Sol-gel transition in biopolymer solutions

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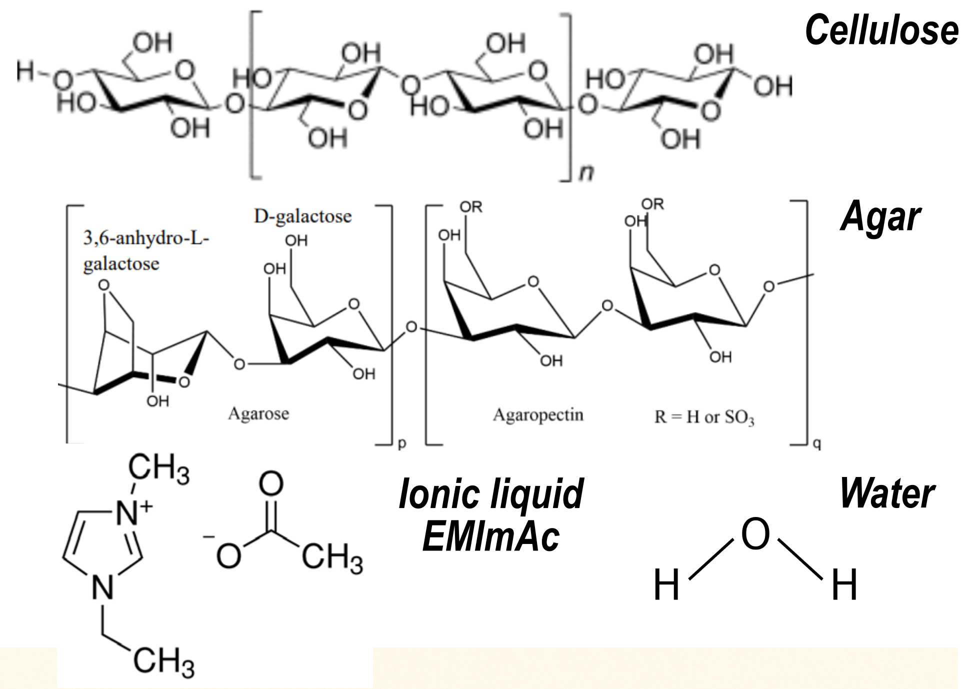


BACKGROUND

Polysaccharides like cellulose and agar are promising sustainable materials but face challenges in solubility and processing. Ionic liquids (IL) such as EMImAc enable their molecular dissolution and open routes to sol-gel transitions. This study examines how polymer structure and water addition can tune intermolecular interactions, allowing control over gel formation and mechanical properties.

METHODOLOGY

We studied the sol-gel transitions of native cellulose and agar in EMImAc induced by water addition. Linear shear rheology quantified viscoelastic behavior and scaling laws. WAXS and Raman spectroscopy confirmed amorphous gel formation, while photon correlation imaging revealed the diffusive gelation process. Linking polymer and water content to rheology, we highlight distinct gelation mechanisms driven by intermolecular interactions and solvent exchange.

RESULTS

Linear viscoelasticity

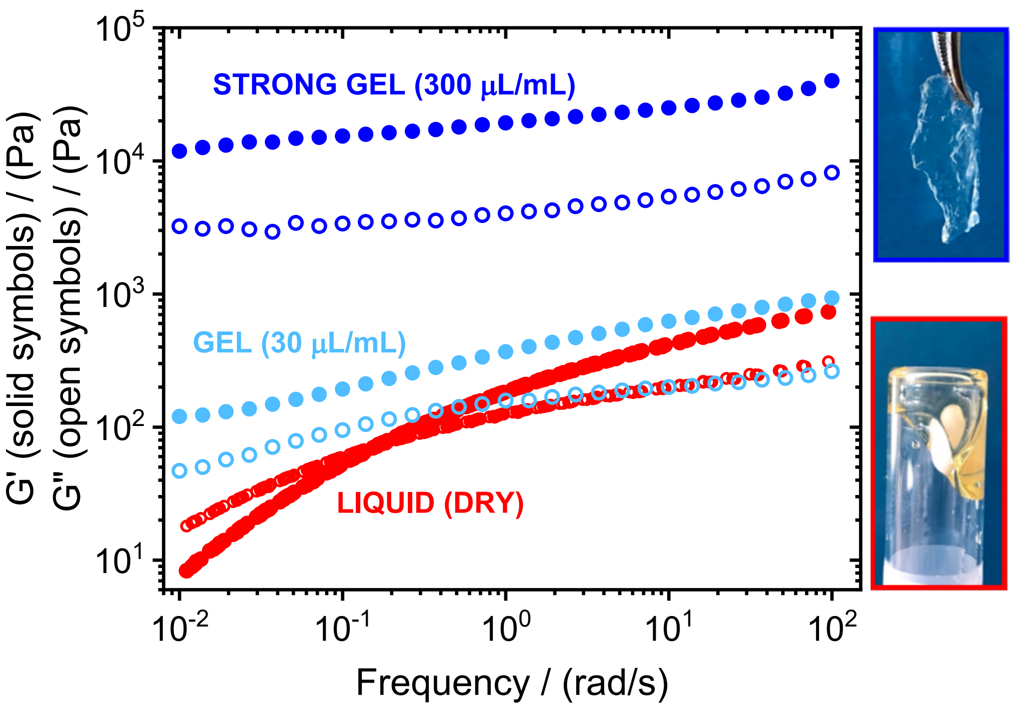


Fig. 1. Linear viscoelastic spectra showing sol–gel transition and gel strengthening of 2 wt.% cellulose/EMImAc upon increasing water content

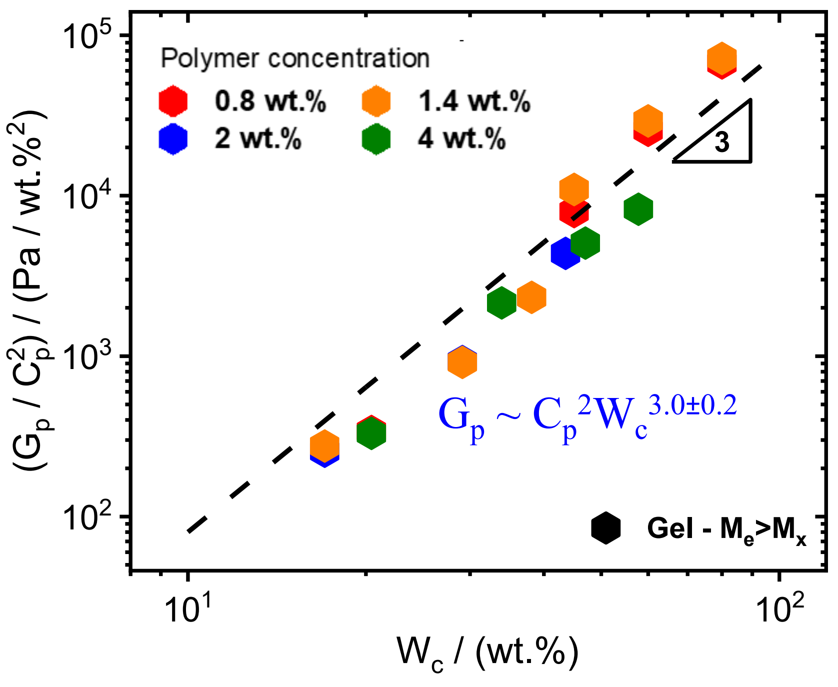


Fig. 2. Plaeau modulus of cellulose/EMImAc as a function of water content, showing gel strengthening across different cellulose concentrations

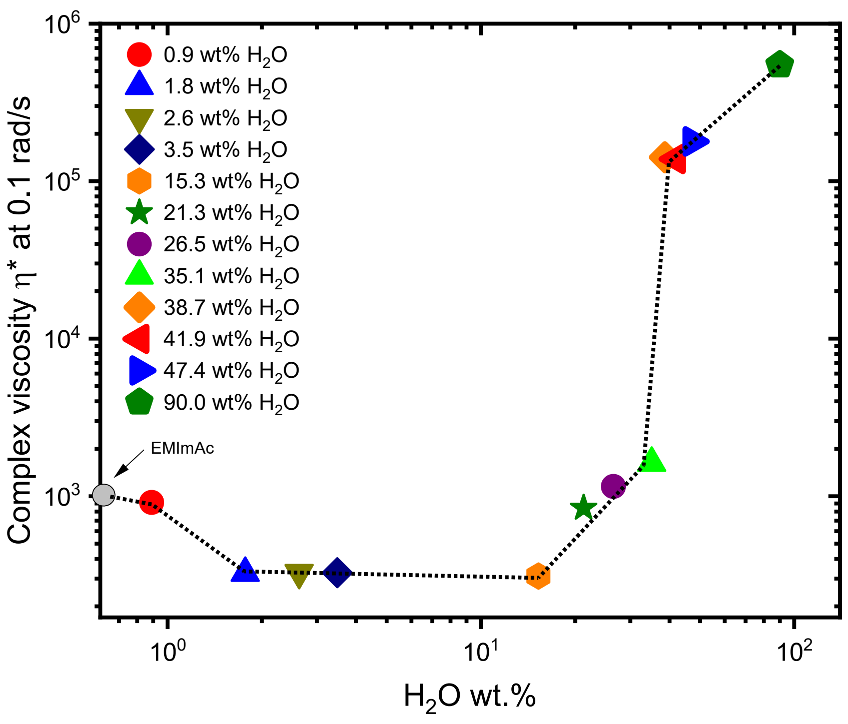
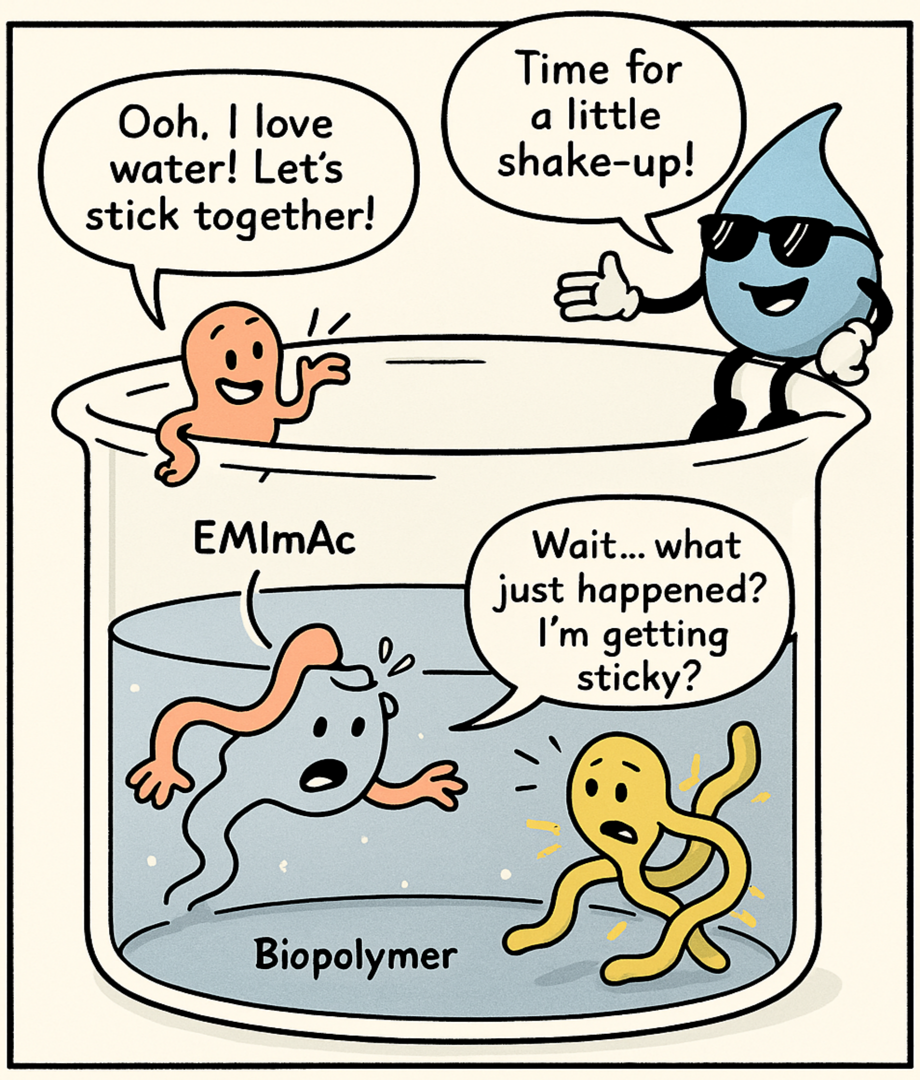


Fig. 3. Complex viscosity of 10 wt.% agar/EMImAc as a function of water content

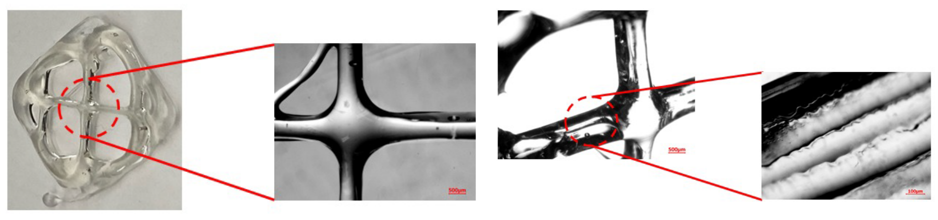
- **Dilute** biopolymer/IL solutions, adding water → **polymer coil shrinkage** and viscosity decrease [1]
- **2 wt.% native cellulose** and **10 wt.% agar** in EMImAc → **entangled solutions** [1-2]
- **At and above entangled** concentrations, water addition → **sol-gel transition** [1]
- Cellulose/IL gels elegantly follow **$G_p \sim C_p^2 W_c^{3\pm0.2}$** → higher cellulose conc. require less water for stronger gels
- Exponent 3 in the above scaling with water → **complex gel network**, likely from **heterogeneous cellulose bundles** or **ordered mesophases** [1]
- **Differs** from **synthetic** physically crosslinked network → conventional scaling is **$G_p \sim C_p^2 \varphi^1$** [3]
- **Agar/IL** exhibits **non-monotonic viscosity changes** with water
- Gelation mechanisms vary due to distinct polymer–solvent interactions

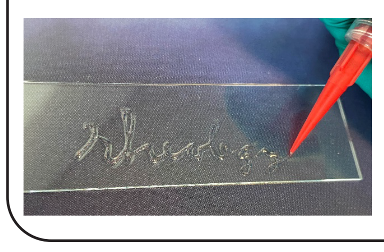
THE WATER SHIFT: HOW GELS FORM



When water enters, the ionic liquid bonds with it, leaving the biopolymer chain ready to link up and form a gel.

Processability





- Well-defined structures via **3D printing**
- Microscopy confirms **precise layering**
- **Injectable** material for easy patterning
- Versatile processing → **customized soft materials**

Raman Spectroscopy

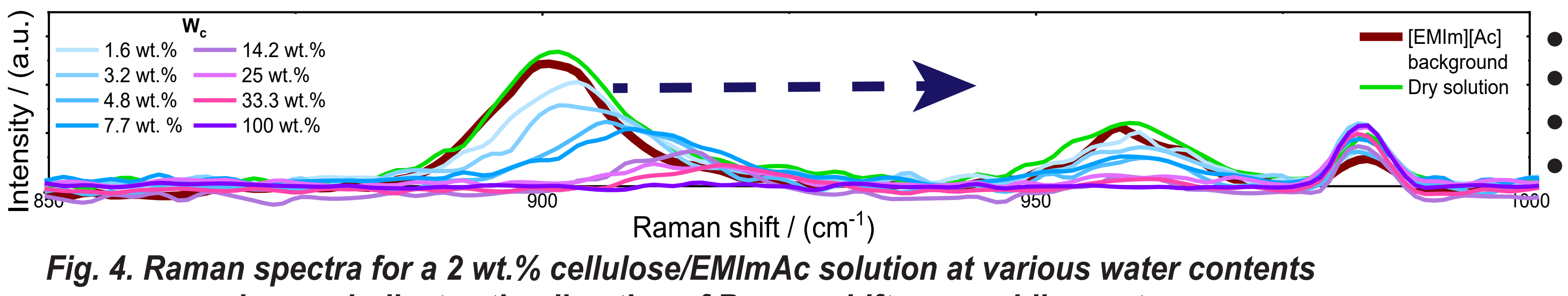


Fig. 4. Raman spectra for a 2 wt.% cellulose/EMImAc solution at various water contents and arrow indicates the direction of Raman shift upon adding water

- Raman peak at **~900 cm^{-1}** corresponds to **O–C–O vibration** of acetate anion of IL
- Peak shifts to **higher wavenumbers** as water binds to anions
- Shift **saturates** at high water content → **dominant anion–water interactions** [1]
- **No Raman signal** after gelation → indicates **complete IL replacement** [1]

WAXS & cryo-TEM

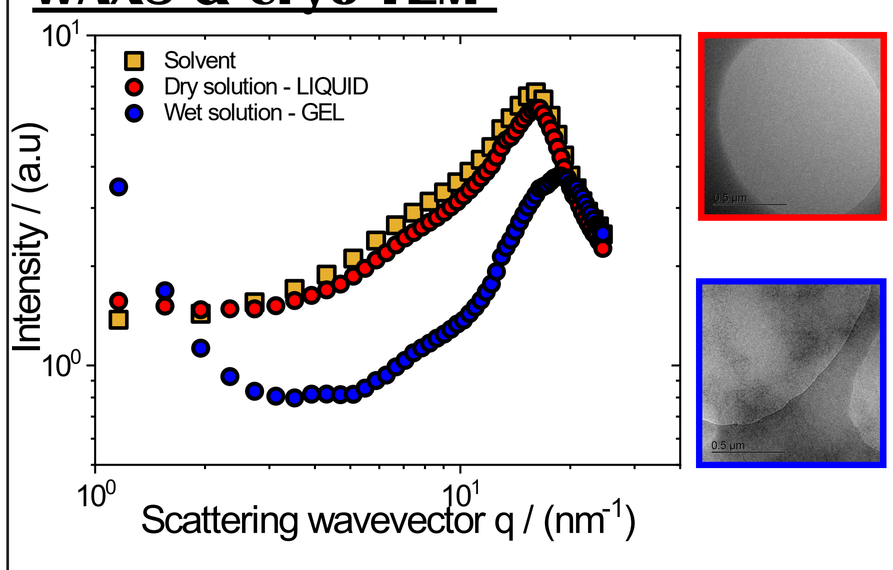


Fig. 5. WAXS and cryo-TEM of 2 wt.% cellulose/EMImAc in dry (red) and wet (blue) states

- **WAXS peak** shifts from **16** → **19 nm^{-1}** with added water
- Corresponding **length scale** decreases: **0.39** → **0.33 nm**
- Suggests **water replaces IL** around cellulose chains
- **No sharp peaks** → lack of crystallinity
- Suggests **amorphous gel** structure
- Submergence of gel in water makes it **opaque** [1]
- **High turbidity** → **polymer aggregation** (local heterogeneities)

- **Dry state** → cryo-TEM shows **homogeneous solution**
- **Gel state** → cryo-TEM reveals **micron-scale aggregates**
- Suggests **heterogeneous gel**

Photon Correlation Imaging (PCI)

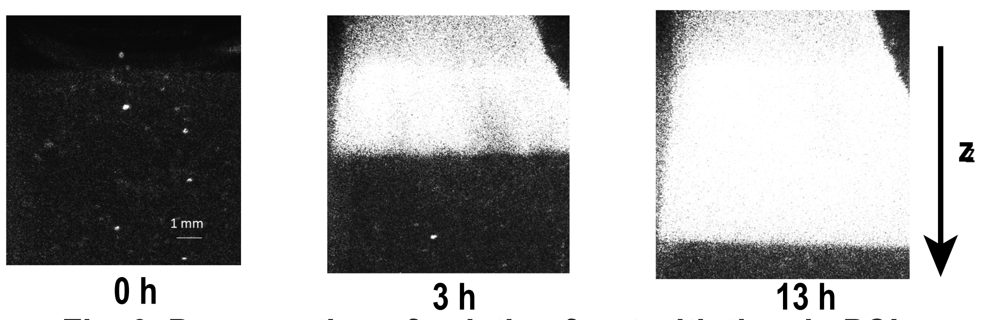


Fig. 6. Propagation of gelation front with time in PCI upon addition of excess water to 2 wt.% cellulose/EMImAc

- **Speckle patterns** from diffusing green laser light imaged at 90°
- **Excess water added**, gelation monitored over several hours
- Turbidity increases and **gelation front propagates vertically**
- Intensity profiles used to track gelation front position
- Gelation dynamics are **purely diffusive**
- Confirmed by **linear z^{*2} vs. time** relationship
- **Diffusion coefficient** → **9*10^{-10} m^2/s**

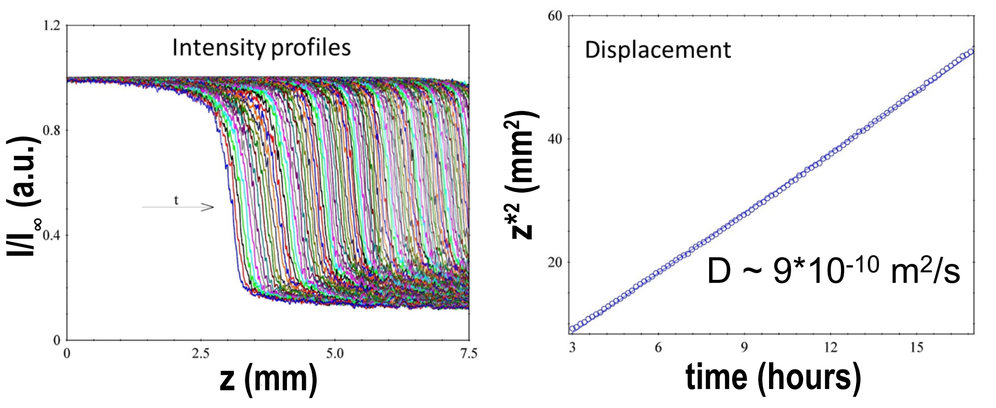


Fig. 7. Intensity profiles and displacement plot for the gelation of 2 wt.% cellulose/EMImAc

CONCLUSIONS

- ▶ Cellulose and agar in the same ionic liquid show distinct sol–gel transitions upon water addition.
- ▶ Cellulose forms tunable, strong gels with modulus scaling beyond traditional crosslinked networks.
- ▶ Agar exhibits a non-monotonic viscosity response, indicating different gelation dynamics.
- ▶ Small solvent changes enable precise control of plant-based biopolymer rheology.

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REFERENCES

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