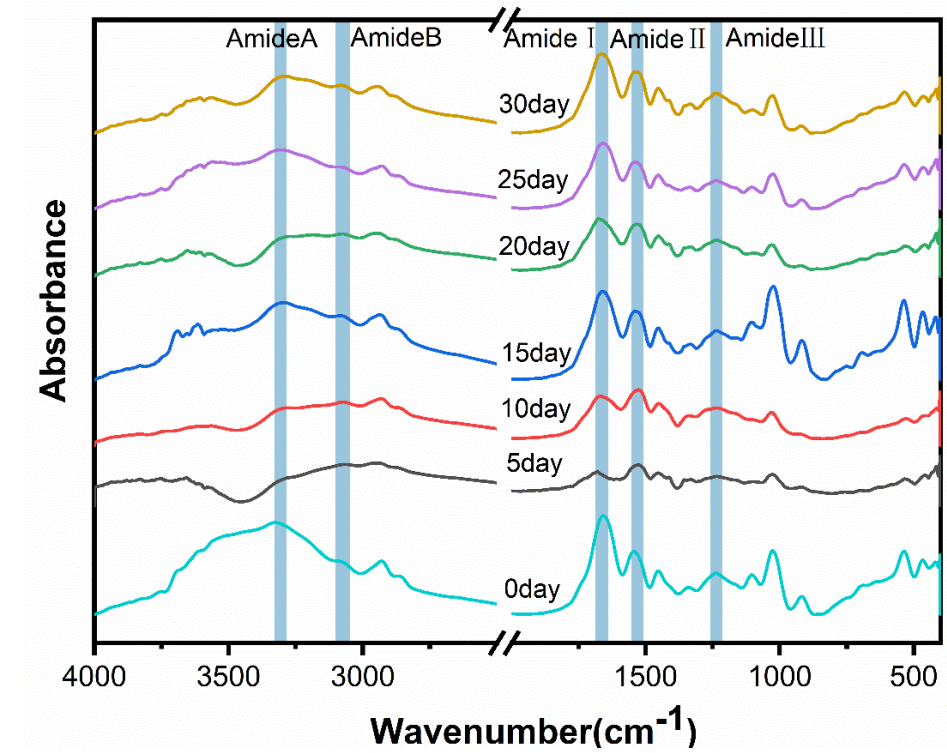


Fig. 6 ATR-FTIR spectra of betel-tanned leather samples after aging treatments.

- Characterization peaks turned blue-shift
- Absorbance ratio showed decreased triple-helix structure in collagen

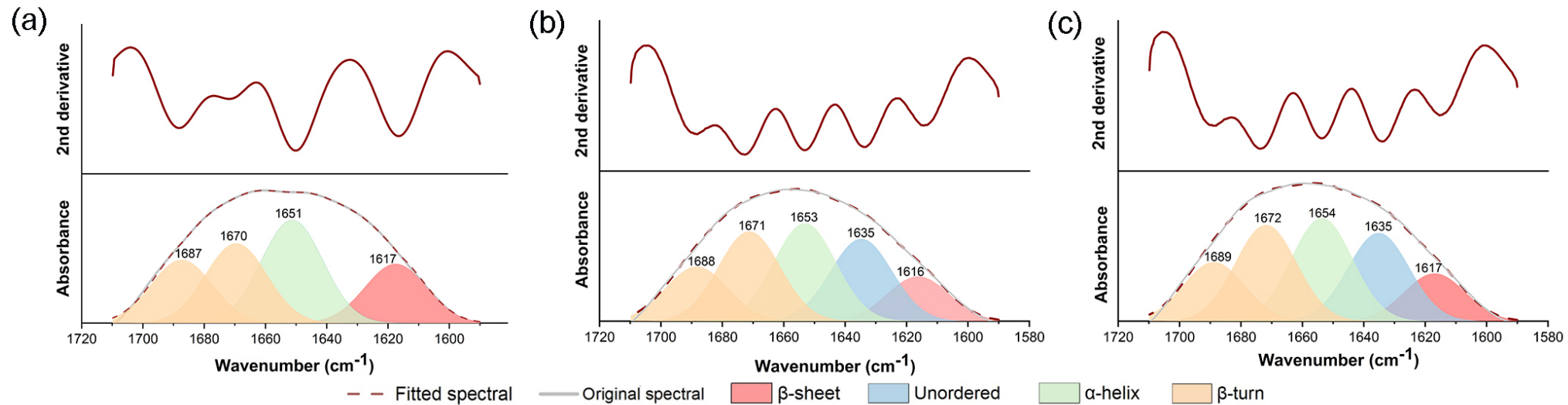


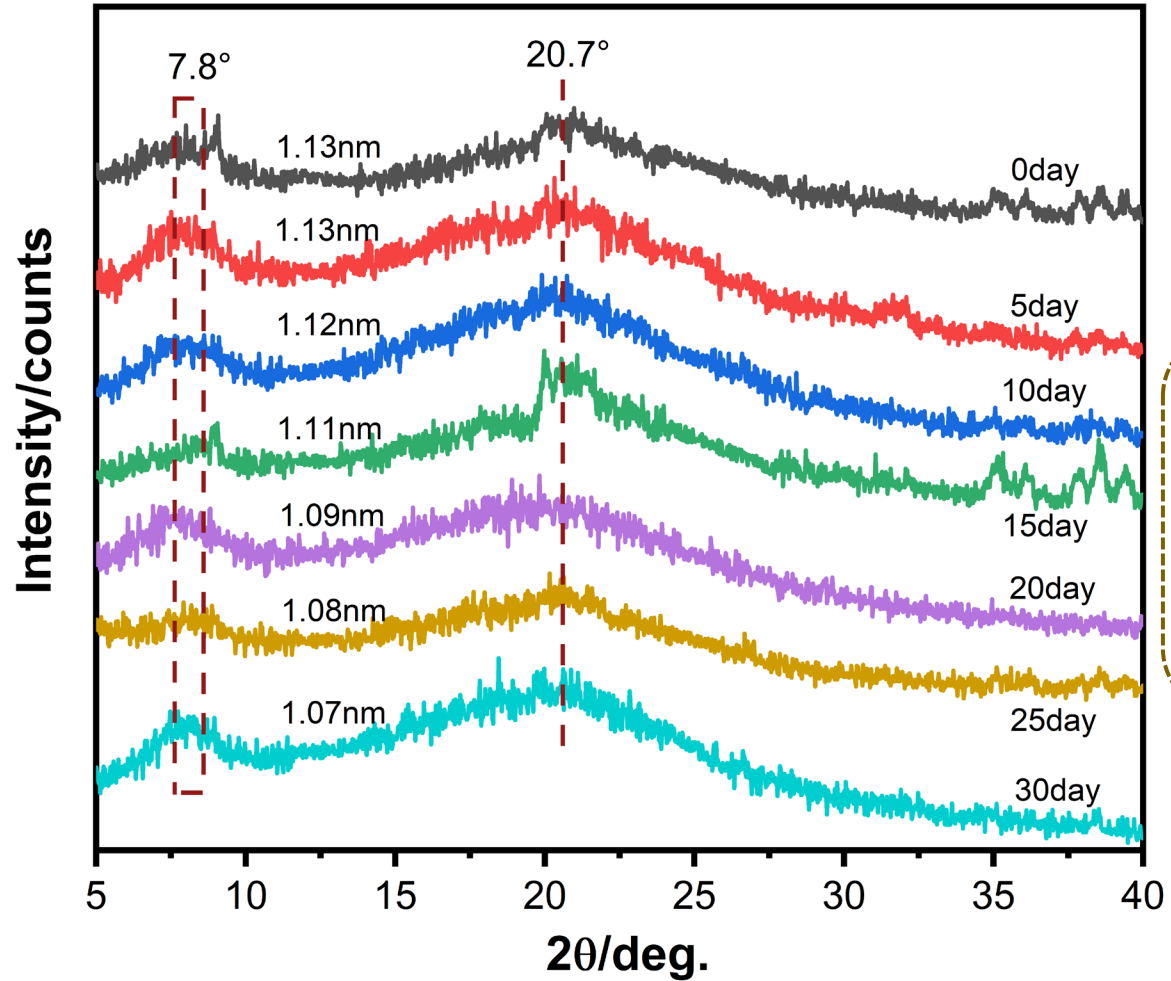
Fig. 7 Deconvolution results of amide I of betel-tanned samples after aging at 80 °C and 65% RH for (a) 0 day, (b) 15 days, and (c) 30 days.

Table 5. The area (%) of the peaks obtained by deconvolution of amide I of betel-tanned samples after aging treatments.

Aging time (day)	α-helix (%)	β-sheet (%)	β-turn (%)	Unordered structure (%)
0	34	19	47	0
15	27	12	39	22
30	26	12	39	23

• Decreased α-helix structure while increased unordered structure in the secondary structure of collagen

XRD



- Decreased distance between the molecular chains (Peak near 7.8°)
- Diffuse scattering of an amorphous region (Peak at 20.7°)

Fig. 8 X-ray diffraction of betel tanning agent and betel-tanned leather samples with or without ageing treatments.

Tensile strength and Elongation at break

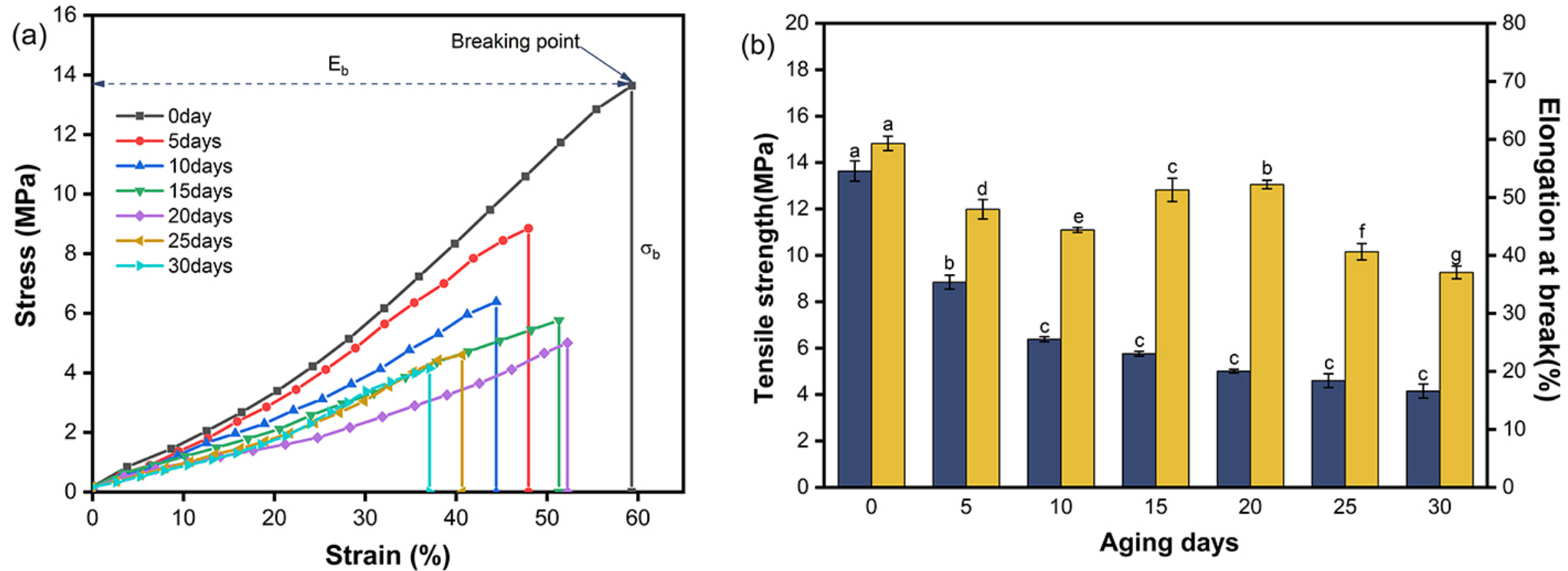


Fig. 9 Stress-strain curves, tensile strength and elongation at break of betel-tanned leather samples after aging treatment among different periods. Different letters mean significance in the same group.

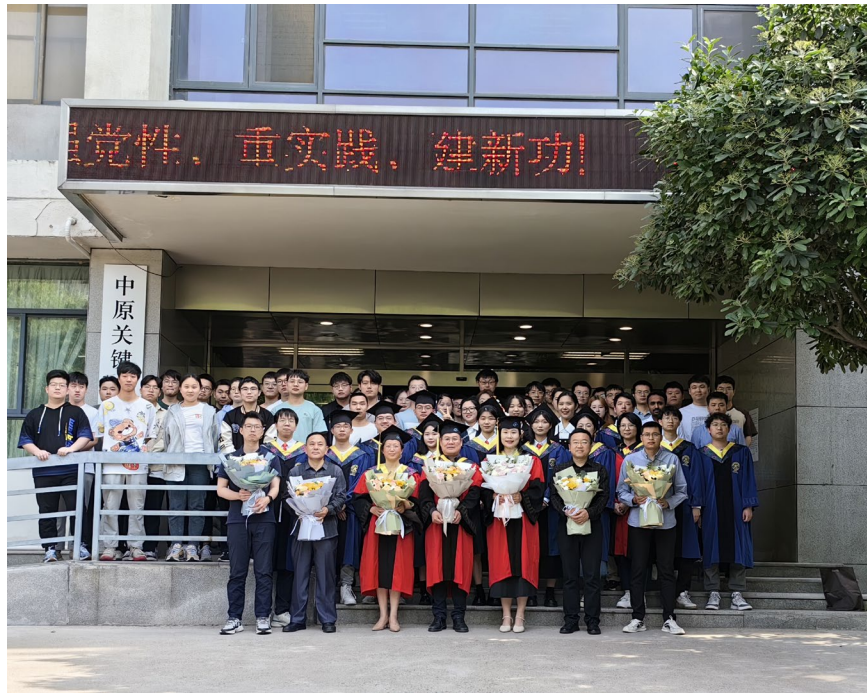
- There denoted an interesting variation (remaining a slight rebound before ultimately decline) as elongation at break of leather samples



Summary

- 1) Aging treatment caused leather deterioration from inside to surface
- 2) Decreased thermal stability and mechanical property led to reduced durability of leather artifacts
- 3) The deterioration of samples includes a decrease in thermal stability and the destruction of the fiber structure.
- 4) Collagen fibers gradually lost cohesion and orientation by time

Welcome to Henan International Joint Laboratory of Biomass Resources & Materials!



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Thank you very much for your attention!