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From dilute polyelectrolyte solutions to entangled polyelectrolyte networks: a study of sodium carboxymethyl cellulose in water by light scattering and rheology

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From dilute polyelectrolyte solutions to entangled polyelectrolyte networks: intriguing ageing phenomena in Sodium Carboxymethyl Cellulose (Na CMC) solutions

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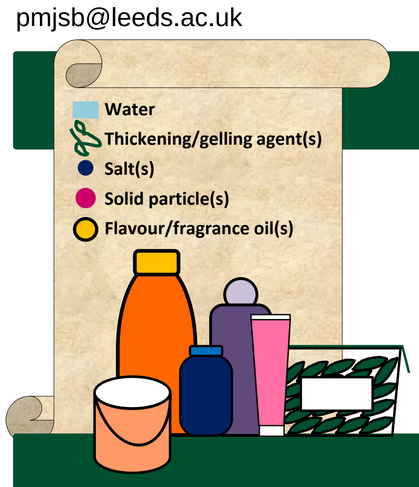
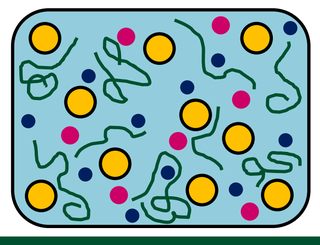
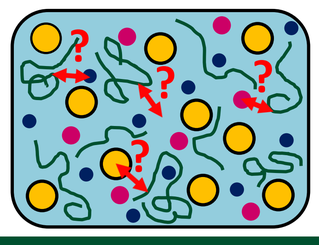
Introduction

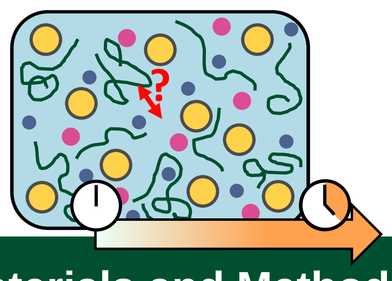


Context



Project objectives





Poster objectives

- Selected thickener: Na CMC (Fig. 1)
- Analysis techniques:
  - Dynamic Light Scattering (DLS)
  - Rheology

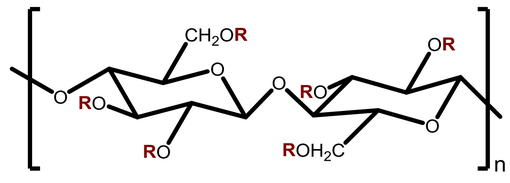
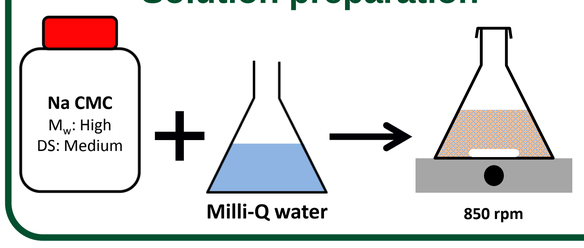


*Figure 1: Na CMC (**R** = H or CH_2COO^-, Na^+)*

Materials and Methods

Solution preparation



Studied solutions	Concentration regime	$\Delta t_{stirring}$
◆ 0.02 wt%	Semi-dilute non-entangled	2 h
■ 0.2 wt%	Semi-dilute entangled	2 h
▼ 1.5 wt%	Concentrated	48 h

Rheology (Stress-controlled)

T: 25°C

- **Flow curves (all solutions)**
  - 20 min pre-shear at 0.1 Pa
  - $\Delta t_{meas.}$ = 30 s
- **Measurements at constant σ (1.5% Na CMC)**
  Solvent trap covered with wet tissue to reduce water evaporation

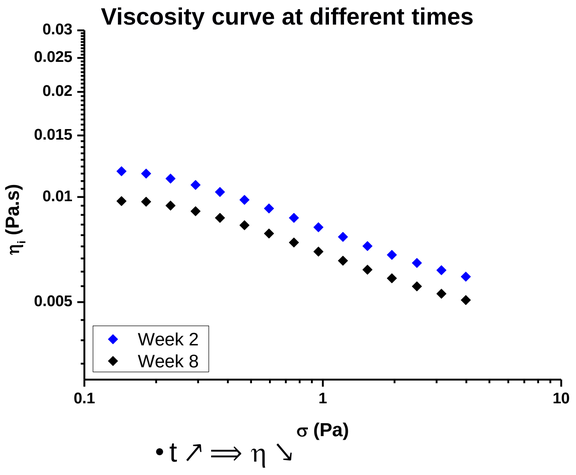
DLS

- Additional preparation steps:
  0.02%: filtration (1-5 µm glass filter)
  0.2%: concentrated from 0.02%
- T: 25°C
- θ: 50°
- Δtmeas: 2 or 5 min

Results and discussion

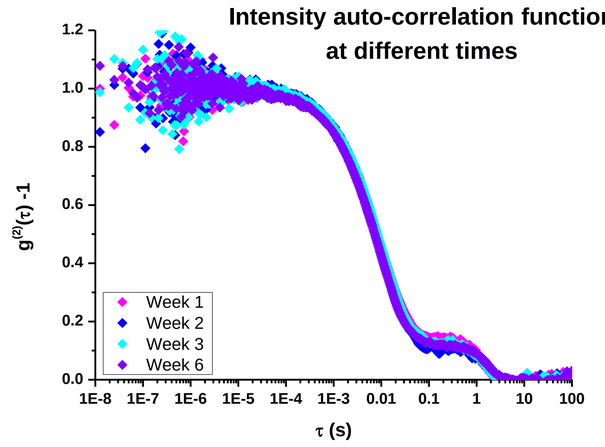
0.02% Na CMC

Viscosity curve at different times



- t ↗ ⟹ η ↘
- $\eta_{Week\ 2} = 81\%\ \eta_{Week\ 8}$

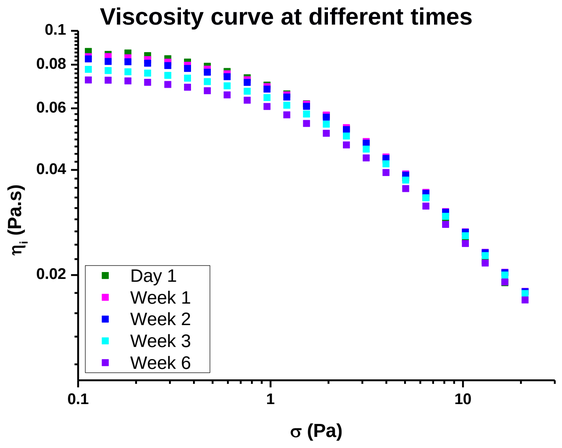
Intensity auto-correlation function at different times



- First 6 weeks: t ↗ ⟹ $\tau_{relaxation}$ ⟶

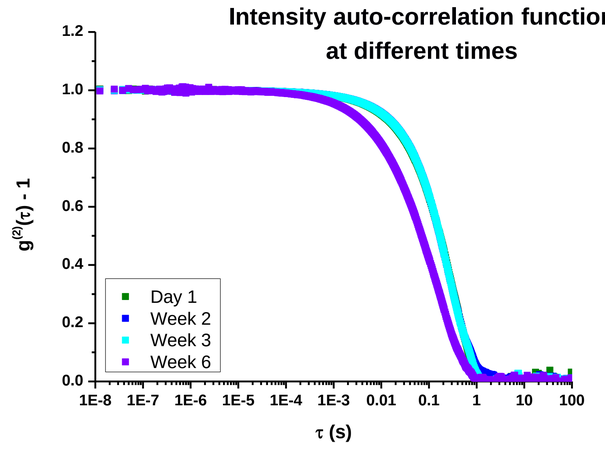
0.2% Na CMC

Viscosity curve at different times



- First 2 weeks: t ↗ ⟹ η ↘ slowly
- From Week 3: t ↗⟹ η ↘↘
- $\eta_{Week\ 6} = 83\%\ \eta_{Day\ 1}$

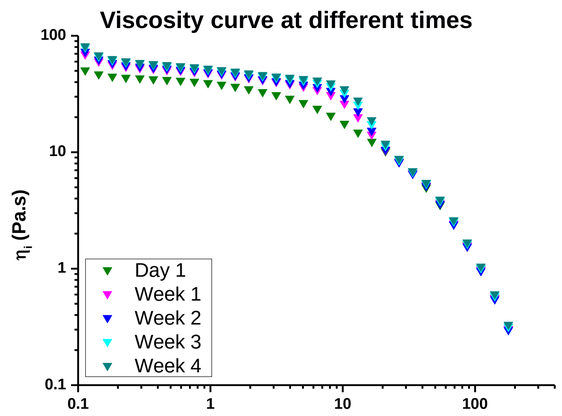
Intensity auto-correlation function at different times



- First 3 weeks: t ↗ ⟹ $\tau_{relaxation}$ ⟶
- Between Weeks 3 and 6: t ↗ ⟹ $\tau_{relaxation}$ ↘

1.5% Na CMC

Viscosity curve at different times



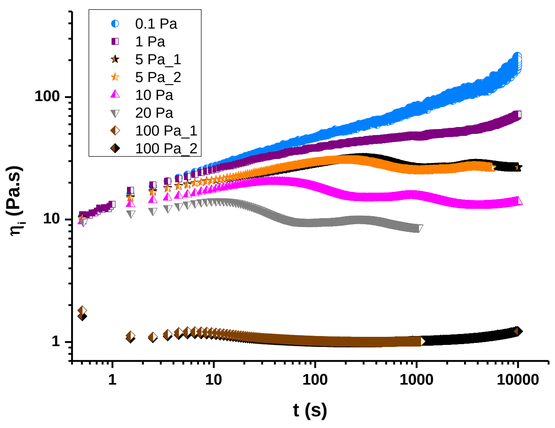
- First week:
  - t ↗ ⟹ η ↗ ↗
  - Significant change in the curve shape
- From Week 2: t ↗ ⟹ η ↗ slightly
- $\eta_{Week\ 4} = 161\%\ \eta_{Day\ 1}$

Possible explanations

- Chain degradation
  (i.e. shorter chains ⟹ η ↘ [1])
  ✓ Could agree with the results of the 0.02% and 0.2% Na CMC solutions
  ✗ Disagrees with the results of the 1.5% Na CMC solution
- Changes in the chain conformation
  ✓ Could agree with the results of the 0.02% and 0.2% Na CMC solutions
  (e.g. chains getting coiled, formation of aggregates)
  ✓ Could agree with the results of the 1.5% Na CMC solution
  (e.g. entanglements ↗ [2]; see opposite)

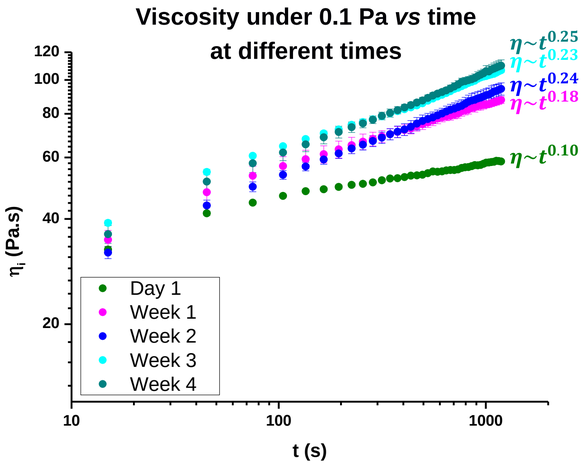
1.5% Na CMC – Other intriguing features

Viscosity under different shear stresses *vs* time



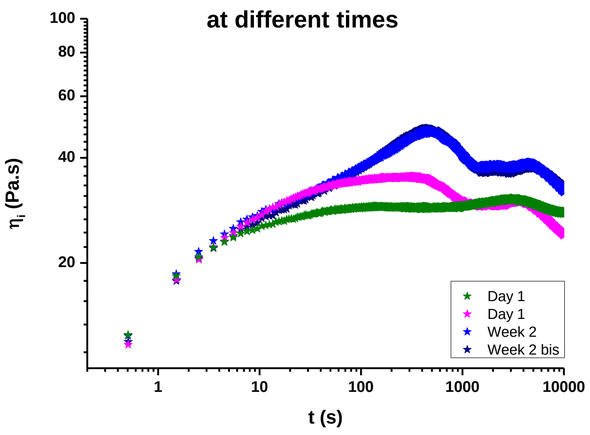
- Low σ: t ↗ ⟹ η ↗
- Intermediate σ: t ↗ ⟹ η ↗ before oscillating
- High σ:
  - t ↗ ⟹ η ↘ before reaching a steady value
  - At high t, η ↗ ⟹ evaporation? Most likely to occur during all long measurements
- Similar behaviour found in the literature [3]

Viscosity under 0.1 Pa *vs* time at different times



- t ↗ ⟹ η ↗
- t_{ageing} ↗ ⟹ power law exponent ↗ before reaching a steady value around 0.24

Viscosity under 5 Pa *vs* time at different times



- Day 1: t ↗ ⟹ η ↗ before reaching a quasi- steady value
- Weeks 1 and 2:
  - t ↗ ⟹ η ↗ before oscillating
  - t_{ageing} ↗ ⟹ η_{max} ↗

Conclusions and perspectives

- Ageing phenomena are concentration-dependent:
  - Low $c_{Na\ CMC}$ (semi-dilute regime): t ↗ ⟹ η ↘
  - High $c_{Na\ CMC}$ (concentrated regime): t ↗ ⟹ η ↗ and significant change in the viscosity curve
- Suggested ageing causes:
  - Chain degradation
  - Changes in chain conformation
- Viscosity of the 1.5% Na CMC solution under constant stresses: stress-dependent
- Further investigations:
  - Size-Exclusion Chromatography (SEC) over time to check for chain degradation
  - Light scattering study on the most concentrated solutions

References

1. F.L. Muller and J.F. Davidson, *Industrial & Engineering Chemistry Research*, 1994. **33**(10)
2. J. Sanchez-Reyes and L.A. Archer, *Journal of Rheology*, 2002. **46**(5)
3. P.C.F. Møller , A. Fall and D. Bonn, *EPL (Europhysics Letters)*, 2009. **87**(3)

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P&G