Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information (ESI)

Thermomechanical relaxation and different water states in cottonseed protein derived bioplastics

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Table S1 Enthalpy of ice-melting and water vaporisation of the cross-linked CPBs after water absorption for 30 min and 2h

Samples	Pure Water	CP-0CL-WA30min	CP-0CL - WA2h	CP-FA-WA30min	CP-FA-WA2h	CP-GX-WA30min	CP-GX-WA2h	CP-GA-WA30min	CP-GA-WA2h
ΔH_m (J/g)[a]	333.5	942	363	783	1029	560	592	336	435
ΔH_v (J/g)[b]	2260	8910	3567	7924	10431	5704	5849	3645	4420
$\Delta H_v/\Delta H_m$	6.7	9.4	9.8	10.1	10.1	10.1	9.8	10.8	10.1

[a] Enthalpy of ice-melting, normalized with water mass; [b] Enthalpy of water vaporisation, normalized with water mass; WA: water absorption

Enthalpy of ice-melting (ΔH_{m}), normalized with the mass of water (absorbed), is obtained from Equation S1.

$$\Delta H_{\mathrm{m}} = \frac{\Delta H_{W_{\mathrm{CPBs}}} \times W_{\mathrm{CPBs}}}{W_{\mathrm{H_2O}}^{\mathrm{abs}}} \tag{S1}$$

where $\Delta H_{W_{\mathrm{CPBs}}}$ is calculated by integrating the ice-melting endothermic peak, related to the total mass of the tested sample (W_{CPBs}); $W_{\mathrm{H_2O}}^{\mathrm{abs}}$ is the weight of water adsorbed onto the CPBs bioplastic. Enthalpy of water vaporization (ΔH_{v}), shown in Table S1, is calculated using the same concept.

Table S2 (A) DSC results related to the CP-0CL bioplastics with different water content

Samples	WC8	WC16	WC28	WC34	WC52	WC53	WC66
ω_{H_2O} (%)	8	16	28	34	52	53	66
Peak temp. (°C)	--	-12.9	-5.3	-3	-0.5	-0.1	1.9
ΔH (J/g)	--	24.5	53.7	75.5	143.1	145.9	210.4
$W_{H_2O}^{free}$ (mg)	0	0.27	0.85	1.49	3.00	3.54	8.01
Water added (mg)	0.47	0.67	1.68	2.50	4.00	4.70	9.24
$W_{H_2O}^{non\text{-}free}$ (mg)	0.47	0.40	0.83	1.01	1.00	1.16	1.23
$\omega_{H_2O}^{free}$ (%)	0	40	51	59	75	75	87
$\omega_{H_2O}^{non\text{-}free}$ (%)	100	60	49	41	25	25	13

Symbol notes: water content, ω_{H_2O} ; melting enthalpy, ΔH; weigh of free water, $W_{H_2O}^{free}$; weight of non-freezable water, $W_{H_2O}^{non\text{-}free}$; weight percentage of free water $\omega_{H_2O}^{free}$; weight percentage of non-free water $\omega_{H_2O}^{non\text{-}free}$. WC: water content.

Table S2 (B) DSC results related to the CP-FA bioplastics with different water content

Samples	WC8	WC16	WC28	WC34	WC52	WC53	WC66
ω_{H_2O} (%)	8	16	28	34	52	53	66
Peak temp. (°C)	--	-12.9	-5.3	-3	-0.5	-0.1	1.9
ΔH (J/g)	--	24.5	53.7	75.5	143.1	145.9	210.4
$W_{H_2O}^{free}$ (mg)	0	0.23	1.18	2.14	4.93	7.84	11.07
Water added (mg)	0.66	1.50	2.30	3.34	6.86	10.37	13.48
$W_{H_2O}^{non\text{-}free}$ (mg)	0.66	1.27	1.12	1.20	1.93	2.53	2.41
$\omega_{H_2O}^{free}$ (%)	0	16	52	64	72	76	82
$\omega_{H_2O}^{non\text{-}free}$ (%)	100	84	48	36	28	24	18

Symbol notes: water content, ω_{H_2O}; melting enthalpy, ΔH; weigh of free water, $W_{H_2O}^{free}$; weight of non-freezable water, $W_{H_2O}^{non\text{-}free}$; weight percentage of free water $\omega_{H_2O}^{free}$; weight percentage of non-free water $\omega_{H_2O}^{non\text{-}free}$. WC: water content.

Table S2 (C) DSC results related to the CP-GX bioplastics with different water content

Samples	WC8	WC16	WC28	WC34	WC52	WC53	WC66
ω_{H_2O} (%)	8	16	28	34	52	53	66
Peak temp. (°C)	--	-12.9	-5.3	-3	-0.5	-0.1	1.9
ΔH (J/g)	--	24.5	53.7	75.5	143.1	145.9	210.4
$W_{H_2O}^{free}$ (mg)	0	0.58	1.23	2.70	4.45	8.11	11.50
Water added (mg)	0.81	1.34	2.28	3.87	6.33	10.02	13.57
$W_{H_2O}^{non\text{-}free}$ (mg)	0.81	0.76	1.05	1.17	1.88	1.91	2.07
$\omega_{H_2O}^{free}$ (%)	0	43	54	70	70	81	85
$\omega_{H_2O}^{non\text{-}free}$ (%)	100	57	46	30	30	19	15

Symbol notes: water content, ω_{H_2O} ; melting enthalpy, ΔH; weigh of free water, $W_{H_2O}^{free}$; weight of non-freezable water, $W_{H_2O}^{non\text{-}free}$; weight percentage of free water $\omega_{H_2O}^{free}$; weight percentage of non-free water $\omega_{H_2O}^{non\text{-}free}$. WC: water content.

Table S2 (D) DSC results related to the CP-GA bioplastics with different water content

Samples	WC8	WC16	WC28	WC34	WC52	WC53	WC66
ω_{H_2O} (%)	8	16	28	34	52	53	66
Peak temp. (°C)	--	-12.9	-5.3	-3	-0.5	-0.1	1.9
ΔH (J/g)	--	24.5	53.7	75.5	143.1	145.9	210.4
$W_{H_2O}^{free}$ (mg)	0.26	0.72	0.83	1.48	3.15	5.06	10.97
Water added (mg)	1.00	1.73	1.73	2.31	4.54	6.75	13.34
$W_{H_2O}^{non\text{-}free}$ (mg)	0.74	1.01	0.90	0.83	1.39	1.69	2.37
$\omega_{H_2O}^{free}$ (%)	26	42	48	64	69	75	82
$\omega_{H_2O}^{non\text{-}free}$ (%)	74	58	52	36	31	25	18

Symbol notes: water content, ω_{H_2O} ; melting enthalpy, ΔH; weigh of free water, $W_{H_2O}^{free}$; weight of non-freezable water, $W_{H_2O}^{non\text{-}free}$; weight percentage of free water $\omega_{H_2O}^{free}$; weight percentage of non-free water $\omega_{H_2O}^{non\text{-}free}$. WC: water content.

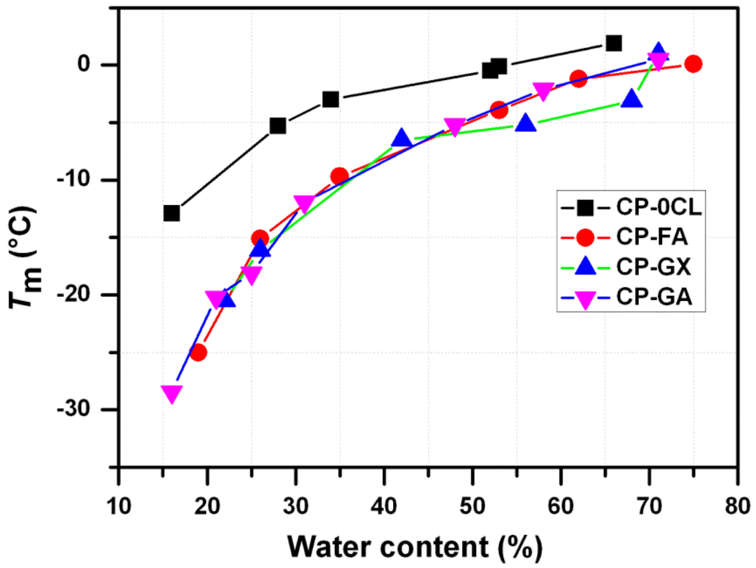


Fig. S1 Plots of the melting temperature (T_m) of water in the CPBs networks versus different water content.

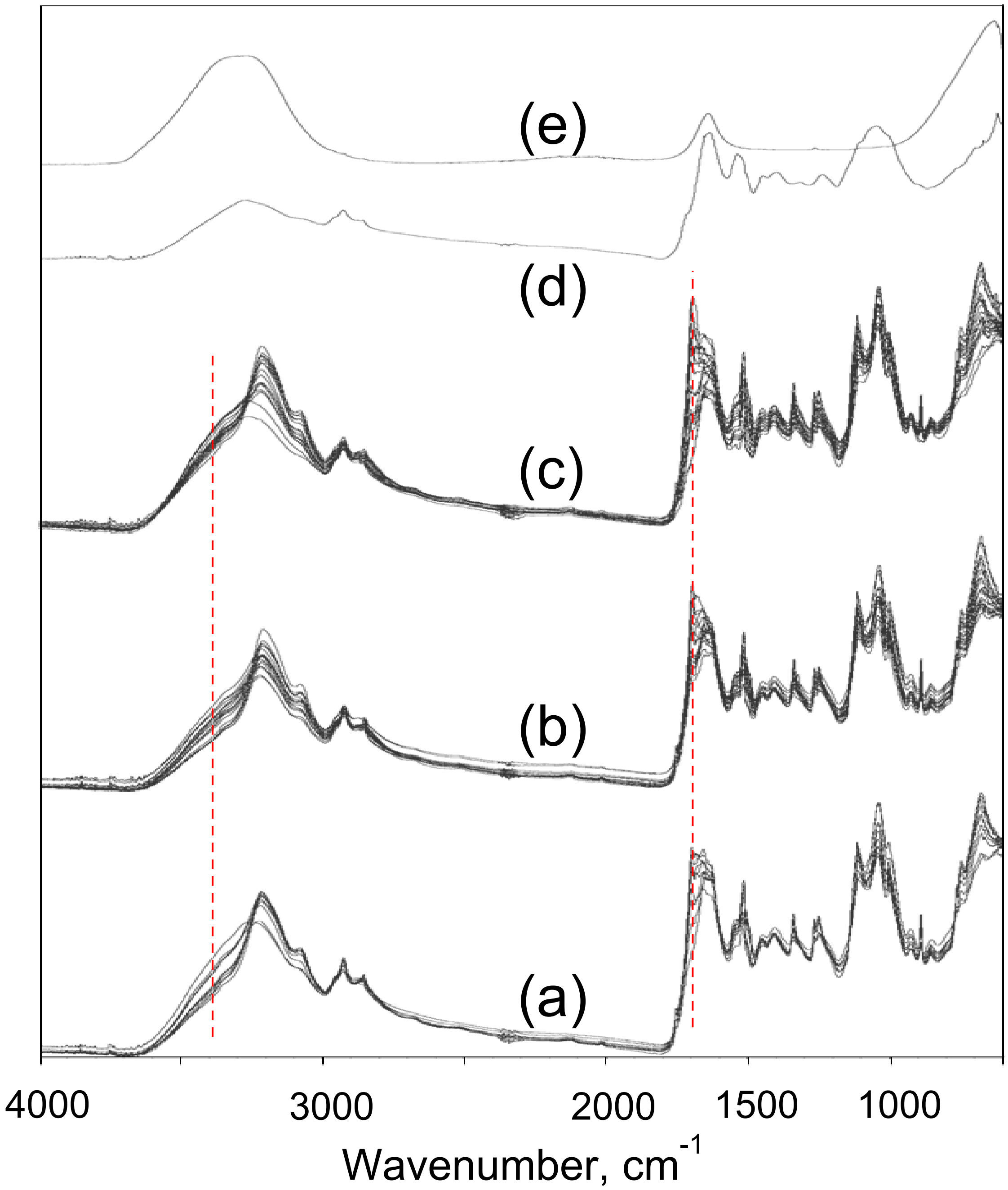


Fig. S2 Infrared spectra recorded from different positions of samples (a) CP-FA, (b) CP-GX and (c) CP-GA. Spectrum of (d) water and (e) CPL-0CL are shown for comparison.

Figure S2 shows infrared spectra recorded from various positions on the different samples using an ATR objective with a Ge crystal with a contact surface of 100 μm diameter. It can be observed that for each cross-linked sample heterogeneity is observed, notably reflected in the relative intensity of the band at 1697 cm^{-1} associated with unreacted or partially reacted aldehyde carbonyl stretching vibration (marked). Along with other band changes, it is also interesting to note the variations in the N-H and O-H stretching region. In this latter region, if we compare the intensity observed for the 1697 cm^{-1} band with that of the OH region (marked), we observe that an inverse correlation exists (see Figure S3), which provides evidence for a heterogeneous water uptake in the system, being lower when more aldehyde is present. Although this was a generalised observation the best correlations were observed for the spectra from CP-FA and CP-GX (shown).

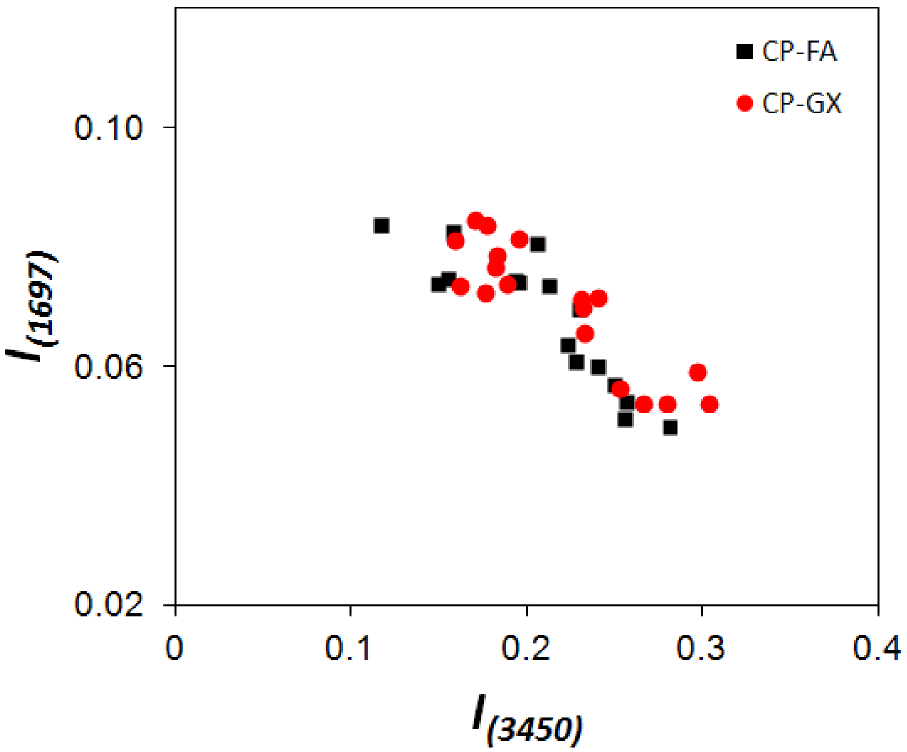
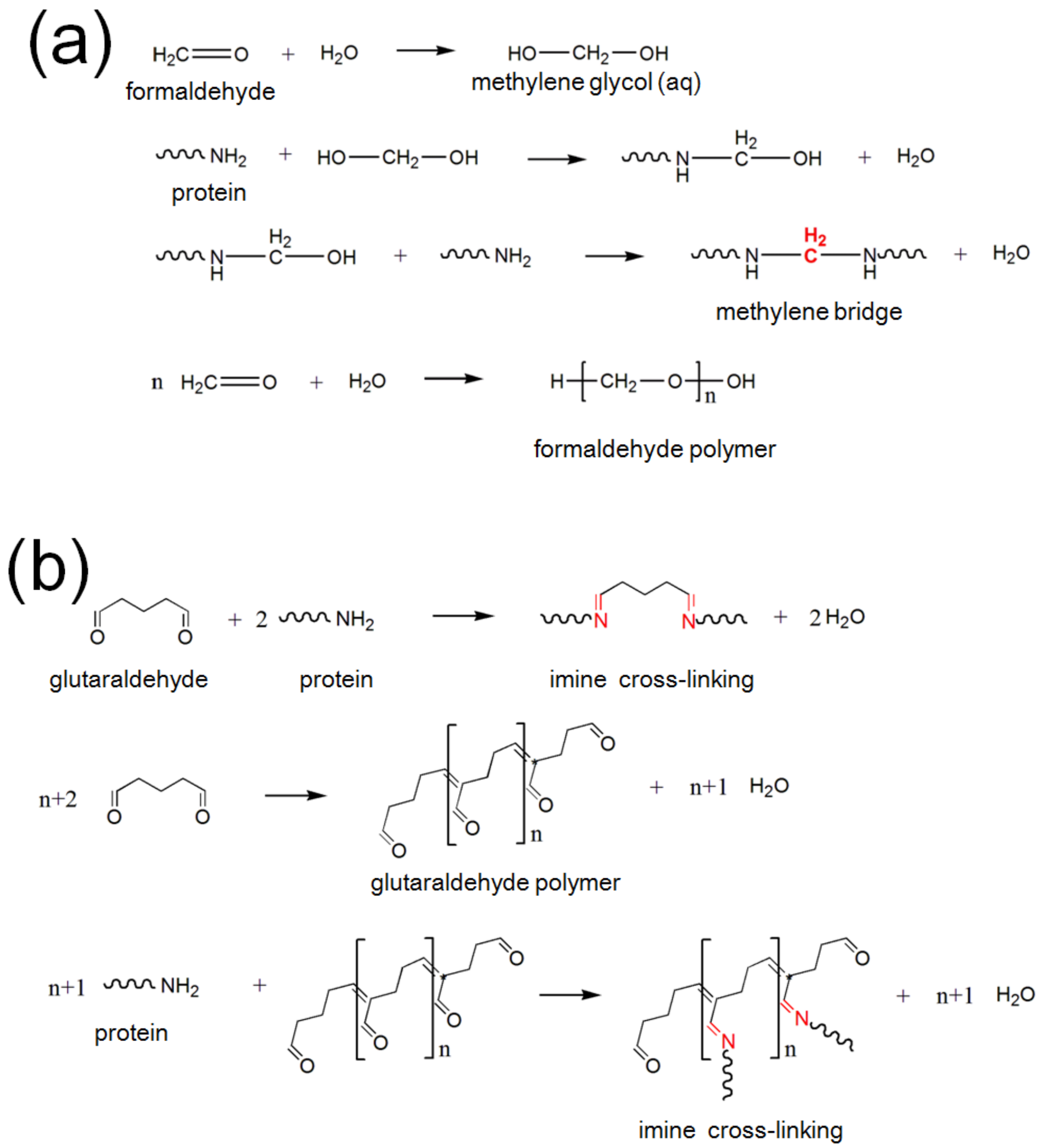


Fig. S3 Plot of the intensity of the aldehyde C=O band at 1697 cm^{-1} vs the intensity observed at 3450 cm^{-1}, reflecting the relative concentration of water.



Scheme S1 Cross-linking reactions of protein molecules with formaldehyde showing the formation of methylene bridge (a); and with glutaraldehyde monomer/polymer, creating imine covalent bonds (b).

Three aldehydes (formaldehyde, glyoxal, and glutaraldehyde) react with protein molecules in a quite different manner, creating the cross-linked structures. Methylene bridge formation is responsible for the formaldehyde cross-linked networks (Scheme S1a)[1]; however the formaldehyde polymer (in FA solution) cannot generate further methylene bridges. As for the glutaraldehyde cross-linked networks (Scheme S1b), both GA monomer and GA polymer are able to react with protein molecules through imine covalent bond formation[1, 2]. Glyoxal maintains the same mechanism as GA.

References

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2. H. B. Yue, Y. D. Cui, P. S. Shuttleworth and J. H. Clark, *Green Chem*, 2012, **14**, 2009-2016.