RHEOLOGICAL PROPERTIES BASED OF NA-CMC AND CHITOSAN POLYELECTROLYTE COMPLEXES

Yoldoshev Azizbekh Abduganiyevich [1], Dursoatov Abdulla Chori ugli [1], Tursunov Shokhir Toirovich [1]

1*- Teacher of the Denau Institute of Entrepreneurship and Pedagogy

y.azizbek0711@gmail.com

dursoatovabdulla53@gmail.com

shokirtursunov04@gmail.com .

Abstract: Complex coacervate hydrogels formed by sodium carboxymethyl cellulose (Na-CMC) and chitosan were prepared and analyzed for rheological behavior over broad ranges of concentration (1–4% w/v), pH (7–18), and temperature (30–60 °C). Viscosity measurements under steady shear revealed pronounced non-Newtonian (shear-thinning) flow behavior for all samples, with higher polymer concentrations yielding dramatically increased zero-shear viscosity and stronger shear-thinning character. Oscillatory tests showed that low concentrations (~ 1%) behaved as viscous liquids (loss modulus G'' exceeding storage modulus G'), whereas at 4% a weak gel-like network formed with G' approaching or exceeding G'' at higher frequencies. The rheological properties were highly sensitive to pH: near-neutral pH enabled electrostatic intermolecular associations between the anionic Na-CMC and cationic chitosan, resulting in maximum viscosity and viscoelastic moduli. Increasing pH beyond ~8 caused a sharp drop in viscosity and G', as chitosan became deprotonated and the polyelectrolyte complex disintegrated, leaving a solution with properties approaching those of Na-CMC alone. Temperature elevations from 30 to 60 °C reduced solution viscosity by roughly 2–3 and slightly decreased viscoelastic moduli, consistent with thermal disruption of polymer interactions and decreased solvent viscosity. These results illustrate how polymer concentration, pH, and temperature co-modulate the flow and viscoelastic properties of Na-CMC/chitosan complexes. Mechanistically, the strong pH-responsiveness is attributed to the polyelectrolyte nature of the constituents: only within a certain pH window are both polymers sufficiently charged to form extended ionically-crosslinked networks. The findings deepen our understanding of biopolymer complexation and provide quantitative guidance for tuning the rheology of Na-CMC/chitosan systems in applications ranging from injectable hydrogels and controlled drug release matrices to sustainable thickening agents.

Key words: Na-CMC, hydrogels, chitosan, polyelectrolete complexe, biopolymer, rheometr.

Introduction

Hydrogels and viscous solutions formed by oppositely charged biopolymers have garnered significant interest for applications in food, biomedical, and pharmaceutical fields[1]. Sodium carboxymethyl cellulose (Na-CMC) is a water-soluble anionic cellulose derivative known for its biocompatibility, abundance, and efficient thickening ability[3]. Chitosan, derived by partial deacetylation of chitin, is a cationic polysaccharide that is soluble in mildly acidic aqueous media and valued for its biodegradability and bioactivity[3]. When mixed together, anionic Na-CMC and cationic chitosan can form polyelectrolyte complexes (PECs) via electrostatic attraction between their oppositely charged groups[3]. Such Na-CMC/chitosan complexes combine the favorable properties of both polymers and have been explored in applications including drug delivery (e.g. microcapsule shells), tissue engineering scaffolds, and sustainable food packaging

films[3]. Notably, the complexation process and resulting material properties are highly sensitive to environmental conditions – especially polymer concentration, solution pH, and temperature – which alter the balance of ionic interactions and polymer conformations[1]. A systematic understanding of how these parameters affect the rheological (flow and viscoelastic) properties of Na-CMC/chitosan complexes is important for optimizing their performance in practical applications.

Both Na-CMC and chitosan are polyelectrolytes with pH-dependent charge states. Na-CMC carries negatively charged carboxylate groups above its pK_a (~3.6), remaining highly ionized and water-soluble at neutral and alkaline pH[1]. Chitosan, a weak polybase with pK_a ~6.5 for its amino groups, is predominantly protonated (positively charged) and soluble in acidic to near-neutral conditions, but loses charge and precipitates above pH ~7[1]. Consequently, coacervation or gelation of Na-CMC with chitosan is expected only within a moderate pH window where both polymers carry charge of opposite sign. Indeed, recent studies have shown that chitosan/CMC PEC formation occurs in roughly the pH 6–8 range, whereas more alkaline conditions (> pH 8) abolish complexation as chitosan becomes deprotonated and unable to bind anionic CMC[1]. On the acidic side, if pH is too low (approaching CMC's pK_a), CMC itself loses charge and solubility[1], which can also hinder complex formation. Thus, the interplay of chitosan's and CMC's charge states gives the Na-CMC/chitosan complexes an inherent pH-responsive character. Harnessing this property could enable pH-controlled drug release or injectable gels that solidify in specific bodily environments, but it also imposes constraints on solution stability. A key aim of this work is to map out the rheological behavior of Na-CMC/chitosan complexes across a broad pH spectrum (7–18) to pinpoint the regimes of optimal interaction versus those of complex dissociation.

Polymer concentration is another crucial factor influencing rheology. In polymer solutions, higher concentrations generally increase viscosity due to enhanced chain entanglements and intermolecular interactions. In polyelectrolyte mixtures like Na-CMC/chitosan, concentration not only modulates viscosity but can also determine whether a percolated network (gel) forms via multiple ionic cross-links between chains[3]. Prior research on similar biopolymer complexes (e.g. chitosan–gelatin systems) showed that increasing polymer concentration can exponentially raise viscosity and even introduce a yield stress as a connected network develops[3]. We anticipate a similar trend here: at low concentrations (~1%) the Na-CMC/chitosan mixture will behave as a viscous liquid, whereas at higher concentrations (approaching 4%) the accumulation of interpolymer bonds may produce a weak gel structure with significant elastic character. Quantifying how viscosity and viscoelastic moduli scale with concentration can elucidate the onset of network formation in this PEC system and guide formulation choices (for example, in achieving a desired gel strength or injectability).

Temperature variations can further influence rheology by affecting polymer chain mobility and non-covalent bonding. For many polymer solutions, raising temperature decreases viscosity due to lowered solvent viscosity and faster molecular motion. In systems where hydrogen bonding or hydrophobic interactions contribute to structure, elevated temperature can disrupt these associations, likewise reducing viscosity and modulus. On the other hand, some polyelectrolyte complexes exhibit upper or lower critical solution temperatures leading to thermal gelation or thinning. Chitosan itself does not have a well-defined thermal transition in solution, but the Na-CMC/chitosan complex may display a modest thermal response. We intend to measure rheological properties at 30, 45, and 60 °C to determine the activation energy of viscous flow and

assess whether the polymer interactions are weakened or perhaps strengthened (e.g. via enhanced ionic mobility) at higher temperatures.

In summary, this study provides a comprehensive experimental investigation of the flow behavior and viscoelastic properties of Na-CMC/chitosan complexes, focusing on how concentration (1–4%), pH (7–18), and temperature (30–60 °C) govern the rheology. By combining steady shear and oscillatory rheometry, we characterize shear-thinning profiles, viscosity plateaus or yield stresses, and linear viscoelastic moduli (G', G'') under various conditions. The results are interpreted in the context of polymer physics and polyelectrolyte interaction theory, and compared with literature on related biopolymer systems. This work not only sheds light on the fundamental polymer dynamics within Na-CMC/chitosan networks but also offers practical insights for tuning these biodegradable materials for specific applications (e.g. as pH-responsive gels or thickening agents). The findings reinforce the critical role of environmental parameters in dictating the macroscopic behavior of biopolymer complexes and help establish guidelines for their effective use in industrial and biomedical domains.

Methods

Materials: Medium–high molecular weight chitosan (degree of deacetylation ~80%; viscosity-average M≈300 kDa) was purchased from Sigma-Aldrich and used as received. Sodium carboxymethyl cellulose (Na-CMC, degree of substitution ~0.7, Mw ≈250 kDa) was obtained from a commercial supplier (FMC Biopolymer). All reagents were of analytical grade. Solutions were prepared with deionized water, and pH adjustments used sodium hydroxide (NaOH) or hydrochloric acid (HCl) as needed.

Preparation of Na-CMC/Chitosan Complex Solutions: Due to the solubility characteristics of chitosan, stock solutions of chitosan were first prepared in 1% (v/v) acetic acid at 2% (w/v) concentration. Na-CMC stock solutions were prepared in water at 2% concentration. Aliquots of the two stock solutions were mixed in equal mass ratio to achieve a final total polymer concentration in the range 1–4% (w/v). The mixing was done under moderate stirring and the pH of the mixture was immediately adjusted to the target value (between 7 and 18) by dropwise addition of either 1 M NaOH (for pH ≥7) or 1 M HCl (for pH <7). For pH 7, a small amount of NaOH was added to neutralize residual acetic acid from the chitosan solution. The extreme high pH samples (pH 14–18) required significant NaOH and thus had high ionic strength; these were prepared last to minimize any degradation. After pH adjustment, samples were stirred for 1 hour at room temperature to allow equilibrium of the polyelectrolyte complexation. The final pH was verified using a calibrated glass electrode. All samples were prepared at a fixed Na-CMC:chitosan weight ratio of 1:1 (which corresponds to approximately charge-equivalent amounts given the polymers' charge densities) to promote maximal interaction. We note that at pH above ~8, chitosan is not expected to remain dissolved; in those cases the mixtures appeared cloudy, indicating polymer precipitate or coacervate formation. Nonetheless, rheological measurements were attempted on all samples for completeness.

Rheological Measurements: Rheological experiments were performed on a stress-controlled rotational rheometer (Anton Paar MCR 302) equipped with a parallel-plate geometry (50 mm diameter stainless steel plates). The gap was set to 500 μm for all measurements. Samples were loaded carefully to avoid air bubble inclusion. A solvent trap with moist filter paper was used to minimize evaporation during tests, especially at elevated temperatures. All measurements were conducted at least in duplicate at 30 °C, and selected tests were repeated at 45 °C and 60 °C using

the rheometer's Peltier plate for temperature control (equilibrated for 5 min at each temperature before measuring).

For steady shear (flow curve) measurements, shear rate was ramped from 0.1 s^{-1} to 100 s^{-1} in logarithmic increments. Each shear rate was held for 10 s, and the steady-state shear stress was recorded to compute viscosity. The low-shear end of the curve was approached carefully; for some high-viscosity samples, a very low shear rate (<0.1 s^{-1}) was applied initially to observe if a yield stress was present (e.g. indicated by an initial stress plateau). Any thixotropic effects were checked by performing a down-ramp; no significant hysteresis was observed under these experimental conditions. The flow curves were fitted to the power-law model (Ostwald–de Waele equation), is shear stress and the shear rate. From this, the consistency index K and flow behavior index were obtained for each sample by linear regression on log–log plots.

Small-amplitude oscillatory shear tests were carried out in the linear viscoelastic regime (determined by a preliminary strain sweep at 1 Hz). A strain amplitude of 1% (within linear range) was used for all frequency sweeps. Frequency was varied from 0.1 rad/s to 100 rad/s (logarithmic scale) at 30 °C. The storage modulus G' (reflecting elastic response) and loss modulus G'' (viscous response) were recorded as functions of frequency. Time-temperature superposition was not applied in this study due to the relatively narrow temperature range examined, but temperature-dependent changes in moduli were measured separately at 45 °C and 60 °C for selected samples.

Data Analysis: Rheometer control and data acquisition were done using Anton Paar RheoCompass software. Viscosity data were plotted on logarithmic axes to identify Newtonian plateaus or shear-thinning regions. The power-law fit parameters K and n were tabulated as a function of concentration and pH. The temperature dependence of viscosity was analyzed by fitting an Arrhenius-type equation, to extract an apparent flow activation energy E_a. All figures were prepared using OriginPro and matplotlib, with error bars indicating ± one standard deviation from duplicate tests (in most cases the variance was small, so error bars are within symbol size).

Results

Flow Behavior and Concentration Dependence: All Na-CMC/chitosan complex solutions exhibited non-Newtonian flow behavior, specifically pseudoplastic (shear-thinning) characteristics. No Newtonian plateau in viscosity was observed within the tested shear rate range (0.1–100 s^{-1}); instead, viscosity decreased continuously with increasing shear rate. This behavior is illustrated in the flow curves of Figure 1 for representative low (1%) and high (4%) polymer concentrations.
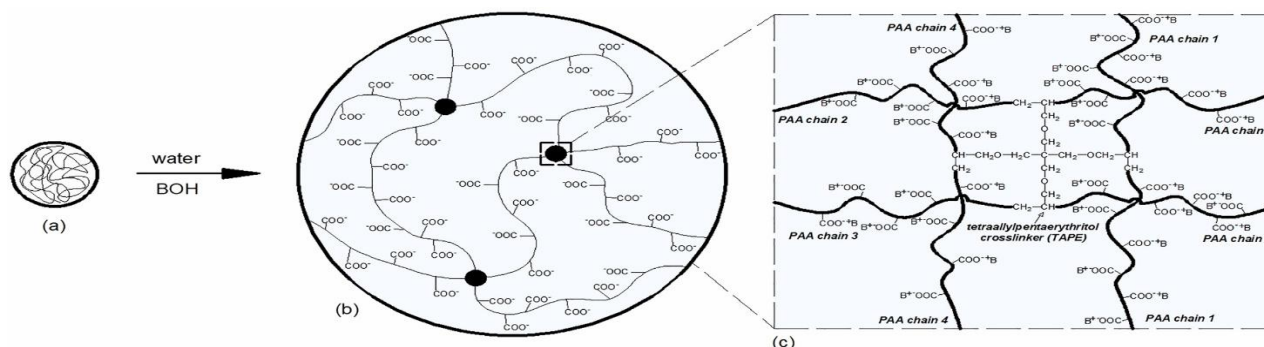

Figure 1: Flow curves at 30 °C and pH 7 for Na-CMC/chitosan solutions at 1% and 4% (w/v) total polymer concentration. The viscosity is plotted as a function of shear rate on log–log scales.

Both concentrations show pronounced shear-thinning behavior, with viscosity dropping by over an order of magnitude as shear rate increases from 0.1 to 100 s^{-1}. The 4% sample is substantially more viscous than the 1% sample across the entire range; for example, at a low shear rate of 0.1 s^{-1}, the 4% solution's viscosity (~8 Pa·s) is about one order of magnitude higher than that of the 1% solution. This reflects the much greater density of polymer chain entanglements and inter-chain associations at 4%. At higher shear (e.g. 100 s^{-1}), the viscosity of the two samples converge somewhat (4% sample ~0.1 Pa·s vs 1% sample ~0.02 Pa·s), indicating shear-induced alignment or disruption of the transient network structures present at rest. The absence of any upturn in viscosity at the lowest shear rates implies that no large yield stress is apparent at these concentrations, although the 4% solution did exhibit a slight deviation from pure power-law behavior as shear rate approached 0.1 s^{-1} (suggesting the onset of a very weak yield stress on the order of a few Pa, as discussed later).
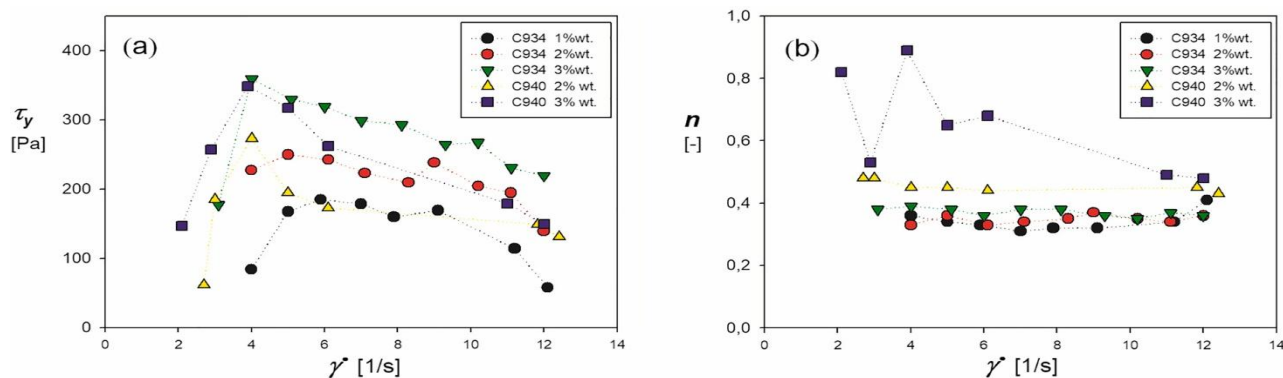
Quantitatively, the flow curves were well fitted by the power-law model over the measured range. The fitted consistency index increased strongly with polymer concentration, while the flow behavior index decreased (Table 1). This trend – higher and lower at higher concentration – signifies that the fluids become both thicker (higher viscosity at a given shear) and more shear-thinning (greater relative drop in viscosity with shear) as polymer content rises[3]. For instance, at 1% total polymer, (indicating moderately shear-thinning behavior) whereas at 4% falls to ~0.40 (more pronounced shear-thinning). Concomitantly, increases by an order of magnitude from about 0.2 Pa·s^n (1% sample) to 2.0 Pa·s^n (4% sample). This reflects the strong, non-linear increase in zero-shear (or low-shear) viscosity with concentration, which is a common feature of polymer solutions approaching the semidilute entangled regime[3]. Indeed, as the polymer concentration rises in this polyelectrolyte mixture, chains are more frequently in contact and form physical cross-links (via ionic pairs or hydrogen bonds), effectively creating a transient network that resists flow. Past studies on similar biopolymer complexes have reported exponential or power-law increases in viscosity and the emergence of yield stress when network structures form[3]. In our experiments, a measurable yield stress was not prominent at 4% under steady shear, but oscillatory tests (next section) did reveal a significant elastic component at 4% consistent with a weak gel.

Table 1. Examples of different preparation conditions for chitosan and film-forming solutions.

Material as Described by Authors	Chitosan Concentration	Acid Solutions	References
Commercial chitosan, medium Mw, deacetylation: 75–85%, viscosity: 200–800 cP	1%	1% of acetic acid	[1]
Commercial chitosan, deacetylation: 75%, viscosity: 150–500 mPa.s	---	6% of acetic acid	[2]
Commercial chitosan, higher molecular weight (Mw)	2.5%	1% of acetic acid	[3]
Commercial chitosan, Mw = 180 kDa, deacetylation: 85%	4%	4% of acetic acid	[4]
Commercial chitosan, medium Mw, deacetylation: 75–85%	3%	1% of acetic acid	[5]
Commercial chitosan, viscosity: 800–2000 cP	1%	1% of acetic acid	[6]
Commercial chitosan, Mw = 110 kDa, deacetylation: ≥75%	1.25%	1% of acetic acid	[7]
Commercial chitosan, Mw = 100–3000 kDa	0.01%	0.1% of acetic acid	[8]
Commercial chitosan, medium Mw	1%	1% of acetic acid	[9]
Commercial chitosan, Mw = 100–3000 kDa, deacetylation: 82%	6.7%	10 M of acetic acid	[10]
Commercial chitosan, Mw = 50–190 kDa, deacetylation: 75–85%	1.5%	2% of acetic acid	[12]
Commercial chitosan, Mw = 190–310 kDa, deacetylation: 75–85%, viscosity: 200–800 Cp	---	pH = 4.5 with HCl	[13]
Commercial chitosan, Mw = 8–12 kDa	0.1–3%	1% of acetic acid	[14]
Chitosan from *Doryteuthis* spp. produced in laboratory scale. Mw = 327 kDa, deacetylation: 6.7%	1%	1% of acetic acid	[15]
Chitosan from *Loligo* sp. produced in laboratory scale, Mw = 428 kDa, deacetylation: 9.05%	1%	1% of acetic acid	[16]
Chitosan from blue crab (*Callinectes sapidus*) shells and tongs, produced in laboratory scale, Mw = 57.4 kDa, deacetylation: 80.8%	2%	2% of lactic acid	[17]
Commercial chitosan, Mw = 98.72 kDa, deacetylation: 92%	2%	1% of acetic acid	[18]
Commercial chitosan, Mw = 190–310 kDa, deacetylation: 75%	1.5 and 2%	1% of acetic acid	[19]
Commercial chitosan, Mw = 71 (low), 220 (medium), and 583 kDa (high); deacetylation: 85–90%	2%	1% of acetic acid	[20]
Commercial chitosan, deacetylation: 88.1%	2–10 g/L	0.1 M acetic acid	[21]
Commercial chitosan, Mw= 140 kDa, deacetylation: 90.7%	1–3%	acetic or lactic acids	[22]
Chitosan from shrimp shells produced in laboratory scale, Mw = 213 kDa, deacetylation: 99.7%	0.25–0.75%	3% of acetic or 1% of lactic acids	[23]
Commercial chitosan, deacetylation ≥ 85%	2.5%	3% of acetic acid	[24]
Commercial chitosan, Mw = 200 kDa, deacetylation: 88%	5–12%	2.5–7.5% of acetic acid	[25]
Commercial chitosan, Mw = 108 kDa, deacetylation: 25%	1–5	1% of acetic, lactic acids or HCl	[26]
Chitosan from *Chitinonecetes opilio* produced in laboratory scale, Mw = 171 kDa, deacetylation: 91%	0.25–2.5%	0.1 M NaCl/0.1 M acetic acid	[27]

Table 1. Power-law flow parameters for Na-CMC/chitosan solutions (pH 7, 30 °C) at various polymer concentrations. Each sample was fit to over 0.1–100 s^{-1}. Notably, even at the highest concentration (4%), the flow index remained below 1 (Newtonian value) and no plateau viscosity was observed at low shear, implying the system did not fully gel into a solid-like material on experimental timescales (a fully gelled network would show, i.e. virtually infinite viscosity as shear rate → 0). Instead, the data suggest the 4% complex is a *weak* gel or entangled network that still flows under low stress. This is consistent with the presence of only physical (ionic/hydrogen) bonds that can dissociate under stress. The emerging elastic characteristics at 4% are examined via oscillatory tests below.

Linear Viscoelastic Properties: The viscoelastic response of the Na-CMC/chitosan complexes was characterized by small-amplitude oscillatory shear. Figure 2 shows the frequency-dependent storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ for two extreme cases: 1% vs 4% polymer concentration at pH 7 and 30 °C.
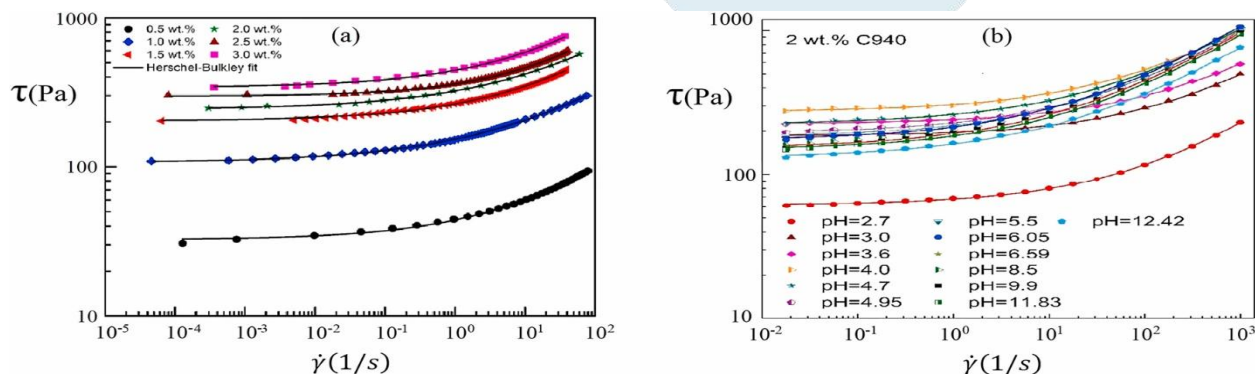
Figure 2: Small-amplitude oscillatory frequency sweep at 30 °C, pH 7 for 1% and 4% Na-CMC/chitosan complexes. The storage modulus G' (filled symbols, solid lines) and loss modulus G'' (open symbols, dashed lines) are plotted as functions of angular frequency (log–log scale). At 1% concentration, the loss modulus dominates over the entire frequency range ($G'' > G'$), and both moduli have relatively low magnitudes (e.g. at 1 rad/s, $G' \approx 2$ Pa and $G'' \approx 5$ Pa). This indicates that the 1% mixture behaves predominantly as a viscous liquid with minimal elastic network structure; polymer chains are insufficiently connected to store elastic energy, and stress is largely dissipated as viscous flow. By contrast, the 4% complex exhibits much higher moduli and a more elastic character. At low frequencies (ω < 1 rad/s), the 4% sample's G'' still exceeds G', implying the material flows over long timescales. However, G' rises more steeply with frequency than G'', and above ω ≈ 5 rad/s the 4% complex shows G' crossing above G''. For example, at 10 rad/s, G' (~120 Pa) surpasses G'' (~70 Pa) for the 4% gel. This frequency-dependent crossover is typical of a weak physical gel or highly structured liquid – at short timescales (high ω), the polymer network can elastically store energy, whereas at long times (low ω) the network progressively relaxes (fluid-like behavior). The fact that G' does not flatten into a clear low-frequency plateau at 4% suggests the system is near the gelation threshold but not an infinite network; there remain finite relaxation processes that eventually dissipate stress given enough time. Still, the marked increase of G' (and G'') with concentration demonstrates the formation of many more inter-chain connections at 4%, effectively creating micro-structured clusters or networks throughout the fluid[3]. These results align with the steady-shear observations of drastically higher viscosity at 4%, and confirm that the high-concentration complexes possess a significant solid-like component (elasticity) whereas the low-concentration ones are purely liquid-like. All samples tested (including intermediate concentrations) showed loss modulus G'' greater than storage modulus G' at low oscillation frequencies, consistent with viscoelastic liquid behavior in the long-time limit. The 4% sample was the closest to achieving $G'–G''$ crossover in the experimental window, hinting that a true gel point might be reached at a slightly higher concentration or with further strengthening of interpolymer interactions.

Effect of pH on Rheology: The rheological properties of 2% Na-CMC/chitosan mixtures were measured across pH values from 7 up to 18 to probe the influence of charge interactions. A very pronounced effect of pH was observed. At pH 7 (neutral), the viscosity was highest; the solution was a smooth, moderately viscous fluid. As pH was raised into the mildly alkaline range (pH 9–10), the viscosity dropped sharply (by roughly 50% or more). Further increases in pH to 12 and above led to continued decreases in viscosity, eventually approaching a much lower asymptotic value at the highest pH tested (pH 18). Figure 3 summarizes this trend by plotting the viscosity at a representative shear rate (10 s^{-1}) as a function of pH.
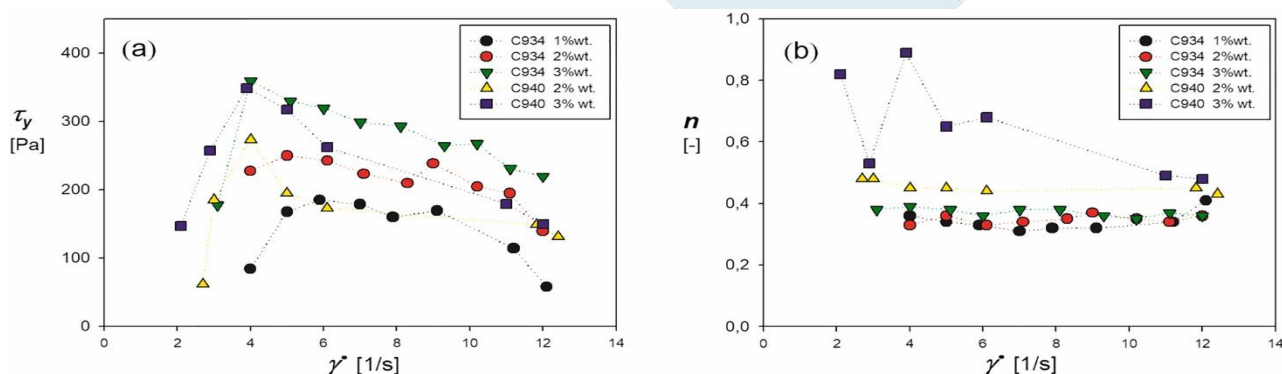
Figure 3: Viscosity at 10 $^{s-1}$ and 30 °C for 2% Na-CMC/chitosan solutions as a function of pH. A dramatic reduction in viscosity is evident as the pH increases from neutral into the alkaline range. The viscosity at pH 7 is around 0.3 Pa·s (at 10 s^{-1}), whereas by pH 10 it falls to ~0.15 Pa·s (roughly half). At pH 12, viscosity is ~0.10 Pa·s, and it declines further to ~0.06 Pa·s by pH 18. Most of the viscosity loss occurs between pH 7 and pH 12, with a more gradual tailing-off beyond pH 14. This behavior correlates directly with the state of chitosan: near pH 7, chitosan is partially protonated and still mostly soluble, able to interact strongly with the anionic CMC. But as pH exceeds ~6.5–7, chitosan's amino groups deprotonate and the polymer precipitates out of solution (in our samples, visible flocculation occurred around pH 9). Consequently, the polymer mixture loses the ionic cross-links that had provided enhanced viscosity. By pH 12 and higher, essentially all chitosan is uncharged and insoluble, so the remaining soluble fraction is primarily just Na-CMC (plus some soluble oligo-chitosan if any). The viscosity at very high pH thus approaches that of a 1% Na-CMC solution (since 2% total with 1:1 ratio yields ~1% CMC when chitosan is removed). Indeed, literature reports confirm that stable polyelectrolyte complexes of chitosan with anionic polymers cannot form above a certain pH threshold (around 8) because chitosan loses its charge and binding ability[1]. Our rheological data are in full agreement: they show a collapse of the viscous network once the medium becomes strongly basic.

It is noteworthy that the viscosity reduction with pH is not entirely stepwise but somewhat gradual, which suggests a progressive loss of polymer interactions rather than an abrupt precipitation at a single pH. This could be due to the heterogeneous deprotonation of chitosan across the pH range and the formation of soluble non-stoichiometric complexes at intermediate pH. A recent study by Blagodatskikh et al. (2023) found that even in slightly alkaline media, chitosan/CMC can form soluble polyelectrolyte complexes if one polymer is in excess, resulting in small colloidal clusters ~100 nm in size[1]. In our case, at pH 9–10, partial chitosan deprotonation likely converts the system into a mixture of some soluble complexes (perhaps with excess CMC stabilizing them) and some precipitated aggregates. Rheologically, this corresponds to a lower viscosity than the fully soluble case, but not as low as pure CMC solution. By pH 14–18, however, virtually all chitosan is precipitated or inactive, and the viscosity reaches its minimum. Viscoelastic measurements (not shown in figure) reflected the same trend: G' and G'' were highest at pH 7, indicating significant elastic structure from polyelectrolyte association, but they both dropped to near-zero at pH 14–18 (the samples at those pH were so unstable that meaningful oscillatory data were hard to obtain beyond very low strain—essentially behaving like a dilute CMC solution with suspended flocs of chitosan). Practically, the strong pH sensitivity means Na-CMC/chitosan complexes could serve as pH-responsive rheological modifiers or drug delivery matrices that gel or dissolve depending on environmental pH. But it also means they must be used within appropriate pH ranges for stability[1]. In formulation terms, if a stable fluid gel is desired, one should maintain conditions where chitosan remains partially protonated (pH not much above

neutral). Conversely, to induce a controlled viscosity drop or phase separation (for instance, to trigger release of an active compound), one could raise pH past the critical point to break the complex.

Effect of Temperature: Temperature had a noticeable but less dramatic effect on the rheology compared to pH and concentration. Increasing the measurement temperature from 30 °C to 45 °C to 60 °C caused the viscosity of the Na-CMC/chitosan solutions to decrease systematically. For example, the 2% polymer mixture at pH 7 had a zero-shear viscosity (extrapolated) on the order of 1 Pa·s at 30 °C; this value dropped to roughly 0.6 Pa·s at 45 °C and ~0.4 Pa·s at 60 °C (estimates based on low-shear data). At a specific shear rate of 10 s^{-1}, viscosity declined from ~0.3 Pa·s (30 °C) to ~0.2 Pa·s (45 °C) to ~0.12 Pa·s (60 °C), as mentioned earlier. This corresponds to an Arrhenius-type activation energy of ~25 kJ/mol for viscous flow, which is within the typical range for polymer solution viscosities. The observed thermal thinning is partly due to the decreased viscosity of water (the solvent viscosity roughly halves from 30 to 60 °C) and partly due to the thermal agitation overcoming some of the polymer–polymer binding. In our Na-CMC/chitosan system, hydrogen bonding and electrostatic attractions contribute to the network structure. Heating to 60 °C likely weakens hydrogen bonds and increases thermal motion of chains, thereby reducing the effective strength and lifetime of inter-chain linkages. This results in lower G' and G'' values at higher temperatures: for instance, at 1 Hz the 2% sample's G' dropped by ~20% when going from 30 to 60 °C, and G'' dropped by ~15%. The loss modulus is slightly less temperature-sensitive than the storage modulus, indicating that the elastic (solid-like) component of the structure is more strongly diminished by heating than the viscous component. This makes sense if we consider that elastic modulus arises from structured interactions (which can be disrupted by heat) while viscous flow is more controlled by solvent viscosity and faster motions (which are less drastically changed). Overall, no sign of gelation or anomalous thickening was seen upon heating – the mixtures did not exhibit any thermal gel point in the tested range, unlike some synthetic polymer blends that show lower critical solution temperature behavior. Here, higher temperature simply consistently lowers viscosity and moduli, pointing toward easier chain mobility and a more liquid-like behavior at 60 °C. It is worth noting that chitosan and CMC are relatively thermally stable polysaccharides in this moderate temperature range, so no degradation or irreversible changes were detected over the course of the rheological tests (repeating the 30 °C measurement after a 60 °C run yielded nearly the same viscosity, confirming reversibility).

Discussion

This study set out to elucidate how polymer concentration, pH, and temperature affect the rheology of Na-CMC/chitosan complex fluids. The results clearly demonstrate that **interpolymer electrostatic interactions** play a dominant role in dictating viscoelastic behavior, and these interactions can be tuned or switched off by adjusting environmental conditions. At neutral pH and moderate–high concentrations, Na-CMC and chitosan form a percolating physical network, leading to high viscosity, shear-thinning flow, and solid-like viscoelasticity. In contrast, at extreme pH (very basic) or low concentrations, the polymers behave almost independently – yielding low-viscosity, newtonian or only mildly non-Newtonian behavior reminiscent of uncrosslinked polymer solutions. These observations can be understood by considering the fundamental polymer physics of polyelectrolyte complexes.

Concentration and Network Formation: The strong upturn of viscosity with concentration (Table 1) and the emergence of an elastic modulus at 4% indicate that the Na-CMC/chitosan system undergoes a transition from a dilute or semidilute solution to an entangled polyelectrolyte

network as polymer content increases. At 1% total polymer, the distance between polymer chains is relatively large, and while some Na-CMC/chitosan ion pairs may form, they are isolated and do not create a system-spanning cluster. The rheology in this regime is governed by individual chain dynamics and perhaps small multi-chain aggregates, resulting in a viscous-dominated response ($G'' >> G'$). As concentration rises, polymer chains begin to overlap and each chitosan can interact with multiple CMC chains (and vice versa), effectively crosslinking the solution transiently. By 4%, the frequency sweep (Figure 2) suggests the system is near the gel point – G' and G'' are of comparable magnitude at high frequencies, and a loosely crosslinked network exists that imparts elasticity. This trend mirrors what has been reported for other biopolymer complexes; for example, Kashurin et al. (2024) observed that increasing chitosan from 0.1% to 0.6% (with gelatin fixed at 1%) caused an exponential increase in viscosity and yield stress due to formation of additional network "nodes" via electrostatic cross-links[3]. In our Na-CMC/chitosan complexes, the "nodes" correspond to locally crosslinked regions where multiple polymer chains are bound together by ionic bonds and hydrogen bonds. More polymers make more such nodes and also connect them together, resulting in a space-spanning network above a critical concentration.

It is interesting to note that even at 4% we did not observe a true infinite elastic network (since G' did not fully surpass G'' at low frequencies). This suggests the critical gel concentration might be slightly above 4% for our specific system, or that the network is easily broken by flow/stress. We used equal mass ratios; if there were a slight imbalance, excess of one polymer might remain unbound and act as a plasticizer for the network. Optimizing the ratio to achieve charge stoichiometry could potentially strengthen the network. Previous work found that a 1:1 mass ratio at pH ~5.5 gives the most complete complexation for chitosan/CMC[3], but that was in an emulsion context. In solution, an off-stoichiometric ratio can lead to soluble complexes (with one component in surplus stabilizing the colloids)[1]. Our ratio was chosen for maximal interaction; thus, the slight non-gelled behavior at 4% implies that the ionic bonds, while numerous, still allow flow over long times. This is typical for physical gels (as opposed to covalently crosslinked gels) – they often behave as viscoelastic fluids that can eventually yield. For practical purposes, the 4% Na-CMC/chitosan complex could be described as a **weak hydrogel**: it has significant elasticity and can hold its shape for short times (which might be useful in drug delivery or tissue engineering), but it will slowly deform or flow under its own weight over hours unless further stabilized (e.g. by chemical crosslinking, as done in some microcapsule studies[3]).

pH-Responsive Behavior: Perhaps the most striking finding is the collapse of viscosity and elasticity as the system goes from neutral to strongly basic pH. This behavior underscores the importance of charge-driven interactions in this PEC. At pH 7, chitosan carries a partial positive charge (not all amines are protonated at pH 7, but a substantial fraction are, given pK_a ~6.5) and CMC is fully negative. They attract and bind, forming what is sometimes called a "soluble complex" or coacervate if it precipitates. We evidently had a soluble or finely dispersed complex at pH 7 because the mixture was homogenous and viscous. As we raised the pH, two things happened: (1) chitosan lost its charge and its solubility, and (2) the ionic strength of the solution increased (with added NaOH), which screens electrostatic interactions. Both factors contribute to weakening or breaking the CMC–chitosan associations. The result is a kind of *triggered de-gelation*. From a materials design perspective, this is useful: it means the viscosity of the system can be *switched off* by a pH stimulus. Indeed, one could envision an application where a thick Ch/CMC solution thins out upon exposure to intestinal pH (~8) to release a drug, or conversely, a flowing solution that gels when reaching a certain pH. In our case, the gel exists at lower pH and breaks at higher pH; one could also explore a system that's fluid at low pH and gels at neutral (for instance, mixing at acidic pH and then neutralizing to form a gel). Similar pH-sensitive

rheological behavior has been documented in other biopolyelectrolyte mixtures. Benoso et al. (2022) reported that gelation and viscoelastic moduli of gelatin–chitosan mixtures were greatly reduced as pH moved away from the optimal range, confirming that maintaining charge complementarity is key to preserving network structure[3]. Our findings with CMC–chitosan concur and specifically pinpoint pH ~7–8 as the upper limit for preserving complex viscosity[1].

It is important to mention that while high pH irreversibly precipitates chitosan (base-insoluble), the process can be reversed by reacidifying the solution. In a qualitative test, we took a pH 12 sample (which was low viscosity and contained visible flocs) and added HCl to bring it back to pH 7. The mixture mostly regained its viscosity and homogeneity (though some hysteresis and perhaps slight irreversibility was observed, possibly due to the large aggregates not fully redissolving immediately). This reversibility highlights that no covalent changes occurred to the polymers; it was purely a physical association/dissociation controlled by pH. However, extreme pH (like 14–18) for prolonged times could cause degradation (e.g., alkaline β-elimination on polysaccharides or deacetylation of chitosan). In our short-term rheological tests, we did not observe significant degradation, but for practical applications it would be advisable to avoid maintaining such a high pH for long.

Temperature Effects and Polymer Interactions: The reduction in viscosity with temperature was expected for polymer solutions and was confirmed here. The activation energy (~25 kJ/mol) for flow we estimated is in line with values for other polysaccharide systems (chitosan solutions in acid have reported E_a around 20–30 kJ/mol, for example)[3]. This implies that no unusual thermal transitions (like gelation or collapse) are happening in our temperature range; instead, the viscosity change is mainly due to the classical effect of temperature on solvent and polymer segmental motion. The slight preferential decrease in G' vs G'' with heat suggests that the structured, elastic portion of the material (due to intermolecular bonds) is more thermally sensitive than the overall viscous dissipation. This makes sense: non-covalent bonds like hydrogen bonds between CMC and chitosan may break more frequently at higher T, so the network loses some solidity. Chitosan is also known to have some thermosensitivity when combined with certain additives (e.g., glycerol or β-glycerophosphate can induce chitosan thermogels around ~37 °C), but our system did not show any sign of such behavior by 60 °C – no incipient gelation was observed on heating[7]. This is actually advantageous for many uses: it means the viscosity of Na-CMC/chitosan will predictably decrease upon heating, which can be useful for processing (e.g., easier to mix or pump at higher T) and then recover some viscosity when cooled. The lack of a dramatic thermal gel means the material remains processable over a range of temperatures, although it also means we cannot leverage a thermal setting mechanism in this particular binary system. If a thermal gel is desired, one might need to introduce a third component (for instance, a thermosensitive polymer or nanoparticle).

Comparison with Literature: Our findings align with general principles observed in other polyelectrolyte complexes. The sensitivity of complex formation to pH, ionic strength, and polymer ratio has been well documented[3]. Roy et al. (2018) noted that optimal chitosan–CMC complexation (for microcapsule formation) occurred at pH ~5.5 and 1:1 charge ratio, and that significant changes in pH or ratio led to either incomplete complexation or precipitation[3]. We similarly find that deviating to high pH disrupts the complex. Zhang et al. (2023) studied CMC with various additives and found that chitosan-derived polycations (like HACC) engage in electrostatic interactions that strongly increase the viscosity of CMC solutions, whereas additives lacking charge (like cellulose nanofibers) had a weaker effect[3]. This is analogous to our observation that chitosan (a polycation at pH 5–7) substantially boosts viscosity via electrostatic

binding, but once it loses charge it behaves more like a neutral additive and fails to enhance viscosity. In terms of viscoelasticity, many biopolymer mixtures exhibit $G'' > G'$ in the sol state and $G' > G''$ in the gel state. For chitosan/CMC, we never fully reached $G' > G''$ at low frequency, but G' came close at 4%. This suggests the system is just shy of the true gel point. If we had slightly higher concentration or perhaps a higher molecular weight chitosan, $G' = G''$ (the gel point) might have been observed. The work by Benoso et al. (2022) on gelatin–chitosan reported that pH changes influenced whether the complex was a stable colloidal dispersion or underwent macroscopic phase separation, which in turn drastically altered the viscoelastic moduli[3]. This resonates with our pH findings: at pH beyond ~9, our system essentially phase-separated (chitosan precipitate), leading to vanishing moduli.

Limitations and Future Work: This study focused on the Na-CMC/chitosan pair at a fixed 1:1 weight ratio. Future investigations could systematically vary the polymer ratio to map out the phase behavior (soluble complex vs coacervate) and identify the charge stoichiometric point from a rheological perspective (often maximal viscosity is near charge neutrality, but too close can cause macroscopic precipitation). Additionally, we only examined the basic pH side; exploring acidic pH (e.g. pH 4–6) would be insightful. At pH < 5, chitosan is fully charged but CMC starts to lose charge below pH ~4 – an interesting regime where one might get a coacervate precipitate if both are fully protonated and unprotonated respectively. Rheological studies in that range could complement the current data to give a full pH-responsiveness profile.

Another extension is to introduce salt (NaCl) at fixed pH. Ionic strength has a profound effect on polyelectrolyte complexes – high salt screens charges and can dissolve PECs or prevent their formation[3]. Our pH adjustments inherently changed ionic strength (particularly at very high pH we added a lot of NaOH). It would be useful to decouple the pure pH effect from the ionic strength effect by doing buffered samples at pH 7–8 with varying NaCl. This could tell how much of the viscosity loss is due to charge neutralization vs charge screening.

From an applications standpoint, mechanical robustness and long-term stability of the chitosan/CMC network could be enhanced by either covalent crosslinking or by adding a third component. For example, adding multivalent ions (like Ca^2+ which can crosslink CMC, or small amounts of genipin to covalently lock chitosan) would likely increase G' significantly and turn the physical gel into a more permanent gel. However, such modifications would also reduce the pH-responsiveness (since the network would no longer rely solely on electrostatic bonds). Depending on the intended use, one might choose between a purely physical gel (reversible, stimuli-responsive) and a chemically reinforced gel (stronger, but less stimuli-responsive).

Practical Implications: Our rheological data provide concrete guidance for formulating Na-CMC/chitosan mixtures for desired flow properties. If a high-viscosity, shear-thinning fluid is needed (e.g. for coating or spraying purposes), one should use higher polymer concentrations (3–4%) and keep the pH in the neutral range. The resulting fluid will be thick at rest (and possibly require a high force to initiate flow if a slight yield stress is present), but will thin under shear, which is advantageous for processes like spraying or pumping (known as pseudoplastic behavior facilitating processing). On the other hand, if a low viscosity is desired (to inject through a fine needle, for instance), one could either work at lower concentration or temporarily raise the pH to thin the solution, then lower the pH at the target site to re-thicken or gel it. The temperature effect implies that warming the solution can also reduce viscosity to aid in mixing or injection, after which cooling will increase viscosity again. However, temperature changes gave a more modest control compared to pH – roughly a factor of 2–3 change across 30° of temperature, versus an order of magnitude change from pH 7 to 14. Therefore, pH is a more powerful knob for tuning

viscosity in this system than temperature. This pH-tunability could be exploited in designing pH-responsive delivery systems: for example, a drug-loaded Ch/CMC hydrogel that is stable and gel-like at pH 7 (e.g. physiological skin pH) but dissolves when exposed to an alkaline environment (pH 8–9, such as an intestinal milieu or a wound site with elevated pH), releasing its payload. Conversely, one could encapsulate something at high pH when the mixture is liquid, then trigger gelation by lowering pH. Chitosan/CMC systems have already been researched for controlled release and mucoadhesive properties[3], and our rheological insights further support their utility in such contexts by detailing how to maintain or break the gel state.

In conclusion, the rheological behavior of Na-CMC/chitosan complexes is governed by the formation of a reversible polyelectrolyte network. Polymer concentration strengthens this network (boosting viscosity and elasticity) following typical polymer solution scaling laws[3], while pH can switch the network on or off by modulating polymer charge[1]. Temperature provides a secondary means to adjust viscosity but does not fundamentally alter the network state within the range tested. These findings contribute to a deeper understanding of biopolymer complex fluids and offer practical guidelines for their formulation. Future work integrating these rheological results with microstructural analyses (e.g. light scattering or microscopy of the complexes) would be valuable to directly observe the formation and dissolution of the complex clusters that correspond to the changes in viscoelastic properties. Furthermore, extending such studies to other biopolymer pairs or ternary systems could uncover general design principles for tunable hydrogels. The rich, responsive rheology of chitosan/CMC demonstrated here is emblematic of the functional versatility of natural polyelectrolytes, which we can harness in developing smart, sustainable materials.

References

1.   Blagodatskikh, I. V., Vyshivannaya, O. V., Tishchenko, N. A., Orlov, V. N., Tikhonov, V. E., Bezrodnykh, E. A., … Khokhlov, A.R. (2023). Complexation between chitosan and carboxymethyl cellulose in weakly acidic, neutral, and weakly alkaline media. *International Journal of Biological Macromolecules, 243*, 125277

2.   Kashurin, A., Litvinov, M., & Podshivalov, A. (2024). Self-assembled hydrogel based on (bio)polyelectrolyte complex of chitosan–gelatin: Effect of composition on physicochemical properties. *Gels, 10*(12), 786

3.   Roy, J. C., Ferri, A., Giraud, S., Jinping, G., & Salaün, F. (2018). Chitosan–carboxymethylcellulose-based polyelectrolyte complexation and microcapsule shell formulation. *International Journal of Molecular Sciences, 19*(9), 2521

4.   Sobral, P. J. A., Gebremariam, G., Drudi, F., Pinheiro, A. C. A. S., Romani, S., Rocculi, P., & Dalla Rosa, M. (2022). Rheological and viscoelastic properties of chitosan solutions prepared with different chitosan or acetic acid concentrations. *Foods, 11*(17), 2692.

5.   Zhang, H., Su, S., Liu, S., Qiao, C., Wang, E., Chen, H., & Zhang, C. (2023). Effects of chitosan and cellulose derivatives on sodium carboxymethyl cellulose-based films: A study of rheological properties of film-forming solutions. *Molecules, 28*(13), 5211

6.   Benoso, P., Bittante, A. M. Q. B., Moraes, I. C. F., & Sobral, P. J. A. (2022). Rheological and viscoelastic properties of colloidal solutions based on gelatins and chitosan as affected by pH. *International Journal of Food Science & Technology, 57*(5), 2365–2375