

The 37th IULTCS congress

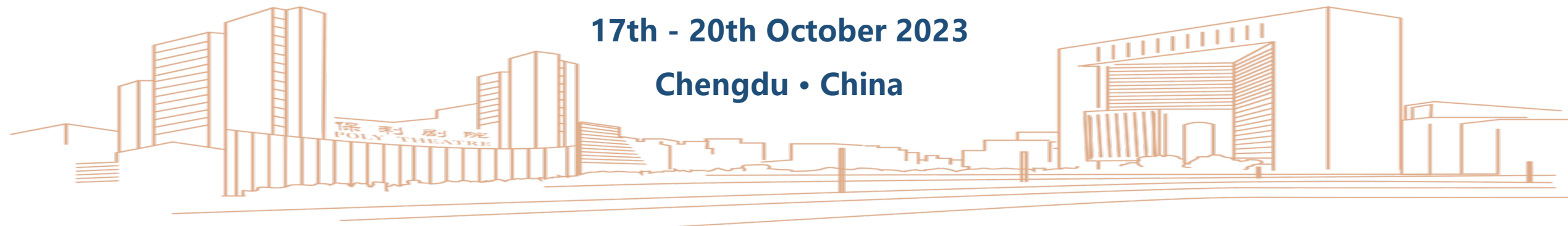
Isocyanate-based polymeric dye for high-performance dyeing of biomass-derived aldehyde tanned leather

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China Leather and Footwear Research Institute

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Chengdu • China



Main Content



Research Background



Synthesis and Application of Isocyanate-based Polymeric Dye



Conclusions, Outlook and Acknowledgements

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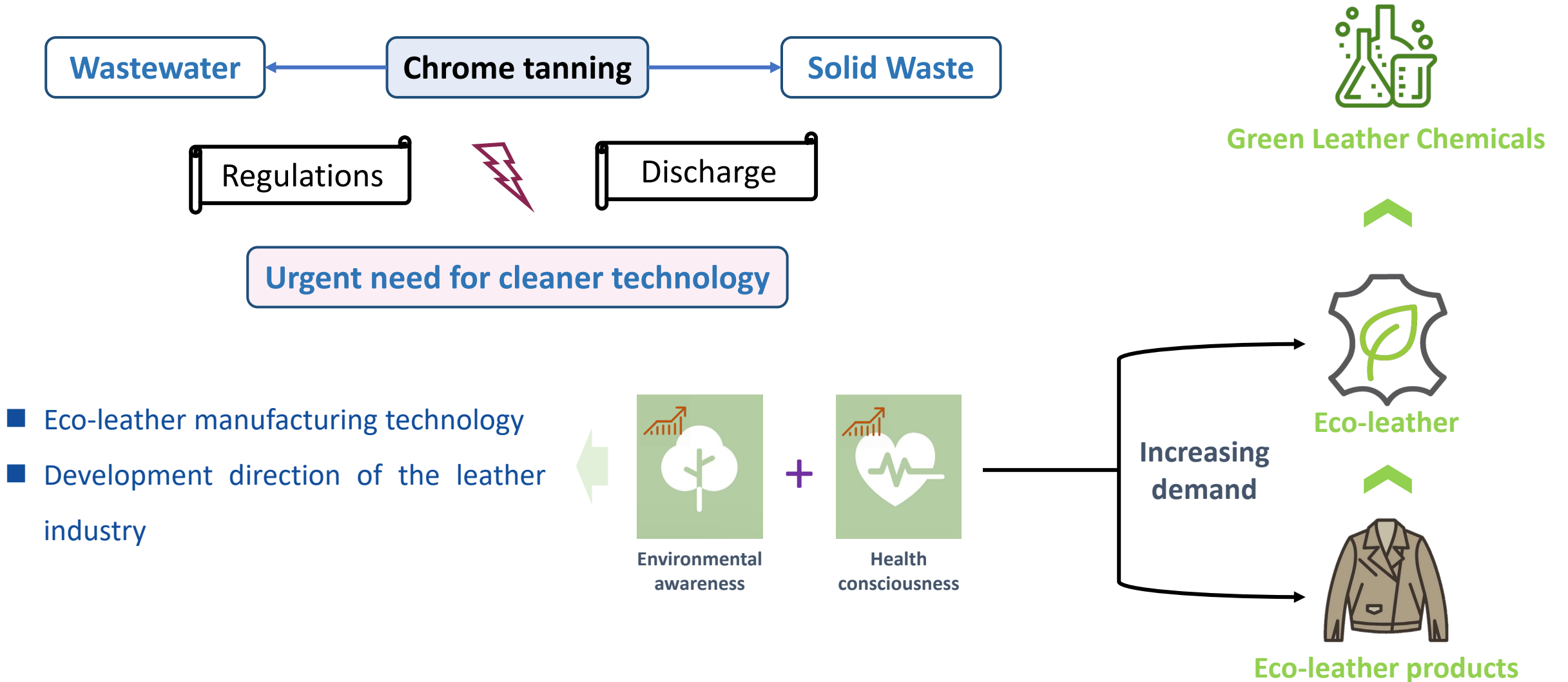
Research Background



1. Research Background



➤ Background



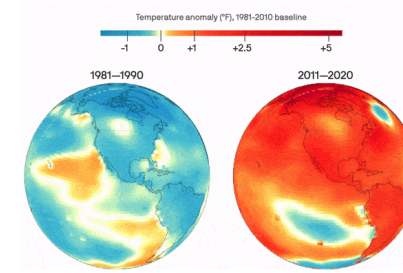
1. Research Background



➤ Background



Excessive exploitation and high dependence on fossil energy



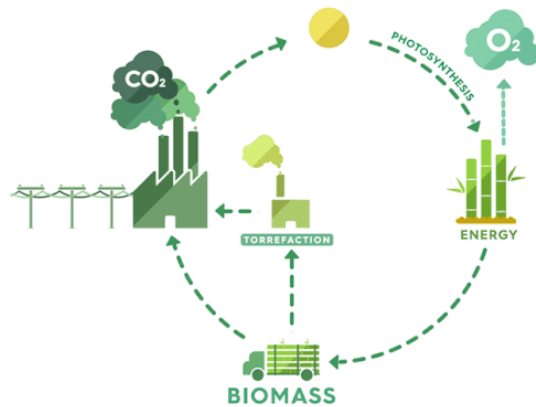
Global warming



Environmental pollution



The global petrochemical resources are increasingly scarce, climate warming, environmental pollution and other problems are worsening



Green and low-carbon renewable biomass energy & materials

➤ Biomass-derived materials:

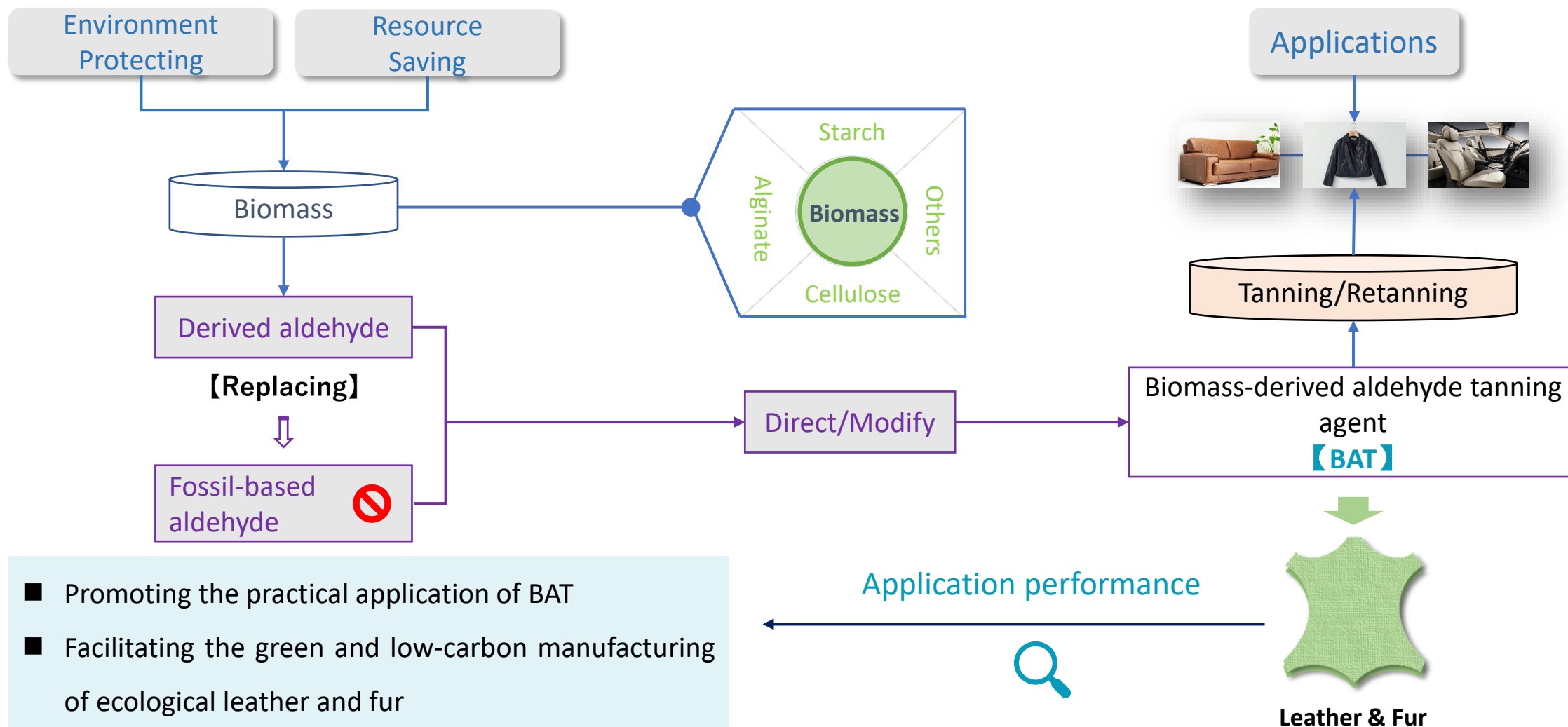
- Renewability, Environmental friendliness, Sustainability
- Scientific and Technological Innovation
- Low Carbon Economy

➤ Biomass-derived materials are becoming one of the most important industries

1. Research Background



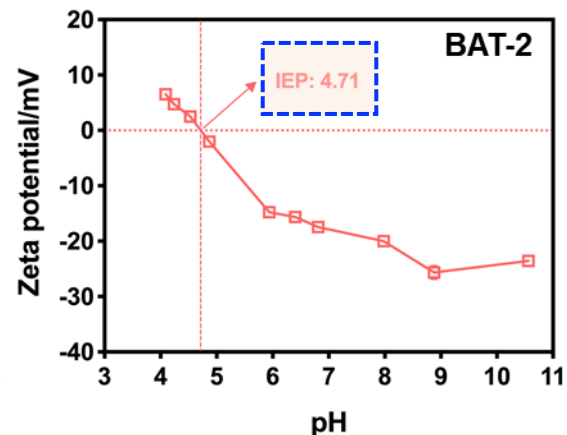
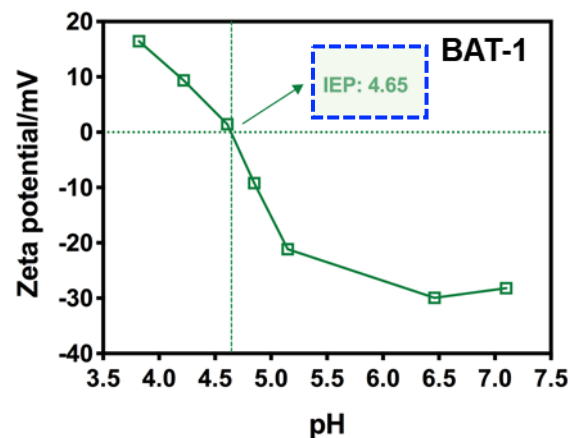
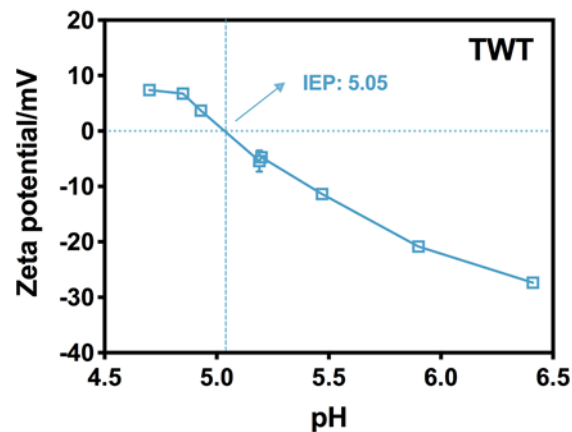
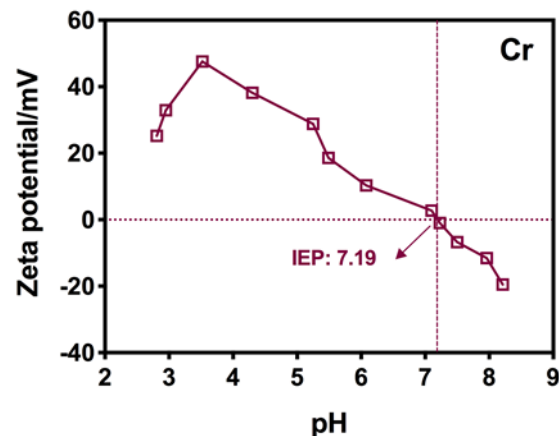
➤ Background



1. Research Background



Questions



Isoelectric point of tanned leather

Low

Isoelectric point of tanned leather



Unfavorable

Uptake and fixation of conventional
post-tanning materials

1. Research Background



➤ Questions



Colorful leather products

- Leather dyes are important industrial source chemical pollutants.
- The decolorization of the leather dyeing wastewater is a challenging task.
- Color migration will affect product quality, and bring potential health hazards to consumers.



Wastewater



Dye transfers from leather



Establishing a high-performance dyeing system to produce high-quality BAT-tanned eco-leather

2

Synthesis and Application of Isocyanate-based Polymeric Dye



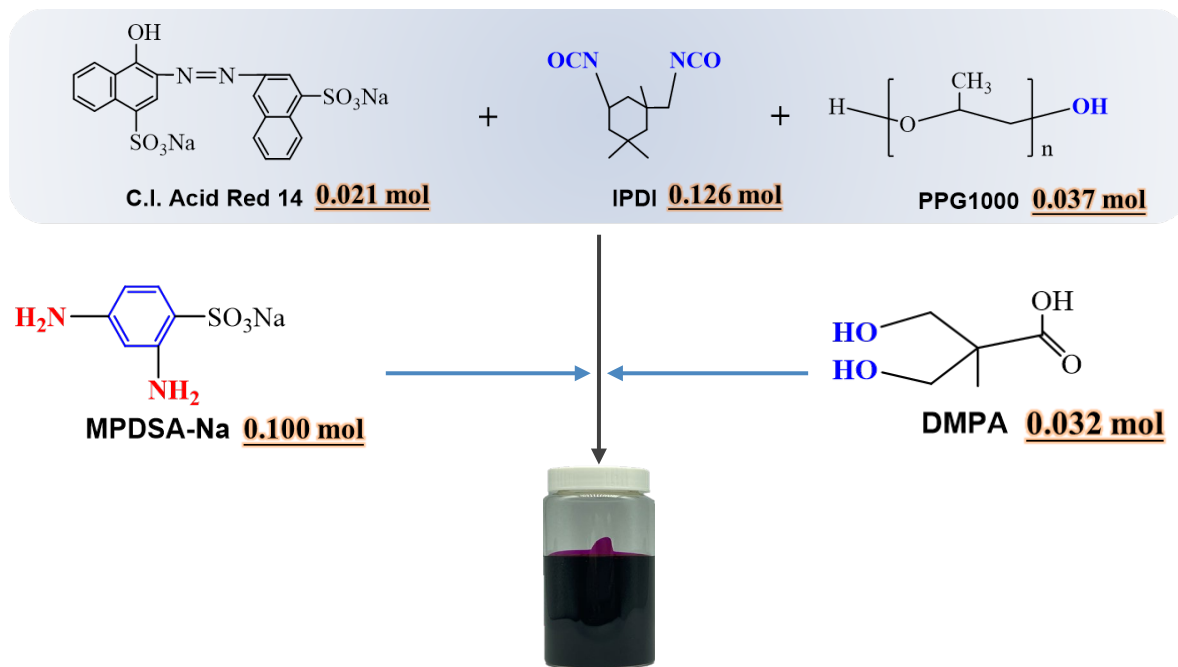
2. Synthesis and Application of Polymeric Dye



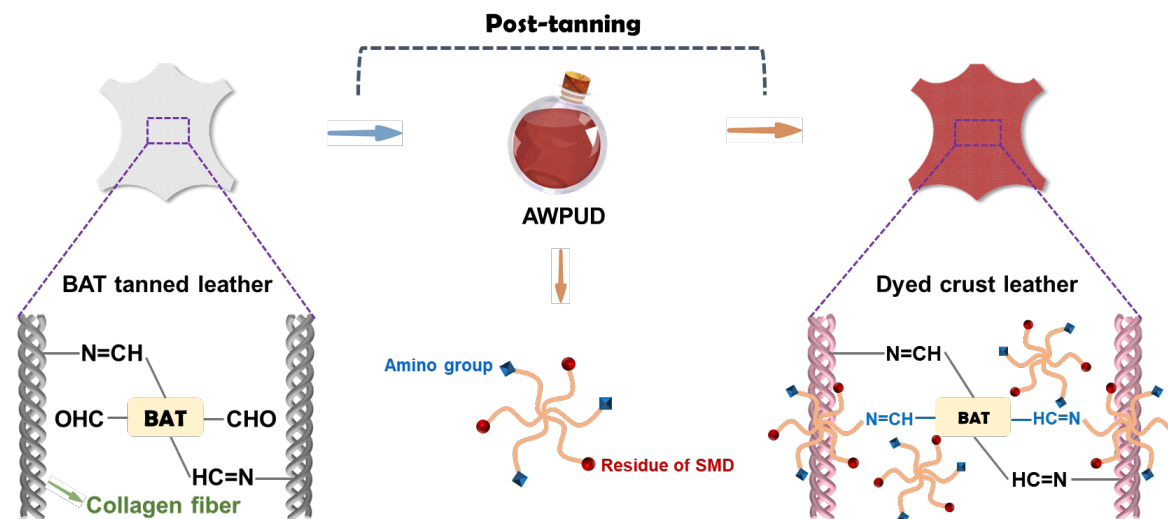
➤ Synthesis and application of polyurethane-based polymeric dye

Basic ideas for the research

■ Synthesis based on conventional route



Waterborne polyurethane-based polymeric dye emulsion (AWPUD)



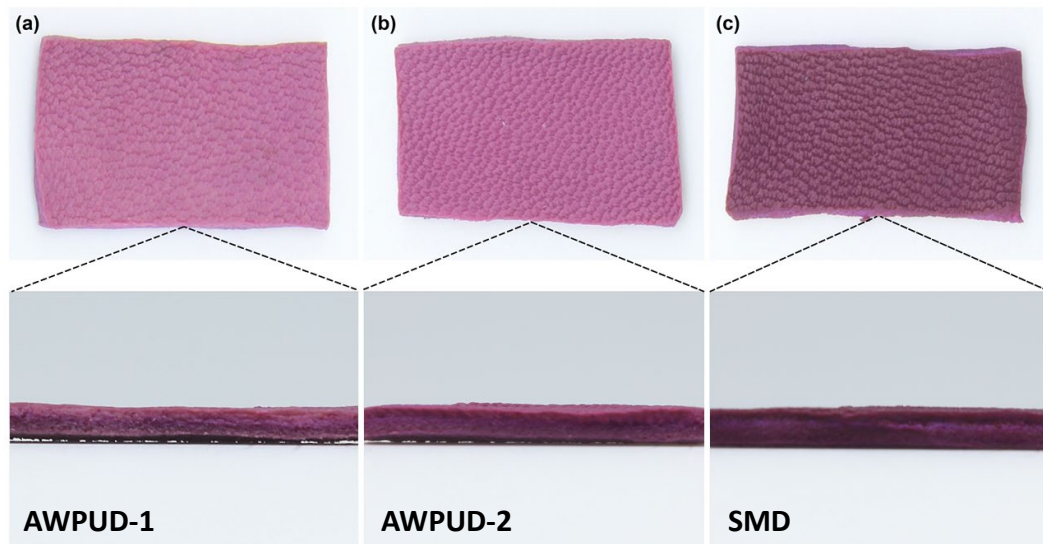
➤ AWPUD was prepared and applied in the dyeing of BAT-tanned chrome-free leather.

2. Synthesis and Application of Polymeric Dye

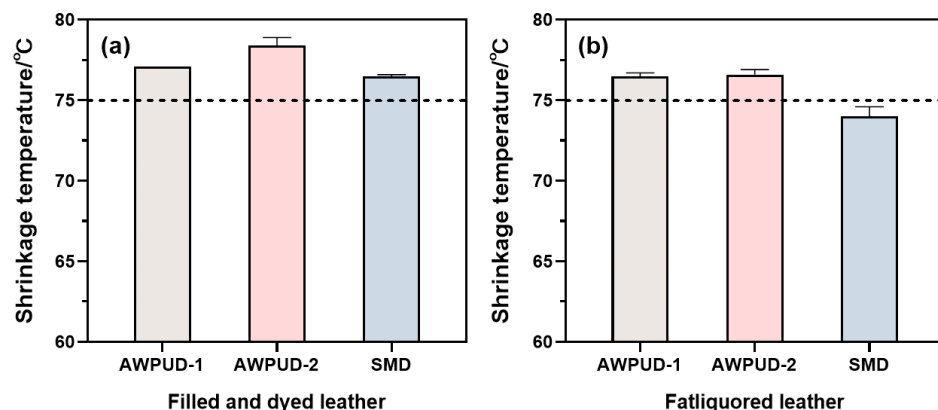


➤ Synthesis and application of polyurethane-based polymeric dye

Post-tanning performance



| Crust leather | AWPUD-1 | AWPUD-2 | SMD (Acid Red 14) |
|----------------------------|----------|----------|-------------------|
| L | 67.5±0.5 | 62.6±0.6 | 45.1±0.8 |
| a | 19.8±0.5 | 25.3±0.1 | 41.0±0.4 |
| b | 1.0±0.5 | -1.9±0.3 | -8.0±0.9 |
| STDEV of ΔE values | 0.7 | 0.1 | 0.9 |



- Good penetrability of AWPUD
- Improved hydrothermal stability of leather crust
- Higher dyeing uniformity but lighter color in comparison with SMD crust leather

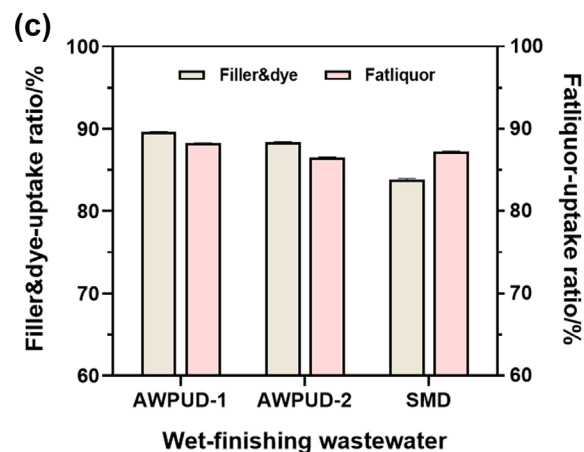
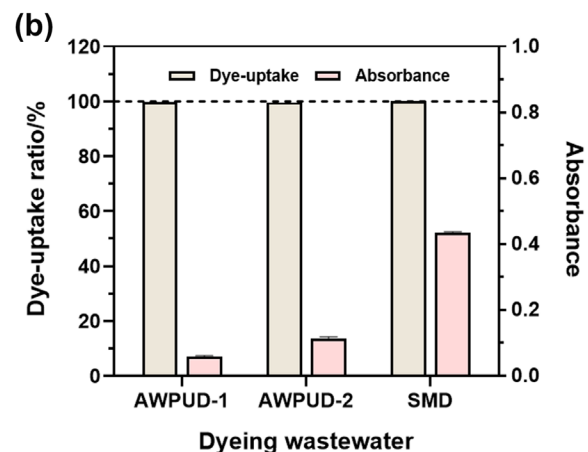
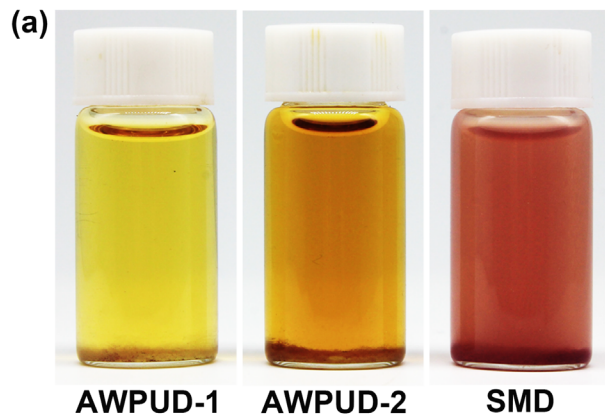
Ding, W., Guo, S., Liu, H., et al. *Materials Today Chemistry*, 2021, 21, 100508.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Post-tanning performance



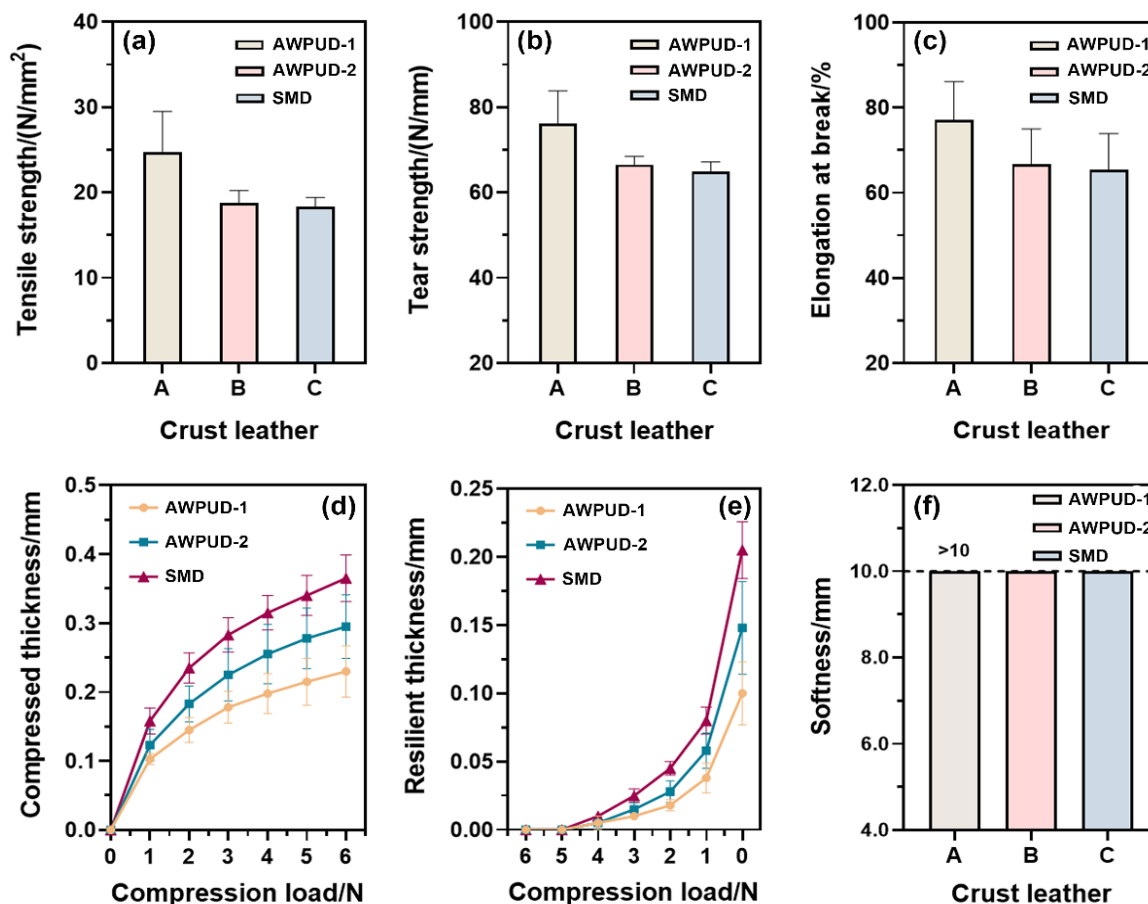
- Favorable uptake
- Promoting the uptake of other post-tanning materials
- Higher color fastness in comparison with SMD crust leather

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Physical and organoleptic properties



In comparison with SMD crust leather

- Higher tensile strength, tear strength and elongation at break
- Lower fullness
- Comparable softness

Low
Coloring Component Content

High
Actual Application Amount

Ding, W., Guo, S., Liu, H., et al. *Materials Today Chemistry*, 2021, 21, 100508.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Basic ideas for the research

■ Synthesis based on new route



TDI:RRD-180=0.8:3



TDI:RRD-180=1.3:3



TDI:RRD-180=1.8:3

Without
polyether or diol polyester

- By altering the molar ratio between TDI (toluene diisocyanate) and reactive small molecule dye RRD-180, three kinds of high molecular dyes (IBD, dye component content was higher than 60%) were synthesized.
- The molecular structure and application properties of the dyes were analyzed and investigated.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Molecular weight

| IBD | Relative molecular mass | | Polydispersity |
|-------|-------------------------|-------|----------------|
| | M_w | M_n | M_w/M_n |
| IBD-1 | 1791 | 1676 | 1.069 |
| IBD-2 | 1817 | 1717 | 1.058 |
| IBD-3 | 1842 | 1729 | 1.065 |

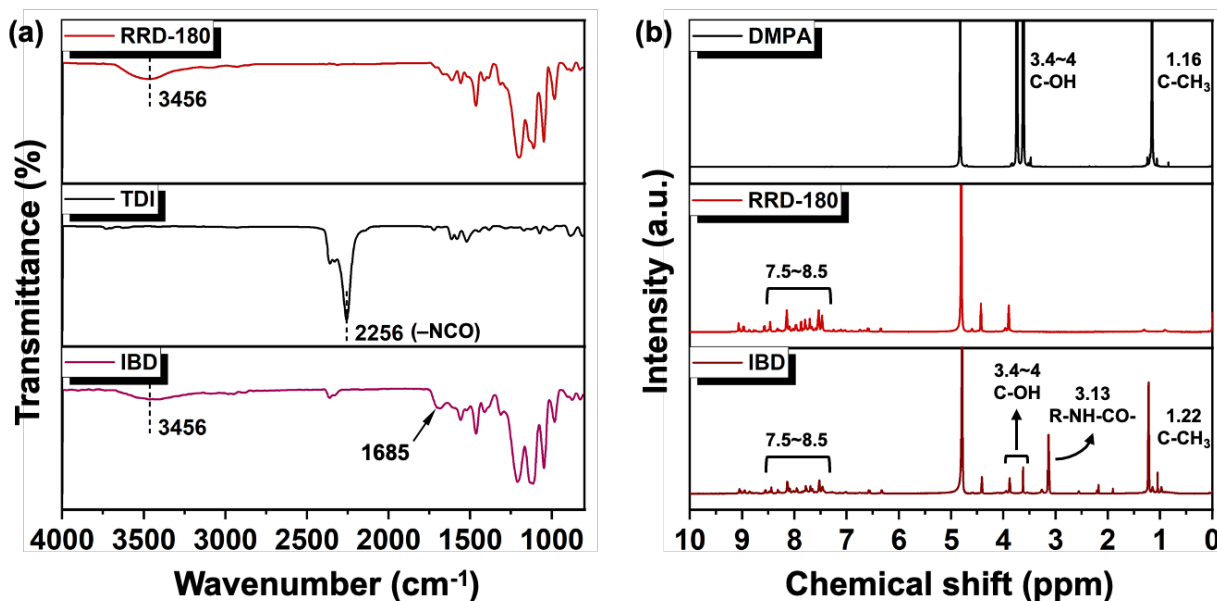
- The polymerization reaction between TDI and RRD-180 proceeded successfully.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

FTIR and NMR spectra



- The -NCO group from TDI appeared at 2256 cm⁻¹, which disappeared after reacting with RRD-180 and DMPA.
- The peak assigned to -NH₂ (3456 cm⁻¹) also decreased obviously.
- A new peak appeared at 3.13 ppm, which might be assigned to the urethane methylene.

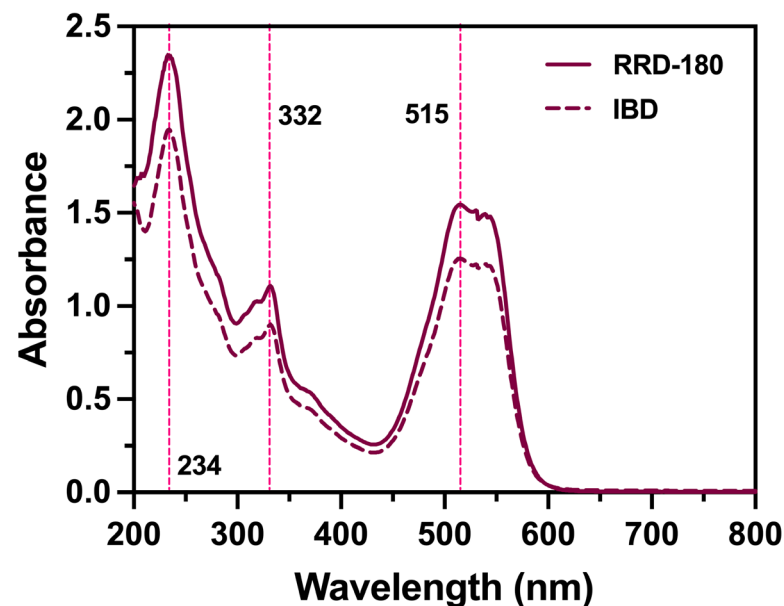
RRD and DMPA had been bonded with TDI, which increased the molecular weight of IBD and potentially improved its hydrophilicity.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

UV-Vis spectra



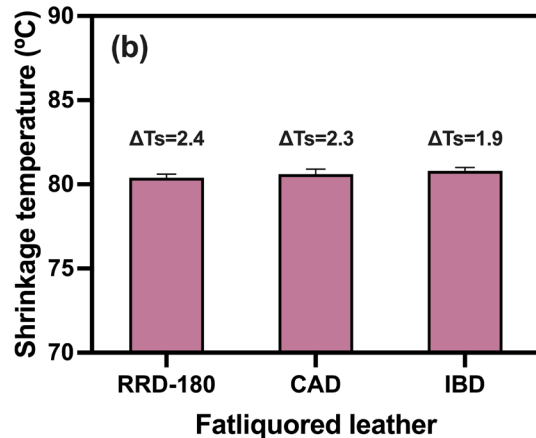
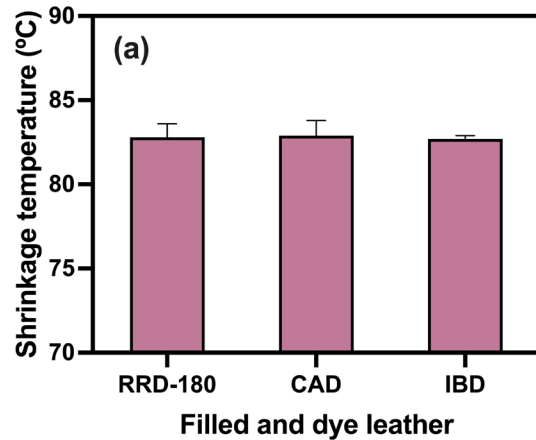
- The reaction did not change the color properties, which was beneficial for ensuring that the resultant crust leather was highly similar in the color of crust leather dyed by RRD-180.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Effect of IBD on the Ts of leather



➤ CAD: conventional anionic dye.

➤ After filling and dyeing, the Ts of three kinds of leathers crust had no obvious difference, which was higher than 80 °C.

➤ After high temperature fatliquoring, the Ts of three kinds of leathers crust decreased slightly, but it was also higher than 80 °C.

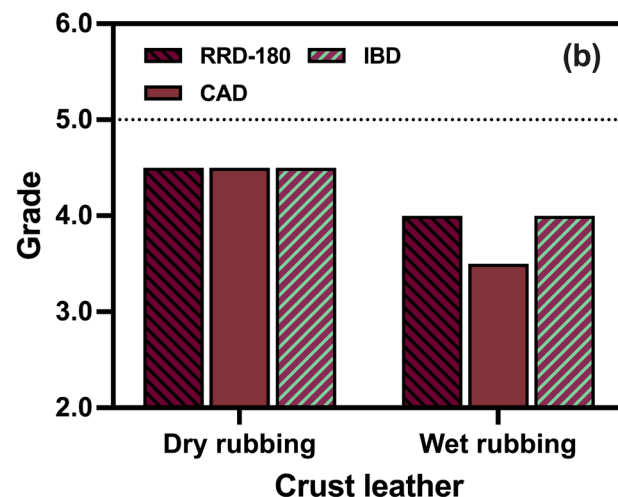
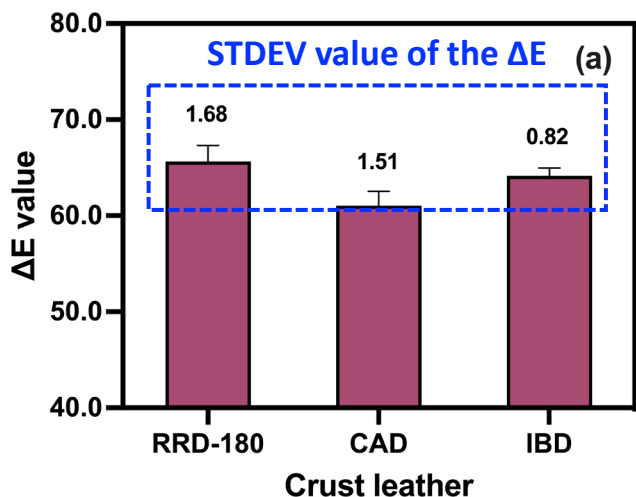
➤ Among them, the Ts decline of IBD-crust leather (1.9°C) was the lowest, suggesting that IBD had a higher stabilizing effect on the collagen fiber network of leather.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Coloring performance



The average total color difference (ΔE) of RRD-180-crust leather and IBD-crust leather compared to standard white ($L=95.26$, $a=-0.64$, $b=2.02$) was comparable, indicating that they had a similar color in the same color system.

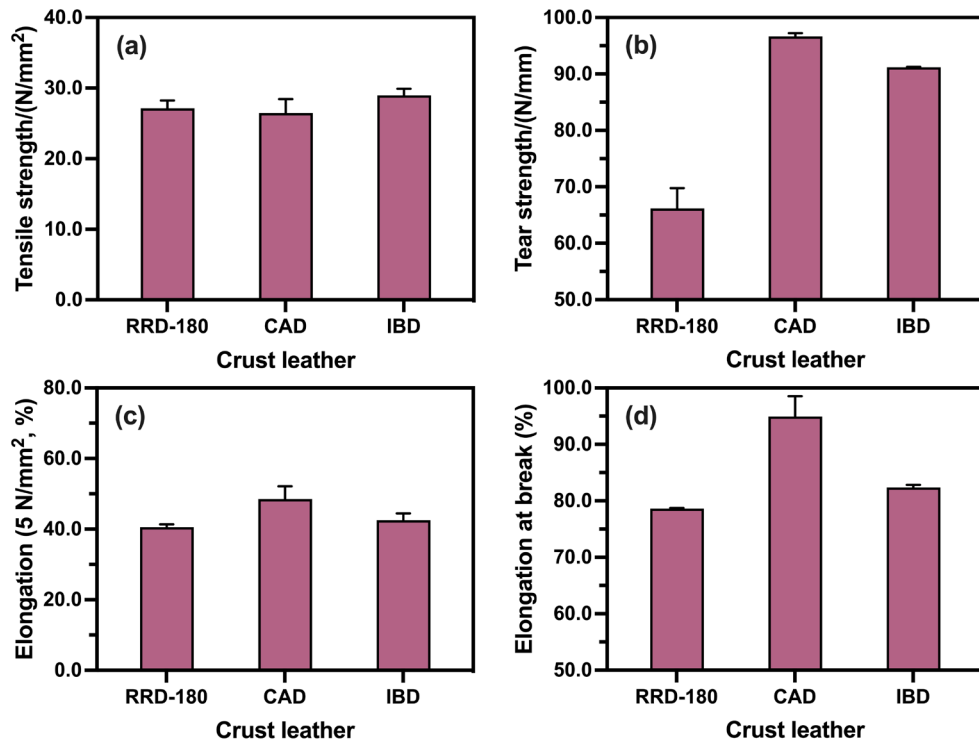
- A lower STDEV value of the ΔE value represents a higher dyeing uniformity.
- IBD-crust leather had the highest dyeing uniformity.
- The three kinds of crust leathers had favorable dry-rubbing fastness, while RRD-180-crust leather and IBD-crust leather had higher wet-rubbing fastness than CAD-crust leather.
- The as-prepared IBD can endow the BAT-tanned crust leather with better coloring performance.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Mechanical strength



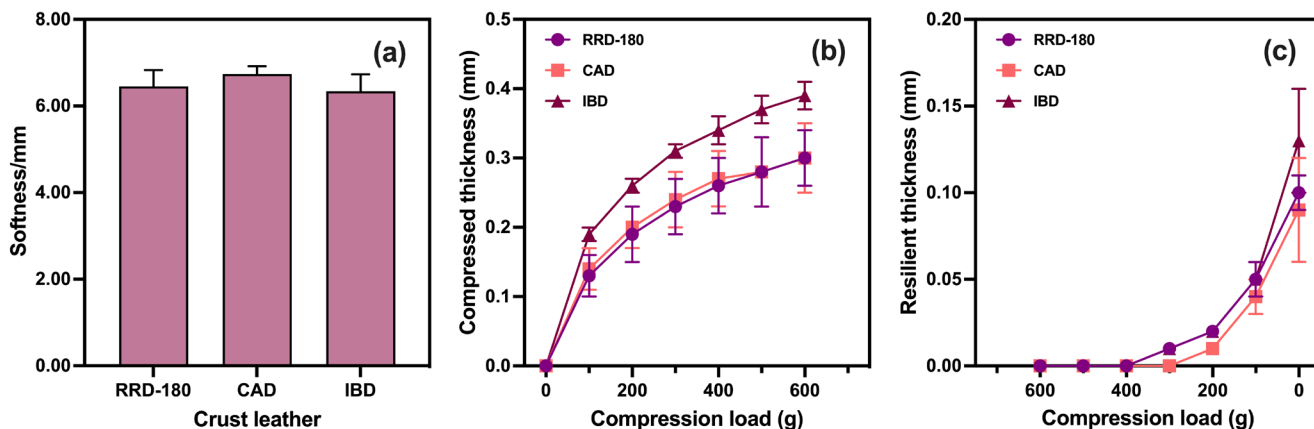
- IBD-crust leather had higher tensile strength and favorable tear strength.
- The handfeel of IBD-crust leather was tighter than that of CAD-crust leather.
- Overall, these results suggested that IBD-crust leather had favorable mechanical strength.

2. Synthesis and Application of Polymeric Dye



➤ Synthesis and application of polyurethane-based polymeric dye

Organoleptic property



➤ Higher compressed and resilient thicknesses of crust leather represent its better fullness.

➤ IBD-crust leather exhibited better fullness than RRD-180-crust leather and CAD-crust leather.

The three crust leathers had comparable and favorable softness, which was higher than 6.00 mm (the highest softness for leather is counted as 7.6 mm).

➤ In summary, IBD-crust leather exhibited satisfactory overall performances, which were better than those of the crust leathers prepared from RRD-180 and CAD dyeing systems.

3

Conclusions, Outlook and Acknowledgements



3. Conclusions, Outlook and Acknowledgements



Conclusions

- ❑ Polymeric dye is an optional functional post-tanning material for the manufacturing of high-performance chrome-free leather. Its structure and application process also need further improvement.



Outlook

- ❑ More functional leather chemicals based on biomass for “full biomass-based leather”.
- ❑ Reconstructed tanning and post-tanning system for eco-leather production.
- ❑ The sustainable and carbon-neutral development of the leather industry.

3. Conclusions, Outlook and Acknowledgements



➤ Acknowledgements

The 37th IULTCS congress organizing committee

国家重点研发计划

2020YFE0203800



22108297



高端外国专家引进计划

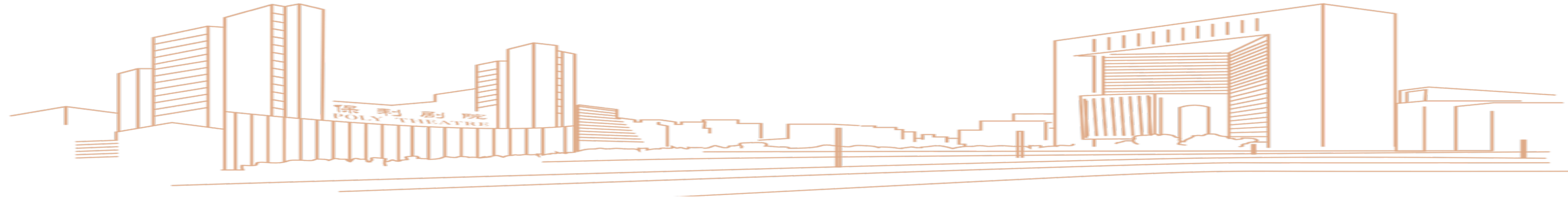
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Support from the leaders and colleagues

The team, the family!

Thanks for your listening!



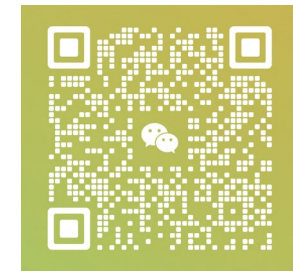
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