Electronic Supplementary Information

Polysaccharide-based Supramolecular Bicomponent Eutectogels as Sustainable Antioxidant Materials

*Salvatore Marullo, Floriana Petta, Giulia Infurna, Nadka T. Dintcheva, Francesca D'Anna**

Università degli Studi di Palermo, Dipartimento di Scienze Biologiche, Chimiche e Farmaceutiche, Viale delle Scienze, Ed. 17, 90128 Palermo, Italia

Table of contents

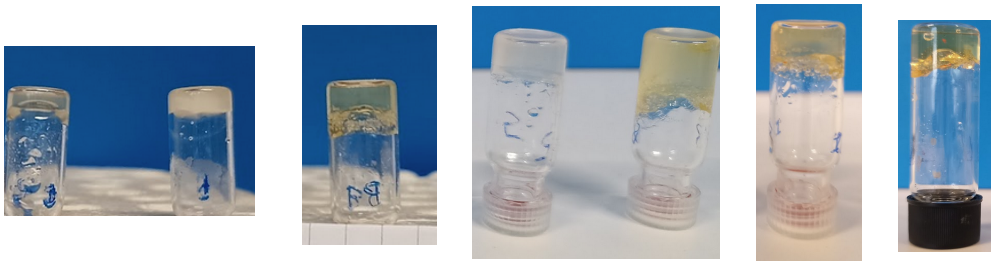
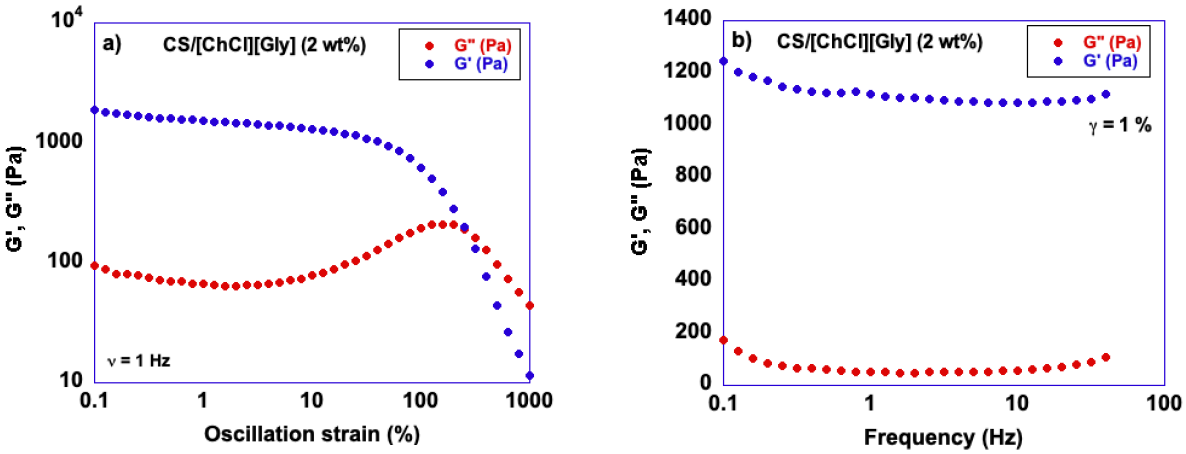
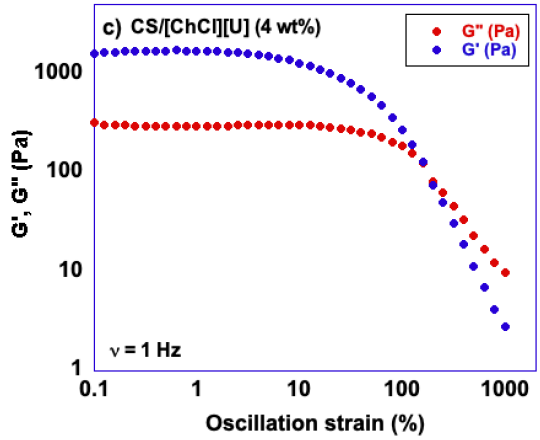
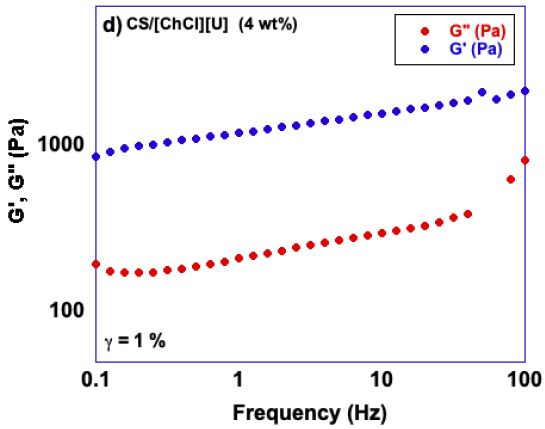


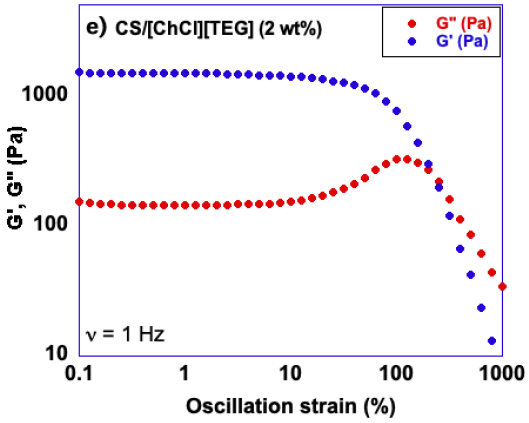
Figure S1. Representative pictures of eutectogels, from left to right: CS/[ChCl][EG], CS/[ChCl][U], CS/[ChCl][DEG], CS:CE (1:0.4)/[ChCl][U], CS:CE (1:0.2)/[ChCl][U] and CS/[ChCl][Gly].

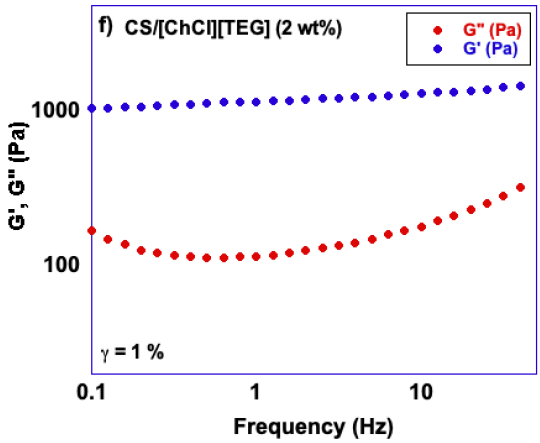
Figure S2. Picture of CS:[ChCl][MA] 2 wt% eutectogel after rheology measurement.

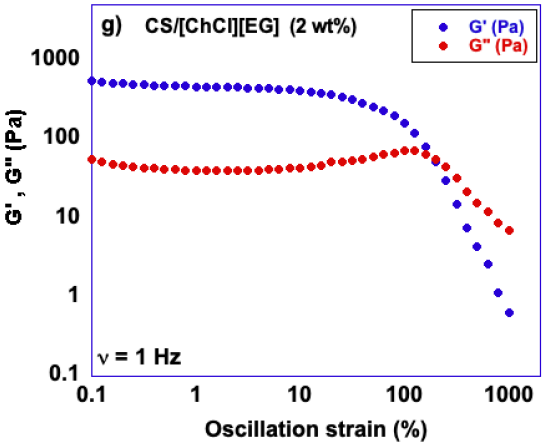


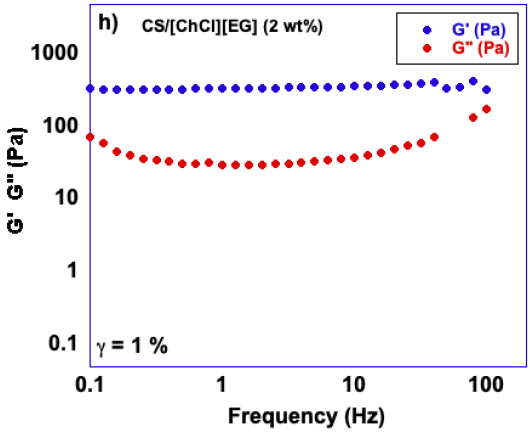

c) CS/[ChCl][U] (4 wt%)
G" (Pa)
G' (Pa)
G', G" (Pa)
1000
100
10
1
ν = 1 Hz
0.1
1
10
100
1000
Oscillation strain (%)

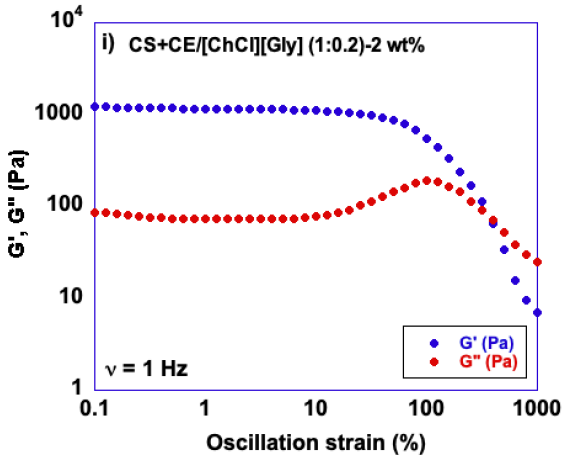

d) CS/[ChCl][U] (4 wt%)
G" (Pa)
G' (Pa)
G', G" (Pa)
1000
100
γ = 1 %
0.1
1
10
100
Frequency (Hz)

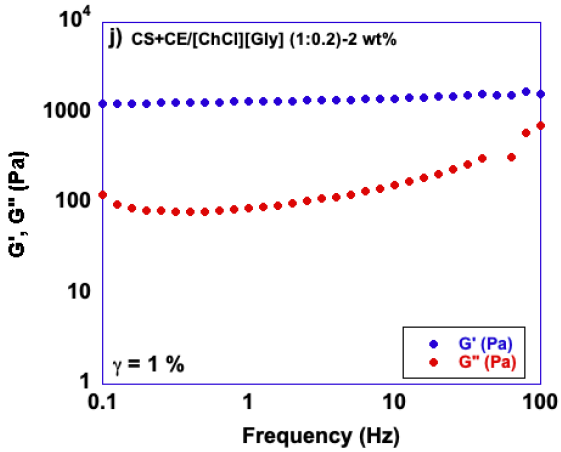

e) CS/[ChCl][TEG] (2 wt%)
G" (Pa)
G' (Pa)
G', G" (Pa)
1000
100
10
ν = 1 Hz
0.1
1
10
100
1000
Oscillation strain (%)

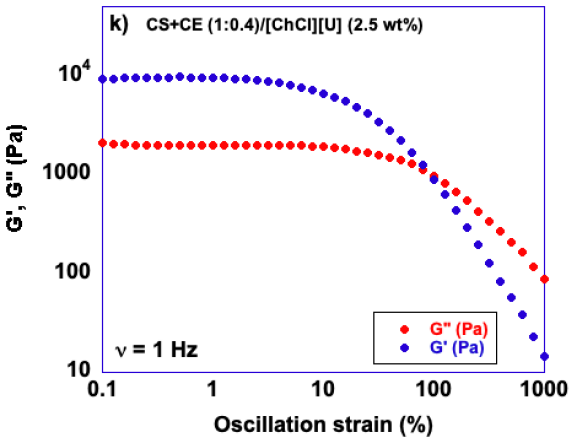

f) CS/[ChCl][TEG] (2 wt%)
G" (Pa)
G' (Pa)
G', G" (Pa)
1000
100
γ = 1 %
0.1
1
10
Frequency (Hz)

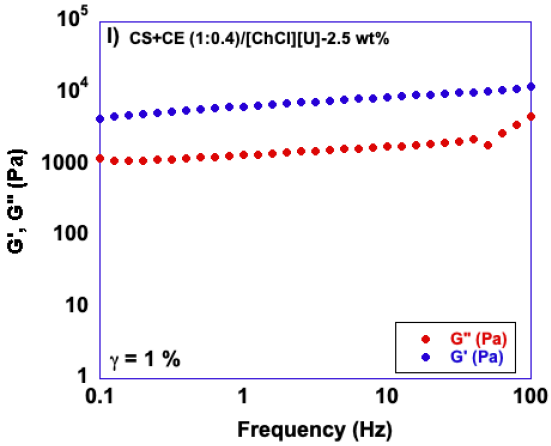

g) CS/[ChCl][EG] (2 wt%)
G' (Pa)
G" (Pa)
G' , G" (Pa)
1000
100
10
1
0.1
ν = 1 Hz
0.1
1
10
100
1000
Oscillation strain (%)

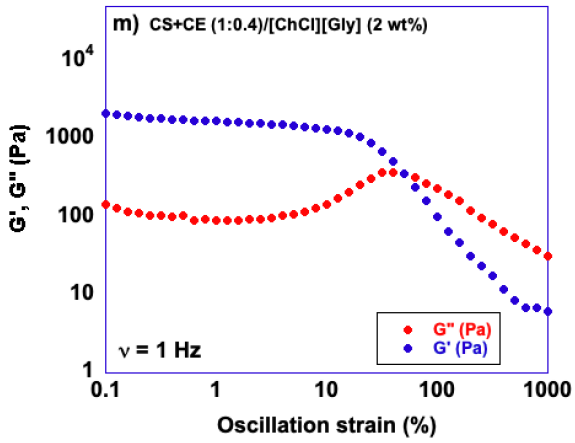

h) CS/[ChCl][EG] (2 wt%)
G' (Pa)
G" (Pa)
G' G" (Pa)
1000
100
10
1
0.1
γ = 1 %
0.1
1
10
100
Frequency (Hz)

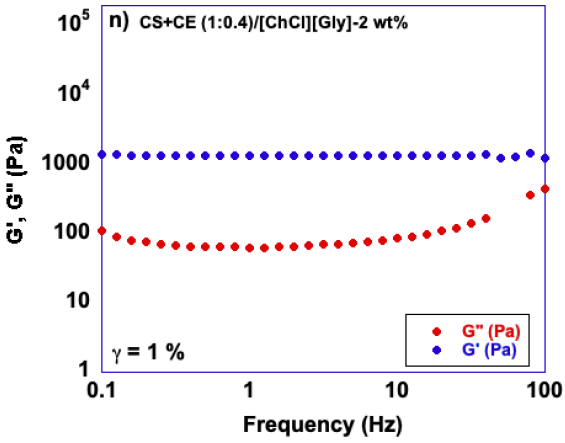

i) CS+CE/[ChCl][Gly] (1:0.2)-2 wt%
G', G" (Pa)
ν = 1 Hz
G' (Pa)
G" (Pa)
Oscillation strain (%)


j) CS+CE/[ChCl][Gly] (1:0.2)-2 wt%
G', G" (Pa)
γ = 1 %
G' (Pa)
G" (Pa)
Frequency (Hz)


k) CS+CE (1:0.4)/[ChCl][U] (2.5 wt%)
G', G" (Pa)
ν = 1 Hz
G" (Pa)
G' (Pa)
Oscillation strain (%)


l) CS+CE (1:0.4)/[ChCl][U]-2.5 wt%
G', G" (Pa)
γ = 1 %
G" (Pa)
G' (Pa)
Frequency (Hz)


m) CS+CE (1:0.4)/[ChCl][Gly] (2 wt%)
G', G" (Pa)
ν = 1 Hz
G" (Pa)
G' (Pa)
Oscillation strain (%)


n) CS+CE (1:0.4)/[ChCl][Gly]-2 wt%
G', G" (Pa)
γ = 1 %
G" (Pa)
G' (Pa)
Frequency (Hz)

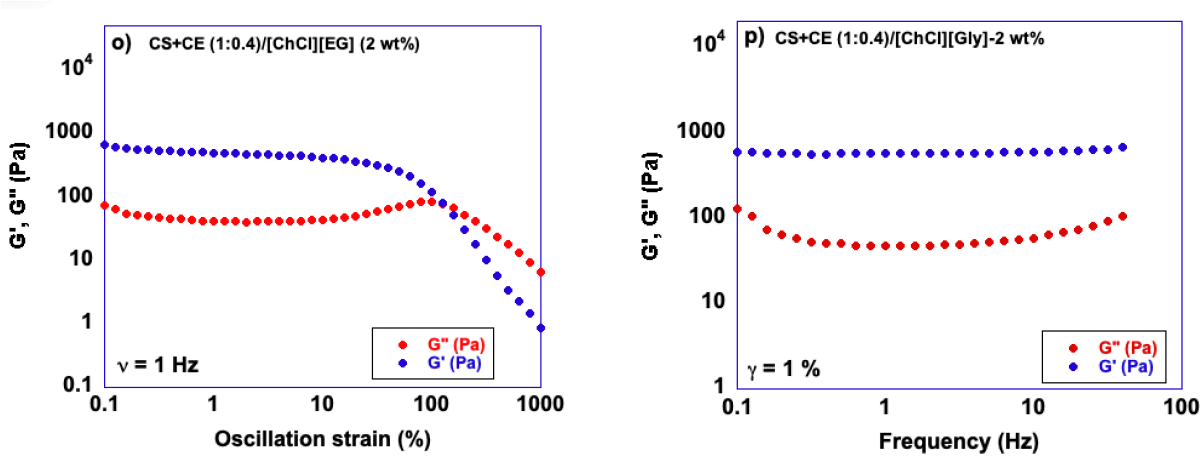
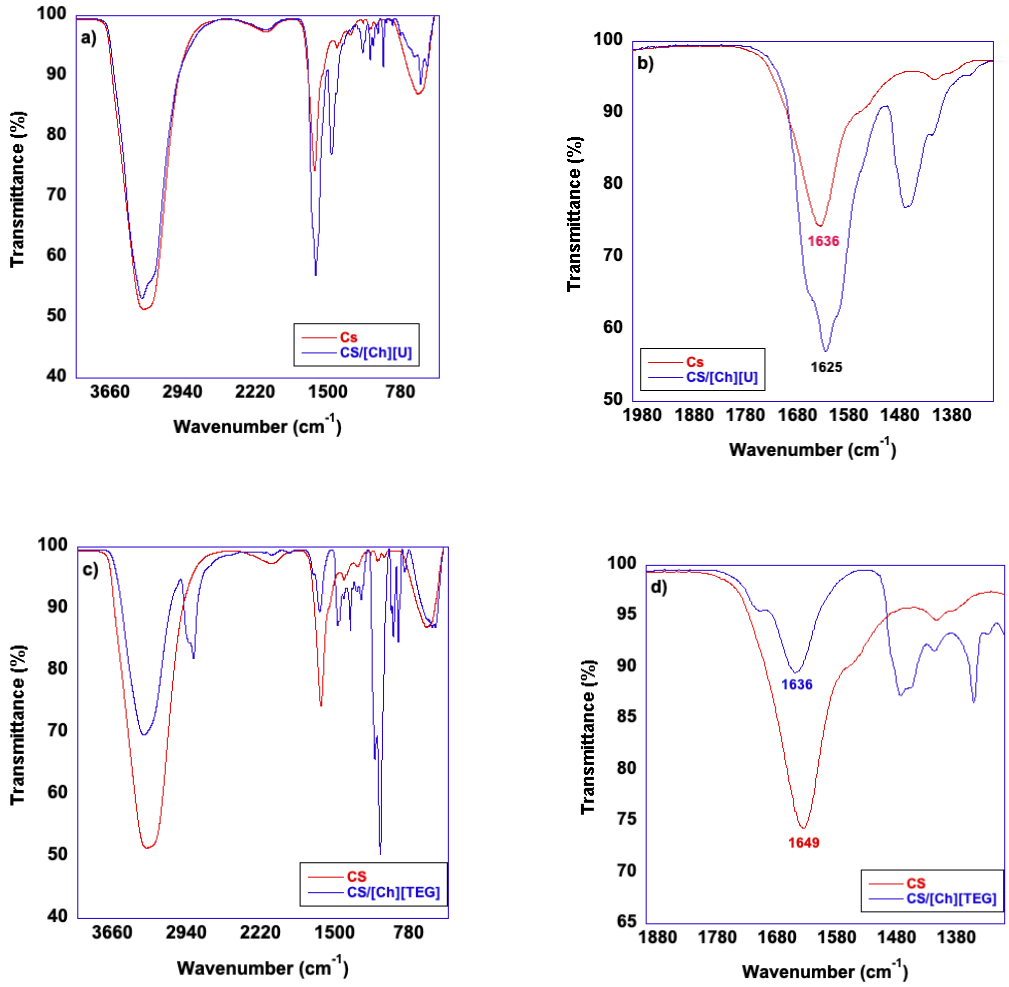
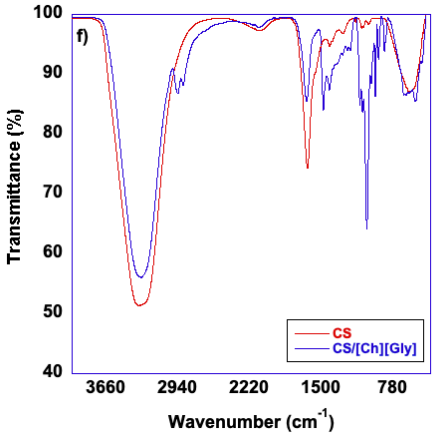
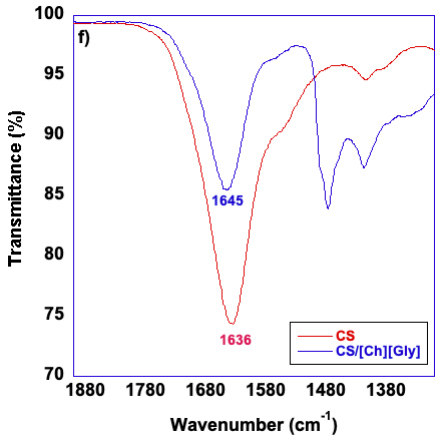
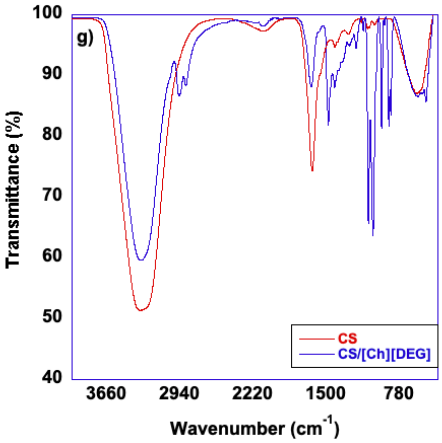


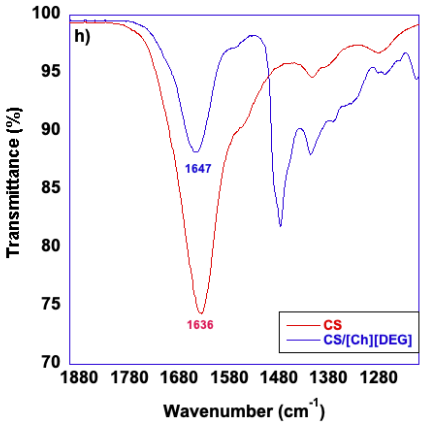
Figure S3. Plots of strain and frequency sweeps measurements for biopolymer-based eutectogels.

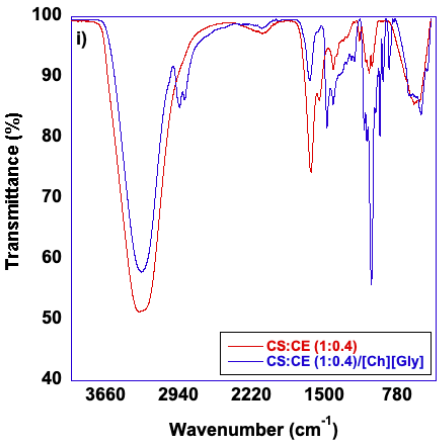


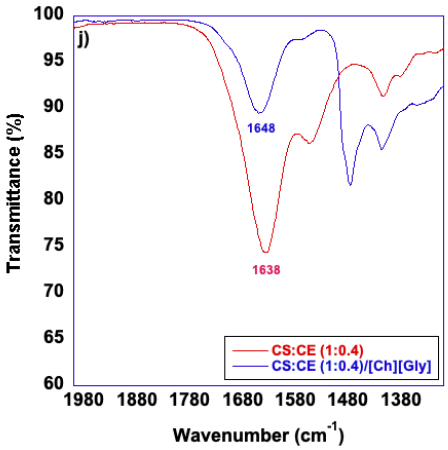

f)
Transmittance (%)
Wavenumber (cm-1)
CS
CS/[Ch][Gly]


f)
1645
1636
Transmittance (%)
Wavenumber (cm-1)
CS
CS/[Ch][Gly]


g)
Transmittance (%)
Wavenumber (cm-1)
CS
CS/[Ch][DEG]


h)
1647
1636
Transmittance (%)
Wavenumber (cm-1)
CS
CS/[Ch][DEG]


i)
Transmittance (%)
Wavenumber (cm-1)
CS:CE (1:0.4)
CS:CE (1:0.4)/[Ch][Gly]


j)
1648
1638
Transmittance (%)
Wavenumber (cm-1)
CS:CE (1:0.4)
CS:CE (1:0.4)/[Ch][Gly]

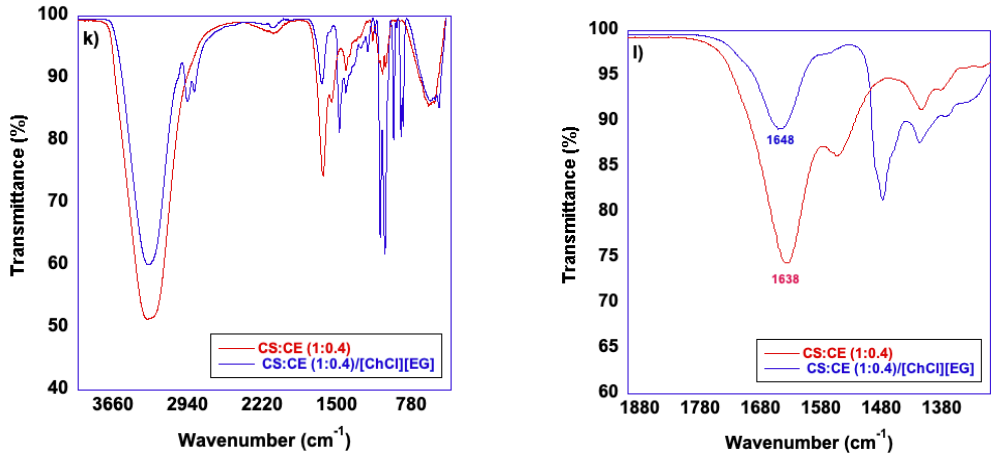


Figure S4. Superimposed FTIR-ATR spectra of polymers and gels (left) and enlargement of the C=O stretching region (right).

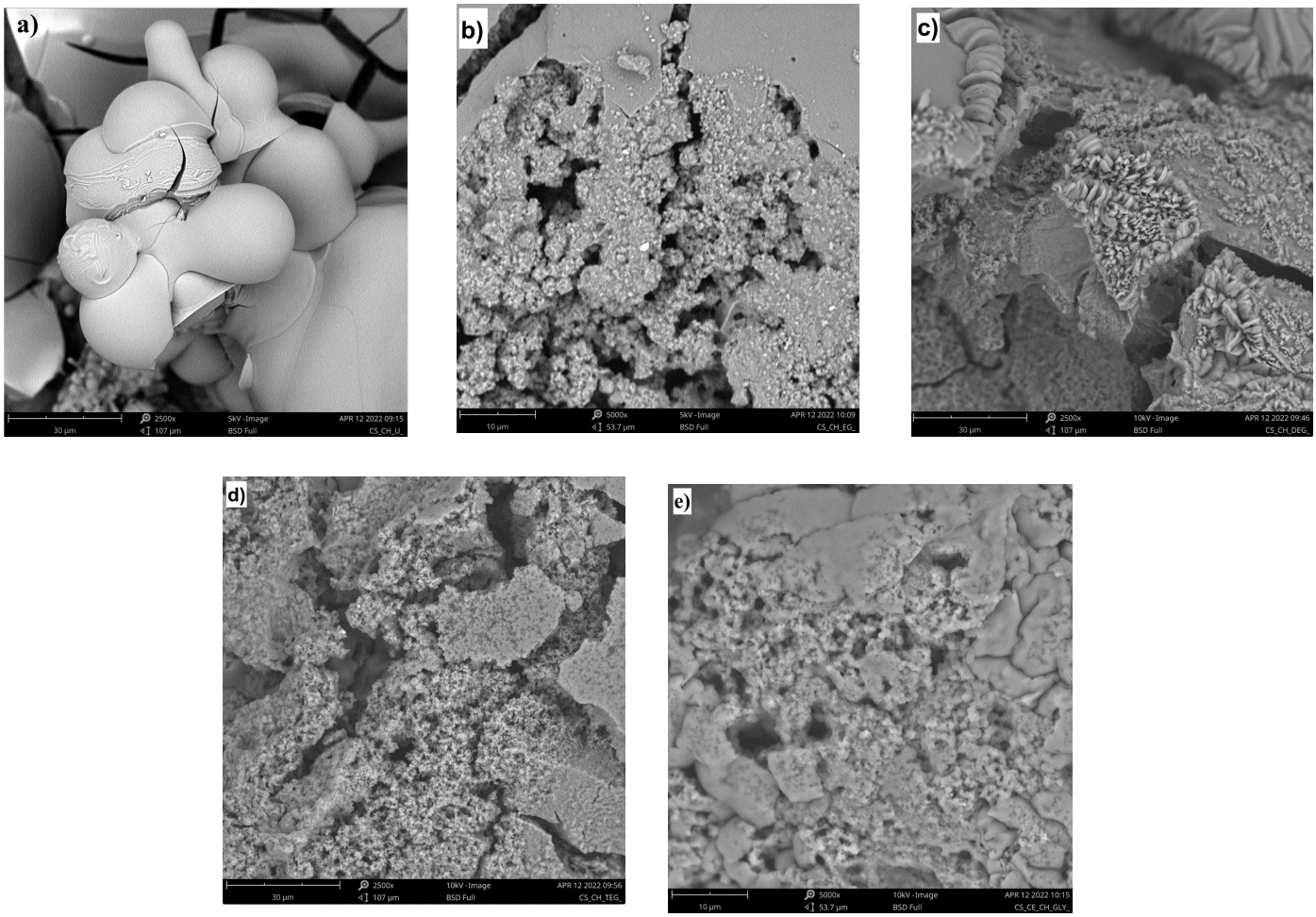


Figure S5. SEM images relevant to xerogels obtained by a) CS/[Ch][U], b) CS/[Ch][EG], c) CS/[Ch][DEG], d) CS/[Ch][TEG] and e) CS+CE (1:0.2)/[ChCl][Gly].

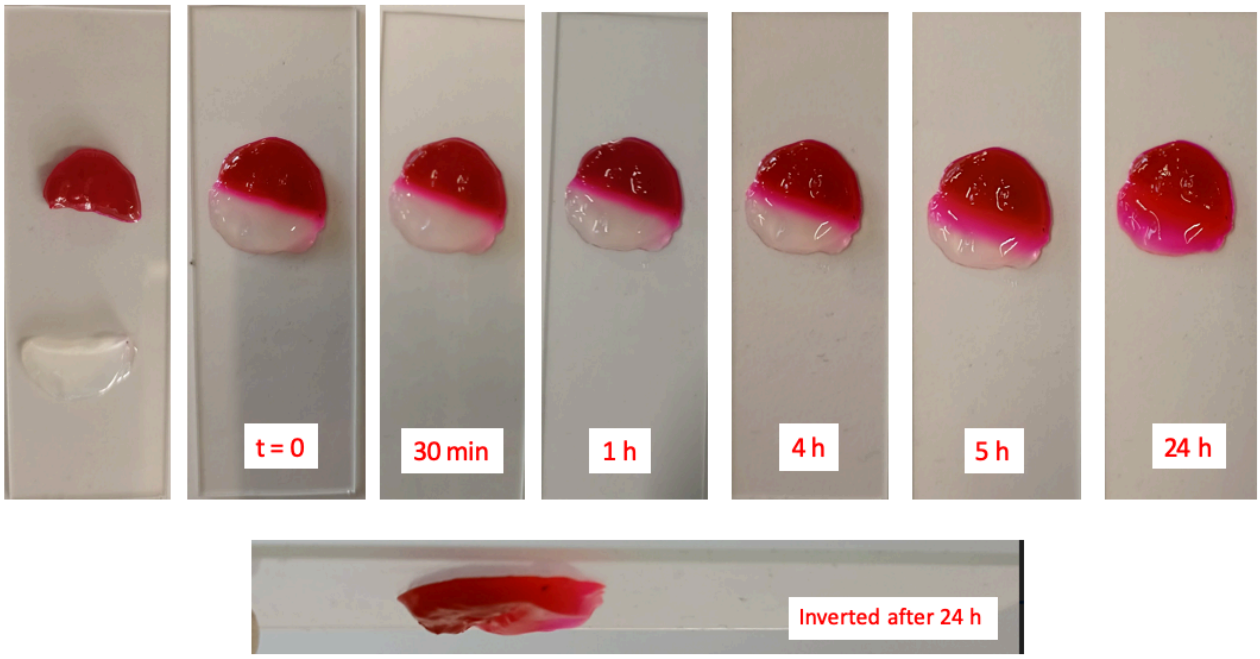


Figure S6. Pictures taken at different times relevant to the evaluation of self-healing ability of CS+CE (1:0.4)/[Ch][EG] (2 wt%) eutectogel.

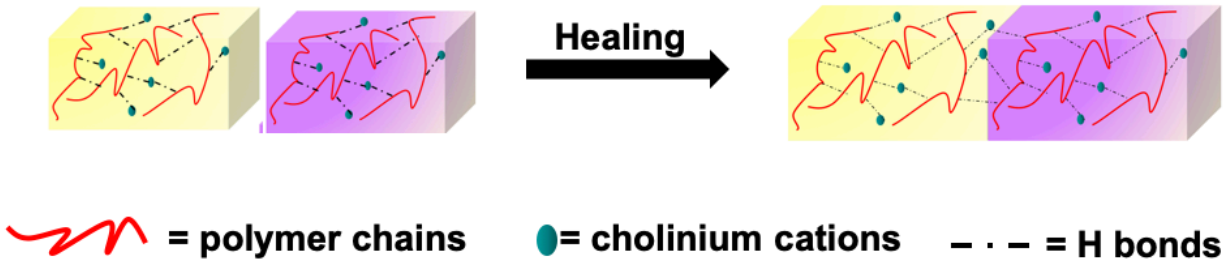


Figure S7. Pictorial representation of self-healing events. HBD and anions are omitted for clarity.

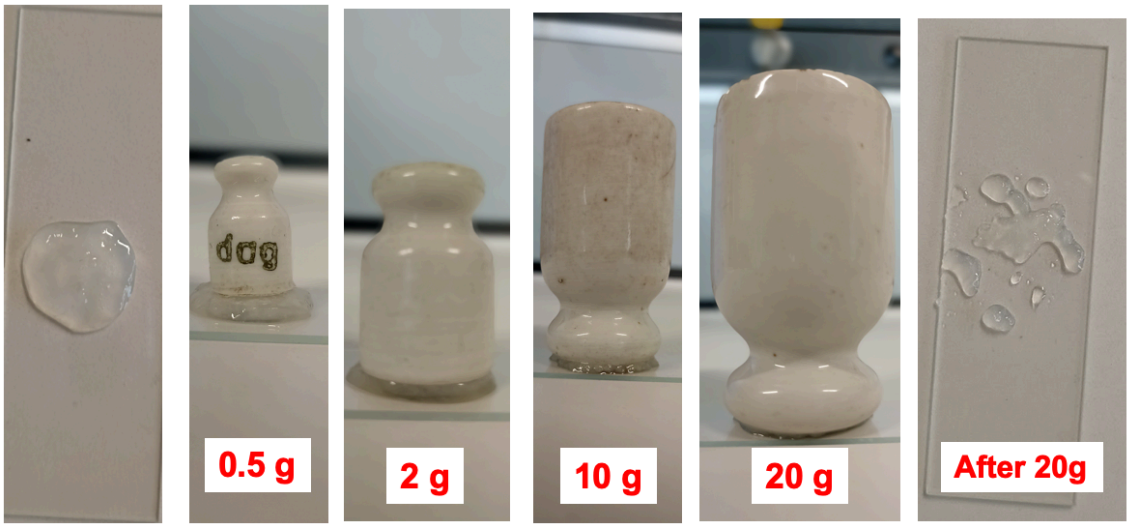


Figure S8. Pictures relevant to the evaluation of load bearing ability of CS+CE (1:0.4)/[Ch][EG] (2 wt%) eutectogel.

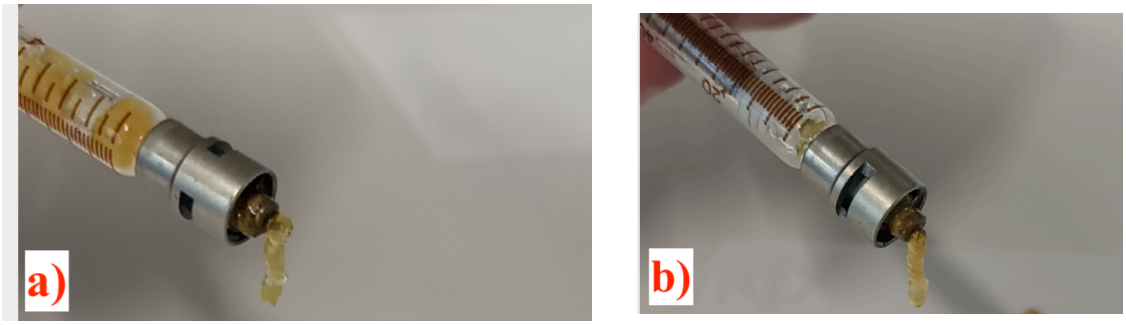


Figure S9. Extrusion from syringe of a) CS/[Ch][Gly] 2 wt% and b) CS+CE (1:0.4)/[Ch][Gly] 2 wt%.

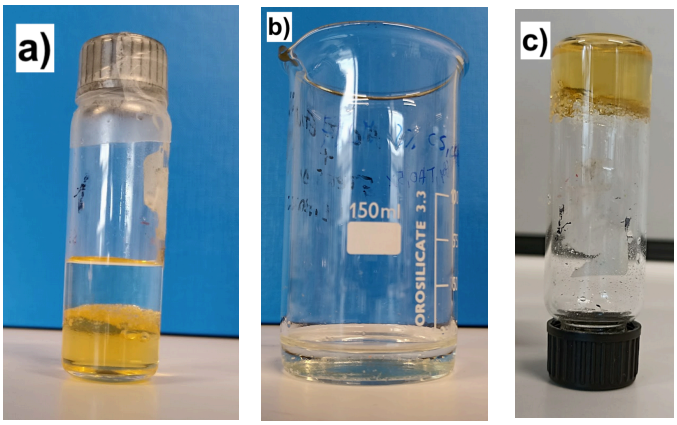


Figure S10. Pictures of CS/[ChCl][Gly] a) gel, b) film in contact with water and c) gel after removal of aqueous phase.

Table S1. Weights and pressures applied to gels in load bearing tests.

Weigth (g)	Upper diameter (cm)	Lower diameter (cm)	Pressure by upper end (g/cm^2)	Pressure by lower end (g/cm^2)
5	0.6	1.1	17.7	5.3
10	1.2	1.5	8.8	5.7
20	1.4	1.9	13.0	7.1
50	1.7	2.4	22.0	11.0
100	2.5	3	20.0	14.2
200	2.7	3.9	34.9	16.8

Table S2. SE% as a function of time for CS/[ChCl][MA] and CS/[ChCl][MA] eutectogels.[a]

CS/[ChCl][MA]	
Time (min)	SE (%)
4	-
10	4
15	4
30	15
45	17
60	26
120	29
180	54
CS/[ChCl][MA]	
Time (min)	SE (%)
60	-
240	7
900	59
1440	41

[a] SE are reproducible within ± 3%.

Table S3. SE% as a function of time for two-component eutectogels.

Time (min)	CS/[ChCl][Gly] + TA (1%)	CS/[ChCl][Gly] + VE (1%)	CS+CE(1:0.4) /[ChCl][U] + TA (1%)	CS/[ChCl][LA] + VE (1%)
5	85	91	92	94
10	85	91	90	94
20	85	93	92	93
30	95	94	90	94
60	93	90	89	
240	94	92		
1440	94	93	87	92

Table S4. Percent amount of TA released a function of time for CS/[ChCl][MA]+TA (0.5 wt%) gel and the relevant film, upon contact with water.[a]

Gel	
Time (h)	TA released (%)
1	11
19	24
26	26
46	41
67	40
115	40
138	42
Film	
Time (h)	TA released (%)
0.167	32
0.33	42
0.5	49
0.66	60
0.83	72
1	70
3	75
4	75
6	78
21	82
46	82

[a] SE are reproducible within ± 3%.