Rheological properties of carboxymethyl cellulose solutions and gels: An overview

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We present a brief overview of the main rheological phenomena associated with solutions and gels of carboxymethyl cellulose, a widely used ionic cellulose ether. When the number of carboxymethyl groups per monomer (DS) exceeds a value of $\simeq 1$, chains behave as hydrophilic polymers with weak associative interactions. Their behaviour is similar to that of other semiflexible polyelectrolytes. For lower degrees of substitution, unsubstituted patches along the chains act as temporary stickers leading to associative solution rheology and weak gel formation at high concentrations. The influence of environmental parameters such as temperature, pH and added salt content is discussed. The rheological properties of mixtures of NaCMC with surfactants and colloids is reviewed.

Keywords: carboxymethyl cellulose, polyelectrolyte, rheology, gel

1. INTRODUCTION

Carboxymethyl cellulose, usually employed as its sodium salt (NaCMC) is the most widely produced ionic cellulose ether.[1–3] It functions as a viscosifying and structuring agent in a multitude of industrial formulations.[4–12] For such products, the rheological properties of CMC solutions and gels are key to its performance. CMC can also be used in the production of various soft materials such as hydrogels.[13, 14] Here we give a short overview of such properties and discuss the main rheological phenomena observed for CMC. For a detailed discussion of the structure and supramolecular aggregation of CMC, see ref. [3]

Etherification of activated cellulose with chloroacetic acid introduces carboxymethyl groups along the cellulose backbone.[15, 16] The extent of substitution is usually quantified by the degree of substitution (DS), defined as the *average* number of substituted hydroxyl groups per anhydroglucose unit. In commercial samples, which are commonly produced by the slurry process, the distribution of substituents can be relatively homogeneous or highly heterogeneous depending on the synthesis conditions and the overall DS. This heterogeneity occurs both along individual chains and across different chains within the sample. As a result, CMC samples contain a distribution of average chain DS values[17–19] and, even for chains with similar average DS, different substitution patterns may exist, ranging from nearly random substitution to highly blocky sequences with long unsubstituted cellulose segments.[20–22]

Broadly speaking, carboxymethyl cellulose samples can be divided into highly substituted grades (DS $\gtrsim$ 1) and weakly substituted grades (DS $\lesssim$ 1).[23, 24] Highly substituted samples are characterised by well-dispersed, molecularly dissolved chains[25, 26] that behave similarly to hydrophilic polyelectrolytes.[27, 28] Weakly substituted grades contain a fraction of chains with long unsubstituted cellulose patches along the backbone, which result supramolecular aggregates[3, 29, 30] and act as interchain stickers.[31] These associations produce rheological behaviour characteristic of hydrophobic polymers, including weak physical gel formation and thixotropy.[32, 33]

We begin by discussing the dilute solution viscosity behaviour of NaCMC, which is important for molar mass characterisation and then introduce the rheological properties of weakly and highly substituted CMC. We discuss the main rheological phenomena associated with changes in environmental conditions (pH, temperature, and salt content) and conclude with examples of the interaction of NaCMC with surfactants, colloids and trivalent ions.

2. DILUTE SOLUTION BEHAVIOUR

The dilute-solution viscosity of NaCMC in excess salt is characterised by the intrinsic viscosity, $[\eta]$, which measures the hydrodynamic volume of the CMC coils, and by the Huggins coefficient, k_H, which describes the concentration dependence of the reduced viscosity, η_{red}. The Huggins equation is:

$$\eta_{red} \equiv \frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c, \qquad (1)$$

where $\eta_{sp} = (\eta - \eta_s)/\eta_s$ is the specific viscosity, η is the solution viscosity, and η_s is the solvent viscosity.

The overlap concentration, defined as the concentration at which chains begin to interpenetrate, can be approximated as $c^* \simeq [\eta]^{-1}$. The product $c^*[\eta]$ is known as the overlap parameter and is used to construct universal functions for several rheological properties, as discussed below.

When expressed in inverse molar concentration units, the intrinsic viscosity depends weakly on the degree of substitution and follows a power law with the degree of polymerisation. If $[\eta]$ is expressed in the usual units of volume per mass, this relation becomes:

$$[\eta]M_0 = KN^{\alpha}, \qquad (2)$$

where $M_0 = 160 + 80 \times DS$ is the molar mass of a monomer and $N = M/M_0$ is the degree of polymerisation. The values of K and α depend on the added salt

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concentration.[34] The exponent α usually takes a value somewhat larger than the Zimm prediction of 0.784, see ref. [35] for a compilation of literature data for NaCMC.

Equation 1 remains valid for $c \lesssim [\eta]^{-1}$, corresponding to the dilute regime, and applies only under excess salt conditions, $2c_S \gg fc$.[36, 37] Here, c_S is the concentration of added salt, assumed to be monovalent, f is the fraction of monomers with a free counterion, $\simeq 0.5$ for NaCMC in water, and c is the polymer concentration expressed as the number concentration of monomers. In the low-salt regime, the reduced viscosity increases upon dilution,[38, 39] which makes extrapolation to zero concentration more involved.[40] In practice, using the criterion that at the overlap concentration the viscosity of a solution is twice that of the solvent, i.e., $\eta_{sp}(c^*) \simeq 1$, the overlap concentration of NaCMC solutions in water can be estimated and a relation of $c^* \propto N^{-2}$ has been found, corresponding to highly extended, rod-like configurations. As salt is added, the chains progressively fold and their hydrodynamic volume decreases, with the corresponding increase in the overlap concentration.

Dilute solutions of NaCMC are non-Newtonian liquids.[41–43] Therefore, the viscosity measured by glass capillary viscometry, which typically applies shear rates of 10^2–10^3 s^{-1}, does not always correspond to the zero-shear, Newtonian limit. Shear thinning becomes more significant as the molar mass increases or the ionic strength of the solvent decreases. Care is therefore required to ensure that viscosity measurements correspond to the Newtonian regime, as discussed in earlier literature.[3, 40, 44, 45]

3. SEMIDILUTE AND CONCENTRATED SOLUTIONS AND GELS

3.1. Highly substituted CMC

3.1.1. General properties

Figure 1 shows the shear-rate dependence of the specific viscosity of NaCMC solutions with DS = 1 at different concentrations. The curves include measurements in DI water and in aqueous NaCl solutions. Addition of NaCl decreases the solution viscosity and shifts the onset of shear thinning to higher shear rates. This effect is most pronounced at low concentrations and becomes negligible at high concentrations.

The shear-rate dependence of the apparent viscosity of NaCMC solutions can be described by the generalised Carreau-Yasuda model,

$$\eta(\dot{\gamma}) = \frac{\eta(0)}{[1 + (\tau\dot{\gamma})^b]^{n/b}}, \tag{3}$$

where $\eta(0)$ is the zero-shear viscosity, τ is the longest relaxation time, $\dot{\gamma}$ is the shear rate, n is the flow index, which describes the power-law dependence of the viscosity at high shear rates, and b determines the sharpness of the crossover between the low-shear Newtonian regime and the high-shear power-law regime.

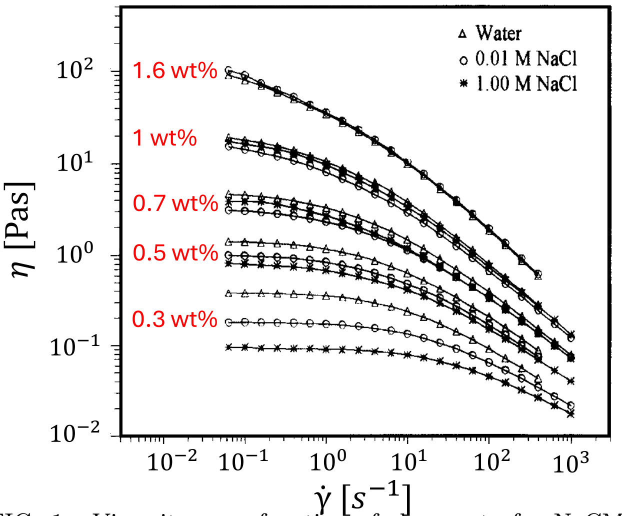

FIG. 1. Viscosity as a function of shear rate for NaCMC solutions in DI water and in aqueous NaCl solutions. Figure adapted from ref. [46].

For low and moderate polymer concentrations, the Carreau model, corresponding to Eq. 3 with $b = 2$, describes the data well. At high concentrations, however, the transition from the Newtonian regime to the power-law regime becomes too broad to be fitted accurately by the Carreau model.[33]

The flow properties of semidilute and concentrated solutions of high-DS CMC are similar to those of other semiflexible, hydrophilic polyelectrolytes.[27, 47–49] Figure 2 plots the specific viscosity as a function of polymer concentration for NaCMC (DS $\simeq$ 1.2) in deionised water and in aqueous NaCl solutions with concentrations of added sodium chloride varying between 5 mM and 2 M. In DI water, which has a low residual salt concentration of $\simeq 4 \times 10^{-6}$ M due to CO_2 in the air which dissolved to form carbonic acid, the viscosity first scales as $\eta_{sp} \propto c^{0.68}$. The 0.68 exponent, which has been observed many times for NaCMCs of varying DS in DI water solution,[33, 50–55] is somewhat larger than the theoretical relation $\eta_{sp} \propto c^{1/2}$ expected for non-entangled polyelectrolytes.[56, 57] The square root dependence of the viscosity on concentration is known as the Fuoss law.[58, 59] The weak dependence of the scaling exponent on the degree of substitution suggests that associative interactions between chains do not strongly modify polymer dynamics in the non-entangled regime.[60]

In salt-containing solutions,[33, 61] the η_{sp}–c exponent in the non-entangled regime is close to 1.3, matching the behaviour of neutral polymers in good solvent, and in agreement with theoretical predictions that in excess salt conditions electrostatic interactions become short ranged and their effect is similar to that of excluded volume in solutions of non-ionic polymers. Above the entanglement concentration, the exponent gradually increases[35, 61, 62] to $\eta_{sp} \sim c^{3-4}$ for both salt-free and

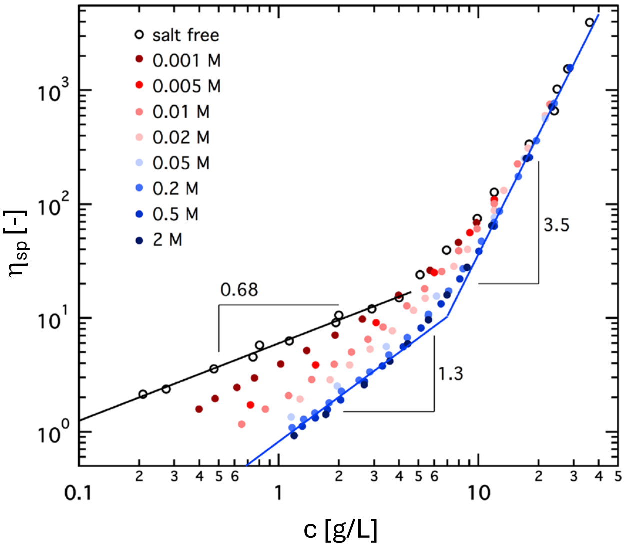

FIG. 2. Viscosity of NaCMC ($M_w \simeq 3.2 \times 10^5$ g/mol. DS $\simeq 1.2$) in DI water and aqueous salt solutions as a function of polymer concentration. Lines are power-law fits, see the text for details. Figure adapted from [35]. The overlap concentration corresponds to the point at which $\eta_{sp} \simeq 1$.

salt-containing solutions. The weak dependence of the viscosity on added salt concentration[63, 64] at high concentrations ($c \gtrsim 20$ g/L) indicates that electrostatics perturb the conformation of chains to a small extent. This regime is sometimes called the concentrated regime or the neutral polymer regime and is usually observed for semiflexible polyelectrolyte systems, where the intrinsic chain rigidity is much larger than the electrostatic one at modest and high ionic strengths.[40, 65]

3.1.2. *Entanglement crossover*

As discussed in the preceding section, the overlap concentration in excess salt decreases with degree of polymerisation as $c^* \sim N^{-0.78}$ and for salt-free solutions as $c^* \sim N^{-2}$.[54] These values are in reasonably good agreement with the theoretical predictions of the scaling model.[56, 57, 66] In excess salt solution the entanglement concentration of NaCMC scales as $c_e \sim N^{-0.78}$, in agreement with theory.[54] The proportionality between c^* and c_e allows the specific viscosity and other rheological properties to be written as a universal function of c/c^*.[27, 67] The molar mass variation of the entanglement concentration in salt-free and low-salt solutions is presently not well understood. Different studies propose different ways of quantifying c_e as well as ways to interpret the existing data for NaCMC and other polyelectrolyte solutions, but no consensus exists on this topic. For an overview of various points of view, see refs.[54, 68–75]. While no consensus exists on the precise nature of the entanglement cross-over, it is clear that once the specific viscosity reaches the regime where it scales as $\eta_{sp} \propto c^{3.75}$, NaCMC is entangled. Measurements over a wide frequency range covering the entanglement plateau region would be helpful towards understanding when CMC solutions become entangled. At present these only exist for ionic liquid solutions.[76]

3.1.3. *Entangled dynamics*

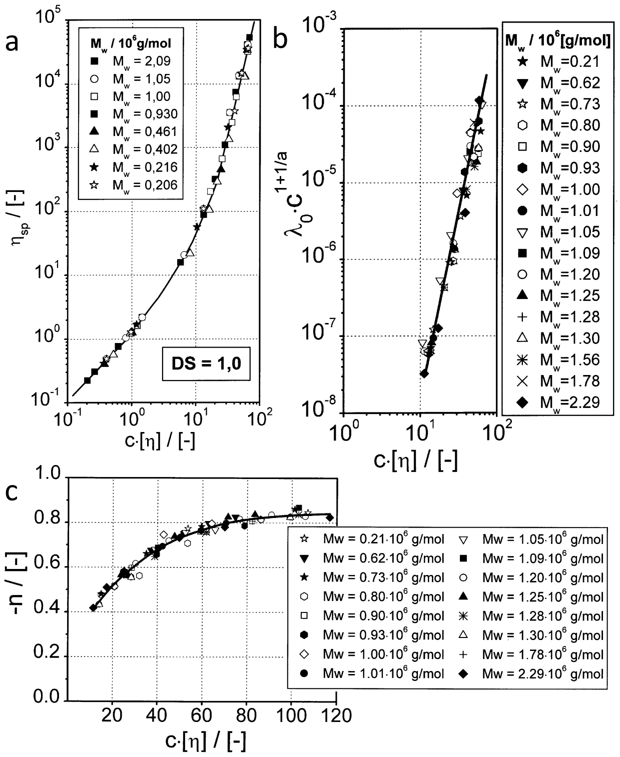

FIG. 3. Dependence of various rheological parameters of NaCMC DS $\simeq 1$ in 0.01 M NaCl solution as a function of the overlap parameter $c[\eta]$. a: specific viscosity, line is Eq. 4. b: longest relaxation time obtained from Carreau-Yasuda model. c: flow index, also obtained from Eq. 3. Solid line is Eq. 5. Weight-averaged molar masses are indicated on the legends. Figure adapted from [67].

Different approaches have been proposed to express the viscosity and other rheological parameters as functions of concentration and molar mass. One approach,[46, 77, 78] extends the Huggins equation (Eq. 1) by adding a term that accounts for the behaviour in the $[\eta]c \gg 1$ limit. The expanded Huggins equation reads:

$$\eta_{sp} = c[\eta] + k_H(c[\eta])^2 + B_\eta(c[\eta])^m \qquad (4)$$

where B_η and m are parameters which depend on the solvent but not the molar mass or DS. Analogous expressions can be written for the longest relaxation time. The flow index n is usually modelled as an exponential function of the overlap parameter:[79, 80]

$$n = 1 - Ae^{-[\eta]c} \qquad (5)$$

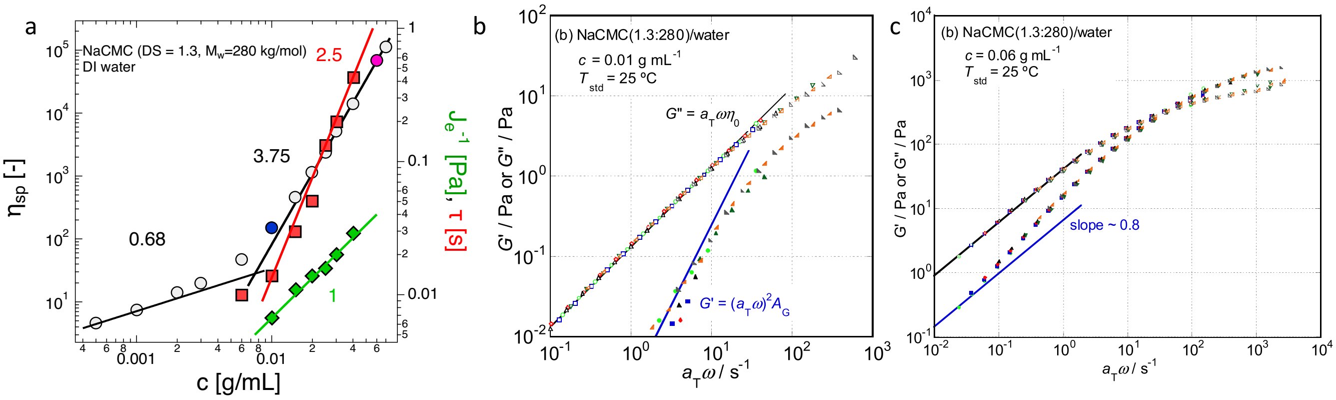

FIG. 4. Rheological properties of NaCMC (DS $= 1.3$, $M_w = 280$ kg/mol) solutions in DI water. a: concentration dependence of the specific viscosity, longest relaxation time, and inverse steady state compliance. Viscosities for concentrated samples were obtained from $\eta = \lim_{\omega\to 0} G''/\omega$. The blue and purple circles indicate the samples whose oscillatory rheology is shown in parts b and c. b: viscoelastic moduli of a 0.01 g/mL solution. Different symbols correspond to temperatures between -5 °C and 55 °C, shifted to a reference temperature of 25 °C. Black and blue lines show the expected behaviour of the storage and loss moduli in the terminal region. c: same as part b, but for a 0.06 g/mL solution. Figure adapted from 62.

where A is a fitting parameter.

Example results for this approach are shown in figure 3. Equation 4 provides a practical method to estimate the viscosity when the intrinsic viscosity is known, but it is largely empirical and the fitting parameters lack a clear physical interpretation. A second approach uses scaling models[56, 57] in which the viscosity is expressed as the product of the non-entangled Rouse viscosity and a cross-over function that recovers the expected scaling behaviour in the entangled regime. Discussion of these approaches and their application to neutral polymers and other polyelectrolytes can be found in [71, 81–83].

The frequency dependence of the storage and loss modulus of a DS $= 1.3$ sample is DI water is plotted in figure 4b. The concentration is $c = 10$ g/L, corresponding to the mid-point between non-entangled and entangled regimes in the $\eta_{sp} - c$ plot, shown in fig. 4a. The storage and loss moduli show the expected frequency dependence in the terminal region. At higher frequencies, the frequency dependence of both quantities weakens, but no cross-over in G' and G'' is observed, suggesting the samples are not entangled, despite deviating significantly from the $\eta_{sp} \propto c^{0.68}$ power-law.[68] For more concentrated samples which are well into the entangled regime, a cross-over in G' and G'' is observed, which is characteristic of reptation dynamics, see fig. 4c. The steady state compliance of the solutions always follows a power-law of $J_e \propto c^{-1}$, and displays no clear sign of entanglements over the measured range. Note that the values of J_e^{-1}, as well as that of the apparent terminal modulus ($G = \eta/\tau$)[28] are much lower than $k_B T$ per chain due to the large molar mass polydispersity of the samples.[84]

3.2. Weakly substituted CMC

Figure 5 compares the oscillatory shear response of NaCMC solutions with DS $= 0.95$ and DS $= 2.4$. The

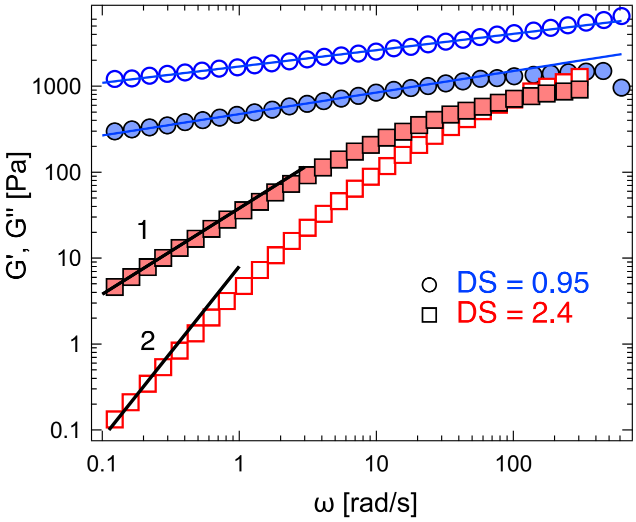

FIG. 5. Oscillatory shear response of NaCMC solutions ($c = 100$ g/L) in aqueous 0.1 M NaCl. The higher substitution grade was obtained by etherifying the DS $= 0.95$ sample for a second time. Data from [85].

lower-DS sample forms a weak physical gel, characteristic of associative polysaccharides,[87, 88] with $G' \sim G'' \sim \omega^{1/3}$. The higher-DS sample displays solution-like behaviour, with the terminal scaling expected for a viscoelastic liquid. At sufficiently low concentrations, usually below the entanglement concentration, both low-DS and high-DS samples display similar solution-like behaviour.[33, 85] This indicates that sufficient chain overlap is required for associative interactions to measurably affect the rheological response.[89–91]

A sol-to-gel transition has been reported for many CMC samples with DS $\lesssim 1$ when the polymer concentration exceeds a critical value, c_{gel}.[33, 92, 93] The precise value of c_{gel} depends on the DS, molar mass, and sub-

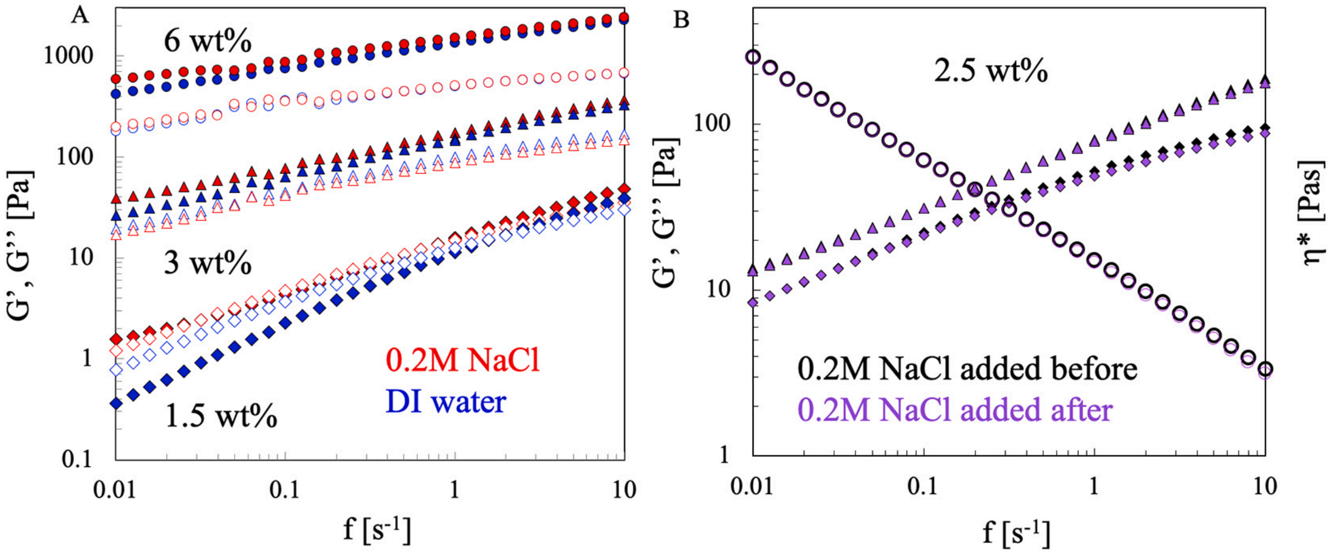

FIG. 6. Oscillatory shear response of NaCMC solutions in the linear viscoelastic region. (a) Frequency dependence of G' and G'' for NaCMC gels in aqueous media. Filled and open symbols correspond to G' and G'', respectively. Red symbols show samples with 0.2 M added NaCl, and blue symbols show samples in DI water. (b) Frequency dependence of G', G'', and η^* for a 2.5 wt% NaCMC solution with 0.2 M added NaCl. Black and purple symbols correspond to NaCl addition before and after polymer dissolution, respectively. Figure from ref. [86].

stitution pattern, but gelation appears to always occur above the entanglement crossover. Gelation is preceded by an associative rheology regime,[94, 95] in which one or more of the following features are observed:

- a rapid increase in the specific viscosity and longest relaxation time with concentration, e.g., $\eta_{sp} \sim c^7$
- a decrease of the apparent modulus ($G = \eta/\tau$) with increasing polymer concentration
- the disappearance of the Newtonian behaviour at low shear rates. Instead, the apparent viscosity increases as the shear rate decreases, reaching no plateau in the measurable shear-rate range.

Above the gelation threshold, the storage and loss moduli display a weak dependence on frequency. The frequency exponent of G' decreases with increasing concentration, indicating an increase in the elastic character of the samples. In the low-frequency region, the elastic modulus scales approximately as $G' \sim c^3$, although substantial variations are observed among samples with different molar masses and substitution patterns.[86] Two theoretical models have been proposed to describe the rheological properties of carboxymethyl cellulose gels.[96, 97] As discussed in earlier work,[3, 31, 98–100] NaCMC gel samples contain two populations that can be separated by ultracentrifugation. Both populations have similar molar mass and average DS, but differ in substitution pattern. One population consists of well-dispersed chains, which form a viscoelastic liquid when dissolved in water. The second population consists of aggregating chains, which form the network responsible for the gelling properties of these grades. An important step towards understanding the rheological properties of NaCMC gels would be to perform systematic measurements on isolated gel-forming fractions, where the well-dispersed chains do not contribute to the measured viscoelastic response. Rheology and scattering data for such networks would be considerably easier to analyse and interpret than for 'mixed' samples.

3.2.1. *Effect of added salts and order of addition*

Several studies[101, 102] have reported that the viscosity of NaCMC + salt solutions depends on whether the low molecular weight salt is added before or after the polymer is dissolved. If the salt is added before, the resulting solution displays lower viscosity than if the salt is added after, which is assigned to greater aggregation of the polymer in the former case. This finding appears to be the result of incomplete polymer dissolution, as dissolution proceeds more slowly in saline media than in salt-free water. If the samples are sufficiently mixed to ensure full dissolution, the solution viscosity is the same regardless of the order of addition.[33, 86] For gel-forming samples, addition of NaCl can enhance the gel strength (G' at low frequencies) to a small degree, see figure 6.

3.3. Temperature and time-dependent behaviour

Relatively little work exists on the temperature dependence of NaCMC viscosity.[62, 103, 104] Polyelectrolytes generally show only a weak temperature dependence of the specific viscosity because electrostatic interactions dominate over thermal energy.[77, 105] The solution viscosity is therefore expected to decrease in approximate proportion to that of the solvent. NaCMC slowly hydrolyses at room temperature, leading to a gradual decrease in solution viscosity with time.[28] This effect is accelerated at higher temperatures because CMC degradation proceeds more rapidly. Time-dependent viscosity is therefore important in formulated products. Commercial brochures report that the viscosity of low-DS samples can continue to increase for several days after dissolution, presumably due to slow structure formation of the associative network, but this effect has not been systematically studied.

3.4. Addition of non-solvents

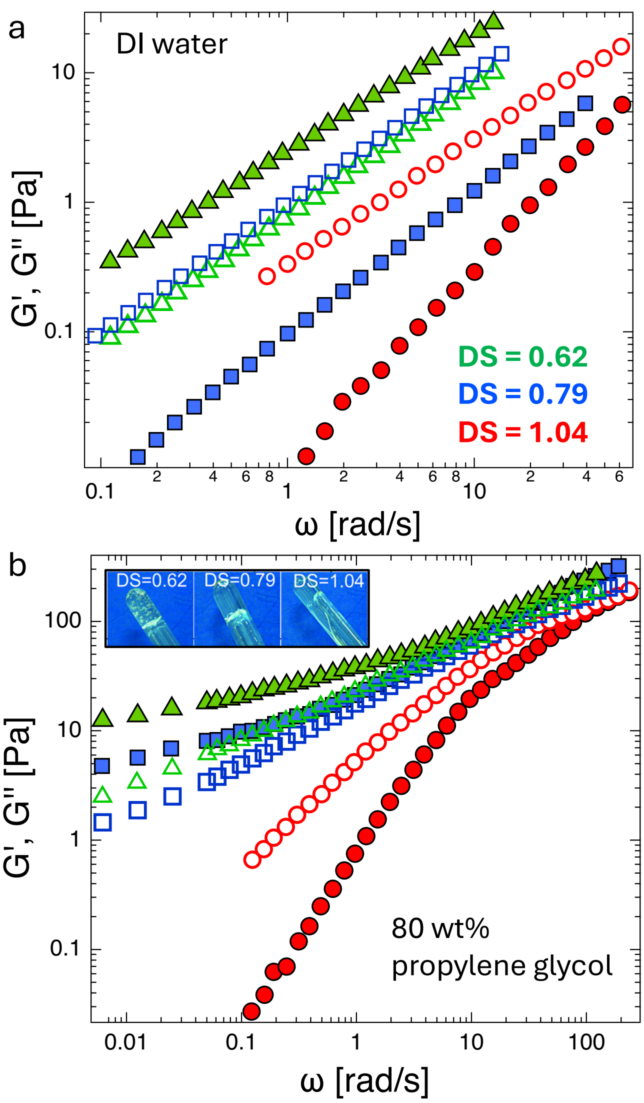

FIG. 7. Oscillatory shear rheology of NaCMC ($c = 2.2$ wt%) with different DS in DI water (a) and in 80 wt% propylene glycol solution (b). All polymers have a molar mass around 250 kg/mol. Figure adapted from ref. [106].

If a non-solvent such as ethanol or propylene glycol is added to NaCMC in aqueous media, two types of behaviour are observed depending on the substitution pattern of the chains: For ‘hydrophilic’ samples with homogeneous substitution patterns, addition of non-solvents leads to either a small decrease or to no change in the specific viscosity. The viscosity of the solution depends on solvent composition through the contribution of the solvent to the solution viscosity. Beyond a critical added non-solvent fraction, the polymer precipitates.[55] By contrast, in CMC samples with heterogeneous substitution patterns, the viscosity and longest relaxation time increase, and for sufficiently high polymer or non-solvent concentrations the system forms a gel. The addition of a non-solvent has an effect similar to lowering the degree of substitution.[107]

Figure 7 compares the oscillatory shear rheology of NaCMC samples with different degrees of substitution in DI water and in 80 wt% propylene glycol, which is a non-solvent for CMC. In DI water, decreasing the degree of substitution produces a transition from liquid-like to weak-gel behaviour, consistent with the mechanisms discussed above. Compared to figure 5, the concentration is $\simeq 5\times$ lower and the gel strength of the low DS samples is therefore weaker. In the presence of propylene glycol, the sol-gel transition upon decreasing DS becomes more pronounced. The low-DS samples show a weaker frequency dependence at low frequency, indicating more developed network formation. By contrast, the more highly substituted sample retains solution-like behaviour. Komorowska et al.[106] proposed that the enhanced gel formation at low DS arises from inter-chain hydrogen bonding.

3.5. Influence of pH

NaCMC is a weak polyelectrolyte, and its charge density depends on the pH of the aqueous medium.[109] At low pH, protonation of carboxylate groups decreases the charge density of the CMC chain, reducing electrostatic repulsion between chains and promoting inter-chain associations which act as temporary stickers that slow down chain dynamics. Lowering the pH can induce a sol-gel transition in non-gelling samples, as shown in Fig. 8e–f, or strengthen an existing weak gel, as shown in Fig. 8a. Acid-induced gelation is accompanied by the development of a weakly frequency-dependent quasi-plateau in G' at low frequencies and by stress overshoot[110] behaviour under medium and large amplitude oscillatory shear.[86, 97, 108] At fixed pH, the gel strength increases with polymer concentration, as expected from the greater number density of inter-chain contacts. At sufficiently low pH, the solutions macroscopically phase separate.

Increasing the solution pH has the opposite effect: NaOH promotes solubilisation of unsubstituted cellulose patches, resulting in a transition from gel-like to solution-like behaviour for weakly substituted samples. Since

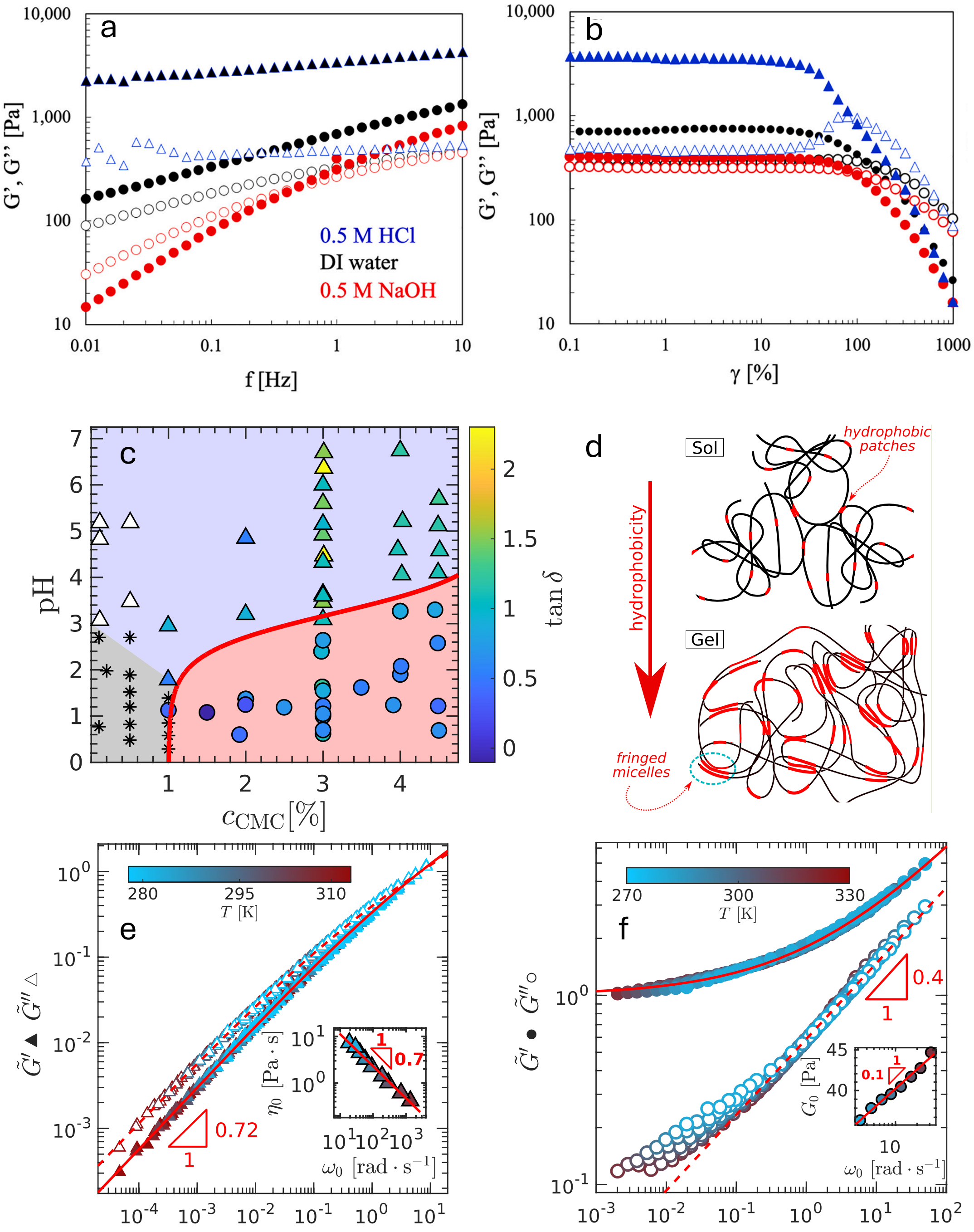

FIG. 8. Influence of pH on the rheology of CMC in aqueous media. (a) Storage and loss moduli of NaCMC (DS $\simeq 0.7$, $c = 2.5$ wt%) in the linear viscoelastic region in DI water (weak gel), 0.5 M NaOH (solution-like), and 0.5 M HCl (stronger gel). (b) Medium and large amplitude oscillatory response of the same samples. (c) pH-polymer concentration phase diagram for NaCMC with DS $= 0.9$. Low values of $\tan\delta \equiv G^{''}/G^{'}$ correspond to stronger gels. The blue region corresponds to solution-like samples, the red region to gel-like samples, and the grey region to phase-separated samples. (d) Schematic of the proposed association model. (e,f) Sol-gel transition for $c = 3$ wt% at pH $= 3.6$ and pH $= 1.6$, respectively (both DS $= 0.9$). At low pH, a rubbery plateau develops at low frequencies. Figure adapted from [86, 97, 108].

CMC is already nearly fully ionised at neutral pH, increased ionisation of the carboxymethyl groups cannot explain this transition. Ionisation of hydroxyl groups on the cellulose backbone may contribute, but this mechanism is not well understood. Note that both high and low pH also promote depolymerisation of CMC.

3.6. Addition of trivalent salts

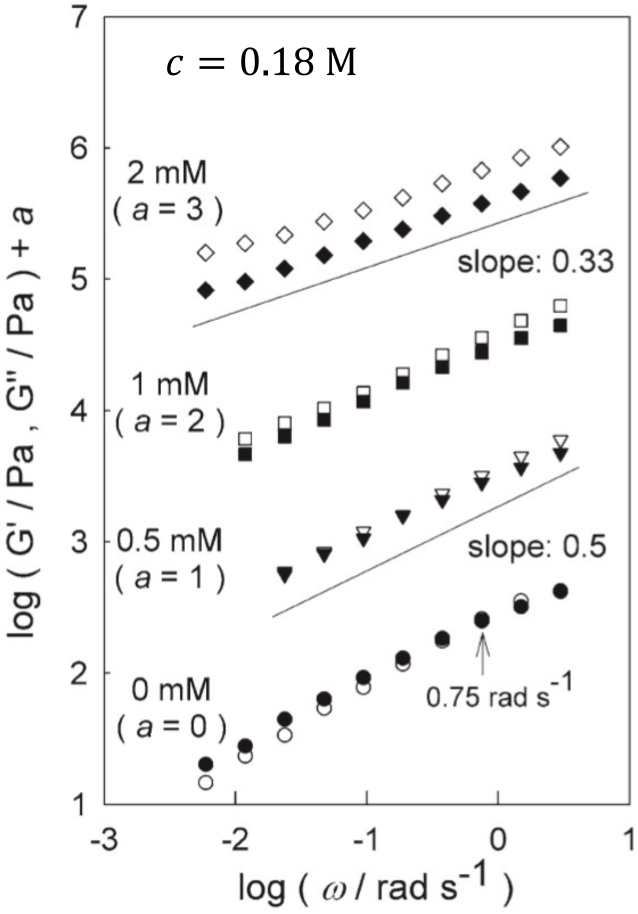

FIG. 9. Oscillatory shear response in the LVE region for CMC with DS = 1.38 at polymer concentration $c \simeq 0.18$ M with different concentrations of added $Al_2(SO_4)_3$. Figure adapted from [111].

Trivalent ions can gel CMC solutions even when present at millimolar concentrations. An example is shown in figure 9, which plots the oscillatory shear response of a NaCMC solution with DS = 1.38 and $c \simeq 180$ mM, and its evolution upon addition of aluminium sulfate. At $c_S = 2$ mM, there is approximately one Al^{3+} ion for every 130 carboxymethyl groups. Under these conditions, the storage and loss moduli have nearly the same frequency dependence, $G' \sim G'' \sim \omega^{0.33}$, indicating that the system is close to the gel point according to the Winter–Chambon criterion.[112] Further addition of aluminium sulfate shifts the response toward more elastic behaviour, with a weaker frequency dependence of G' and a larger separation between G' and G''. This shift is consistent with an increase in the density or lifetime of ionic junctions. The mechanism by which trivalent ions gel CMC is not fully understood, but it is reasonable to suggest that Al^{3+} ions form transient or permanent junctions by coordinating carboxymethyl groups from different chains.

One difficulty in studying ionically cross-linked CMC gels is that direct exposure of the polymer solution to a high concentration of trivalent ions can form a brittle skin.[113, 114] This produces spatially inhomogeneous cross-linking, which can remain stable over very long timescales. A common strategy to avoid this problem is to use chelating agents that slowly release trivalent ions into solution, allowing the gel to form more homogeneously. Divalent ions precipitate NaCMC at much higher than trivalent ones[115] and their influence on the rheological properties of CMC is more mild.[80]

3.7. Complexation with oppositely charged surfactants

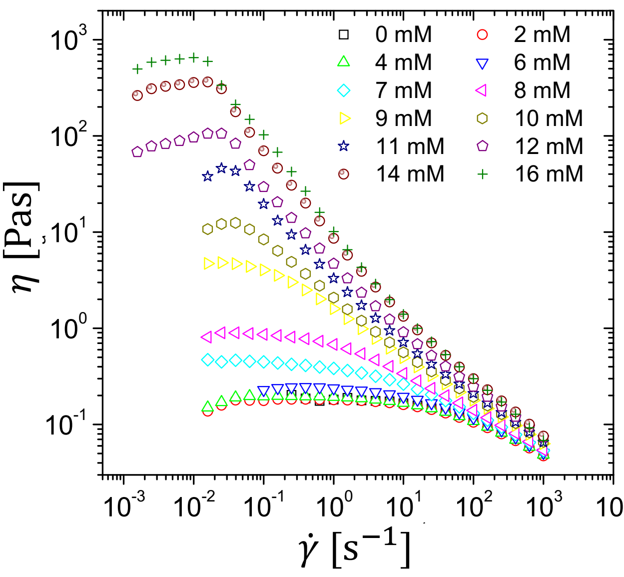

FIG. 10. Apparent viscosity of 1 wt% NaCMC aqueous solutions with DS $\simeq$ 0.7 as a function of added dodecyltrimethylammonium bromide, C_{12}TAB, concentration. Figure adapted from ref. [116].

Polyelectrolytes complex with oppositely charged surfactants to form structures that are often out of equilibrium.[118] Studies on CMC with cationic surfactants have reported a wide range of morphologies, from nanoparticles with ordered cores[119–121] to physically crosslinked networks. Aggregation above a critical surfactant concentration is usually observed.[122, 123] The effect of preparation method on the resulting aggregate structure is discussed in ref. [124]. Interfacial rheology has also been examined for CMC-surfactant mixtures.[125, 126]

Wu et al. studied the rheology of NaCMC solutions with added cationic surfactants, C_{12}TAB and C_{16}TAB.[116] For non-entangled NaCMC solutions, the viscosity decreased with increasing surfactant concentration, consistent with the theory of Colby and coworkers[127] This is also consistent with other studies

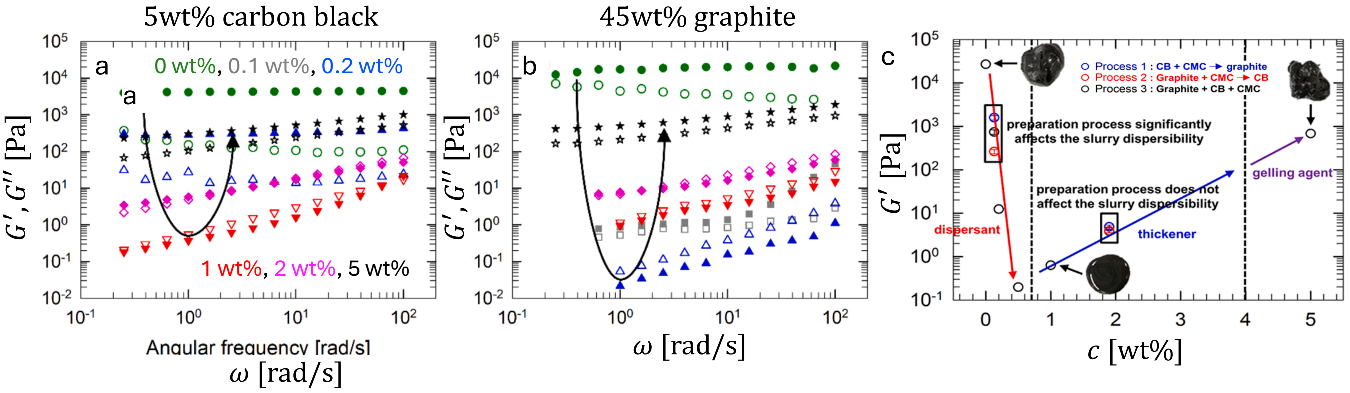

FIG. 11. Rheological properties of NaCMC/carbon black/graphite slurries. a-b: oscillatory shear viscoelasticity of carbon black and graphite dispersions with different concentrations of added NaCMC. The storage modulus in the low frequency region for ternary mixtures is plotted as a function of concentration for different mixing protocols in part c. Figure adapted from [117]

quantifying the surface tension and conductivity measurements on NaCMC-surfactant mixtures.[128, 129] By contrast, addition of cationic surfactant to entangled NaCMC solutions caused a rapid increase in viscosity and longest relaxation time, as shown in figure 10. This increase is generally attributed to the formation of transient network structures in which polymer chains are bridged by surfactant micelles or surfactant-polymer aggregates.[130–132]

3.8. Mixtures of NaCMC and colloidal particles

Sodium carboxymethyl cellulose (NaCMC) is widely used in aqueous Lithium ion battery anode slurries, where it serves as a binder, dispersant, and rheology modifier. The dense, hydrophobic active particles (graphite and carbon black) tend to aggregate or sediment. NaCMC adsorbs onto these surfaces, likely via hydrophobic interactions, stabilizing the particle network. The slurry's structure and rheological properties determine its processability [93, 117, 133–136] as well as the dispersion state of the particles [137].

Figures 11a–b plot the oscillatory shear response of carbon black and graphite slurries at different concentrations of added NaCMC [117]. Addition of low concentrations of NaCMC to a graphite dispersion initially decreases the viscosity, indicating particle stabilization via NaCMC adsorption onto the particle surfaces. Above a certain concentration, this trend reverses: the apparent viscosity and gel strength of the mixture increase with CMC concentration as the contribution of the viscoelastic CMC network becomes more significant. Similar behavior was observed by Lim et al. [93]. Park et al. also found that, depending on the polymer concentration, the mixing order influences the rheological properties of the slurry [117]. As shown in Figure 11c, this effect is particularly pronounced at low CMC concentrations, which is consistent with the findings of Kitamura et al. for CMC/graphite/styrene-butadiene rubber dispersions [138].

Recently, Gwag et al. [137] used small-angle neutron scattering (SANS) to study the structure of NaCMC–carbon black mixtures, correlating these structural findings with the flow properties of the systems. Adding carbon black causes a large decrease in solution viscosity for both the DS $= 1.2$ and 0.7 CMC samples. For the more highly substituted sample, the viscosity is essentially independent of the carbon black concentration for the ratios studied. In contrast, for DS $= 0.7$, the viscosity initially decreases but then increases with further carbon black addition. The viscosity decrease upon filler addition is unusual and may be the result of the sonication used to disperse the particles, which causes scission of the CMC chains, thereby lowering their molar mass. Based on the SANS results, Gwag et al. [137] concluded that the DS $= 0.7$ CMC promotes aggregation and network formation of the carbon black particles, whereas the primary role of DS $= 1.2$ is to stabilize the particles.

Studies on the flow properties of NaCMC mixed with aggregating colloidal particles, such as bentonite clays,[139–143] or microcrystalline cellulose,[32, 144] show synergistic behaviour between CMC and the added particulate phase. An example is shown in figure 12, which displays the stress–shear-rate response of aqueous bentonite dispersions with added CMC.[142] Addition of NaCMC strongly increases the yield stress of the bentonite dispersions and enhances their thixotropic response. Thixotropy has also been reported for NaCMC solutions in water without additives,[145] and is frequently mentioned in commercial brochures. However, it appears to be relatively rare among the NaCMC samples examined in the academic literature.

4. CONCLUSIONS AND OPEN QUESTIONS

The rheological properties of carboxymethyl cellulose are governed by the molar mass, concentration and substitution pattern along the backbone. Highly substituted

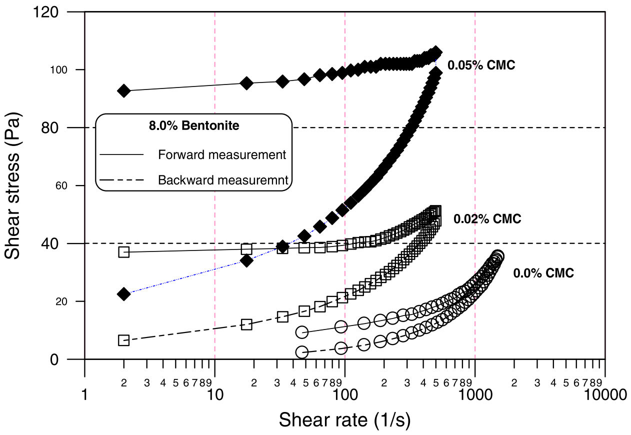

FIG. 12. Rheology of 8 wt% bentonite dispersions in aqueous media with different concentrations of added NaCMC. Figure adapted from [142].

grades (DS $\gtrsim 1$) display relatively homogeneous substitution and are characterized by well-dispersed, molecularly dissolved chains whose dynamics mimic those of classic hydrophilic, semiflexible polyelectrolytes. Weakly substituted grades (DS $\lesssim 1$) contain blocks of unsubstituted cellulose along the backbone which act as 'stickers' between chains. For sufficiently concentrated solutions, these generate a range of rheological phenomena which are absent in the more substituted polymers.

Several open questions remain. First, the relation between substituent distribution and macroscopic rheological properties is still largely qualitative. Weakly substituted CMC samples are known to contain gelling and non-gelling fractions, but the rheological properties of these isolated fractions have not been studied in detail. Measurements on separated fractions would help determine how much of the measured viscosity, elasticity, and gel strength arises from the aggregating chains rather than from the well-dispersed chains. More generally, a quantitative measure of substitution heterogeneity or blockiness would be useful for connecting chemical structure with rheological behaviour.

Second, the influence of preparation history requires more systematic study. Early literature showed that mixing conditions, such as low- versus high-shear mixing, can have a large influence on the rheological properties of CMC gels. These effects have not been reproduced or systematically quantified using modern rheometers and well-defined preparation protocols.

Third, CMC is frequently described as thixotropic in commercial brochures, and thixotropy has been reported for NaCMC solutions and for mixtures with colloidal particles such as bentonite and microcrystalline cellulose. However, quantitative studies of thixotropic behaviour in well-characterised samples are relatively limited. Further work on structure formation, breakdown under shear, and recovery after shear would help clarify when thixotropy is an intrinsic property of CMC solutions and when it arises from aggregates, gels, or added colloidal components.

5. DECLARATION OF INTEREST STATEMENT

The author declares no conflicts of interest.

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