Supporting Information

Ionic Liquid Capsules for Cold-Resistant Leather: Connecting Three Pillars of Green Chemicals, Clean Process and Green Products

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Table S1 Process recipe for making garment leather using chrome and zeolite tanned leathers

Raw Materials: Chrome tanned and zeolite tanned leather (sheep) – Shaved thickness -0.9 mm										
Process	*Chemical Name*	*% Offered* [#]				*Duration (drumming time)*				*Remarks*
		ENS	*CTAB*	*SSE*	*SSP*	*ENS*	*CTAB*	*SSE*	*SSP*	
Neutralization	Water Sodium formate Sodium bicarbonate	100 1 1	100 1 1	100 1 1	100 1 1	(3 x 10 min) + 60 min	(3 x 10 min) + 60 min	(3 x 10 min) + 60 min	(3 x 10 min) + 60 min	Cross-section pH 6.5 ±0.2 Drain/Wash/Drain
Retanning	Low molecular weight phenolic syntan Melamine resin syntan Protein filler	3 3 2	- - -	- - -	- - -	(40 + 20 min)+ 30 min				
Fatliquoring	Synthetic fatliquor Semi synthetic fatliquor ENS SS capsules system	6 6 12 	4 4 - 14	4 4 - 14	4 4 - 14	2 x 60 min	2 x 60 min	2 x 60 min	2 x 60 min	
Dyeing	Acid Blue 9 dye	2*	2*	2*	2*	60 min	45 min	30 min	30 min	Check penetration
Fixing	Formic acid	3.5	3.5	3.5	3.5	(3 x 10 min) + 30 min	(3 x 10 min) + 30 min	(3 x 10 min) + 30 min	(3 x 10 min) + 30 min	Check exhaustion /Drain
Next day: - Hooking/ Stacking/Toggling/Trimming/Buffing. [#] Offer of chemicals based on the shaved weight *Offer of chemicals based on the crust weight										

Analytical Data:

Oleic acid: 1H NMR (400 MHz, DMSO-d6) δ 11.46 (s, 1H), 5.14 – 4.99 (m, 2H), 1.93 (t, J = 7.5 Hz, 2H), 1.76 (q, J = 6.3 Hz, 4H), 1.28 (t, J = 7.2 Hz, 2H), 1.15 – 0.92 (m, 20H), 0.62 (t, 3H). 13C NMR (101 MHz, DMSO-d6) δ 176.09, 129.70, 129.60, 55.01, 53.18, 53.14, 53.10, 31.34, 29.47, 29.28, 29.15, 29.09, 28.89, 28.81, 28.75, 28.64, 26.71, 26.61, 26.40, 22.15, 13.97.

Cholinium Oleate: 1H NMR (400 MHz, DMSO-d6) δ 5.33 – 5.29 (m, 2H), 3.85 – 3.82 (m, 3H), 3.44 – 3.41 (m, 2H), 3.12 (s, 8H), 1.96 (td, J = 7.3, 3.7 Hz, 4H), 1.86 (t, J = 7.5 Hz, 2H), 1.39 (t, J = 7.2 Hz, 2H), 1.29 – 1.17 (m, 20H), 1.05 (t, J = 7.0 Hz, 1H), 0.86 – 0.82 (m, 3H). 13C NMR (101 MHz, DMSO-d6) δ 174.84, 129.86, 34.26, 32.16, 29.98, 29.97, 29.80, 29.61, 29.58, 29.53, 29.47, 29.44, 27.36, 25.21, 22.89, 14.26.

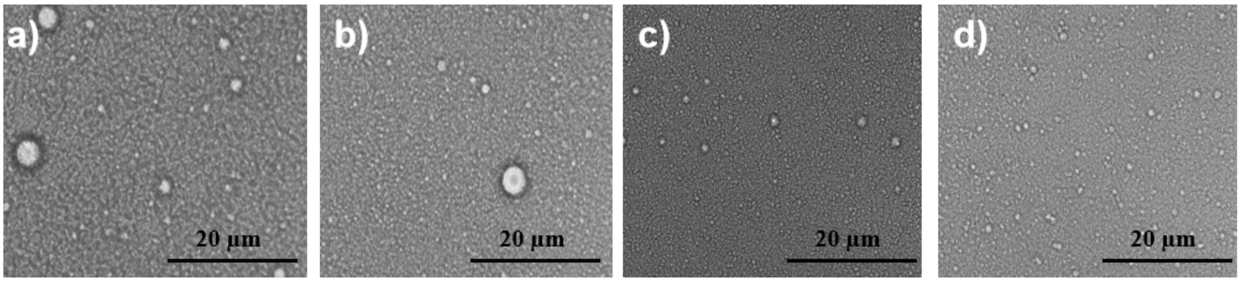

Figure S1 Optical microscope images of silicone oil emulsion using a) CTAB, b) [Cho][Ole], c) [Cho][Ole]/EMIm $EtSO_4$ and d) [Cho][Ole]/[P_{66614}][Dec].

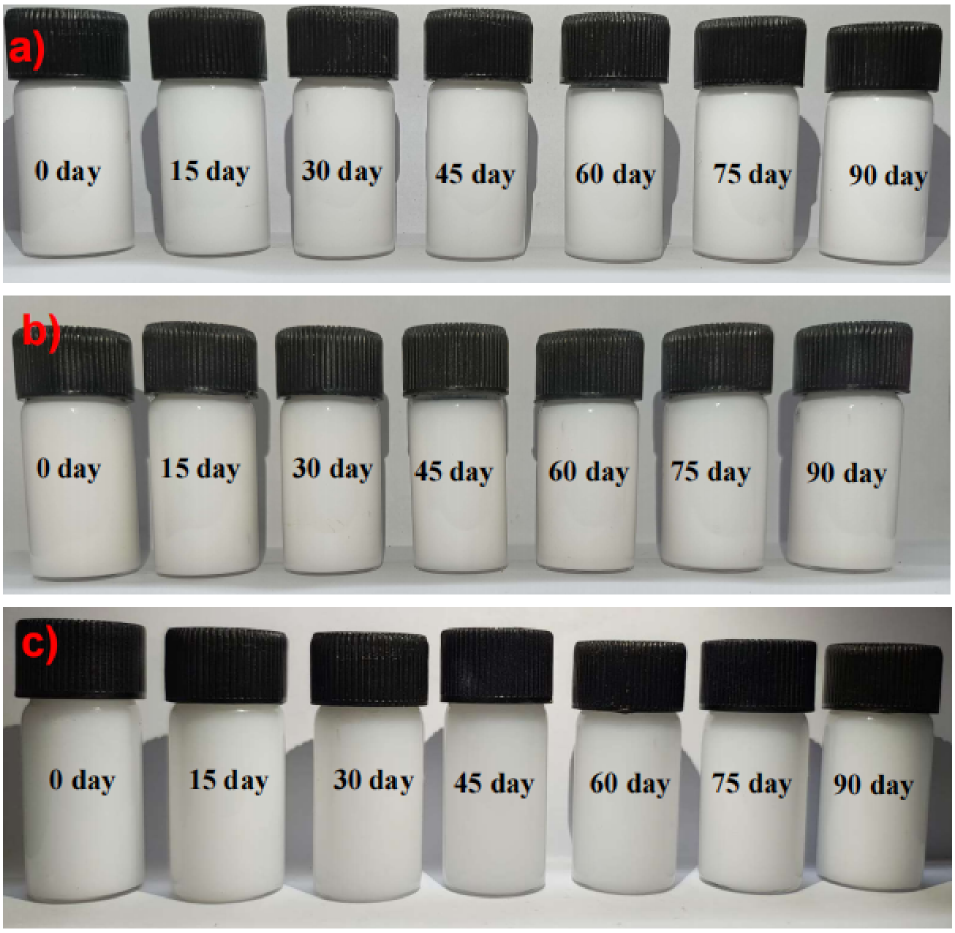

Figure S2 Colour photographs of [Cho][Ole] ILs emulsion a) containing EMIm EtSO4, b) emulsion containing [P_{66614}][Dec] and c) CTAB containing EMIm EtSO4 for 90 days.

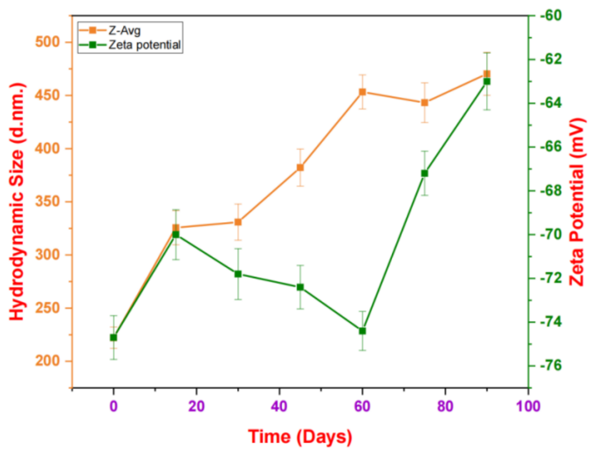

Figure S3 Stability of CTAB emulsion for 90 days

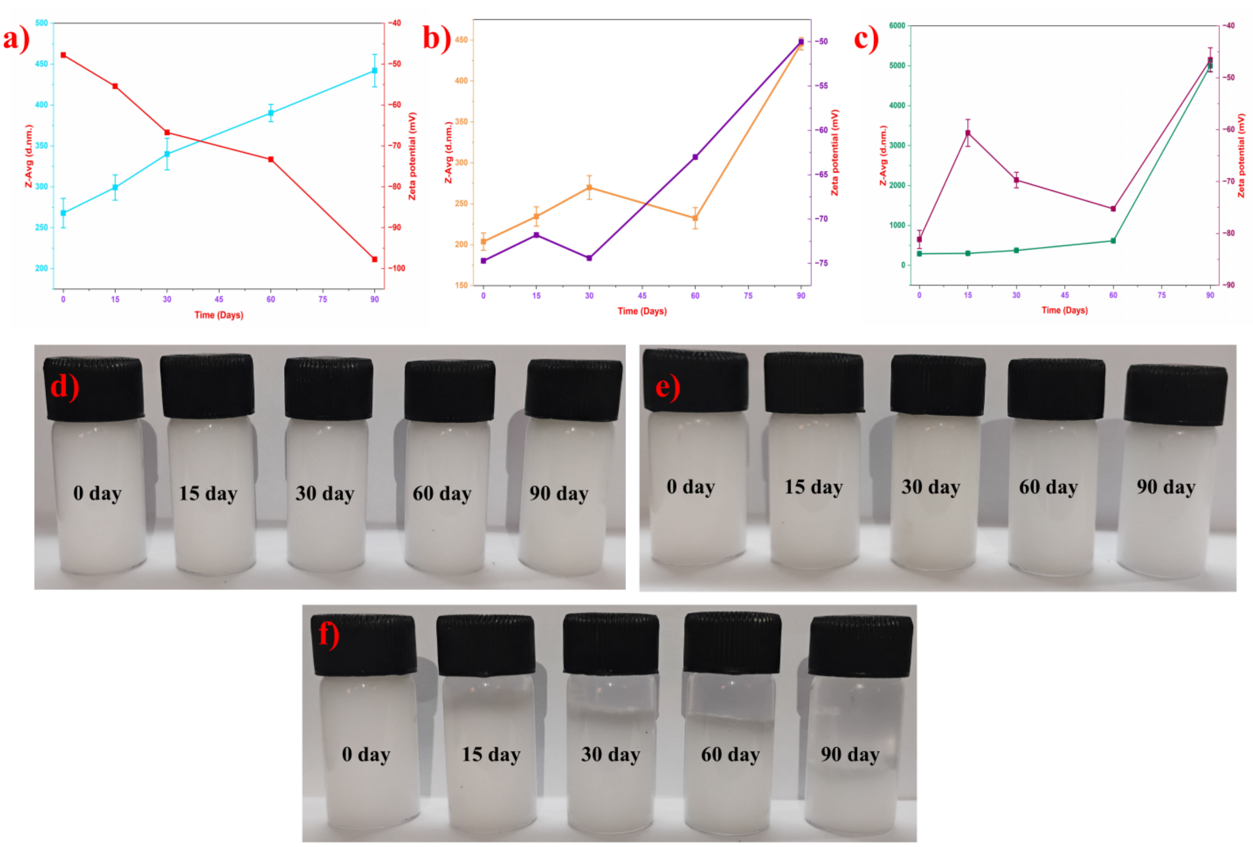

Figure S4 Stability of a, d) SSE, b, e) SSP and c, f) CTAB capsules for 90 days and its respective colour photographs.

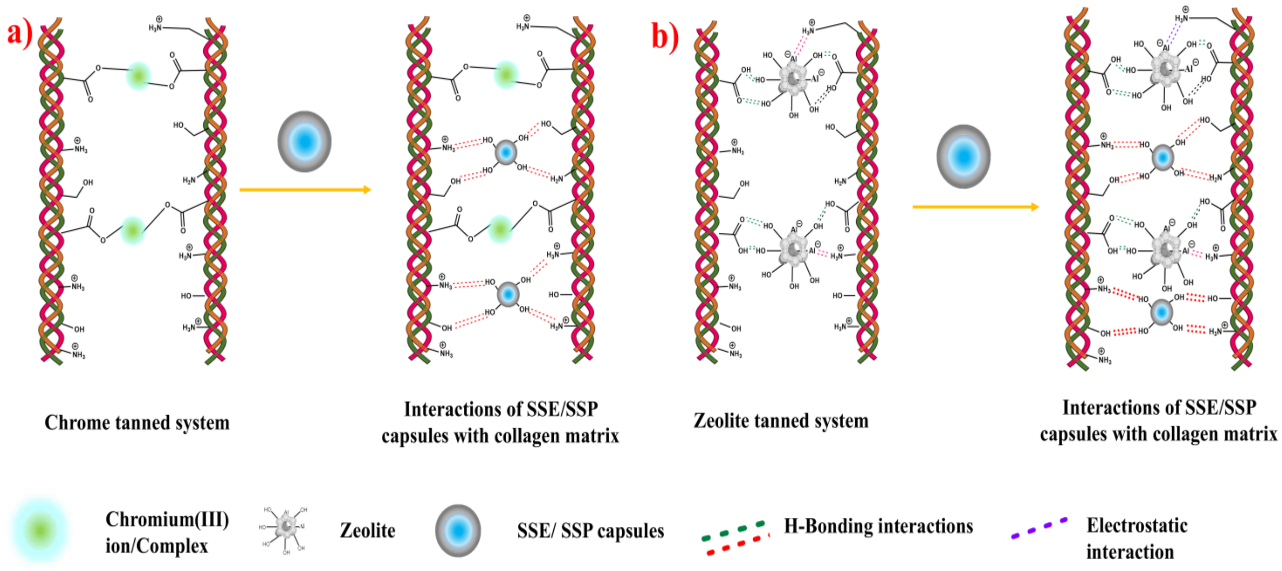

Figure S5 Possible interactions of silica capsules (SSE/SSP) with chrome and zeolite tanned leathers

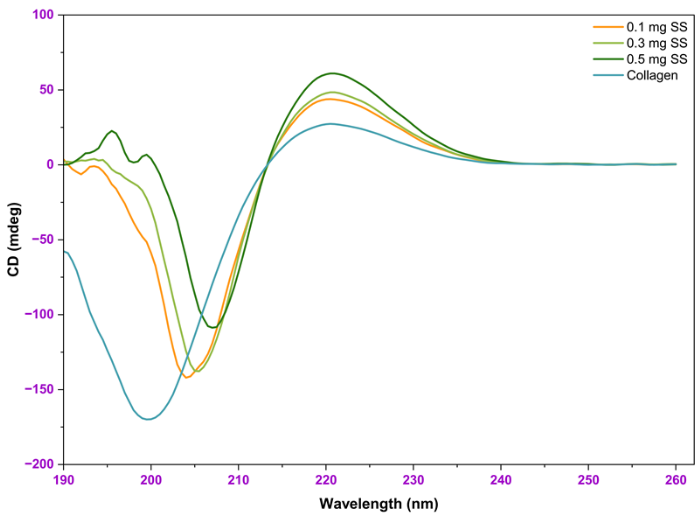

Figure S6 Circular Dichroism (CD) spectra of collagen with silica capsules

Table S2 Cold-resistant behaviour of IL-treated leathers in repeated room temperature to -20°C (thermal-cooling) Cycles.

System	Cycles	Initial Temperature (°C)	Final Temperature (°C)	Temperature Difference (°C)
	Cycle I	23.2	2.1	21.1
ENS-C	**Cycle II**	23.1	1.8	21.3
	Cycle III	23.0	1.8	21.2
	Cycle I	23.2	4.1	19.1
CTAB-C	**Cycle II**	25.2	4.0	21.2
	Cycle III	23.4	4.2	19.2
	Cycle I	25.8	11.5	14.3
SSE-C	**Cycle II**	24.3	9.2	15.1
	Cycle III	24.5	10	14.5
	Cycle I	24.7	9.5	15.2
SSP-C	**Cycle II**	25.1	8.6	16.5
	Cycle III	25.5	7.9	17.6
	Cycle I	24.3	4.4	19.9
ENS-Z	**Cycle II**	24.5	5.0	19.5
	Cycle III	25.5	4.7	20.8
	Cycle I	24.2	4.7	19.5
CTAB-Z	**Cycle II**	24.0	4.6	19.4
	Cycle III	24.0	4.0	20
	Cycle I	23.7	9.6	14.1
SSE-Z	**Cycle II**	23.5	10.2	13.3
	Cycle III	24.0	9.9	14.1
	Cycle I	24.0	5.1	18.9
SSP-Z	**Cycle II**	24.2	4.2	19
	Cycle III	25.2	5.8	19.4

Table S3 Cold-resistant behaviour of IL-treated leathers at -20°C after 3 months.

System	Initial Temperature (°C)	Final Temperature (°C)	Temperature Difference (°C)
ENS-C	24.2 ± 0.1	0.7 ± 1.3	23.5 ± 1.2
CTAB-C	24 ± 0.1	1.2 ± 1.6	22.8 ± 1.5
SSE-C	24.3 ± 0.3	7.3 ± 1.1	17.0 ± 0.8
SSP-C	24.7 ± 0.1	5.9 ± 1.2	18.8 ± 1.1
ENS-Z	24.3 ± 0.3	- 0.5 ± 1.3	24.8 ± 1
CTAB-Z	24.2 ± 0.2	- 1.0 ± 1.2	25.2 ± 1
SSE-Z	23.7 ± 0.1	7.5 ± 1.4	16.2 ± 1.3
SSP-Z	24.0 ± 0.2	3.6 ± 1.1	20.4 ± 0.9

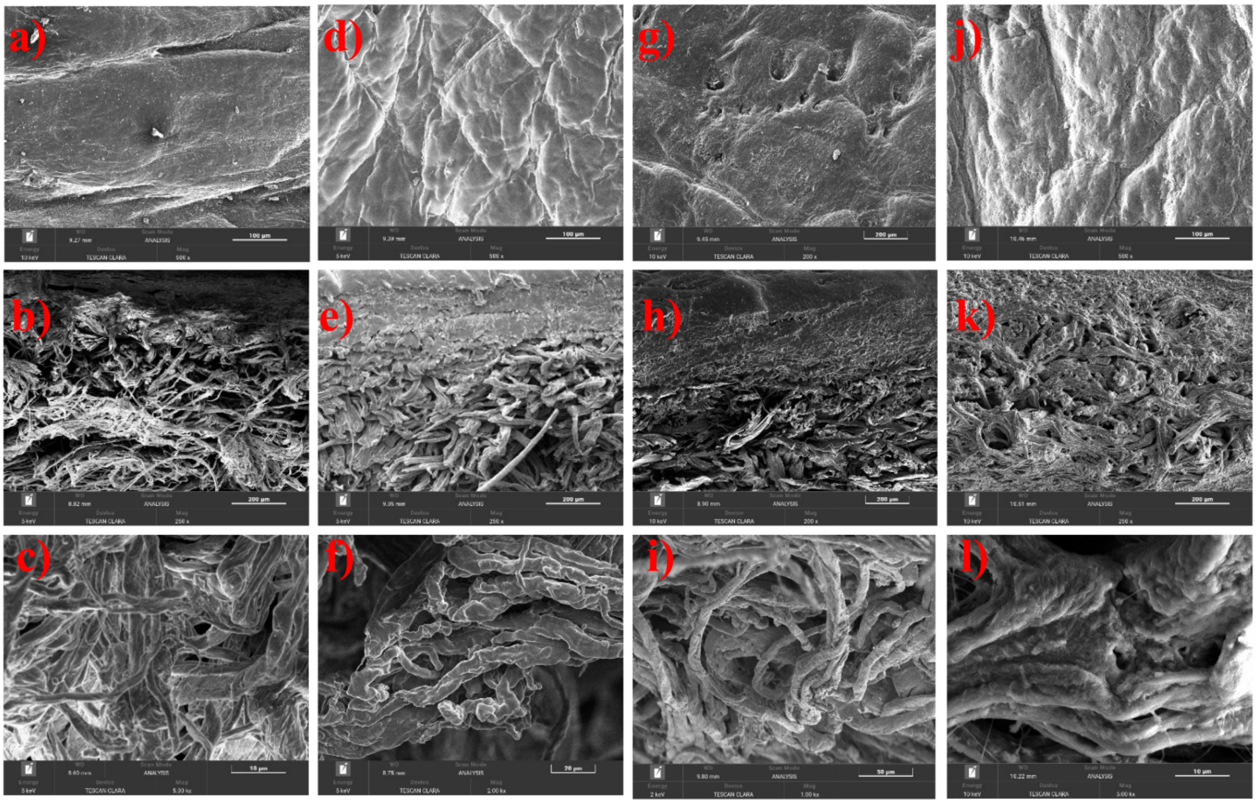

Figure S7 SEM images of surface and cross section of chrome tanned a-c) ENS, d-f) CTAB and zeolite tanned g-i) ENS and j-l) CTAB systems

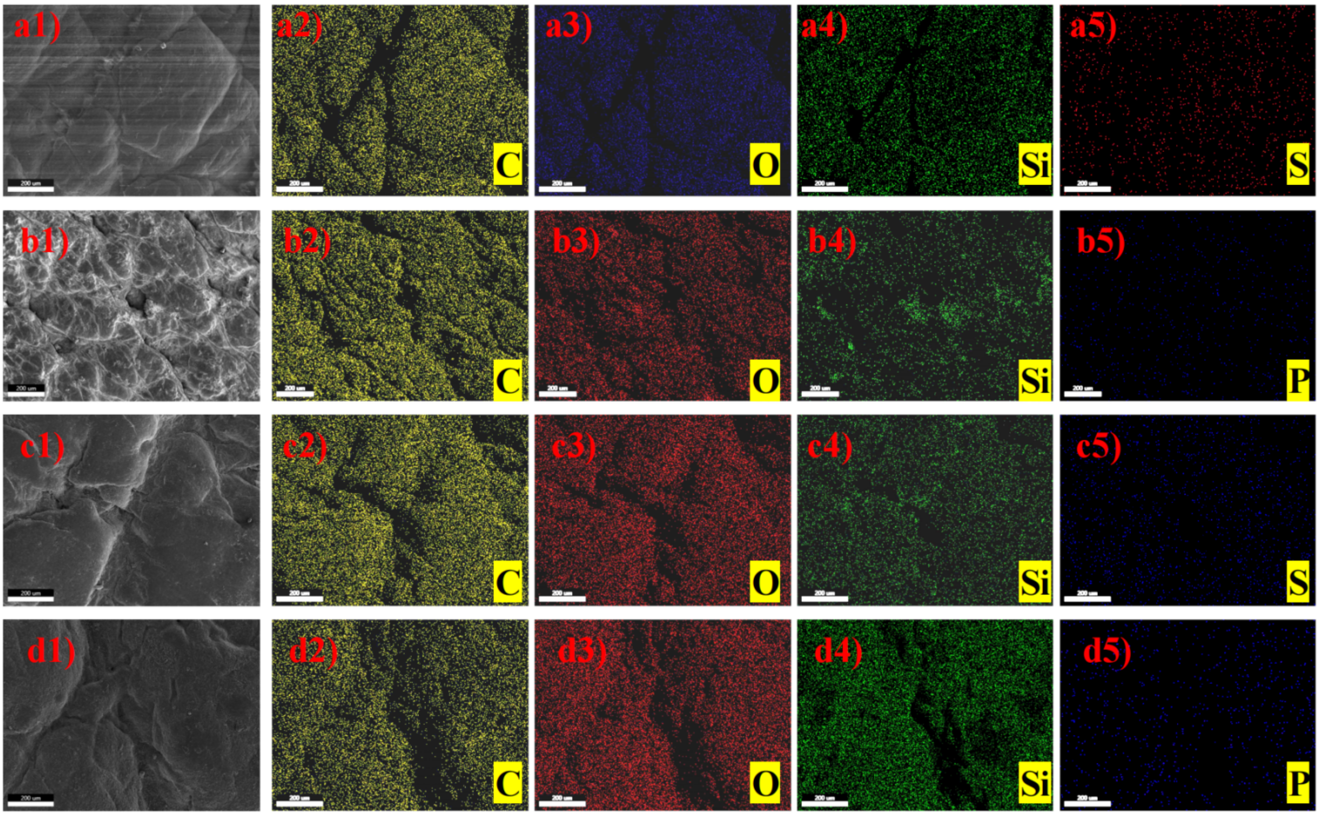

Figure S8 SEM EDAX mapping of chrome tanned a1-a5) SSE, b1-b5) SSP and zeolite tanned c1-c5) SSE and d1-d5) SSP nanocapsules system

Table S4 Colourfastness to circular rubbing, colourfastness to perspiration and lightfastness for SS treated chrome tanned and zeolite tanned systems

Sample	Colourfastness to circular rubbing		Colourfastness to perspiration		Lightfastness to xenon lamp (Blue wool rating)
	Dry-256	Wet-512	Acid	Alkali	
ENS-C	4	4	4/5	4/5	7
CTAB-C	4	4	4/5	4/5	7
SSE-C	4/5	4	4/5	4/5	7
SSP-C	4/5	4	4/5	4/5	7
ENS-Z	4	2/3	4/5	4/5	7
CTAB-Z	4	3	4/5	4/5	7
SSE-Z	4/5	3/4	4/5	4/5	7
SSP-Z	4/5	3/4	4/5	4/5	7

Table S5 Comparison of cold-insulation materials reported in the literature with the current work.

Material	**Cold Insulation Tested**	**Cold crack resistance Tested**	**Brethability Tested**	**Treatment strategy**
silicone oil–PMMA capsules[1]	Yes (-25 ℃)	No	No	Surface coating
microencapsulated phase change materials based on hydrocarbons[2]	No	Yes (evaluated interms of thermoregulation)	-	Surface coating
hexagonal boron nitride–PEG composites[3]	−17 ± 2 ℃	No	No	Surface coating
dioctyl adipate plasticizers[4]	-	-60 ℃	No	Surface coating
IL-silicone oil loaded silica capsules	-20 ℃	-20 ℃	Yes	Fiber penetration-This work

Table S6 Estimated Cost for Synthesis of Cholinium Oleate Ionic Liquid

Reagents	**Required quantity (g)**	**Cost / Kg ($)**	**Cost ($)**
Oleic acid	77.25	2.26	0.174
Choline hydroxide	33.14	1.45	0.0480
Ethanol	300 mL	1.04	0.31
Product			**0.532**
Cholinium Oleate (95 %)	100		

*For synthesis of 100g of Cholinium oleate

Table S7 Estimated Cost for Emulsification of Silicone Oil using IL and CTAB

Reagents	Required quantity (g)	Cost / Kg ($)	Cost ($)	
			IL system	CTAB system
Cholinium Oleate	15.42	5.32	0.0820	-
Cetyltrimethylammonium bromide	36.45	20	-	0.729
Silicone oil	1000g	3.39	3.39	3.39
Total cost			**3.472**	**4.119**

*All the prices were directly quoted from Indiamart.

Table S8 Amount of surfactant and required for emulsification of Silicone oil (100 CPS) using Cholinium Oleate and Cetyltrimethylammonium bromide

Reagents	Conventional Surfactant System	Ionic Liquid System
Silicone oil	1000 g	1000 g
Cetyltrimethylammonium bromide	36.45 g	-
Cholinium Oleate	-	15.42 g
Water	2300 mL	1000 mL
Product		
Silicone emulsion	3075 mL	2040 mL

*For emulsifying 1000 g of oil

Table S9 Ecoscale score calculation for preparation of IL and CTAB assisted emulsion

SI.No.	Parameters	Penalty Points	
		ILs assisted silicone emulsion	**CTAB assisted silicone emulsion**
1	Yield	0 (100 %)	-1.5 (97%)
2	Price/availability	0	(CTAB) -2
3	Safety	0	(CTAB) -2
4	Technical setup: unconventional activation technique (Ultrasonic homoginizer)	-2	-2
5	Temperature/time: RT/ <1hr	0	0
6	Workup and purification: None	0	0
Ecoscale score		**98**	**92.5**

Table S10 Estimated Cost for Emulsification of Silica encapsulated Silicone Oil emulsion using IL and CTAB (with additional IL)

Reagents	Required quantity (g)	Cost / Kg ($)	Cost ($)		
			IL system		CTAB system (with EMIM $EtSO_4$)
			SSE	SSP	
Cholinium Oleate	15.42	5.32	0.0820	0.0820	-
Cetyltrimethylammonium bromide	36.45	20	-	-	0.729
Silicone oil	1000	3.39	3.39	3.39	3.39
1-Ethyl-3-methylimidazolium ethyl sulfate	50	81.99	4.099	-	4.099
Trihexyltetradecylphosphonium decanoate	50	163.99	-	8.199	-
TEOS	2000 mL	1.16	2.32	2.32	2.32
Aqueous ammonia	1000 mL	0.31	0.31	0.31	0.31
Total cost			**10.201**	**14.301**	**10.848**

* for producing 10kg of leather

Table S11 Estimated cost for producing 1 ton of cold resistant leather

Chemicals	***Price per Kg ($)***	***ENS***	***CTAB***	***IL system***	
				SSE	***SSP***
Retanning					
Low weight phenolic syntan	4.08	122.4	-	-	-
Melamin resin syntan	3.78	113.4	-	-	-
Protein filler	4.67	93.4	-	-	-
Fatliquoring					
Synthetic fatliquors	6.2	496	248	248	248
Semi-synthetic fatliquors	5.60	448	224	224	224
ENS	7.45	894	-	-	-
SSE capsules	8.05	-	-	1020.10	-
SSP capsules	11.28	-	-	-	1430.10
CTAB capsules	8.75	-	1084.80	-	-
Dyeing & fixing					
Acid blue 9	104.8	104.8	104.8	104.8	104.8
Formic acid	22.40	22.40	22.40	22.40	22.40
Total cost		2295.4	1684	1619.3	2029.3

Green Metrics

For Emulsification

1. Water Intensity (WI) = $\frac{Tatal\ Water\ used\ (mL)}{Mass\ of\ the\ Product\ (g)}$

WI $_{(IL)}$ = $\frac{50}{102}$ = 0.490

WI $_{(CTAB)}$ = $\frac{115}{154}$ = 0.746

2. Reaction Mass Efficiency (RME) = $\frac{Mass\ of\ the\ product\ (g)}{Total\ Mass\ of\ the\ reactants\ (g)}$ **x100**

RME $_{(IL)}$ = $\frac{50}{50.771}$ = 99.23

RME $_{(CTAB)}$ = $\frac{47.5}{51.822}$ = 91.65

3. Energy Intensity (WI) = $\frac{Total\ Energy\ Used\ (kWh)}{Mass\ of\ the\ Product\ (Kg)}$

EI $_{(IL)}$ = $\frac{0.25}{0.1}$ = 2.5

EI $_{(CTAB)}$ = $\frac{0.375}{0.095}$ = 3.94

For Leather Processing

1. **Water Intensity (WI) =** $\frac{Tatal\ Water\ used\ (mL)}{Mass\ of\ the\ Product\ (g)}$

WI $_{(IL)}$ = $\frac{300}{520}$ = 0.576

WI $_{(CTAB)}$ = $\frac{375}{515}$ = 0.728

WI $_{(ENS)}$ = $\frac{500}{510}$ = 0.980

2. Energy Intensity (WI) = $\frac{Total\ Energy\ Used\ (kWh)}{Mass\ of\ the\ Product\ (Kg)}$

$$EI_{(IL)} = \frac{5}{1.04} = 4.80$$

$$EI_{(CTAB)} = \frac{5}{1.03} = 4.85$$

$$EI_{(ENS)} = \frac{7}{1.03} = 6.79$$

Table S12a Green Metrics Comparison for ILs and conventional surfactant based Emulsion Preparation

Green Metrics	CTAB System (Conventional)	IL System ([Cho][Ole])	Improvement
Reaction Mass Efficiency (%)	91.65	99.23	8.3%
Eco-Scale Score	92.5	98	5.9
Water Intensity (WI)	0.746	0.490	34.3 %
Surfactant Consumption (g/Kg of oil)	36.45	15.42	57.69%
Emulsification Time (min.)	30	20	33%
Energy Consumption for Emulsification (kWh /Oil)	3.94	2.5	36.5 %
Cost of Emulsion Preparation ($ / kg)	4.12	3.47	16%

Table S12b Green Metrics Comparison for Leather processing (conventional and present report).

Green Metrics	Conventional ENS multi-step	IL-assisted single-step	Improvement
Water Usage in Post-Tanning (L)	1.0	0.6	41%
Processing Time (h)	7	5.5	21%
Energy Consumption (kWh)	6.79	4.80	29%
Carbon Footprint (process only) (CO_2 kg)	4.86	3.43	29%
Total Production Cost (1 tonne leather, $)	2,295.5	1,684	26.6%

Wastewater COD (mg/L)	17600 (Chrome) 15200 (Zeolite)	15200 (Chrome) 8000 (Zeolite)	13.6 % (Chrome) 47.3 % (Zeolite)

References

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3. A. P Bhasi, N. Hanna Wilson and T. Palanisamy, *ACS omega*, 2022, **7**, 45120-45128.
4. *China Pat.,* CN102168382A, 2011.