Supplementary Information (SI) for Soft Matter.

Supporting Information
Understanding Polymer-Colloid Gels: A Solvent Perspective Using Low-Field NMR

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1. Impact of the CB content on T_2

Figure S1 shows the impact of the CMC concentration on the transverse relaxation rate $1/T_2$ for hydrogels containing 0, 2, 4, 6 and 8 wt.% in CB. Data were measured at various temperatures, every 10°C between 10 to 80°C. Following Eq. (3) in the main text, the low and high c_{cmc} limit values represent $1/T_2^{bulk}$ and $1/T_2^{bound}$. For each CB content, it is worth noting that while $1/T_2^{bulk}$ tends to decrease with increasing temperature (corresponding to longer T_2), the extrapolated values of $1/T_2^{bound}$ mostly collapse in a narrow interval close to $1/T_2^{bound} \approx 10\ \mathrm{s}^{-1}$ corresponding to $T_2^{bound} \ll 2$ s, in agreement with a strongly reduced molecular mobility of the water molecules. This dichotomy is further reminiscent of the two mechanisms impacting the T_2 values evoked in the main text: i) the presence of a 3D network limiting long-range water diffusion (mostly observed at low CB and CMC contents), and ii) short-range attractive interactions between the CMC and the water molecules (dominating T_2 at large CMC content).

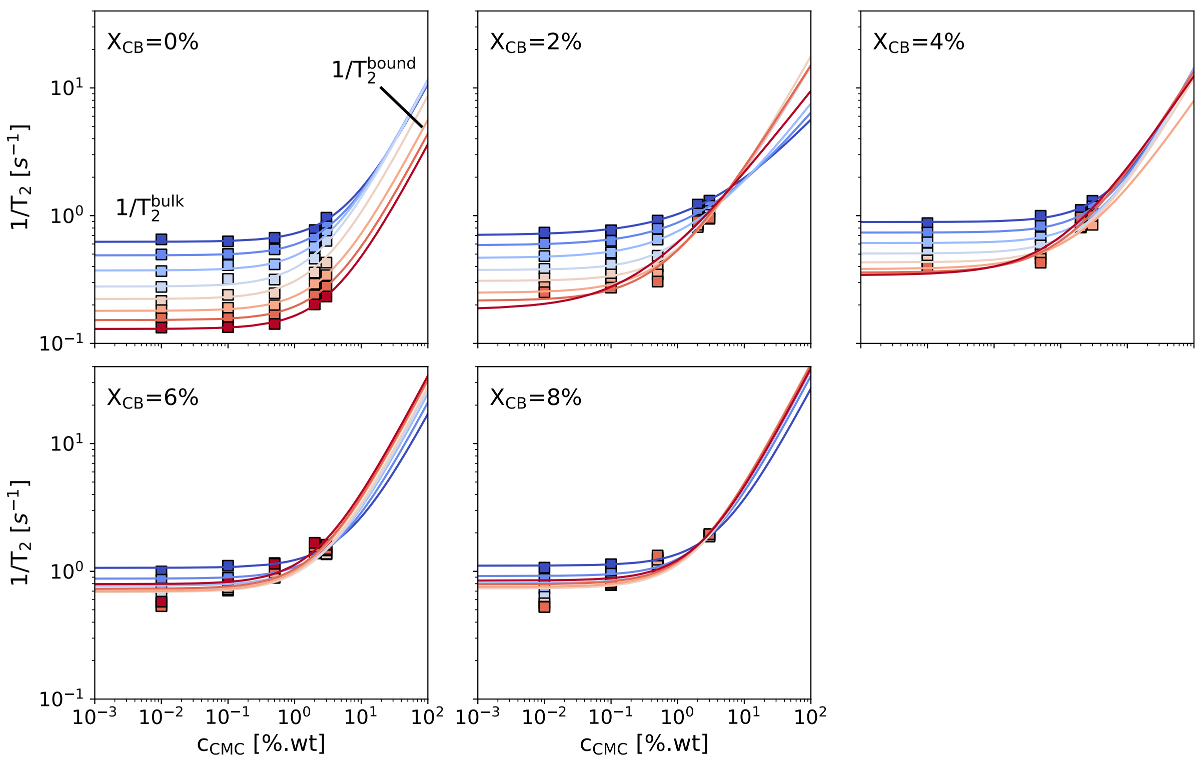

Figure S1: Spin-spin relaxation rate $1/T_2$ vs. CMC concentration c_{CMC} measured at various temperatures, every 10 °C between 10 °C and 80 °C (see color code from dark blue to red) for the pure CMC solution, and hybrid hydrogels containing x_{CB} =2, 4, 6, and 8 wt.% of carbon black particles. Solid lines show the best fit to the data with Eq.(3) from the main text.

2. E_a table used to build the Rheo-NMR diagram

We list below the activation energy E_a in kJ.mol^{-1} for all the samples investigated in the present study. These values are used to build the Rheo-NMR diagram (Figure 3) in the main text. For each concentration in CMC (column), we refer to the concentration in CB and the corresponding E_a (rows).

Table S1: E_a (kJ.mol^{-1}) extracted from CPMG experiments performed between 10°C and 50°C for various CMC and CB concentrations.

CMC0.01	E_a	CMC0.1	E_a	CMC0.5	E_a	CMC2	E_a	CMC3	E_a
CB0	19.2	CB0	19.1	CB0	14.0	CB0	19.0	CB0	16.5
CB2	15.8	CB2	15.7	CB2	6.0	CB2	15.3	CB2	7.6
CB4	13.0	CB4	11.7	CB4	7.3	CB4	-	CB4	7.6
CB6	11.0	CB6	6.4	CB6	2.0	CB6	10.6	CB6	1.4
CB8	12.3	CB8	4.0	CB8	0.0	CB8	8.7	CB8	-

3. Heating vs. Cooling $\mathrm{T_2}$ measurements

Figure S2 shows the impact of the thermal history on T_2 measured on samples containing $c_{\mathrm{CMC}} =$ 0.01 wt.% and various fractions of CB. The measurements are performed in a stepwise manner by increasing the temperature from 10 to 80°C and subsequently cooling down from 80 to 10°C. While no significant effect is observed at $x_{\mathrm{CB}} = 2$ wt.%, the data on the *cooling* branch systematically exhibit lower T_2 values corresponding to a growing degree of aging when increasing the gel density. Figure S3 confirms this result by showing even stronger effects for $c_{\mathrm{CMC}} = 0.1$ wt.%.

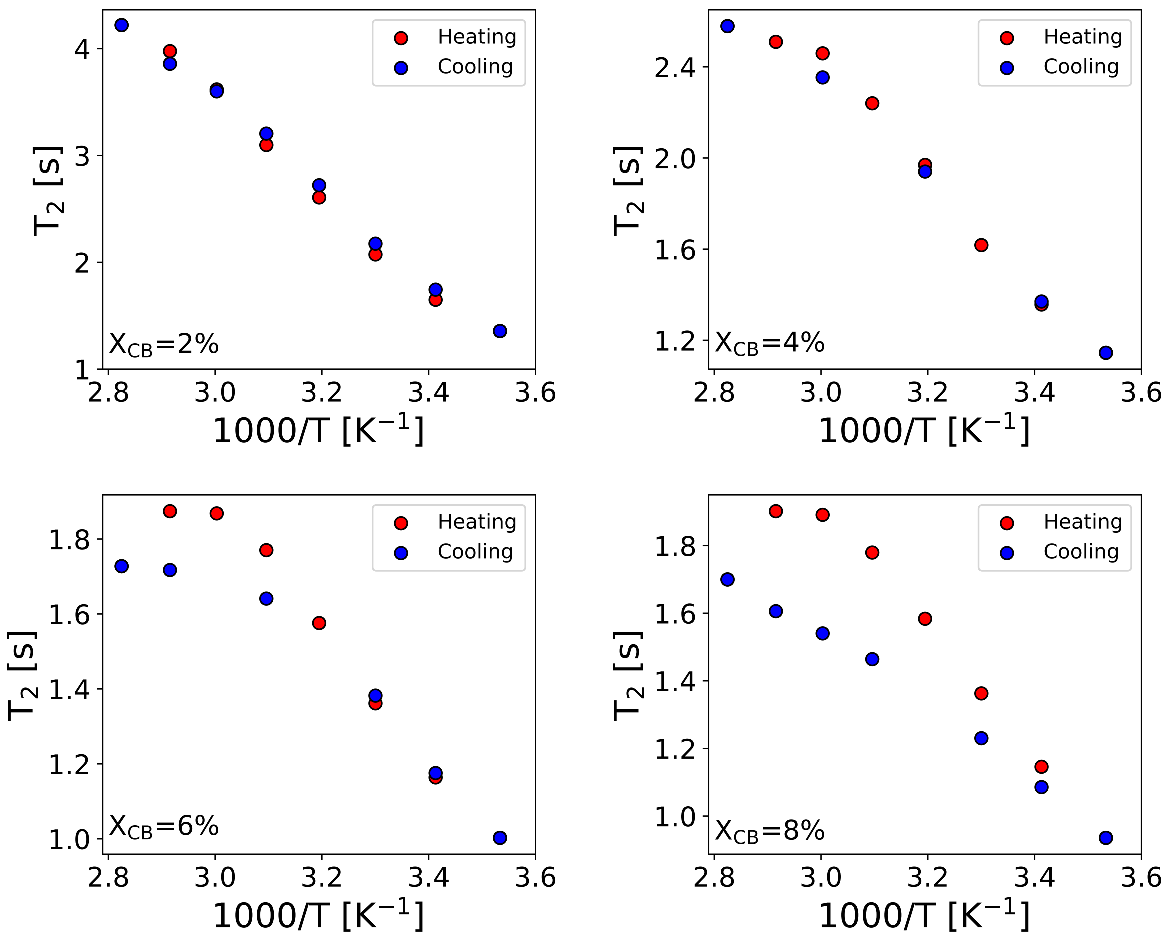

Figure S2: Spin-spin relaxation time T_2 vs. reciprocal temperature measured upon heating from 10 to 80°C and subsequent cooling over the same temperature range. Experiments performed on selected formulations where $c_{\mathrm{CMC}} = 0.01$ wt.% and x_{CB} =2, 4, 6, and 8 wt.%.

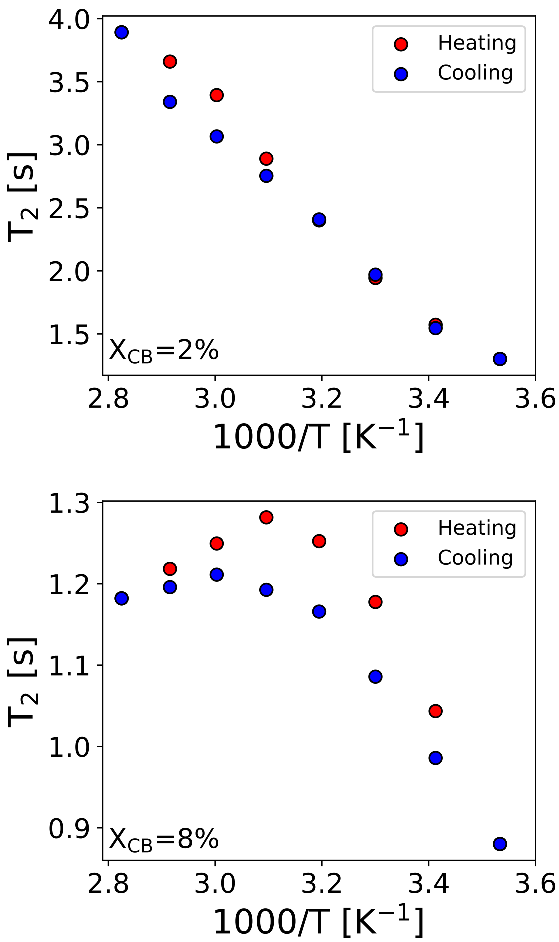

Figure S3: Spin-spin relaxation time T_2 vs. reciprocal temperature measured upon heating from 10 to 80°C and subsequent cooling over the same temperature range. Experiments performed on selected formulations where $c_{\mathrm{CMC}} = 0.1$wt.% and x_{CB} =2, 6 and 8 wt.%.

4. Loss modulus and loss factor of CMC3-CB8 at various temperatures

Figure S4 shows the loss modulus, G'', and loss factor, $\tan\delta = G''/G'$, of the CMC3-CB8 hydrogel corresponding to the storage modulus G' reported in Figure 4 in the main text. These data confirm the non-monotonic behavior of the viscoelastic properties upon increasing the temperature, particularly emphasizing the relative decrease of its viscous character at 70°C.

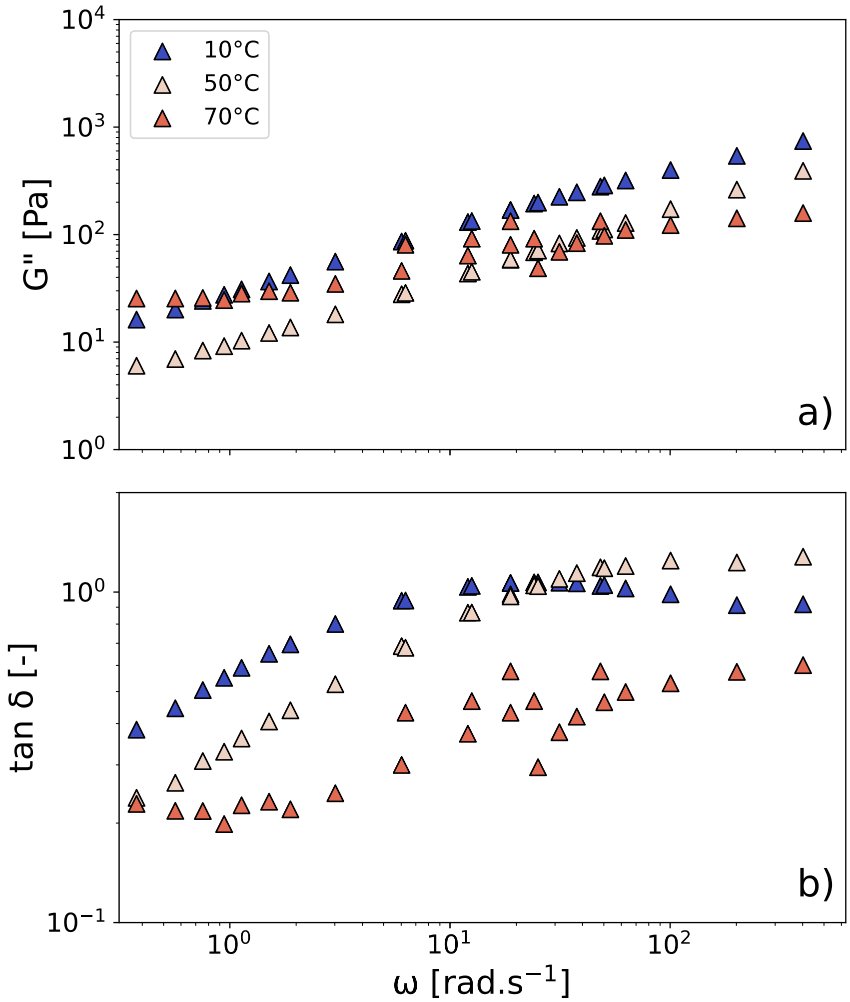

Figure S4: Frequency dependence of (a) the loss modulus G'' and (b) loss factor $\tan\delta = G''/G'$ of the CMC3-CB8 sample measured at 10, 50, and 70 °C for $\gamma = 0.1\%$.

5. Impact of the CPMG echo time on the T_2 values at low and high temperatures.

Figure S5 shows T_2 values obtained for the sample CMC2-CB2 at 10°C and 80°C across different CPMG echo-times (2τ). Although a slight decrease in T_2 is observed with increasing echo-time in both cases, it only corresponds to a relative variation of about −4% and −16%, respectively. These variations are negligible compared to the potential aging effects and the significant T_2 changes with temperature reported in Figure 2 of the main text. This key observation confirms that our CPMG measurements are not impacted by technical artefacts related to the nature of the material.[1]

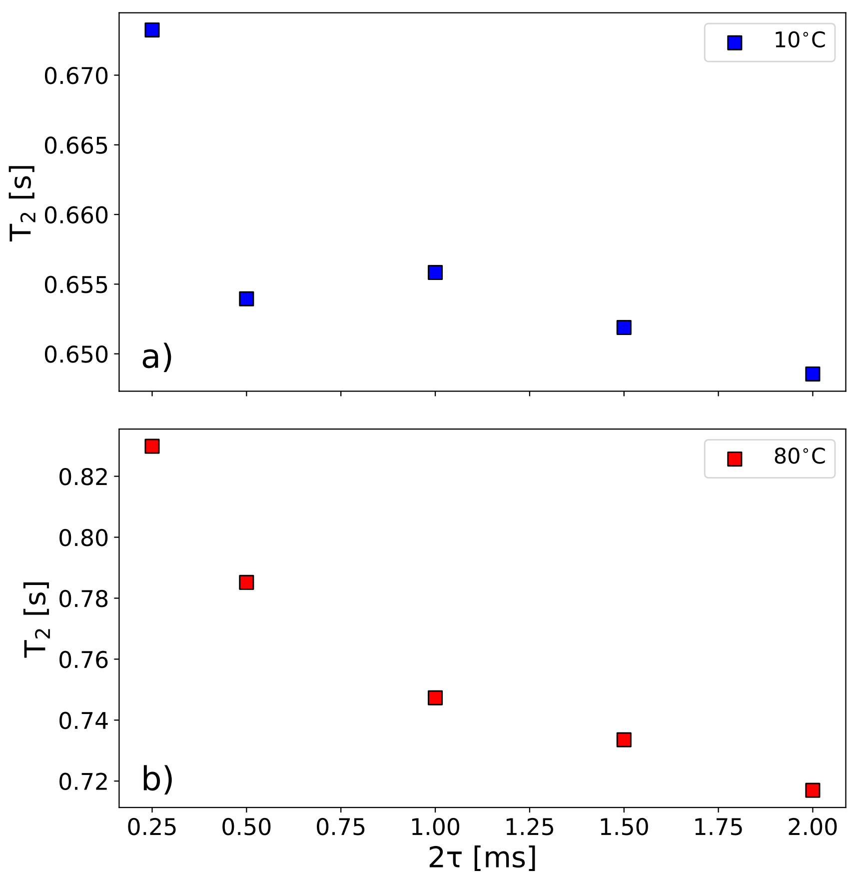

Figure S5: Spin-spin relaxation time T_2 vs. CPMG echo-time 2τ for CMC2-CB2 measured at (a) 10°C and (b) 80°C on independent samples.

References

(1) Jarenwattananon, N. N.; Bouchard, L.-S. Breakdown of Carr-Purcell Meiboom-Gill spin echoes in inhomogeneous fields. *J. Chem. Phys.* **2018**, *149*.