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Rheology of concentrated CNF suspensions following PEG and NaOH modification

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Abstract

The rheology of cellulose nanofibril (CNF) suspensions governs their processability in scalable manufacturing operations such as coating, casting, and film formation, particularly at high solids loadings. However, the combined influence of CNF concentration, polymer additives, and alkaline conditions on network structure and deformation behaviour remains insufficiently understood. In this study, the steady and oscillatory shear responses of concentrated CNF suspensions (2–7 wt%) were examined with controlled additions of polyethylene glycol (PEG) and sodium hydroxide (NaOH) across processing-relevant concentration ranges, aiming to establish a quantitative rheological framework for CNF processing and manufacturing applications. All formulations exhibited shear-thinning behaviour, with increasing CNF concentration substantially increasing viscosity, yield stress, and viscoelastic stiffness, consistent with the formation of progressively denser fibrillar networks. PEG addition reduced viscosity and network strength; however, most PEG-induced changes occurred upon initial addition, with only minor further changes at higher PEG concentrations, suggesting a surface-site-limited interaction mechanism. In contrast, NaOH addition caused substantially stronger rheological changes, suggesting hydroxide-driven swelling and disruption of inter-fibrillar contacts. When PEG and NaOH were combined, the resulting suspension exhibited a weakly connected but highly deformable network. However, the retained stiffness remained slightly higher than that of equivalent highly alkaline NaOH-only suspensions, suggesting PEG could partially moderate alkali-induced network disruption through residual fibril interactions.

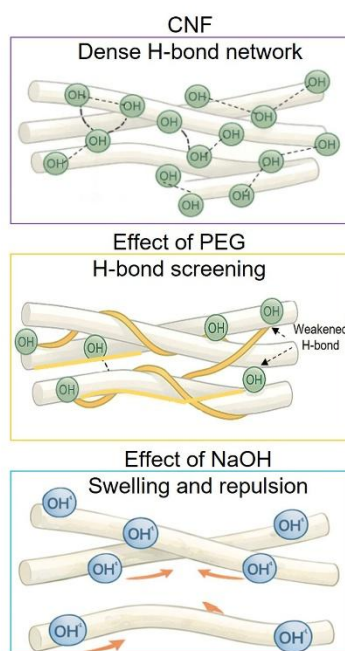
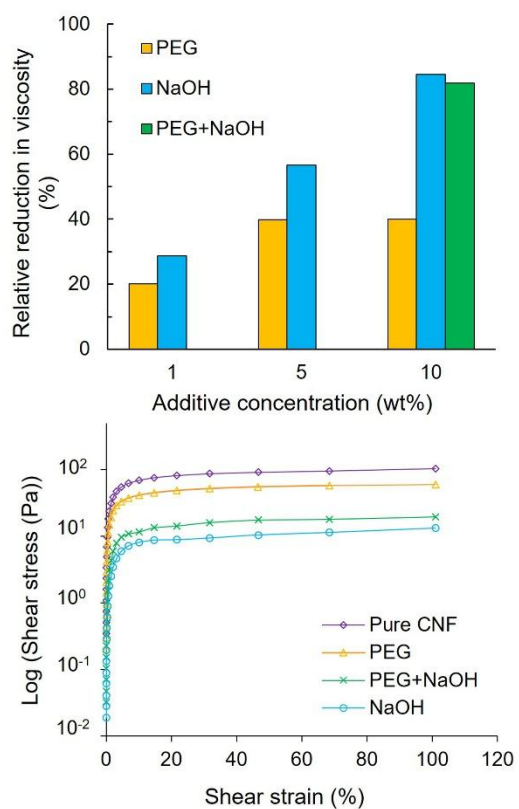
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33 Graphical Abstract



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Introduction

Cellulose nanofibrils (CNFs) are renewable, high-aspect-ratio nanomaterials with strong potential in biodegradable packaging, coatings, filtration media, biomedical scaffolds, and rheology-modifying formulations (Klemm et al., 2011; Moon et al., 2011; Siró & Plackett, 2010). In many of these applications, CNFs are processed from aqueous suspensions through coating, printing, casting, or wet-spinning routes; therefore, their flow and deformation behaviour directly influence processability, structural development, and final material performance (Song et al., 2022; Vadodaria et al., 2018).

Rheological characterisation provides a direct means of probing CNF network structure in suspension. Steady shear measurements describe viscosity, flow onset, and shear-thinning behaviour, whereas oscillatory tests provide insight into viscoelasticity, gel-like response, and yielding under small and large deformations (Mezger, 2014; O'Banion & Shams Es-haghi, 2023). CNF suspensions commonly exhibit shear-thinning behaviour arising from fibril alignment, network disruption, and partial disentanglement under shear (Moon et al., 2011; Rezayati Charani et al., 2013; Thompson Towell & Asenath-Smith, 2024). Their rheological response is strongly influenced by concentration (O'Banion & Shams Es-haghi, 2023), fibril morphology (Tanaka et al., 2014), surface chemistry (Liao et al., 2021), pH (Kobayashi et al., 2022), ionic strength (Wattana et al., 2025), and chemical additives (Žepič et al., 2022).

Although the rheology of dilute and semi-dilute CNF suspensions has been widely investigated, concentrated CNF suspensions remain less fully understood, particularly at concentrations relevant to coatings, printable hydrogels, film precursors, and filtration-material fabrication (Barrulas & Corvo, 2023; Yadav et al., 2021). Recent studies on concentrated CNF hydrogels have reported complex viscoelastic and yielding behaviour over the 3–13.6 wt% range, highlighting the need for more quantitative evaluation of structure–rheology relationships in this concentration regime (Dumont et al., 2023; Martoia et al., 2022; Sellman et al., 2024).

In addition to concentration, chemical additives are frequently used to tailor the rheology and processability of concentrated CNF formulations. Among these, polyethylene glycol (PEG) and sodium hydroxide (NaOH) are widely used in cellulose-based processing and formulation systems (Peng et al., 2025; Safdari et al., 2017; Sharifi Zamani et al., 2025; Yan & Gao, 2008). PEG is commonly applied in cellulose processing, coatings, and hydrogel formulations due to its water solubility and compatibility with cellulose systems (Getya et al., 2023), while NaOH is a long-established reagent in cellulose swelling, mercerisation, scouring, and regenerated-cellulose production.

However, despite their widespread use, the effects of PEG and NaOH on CNF rheology have generally been examined indirectly through dispersion quality, fibrillation efficiency, chemical pretreatment, or gel formation, rather than through systematic rheological characterisation of concentrated CNF networks (Moberg et al., 2017; Nechyporchuk, Belgacem, & Bras, 2016). Existing PEG studies have mainly focused on grafted CNFs or dilute suspensions (Moberg et al., 2017), whereas alkaline studies

have generally investigated electrolyte effects or chemical pretreatment rather than direct modification of concentrated CNF networks (Wattana et al., 2025). Consequently, the individual and combined effects of PEG and NaOH on viscosity, viscoelasticity, and yielding behaviour in concentrated CNF suspensions remain poorly understood.

To address these gaps, this study systematically investigated the rheological behaviour of concentrated CNF suspensions as a function of concentration, pH, and additive composition. Steady shear tests were performed to measure apparent viscosity and shear stress behaviour, and the resulting data were fitted using the Herschel–Bulkley (HB) model to determine yield stress and HB model parameters. Frequency- and amplitude-sweep measurements were used to evaluate viscoelastic response and non-linear yielding behaviour.

The primary objective was to establish quantitative rheological framework and develop a mechanistic understanding of how PEG and NaOH modify concentrated CNF networks. It was hypothesised that PEG and NaOH alter the CNF network through fundamentally different mechanisms, with PEG primarily modifying inter-fibrillar surface interactions, whereas NaOH induces stronger structural disruption through hydroxide-driven swelling and weakening of hydrogen-bonded contacts. Through this combined rheological approach, the study aimed to clarify how concentration-dependent network mechanics and chemical modification govern flow resistance, deformability, and structural integrity in concentrated CNF suspensions. The results provided a framework for formulation design in coating, printing, and film fabrication applications (Nechyporchuk, Belgacem, & Bras, 2016; Spence et al., 2011).

Theory

To support the interpretation of experimental rheological behaviour, this section briefly outlines the theoretical concepts and rheological parameters used in this study.

The rheology of CNF suspensions is governed by fibril aspect ratio, network structure, and deformation mode. As concentration increases, fibrils collide, entangle, and eventually form a continuous network once the crowding factor (N) exceeds the percolation threshold (≈ 60) (Song et al., 2022; Varanasi et al., 2013). N can be estimated from Equation (1):

$$N = 2/3\Phi(L/d)^2 \quad (1)$$

Where Φ is the CNF volume fraction, and L/d is the fibril aspect ratio. Beyond this threshold, fibrils form an interconnected network capable of sustaining elastic stress. The mechanical response in this regime is largely controlled by the density of inter-fibrillar contacts, defined as the points where fibrils physically entangle or interact through hydrogen-bonding. These contacts points act as temporary physical crosslinks and control network stiffness and resistance to flow (Pokrovskii, 2010).

Steady-shear response

The flow behaviour of CNF suspensions is commonly described using the Herschel–Bulkley (HB) model (Equation 2), which is a constitutive equation for non-Newtonian fluids describing yield stress and shear-thinning behaviour.

$$\tau = \tau_y + k\dot{\gamma}^n \quad (2)$$

where τ is the shear stress (Pa), τ_y is yield stress (Pa), k is the consistency index ($\text{Pa}\cdot\text{s}^n$), $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the flow index ($0 < n < 1$ for shear-thinning systems) (Raja et al., 2024).

τ_y represents the minimum stress required to initiate flow and indicates network strength and integrity. k reflects the resistance to flow after yielding, where higher values mean a more viscous suspension. n describes shear thinning behaviour, as lower values cause a sharper viscosity drop at high shear rates, offering insight into suspension processability.

Oscillatory response

Oscillatory rheology characterises the viscoelastic behaviour of CNF networks under cyclic deformation through the storage modulus (G') and loss modulus (G''). G' represents elastic energy storage and network stiffness, while G'' represents viscous energy dissipation. Their ratio, damping factor ($\tan\delta = G''/G'$), indicates the relative dominance of elastic and viscous behavior, with $\tan\delta < 1$ corresponding to predominantly solid-like response (Mezger, 2014).

Frequency sweeps were used to evaluate network dynamics through the low-frequency storage modulus (G'_{LF}), low-frequency damping factor ($\tan\delta_{LF}$), crossover frequency (ω_c), relaxation time ($\tau_c = 1/\omega_c$), and the power-law exponents a and b from the relations $G' \sim \omega^a$ and $G'' \sim \omega^b$. Higher G'_{LF} and lower $\tan\delta_{LF}$ indicate stronger and more elastic networks, while ω_c and τ_c provide measure of structural relaxation. Small values of a and b are characteristic of weak-gel networks with broad relaxation-time distributions (Mulla et al., 2019; Sollich et al., 1997).

Amplitude sweeps were used to evaluate nonlinear deformation and yielding behaviour. The linear viscoelastic (LVE) limit (γ_{LVE}^*), was defined as the strain where G' decreased below 95% of its initial value. The plateau storage modulus (G'_0), calculated as the average G' between 0.01 and 0.05% strain, was used as a measure of network stiffness before yielding. The crossover strain (γ_f^*), defined by $G'=G''$, represents the transition from elastic- to viscous-dominated behaviour.

The apparent oscillatory yield stress (τ_f^*) was estimated using Equation (3):

$$\tau_f^* = \sqrt{(G')^2 + (G'')^2} \gamma_f^* \quad (3)$$

The strain-sensitivity index (S'), determined from the logarithmic decay of G' beyond the LVE region, was used to quantify the susceptibility of the network to strain-induced softening. More negative values of S' indicate faster structural breakdown under deformation.

Energy-based descriptors

Network toughness and deformation behaviour were further assessed using energy-based descriptors. The recoverable elastic energy density (U_C^*) was estimated using Equation (4) (Ferry, 1980):

$$U_C^* = 1/2 G'_0 (\gamma_f^*)^2 \quad (4)$$

while the dissipated energy density (W_d) was estimated using Equation (5) (Ewoldt et al., 2010; Schreuders et al., 2021; Tschoegl, 1989):

$$W_d = \pi G'' (\gamma_f^*)^2 \quad (5)$$

Higher U_C^* indicates a greater ability to store elastic energy before yielding, whereas higher W_d reflects increased viscous energy dissipation during deformation.

Materials and Methods

Materials

Wood extracted CNF pulp (Celova M250R-P grade, 12.6% solid content) was obtained from Weidmann Fiber Technology (Switzerland) and used without further treatment. NaOH pellets ($\geq 99\%$) were purchased from Thermo Fisher Scientific (Australia). PEG (average molecular weight 8,000 g/mol) was purchased from Sigma-Aldrich, selected due to its wide application in cellulose processing and hydrogel formulations (Yazdani et al., 2021). Analytical grade orthophosphoric acid (H_3PO_4 , 85%) was supplied by Merck. All solutions were prepared using ultrapure water from a Milli-Q purification system (IQ-7000).

Sample preparation

CNF suspensions of 2, 4, 6, and 7 wt% (dry weight basis) were prepared by dispersing the wet pulp in Milli-Q water under mechanical stirring until homogeneous. A 6 wt% CNF suspension was selected as the baseline for additive and pH studies, because it provided a stable fibrillar network while remaining suitable for rheological characterisation in the concentrated regime.

PEG was incorporated into the base CNF suspension at 1, 3, 5, and 10 wt%, while NaOH was added separately at 1, 5, 9, and 10 wt%. Combined PEG-NaOH effects were evaluated using 1 wt% PEG and 9 wt% NaOH, based on ratios reported for cellulose dissolution studies (Yan & Gao, 2008).

For pH-controlled experiments, phosphate buffered media (pH 5, 8, and 10) were prepared using 0.1 M H_3PO_4 and 0.1 M NaOH solutions, following the approach of a prior study (Jowkarderis & van de Ven, 2014). The resulting buffers contained ≤ 0.05 wt% NaOH equivalent, allowing pH effects to be isolated from alkaline concentration. The pH 3 suspension was prepared using H_3PO_4 alone.

Finally, prepared samples were coded as $C_xP_yN_z$, where x denotes CNF wt%, y the PEG wt%, and z the NaOH wt%. For pH-controlled suspensions, the notation of C_xpH_y was used.

Aspect ratio estimation

The CNF aspect ratio was estimated using a sedimentation-based method adapted from previous studies (Song et al., 2022). Dilute suspensions (0.01–0.08 wt%) were prepared and left undisturbed for 48 h. The sedimentation ratio, i.e. sediment height (h_s) to initial height (h_0), was plotted against the initial concentration (C_0). Then, the gel point concentration in mass fraction (C_c) was obtained from a quadratic fit. The corresponding volume fraction (ϕ_c) was calculated using Equation (6) (Varanasi et al., 2013):

$$\phi_c = C_c(\rho_l/\rho_c) \quad (6)$$

Where ρ_l is the density of water (assumed 1.0 g/cm³) and ρ_c is the density of cellulose (1.5 g/cm³). The CNF aspect ratio (A) was then estimated using the crowding number relationship shown in Equation (7) (Rahimi Kord Sofla et al., 2019; Song et al., 2022; Varanasi et al., 2013):

$$A = 4.90\phi_c^{-0.5} \quad (7)$$

Rheological characterisation

Rheological tests were performed using an Anton Paar MCR 302 rheometer in normal force–controlled mode using a 25 mm parallel-plate geometry (1 mm gap) at 25°C and 35 ± 2% relative humidity. All measurements were conducted using a minimum of three independent replicates, and results are reported as mean ± standard deviation.

Steady shear tests (0.1–1000 s⁻¹) were performed to determine apparent viscosity and flow behaviour. The resulting shear stress data were fitted to the HB model (Equation 2) using non-linear optimisation (Microsoft Excel Solver) by minimising the residuals sum of squares between measured and predicted shear stresses, with the constraints $\tau_y \geq 0$, $k > 0$, $0 < n < 1$.

Oscillatory tests included amplitude sweeps at 10 rad/s over a strain range of 0.01–100% to identify the linear viscoelastic region (LVER), followed by frequency-sweep measurements over an angular frequency range of 0.1–628 rad/s to determine the storage (G') and loss (G'') moduli.

Statistical analysis

Rheological parameters derived from steady and oscillatory measurements are reported as mean ± standard deviation from a minimum of three independent replicates of each sample. Statistical significance was evaluated using one-way analysis of variance (ANOVA), with $p < 0.05$ considered significant. MATLAB (MathWorks, USA) was used for parameter extraction and statistical analysis.

Results

CNF characteristics

Fibril morphology was evaluated indirectly via sedimentation-based gel point analysis. The CNF suspension exhibited a gel point (C_g) of 0.0021, corresponding to a volume fraction of 0.0014 (**Fig. S1**). From this, the fibril aspect ratio was estimated as 131, consistent with literature ranges for mechanically fibrillated CNF pulps (≈ 100 –150) (Song et al., 2022; Varanasi et al., 2013). This high aspect ratio suggested the formation of interconnected networks at low solid contents, mirroring the gel-like behaviour observed in the concentrated suspensions (Sellman et al., 2024; Varanasi et al., 2013).

To quantify network crowding, N was calculated using Equation (1). For 2, 4, 6 and 7 wt% CNF suspensions, the derived N values were 152, 305, 457, and 534, respectively. Because these values far exceed the typical gelation thresholds ($N \approx 60$ (Varanasi et al., 2013)), all studied suspensions likely operated within a fully percolated regime where fibril entanglement governs both elastic structure and flow behaviour.

Steady shear rheological behaviour of CNF suspensions

Figure 1 shows the apparent viscosity of CNF suspensions as a function of shear rate for varying CNF concentration, PEG concentration, pH, NaOH concentration, and combined PEG–NaOH modification. All formulations exhibited continuous non-Newtonian shear-thinning behavior without the flow-regime transitions or plateaus sometimes reported in literature (Li et al., 2021; Li et al., 2015). The observed trend suggested a relatively homogeneous and well-dispersed fibrillar network (Iotti et al., 2011; Xu et al., 2024).

For pure CNF formulations (2–7 wt%), viscosity expectedly increased with concentration across the entire shear rate range (**Fig. 1(a)**), reflecting a progressively denser fibrillar network. At a low shear (0.1 s^{-1}), viscosity increased by nearly two orders of magnitude, from $2.8 \times 10^4 \text{ mPa.s}$ (2 wt%) to $9.1 \times 10^5 \text{ mPa.s}$ (7 wt%). This relationship was well described by the Ostwald-de Waele power-law model (**Fig. 1(a)** inset), where the flow behaviour index (n) remained below 1 for all formulations. Increasing CNF concentration caused a modest increase in n from 0.77 to ~ 0.83 , suggesting slightly weaker shear-thinning at higher concentrations. This behaviour likely stemmed from enhanced fibre–fibre interactions and reduced mobility within the denser network, which restricted structural breakdown under shear.

Modifying the network strength via chemical additives or pH alterations consistently reduced suspension viscosity without changing the underlying flow mechanism. Introducing PEG uniformly decreased viscosity across all shear rates (**Fig. 1(b)**); at 0.1 s^{-1} , a 40% reduction was achieved with 3 wt% PEG (from $\sim 6.22 \times 10^5$ to $3.75 \times 10^5 \text{ mPa.s}$), indicating a weakening of inter-fibrillar interactions. However, higher PEG loadings (3–10 wt%) yielded negligible further changes. This

plateau could reflect a saturation-type behavior where accessible surface interaction sites were fully occupied at low polymer concentrations, mirroring surface-site-limited mechanisms described for other polymer-cellulose systems (Pellegrino et al., 2025).

Electrostatic modifications induced by pH adjustments similarly altered network structure (**Fig. 1(c)**). Viscosity progressively decreased with increasing pH; at 0.1 s^{-1} , it dropped by $\sim 60\%$ from $\sim 7.66 \times 10^5 \text{ mPa.s}$ at pH 3 to $\sim 3.03 \times 10^5 \text{ mPa.s}$ at pH 10, while intermediate conditions (pH 5 and 8) yielded transitional viscosities ($\sim 4.2\text{-}3.7 \times 10^5 \text{ mPa.s}$). This elevated viscosity under acidic conditions and subsequent reduction at higher pH suggested that increased surface ionisation promoted fibril–fibril repulsion and reduced flow resistance via charge regulation (Jowkarderis & van de Ven, 2014). However, the overall effect remained moderate likely because the phosphate-buffers introduced only trace Na^+/OH^- concentrations.

In contrast, NaOH additions yielded a stronger response than either PEG or pH control (**Fig. 1(d)**). At 0.1 s^{-1} , viscosity dropped to $9.60 \times 10^4 \text{ mPa.s}$ at 10 wt%, corresponding to an $\sim 84\%$ reduction. At an equivalent 1 wt% loading, NaOH caused a 9% greater viscosity drop than PEG, suggesting a more pronounced disruption of fibril–fibril interactions. Remarkably, whereas the pH-adjusted suspensions leveled-off, the alkali-treated suspensions continued to decrease with higher NaOH concentrations despite sharing an identical bulk pH (≈ 14). This suggested that hydroxide concentration, rather than pH alone, governed the observed network weakening, a phenomenon commonly attributed to alkali-induced fibril swelling and structural cohesion loss (Jarvis, 2023; Wattana et al., 2025).

This dominance was further apparent in the combined formulation ($\text{C}_6\text{P}_1\text{N}_9$; **Fig. 1(e)**), which exhibited a low-shear viscosity of $\sim 1.13 \times 10^5 \text{ mPa.s}$, representing $\sim 82\%$ reduction relative to the additive-free suspension. While this value was substantially lower than the PEG-only baseline ($\text{C}_6\text{P}_1\text{N}_0$, $\sim 4.97 \times 10^5 \text{ mPa.s}$), it was nearly identical to the NaOH-only suspension ($\text{C}_6\text{P}_0\text{N}_9$, $1.12 \times 10^5 \text{ mPa.s}$). This close alignment might be explained by the polymer–alkali synergism observed in some cellulose dissolution media (Wan & Li, 2015; Yan & Gao, 2008) was minimal under these conditions. Because the combined suspension was more viscous than the 10 wt% NaOH formulation ($\text{C}_6\text{P}_0\text{N}_{10}$), hydroxide concentration remained the primary factor governing the rheological response and network breakdown.

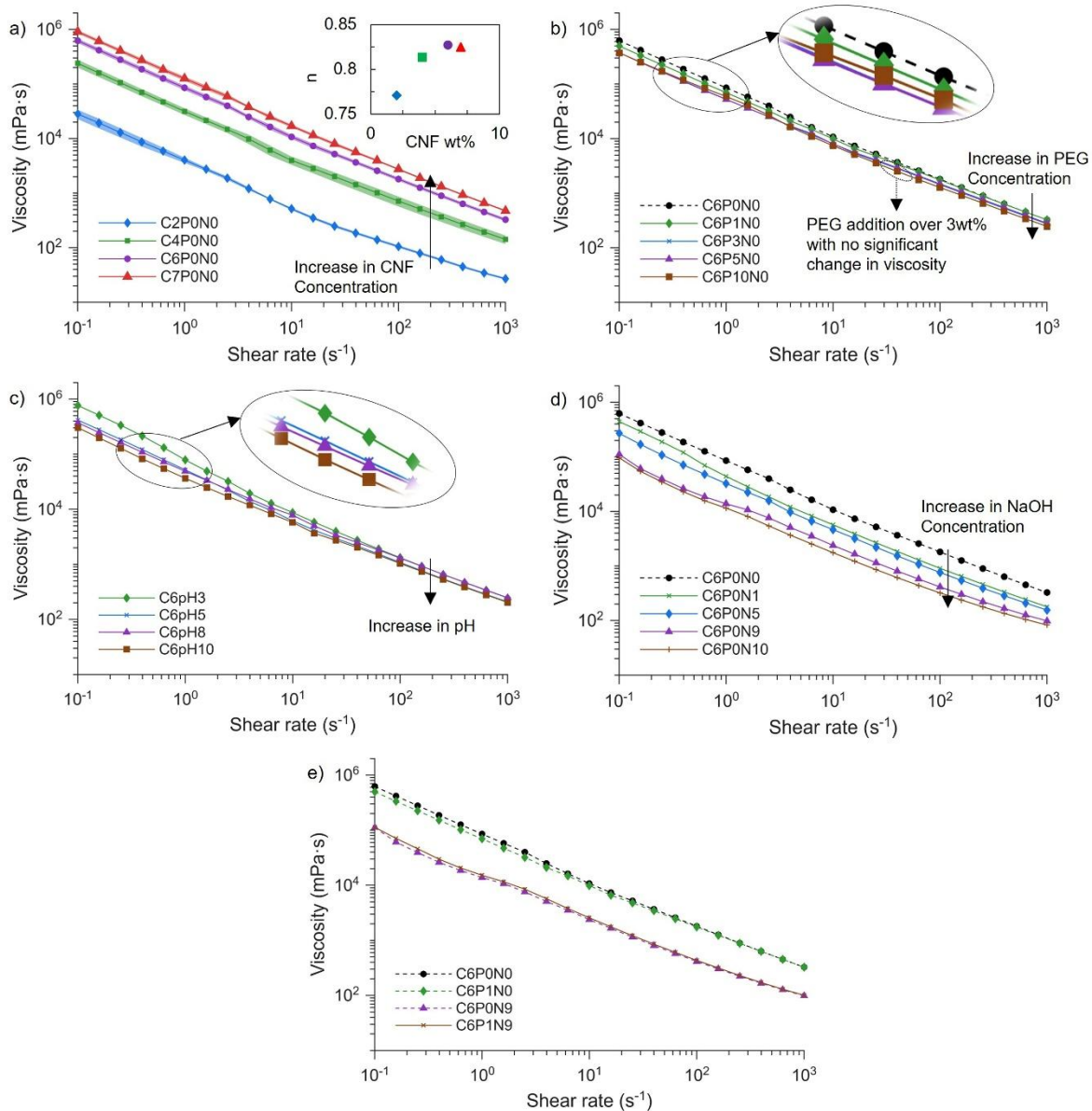


Fig. 1 Steady shear viscosity of CNF suspensions as a function of shear rate: (a) effect of CNF concentration (shaded regions indicate $\pm$ standard deviation; inset shows the dependence of n to CNF concentration); (b) effect of PEG concentration; (c) effect of pH; (d) effect of NaOH concentration; and (e) combined effect of PEG–NaOH in 6wt% CNF suspensions. For clarity, standard deviations for panels (b–e) are reported in Table S2

Yield stress and flow behaviour

Experimental shear stress data for all formulations were successfully captured by the HB model (**Fig. 2(a–e)**), as confirmed by near-linear parity correlations (**Fig. 2(f–j)**). The extracted yield stress (τ_y), consistency index (k), and flow index (n) are shown in **Fig. 3**. All model parameters across the studied formulations were statistically significant ($p < 0.05$), with the sole exception of n under varying PEG concentrations.

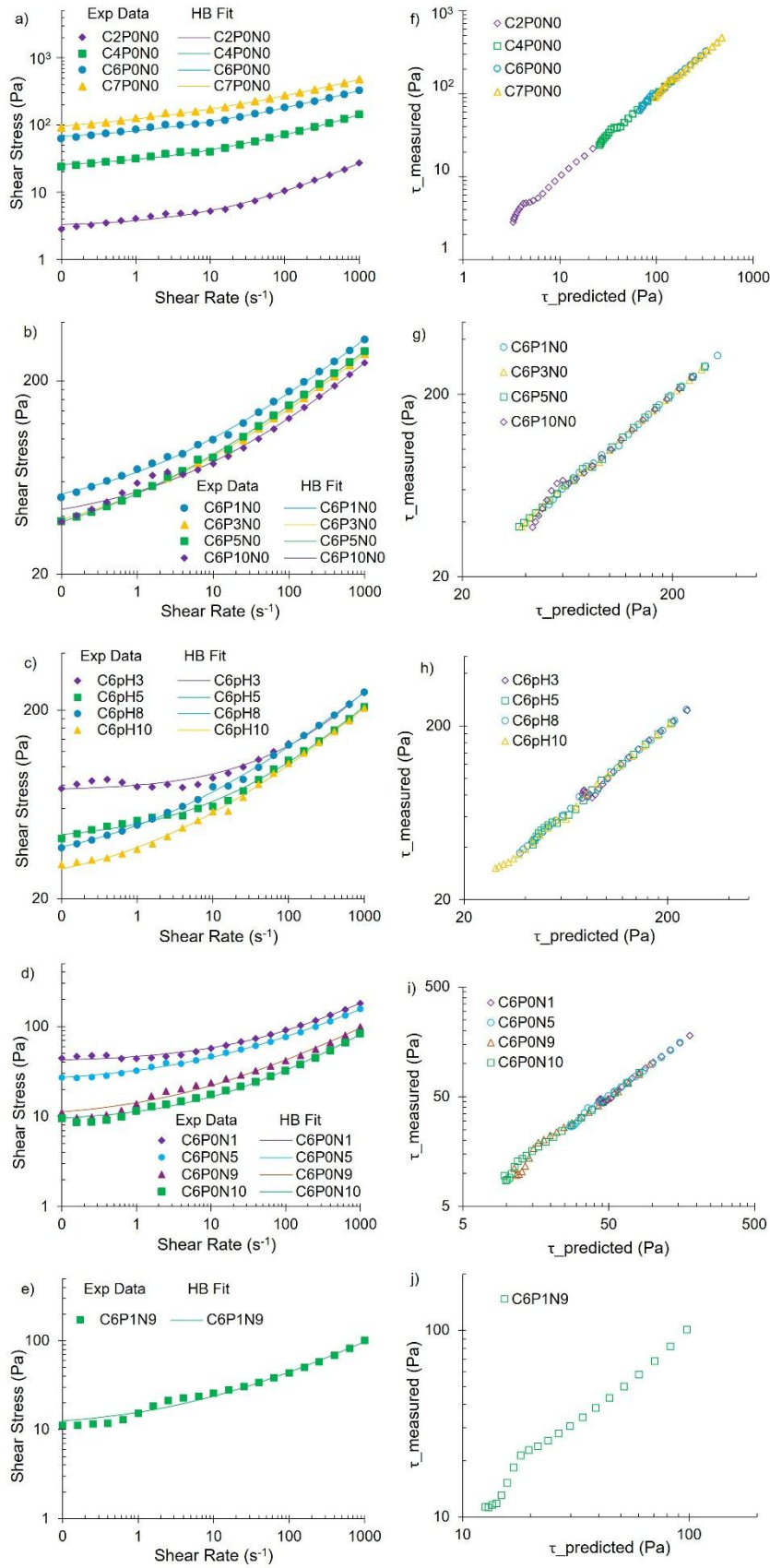


Fig. 2 Experimental shear stress (symbols) and HB fits (solid lines) for CNF suspensions: (a) effect of CNF concentration; (b) effect of PEG concentration; (c) effect of pH; (d) effect of NaOH concentration; and (e) combined effect of PEG–NaOH in 6 wt% CNF suspension; (f–j) parity plots comparing measured and HB-predicted shear stresses ($R^2 > 0.99$)

Increasing CNF concentration increased τ_y markedly from 3.05 Pa at 2 wt% to 70.96 Pa at 7 wt%, driven by network densification and fibrillar entanglement. This trend was accompanied by a substantial increase in k and a decrease in n from 0.52 to 0.30 (**Fig. 3(a)**), in agreement with scaling arguments for fibrillar gels (Iotti et al., 2011; Moberg et al., 2017; Sellman et al., 2024). Furthermore, yield stress exhibited a power-law relationship with crowding factor ($\tau_y \propto N^{2.54}$; **Fig. S2**). This exponent is slightly higher than values reported for typical cellulose suspensions ($\tau_y \propto C^{2.26}$, where $N = \kappa C$) (Koponen, 2020), likely reflecting the high aspect ratio of CNFs and the concentrated regime investigated in this study.

While both PEG and NaOH reduced τ_y and k , signaling weaker structures, their impacts on the yielding mechanisms diverged. Adding PEG decreased τ_y from 54.41 Pa to 38.21 Pa at 1 wt% PEG, before stabilizing between 23-35 Pa at higher loadings (**Fig. 3(b)**). Accompanying this was a similar reduction in k but a nearly constant n (0.33-0.36), suggesting that PEG weakened inter-fibrillar interactions via the surface-saturation mechanism identified in the steady-shear data without altering the post-yield deformation mode. In contrast, NaOH addition triggered a more aggressive network breakdown (**Fig. 3(d)**). Yield stress progressively decreased to ~ 9 Pa at 9-10 wt% NaOH, while k and displayed non-monotonic trends, governed by the interplay between alkali-induced fibril swelling and structural delamination (Jarvis, 2023; Wattana et al., 2025), as discussed previously. This structural disruption was dominated by alkaline effects in the combined formulation ($C_6P_1N_9$) which exhibited a low yield stress of ~ 10 Pa, a k of 5.6 Pa.sⁿ, and an n of ~ 0.42 . These parameters were virtually identical to those of the NaOH-only baseline, suggesting that NaOH governed the network weakening while PEG provided a negligible contribution under highly alkaline conditions.

Electrostatic modulation via pH adjustment revealed a complementary control path (**Fig. 3(c)**). Acidic conditions (pH 3–5) elevated yield stress up to ~ 73 Pa likely related to protonation-induced aggregation, whereas alkaline conditions (pH 10) lowered τ_y to ~ 21.6 Pa, likely via electrostatic repulsion (Alves et al., 2024). The stable k and narrow n ranges (0.34–0.51) suggested that pH modulated baseline network strength rather than post-yield viscous resistance.

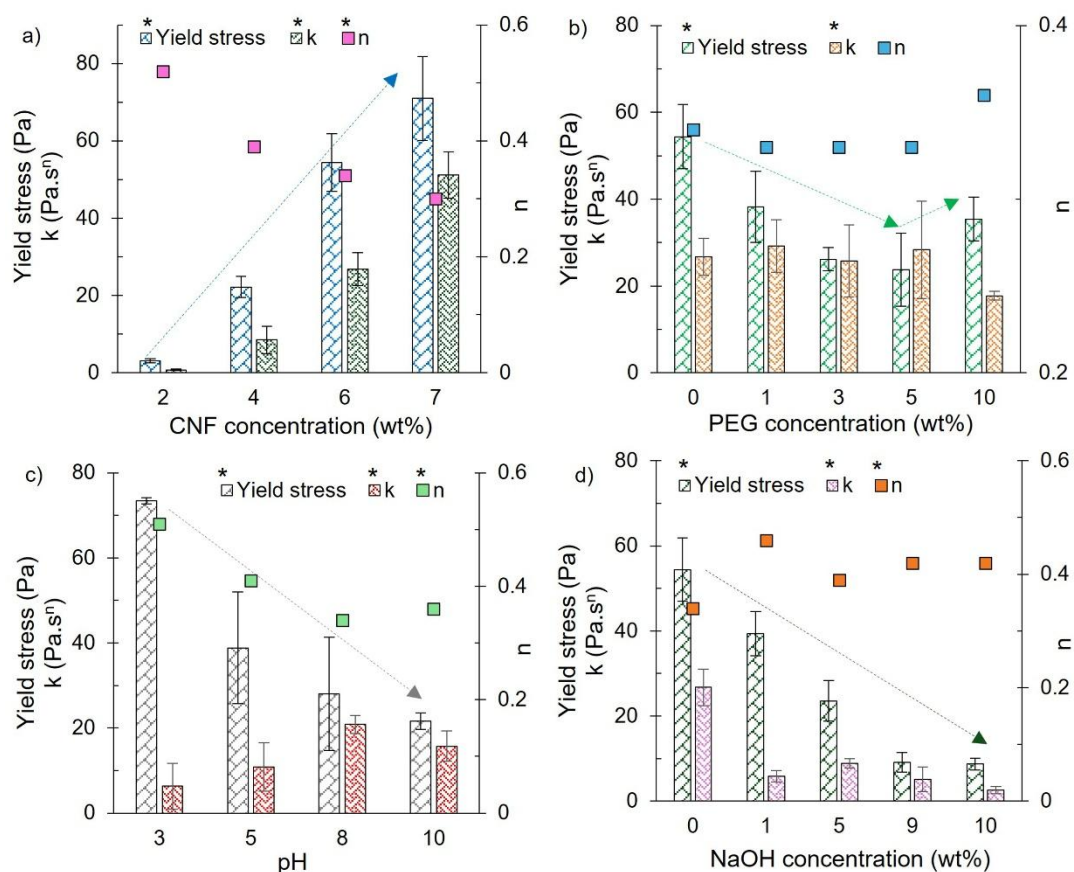


Fig. 3. The HB model fit values for yield stress, consistency (k) and flow (n) indices. P-value < 0.05 is considered significant noted by (*)

Oscillatory shear behaviour of CNF suspensions

The frequency-dependent viscoelastic behaviour of CNF suspensions is presented in **Fig. 4**, with key derived quantitative parameters summarized in **Table 1**. Across all formulations, the storage modulus (G') consistently exceeded the loss modulus (G'') within the low-to-intermediate frequency range ($\omega \leq 100 \text{ rad.s}^{-1}$), confirming that CNF suspensions behaved as percolated, elastic networks rather than viscous dispersions. All $G'-G''$ crossover frequencies occurred at $\omega > 100 \text{ rad.s}^{-1}$, where increased scatter in the rheological response was observed, consistent with previous reports for concentrated fibrillar and soft-gel systems (Chan et al., 2023; Cho et al., 2005). Consequently, the low-frequency storage modulus (G'_{LF}), damping factor ($\tan\delta_{LF}$), and frequency-scaling exponents (a and b) were considered the most representative descriptors of bulk network structure.

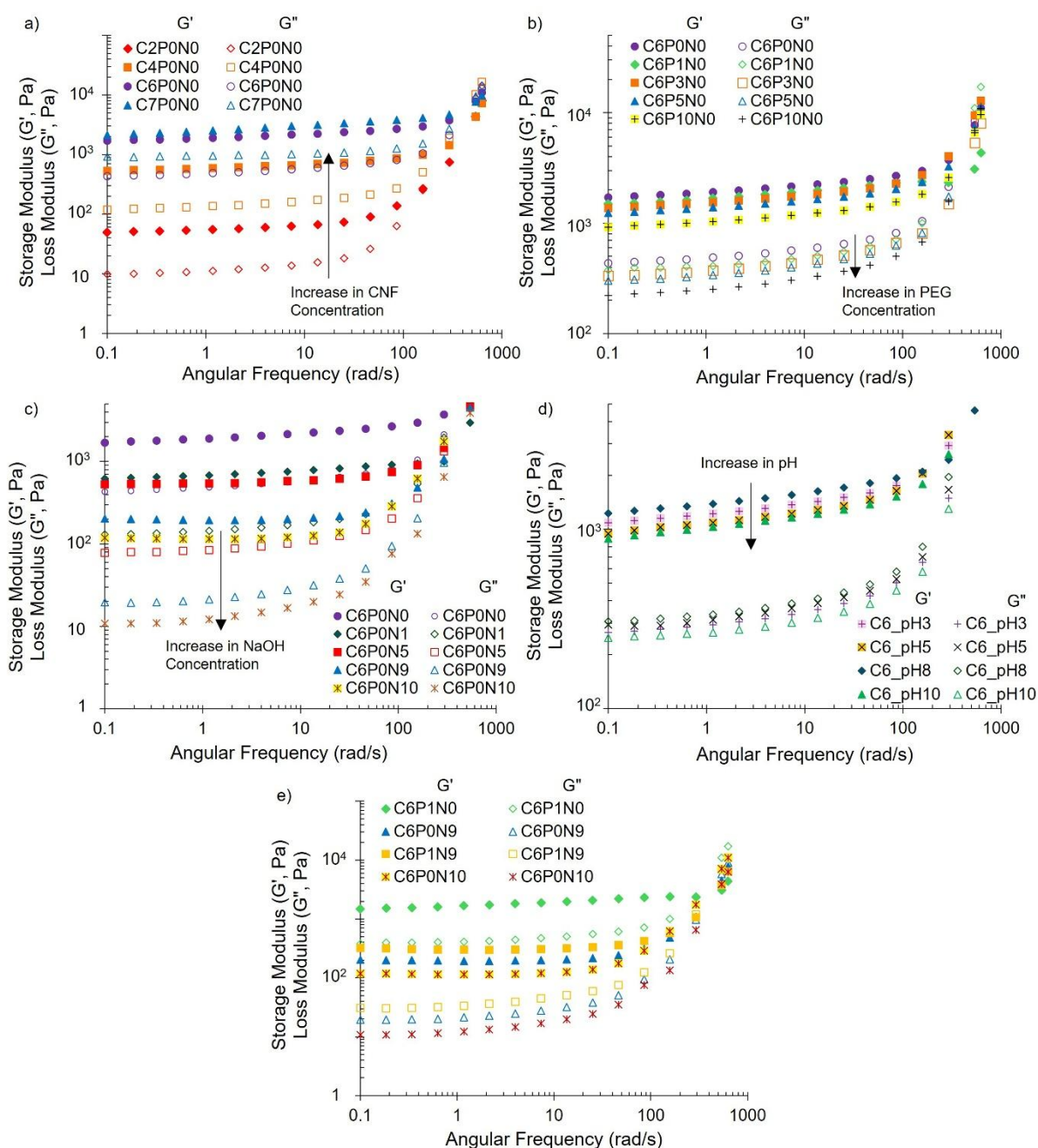


Fig. 4 Frequency-dependent storage modulus (G') and loss modulus (G'') of CNF suspensions showing the (a) effect of CNF concentration; (b) effect of PEG concentration; (c) effect of NaOH concentration; (d) effect of pH; and (e) the combined effect of PEG–NaOH in 6 wt% CNF suspensions. Corresponding standard deviations for panels (a-e) are provided in Tables S4 and S5 for clarity

Increasing CNF concentration sharply increased viscoelastic stiffness. The low-frequency storage modulus (G'_{LF}) increased by 98%, from ~ 0.05 kPa (2 wt%) to ~ 2.3 kPa (7 wt%), consistent with the increases in viscosity and yield stress observed under steady shear (**Fig. 5(a)**). The $\tan\delta_{LF}$ also increased from 0.20 to 0.41, indicating a greater contribution of viscous dissipation within the denser fibrillar networks. Despite this increase, G' remained dominant across the investigated frequency range, suggesting the suspensions retained their weak-gel behaviour.

Although all crossover frequencies occurred above the stable measurement regime, ω_c increased and τ_c decreased with increasing concentration (**Table 1**), suggesting progressively faster network relaxation. The change became less pronounced between 6 and 7 wt%, indicating diminishing sensitivity at high solids loading, similar to those reported for dense semiflexible biopolymer networks (Li et al., 2015; Nechyporchuk, Belgacem, & Pignon, 2016). ANOVA confirmed that all evaluated viscoelastic parameters were significantly affected by CNF concentration ($p < 0.05$; **Table S6**), indicating that solids loading strongly governed both network stiffness and viscoelastic response.

Table 1. Summary of viscoelastic parameters derived from frequency-sweep data. One-way ANOVA results are provided in Table S6. Parameters without a standard deviation rounded to zero at two decimal places

Studied Parameter	Sample Code	G'_{LF} (Pa)	$\tan\delta_{LF}$	ω_c (rad/s)	τ_c (ms)	a (G' scaling exponent)	b (G'' scaling exponent)
CNF Concentration	C ₂ P ₀ N ₀	53.05±4.33	0.20	166.63±64.14	6.83±3.25	0.04	0.06
	C ₄ P ₀ N ₀	568.08±17.21	0.23	237.44±46.84	4.32±0.80	0.04	0.06
	C ₆ P ₀ N ₀	1823±64.59	0.25±0.02	391.25±104.59	2.67±0.63	0.05	0.05±0.01
	C ₇ P ₀ N ₀	2347.96±383.31	0.41±0.08	337.19±17.39	2.97±0.15	0.07	0.03±0.01
PEG Concentration	C ₆ P ₁ N ₀	1587.53±208.41	0.25±0.03	279.02±29.05	3.61±0.34	0.05±0.02	0.02±0.06
	C ₆ P ₃ N ₀	1554.05±143.50	0.37±0.26	363.35±253.31	3.64±2.53	0.06±0.02	0.05
	C ₆ P ₅ N ₀	1329±369.85	0.24	257.21±55.17	3.98±0.85	0.05	0.05±0.02
	C ₆ P ₁₀ N ₀	988.58±79.25	0.24±0.01	439.02±0.47	2.28	0.05	0.05±0.01
NaOH Concentration	C ₆ P ₀ N ₁	657±85.34	0.21±0.01	202.37±25.67	5.00±0.62	0.04	0.05
	C ₆ P ₀ N ₅	538.77±102.77	0.15±0.01	183.52±32.03	5.53±0.97	0.01±0.02	0.03
	C ₆ P ₀ N ₉	197.61±109.92	0.10±0.01	130.07±11.58	7.72±0.69	-0.02±0.01	0.05±0.01
	C ₆ P ₀ N ₁₀	115.51±20.62	0.10	307.10	3.26	-0.01±0.01	0.07±0.01
pH	C ₆ pH ₃	1167.15±140.68	0.24	503.93±171.26	2.11±0.72	0.05	0.04±0.01
	C ₆ pH ₅	1041±33.24	0.29±0.02	356.41	2.81	0.05	0.04±0.02
	C ₆ pH ₈	1322.52±57.96	0.24±0.01	244.09±26.15	4.12±0.44	0.05	0.04
	C ₆ pH ₁₀	978.47±22.38	0.27±0.03	223.08	4.48	0.06±0.01	0.03±0.03
Combined PEG NaOH	C ₆ P ₁ N ₉	307.12±3.96	0.10	184.81±2.20	5.41±0.06	-0.03	0.05±0.01

Both PEG and NaOH reduced network stiffness relative to the untreated suspension, although their effects differed substantially. PEG produced a gradual reduction in G'_{LF} from ~1.8 kPa to ~1 kPa as concentration increased from 0 to 10 wt% (**Fig. 5(b)**). However, $\tan\delta_{LF}$, ω_c , and the frequency-scaling exponents showed no statistically significant changes ($p > 0.05$; **Table S6**), indicating that PEG primarily reduced network strength while preserving the underlying relaxation behaviour. In contrast, NaOH produced a much stronger response (**Fig. 5(c)**). The G'_{LF} decreased from ~1.8 kPa to 0.7 kPa at

10 wt% NaOH (a ~64% reduction). Unlike PEG, NaOH significantly affected all evaluated frequency-sweep parameters ($p < 0.05$; **Table S6**). The accompanying changes in $\tan\delta_{LF}$, ω_c , τ_c , and the scaling exponents may suggest that NaOH altered both network strength and relaxation behaviour, consistent with substantial modification of the fibrillar network structure.

The combined PEG–NaOH suspension exhibited a low G'_{LF} of ~0.3 kPa, suggesting extensive network weakening. However, this value remained higher than those of the corresponding high-NaOH suspensions ($C_6P_0N_9$ and $C_6P_0N_{10}$), suggesting that PEG did not further weaken the network under strongly alkaline conditions. The corresponding $\tan\delta_{LF}$ and scaling exponents were comparable to those of the highly alkaline suspensions, indicating that the viscoelastic response remained largely governed by hydroxide-induced structural changes, and PEG acted as a secondary modifier of network strength.

Independent pH adjustments produced comparatively modest changes in viscoelastic behavior. The G'_{LF} remained relatively high under acidic conditions and decreased moderately with increasing pH (**Fig. 5(d)**), indicating some weakening of the fibrillar network. In contrast, $\tan\delta_{LF}$, ω_c , and the frequency-scaling exponents varied only slightly across the investigated pH range. ANOVA confirmed that pH significantly affected G'_{LF} but did not significantly affect other studied parameters ($p > 0.05$; **Table S6**). These results may indicate that pH likely influenced network strength through electrostatic regulation while having a limited effect on the underlying viscoelastic and relaxation behaviour. The magnitude of these changes remained substantially lower than those produced by direct NaOH addition.

Amplitude-sweep viscoelastic response

The amplitude-dependent viscoelastic behaviour of CNF suspensions is presented in **Fig. 6**, with the derived parameters summarized in **Table 2**. Across all formulations, a characteristic three-regime response was observed, consisting of a linear viscoelastic region (LVER), followed by gradual modulus decay and eventual yielding, consistent with entangled fibrillar networks reported previously (Nechyporchuk, Belgacem, & Pignon, 2016).

Increasing CNF concentration substantially increased network strength (**Fig. 6(a)**). The plateau storage modulus (G'_0) increased from ~90 Pa (2 wt%) to ~5018 Pa (7 wt%) (**Fig. 5(a)**), while the oscillatory yield stress (τ_f^*) increased from 3.7 to 96 Pa (**Table 2**). Both parameters were significantly affected by concentration ($p < 0.05$; **Table S7**), consistent with the increases in viscosity, yield stress, and viscoelastic stiffness observed in the preceding sections. Furthermore, τ_f^* followed a power-law dependence on concentration ($\tau_f^* \propto C^{2.64}$), with an identical scaling obtained using the crowding factor ($\tau_f^* \propto N^{2.64}$; **Fig. S3**). The fitted proportionality constant ($\kappa=77.8$; Equation S7) closely matched the theoretical estimate ($\kappa \approx 76.3$) based on the measured fibril aspect ratio ($L/d=131$), suggesting that oscillatory and steady-shear yielding were governed by the same connectivity-controlled mechanism.

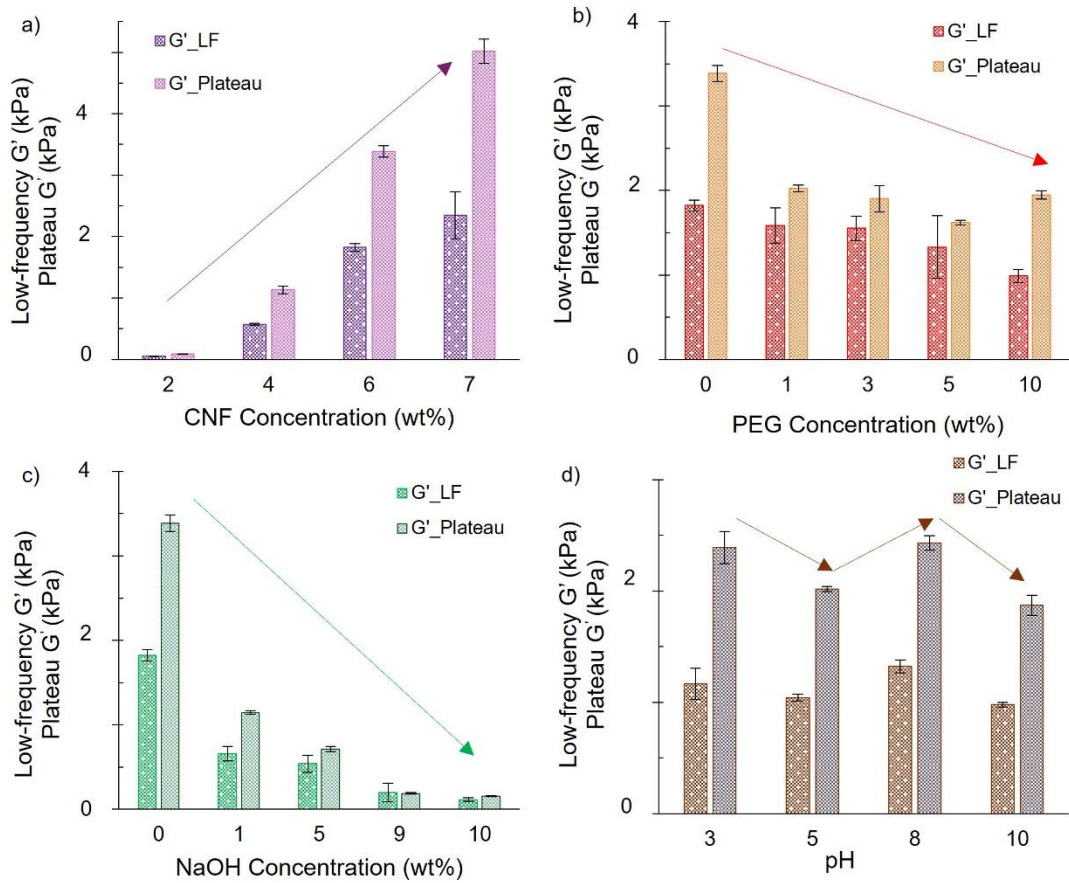


Fig. 5 Low frequency storage modulus (G'_{LF}) and Plateau modulus (G'_0) showing the (a) effect of CNF concentration; (b) effect of PEG concentration; (c) effect of NaOH concentration; and (d) effect of pH in 6 wt% CNF suspensions

In contrast, the strain limit of linearity (γ_{LVE}^*) remained relatively constant (~ 0.17 – 0.19%) and was not significantly affected by concentration ($p > 0.05$; **Table S7**), indicating that increased network stiffness did not improve strain tolerance. The strain-sensitivity index (S') became more negative between 2 and 4 wt% and then stabilised, suggesting that the mode of structural breakdown changed little once a well-developed fibrillar network had formed. Both the recoverable elastic energy density (U_c^*) and structural dissipation energy (W_d) increased significantly with concentration ($p < 0.05$) suggesting an enhanced capacity to store and dissipate energy prior to yielding.

Both PEG and NaOH reduced network strength, as reflected by decreases in G'_0 and τ_f^* (**Fig. 5(b,d)**, **Table 2**), although their effects differed substantially. PEG led to a progressive reduction in G'_0 decreasing from ~ 3386 Pa (additive-free) to ~ 2024 Pa at 1 wt% PEG ($\sim 40\%$ reduction) and to ~ 940 Pa at 10 wt% (**Fig. 5(b)**), with corresponding decreases in τ_f^* . Most of the reduction occurred upon initial PEG addition, while further increases in PEG concentration produced comparatively minor changes. Similar behaviour was observed for U_c^* and W_d , which decreased sharply at 1 wt% PEG before approaching near-constant values at higher PEG concentrations. Despite these reductions, γ_{LVE}^* and S' remained statistically unchanged ($p > 0.05$), indicating that PEG primarily reduced network strength while having little influence on the yielding mechanism.

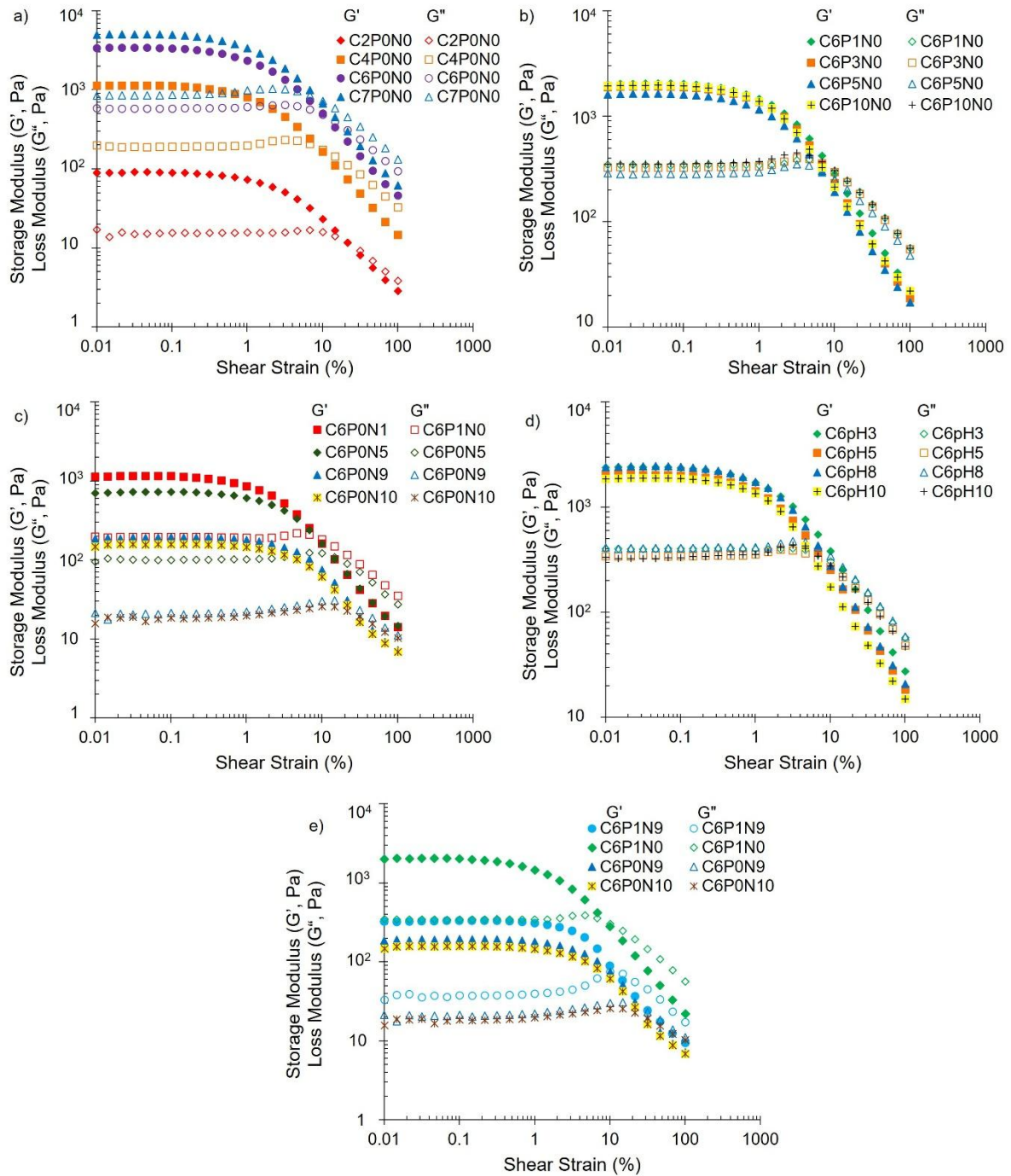


Fig. 6 Amplitude sweep response of CNF suspension on storage modulus (G') and loss modulus (G'') showing the (a) effect of CNF concentration; (b) effect of PEG concentration; (c) effect of NaOH concentration; (d) effect of pH; and (e) the combined effect of PEG–NaOH in 6 wt% CNF suspension

In contrast, NaOH addition produced a much stronger response (**Fig. 5(d)**); G'_0 dropped to ~ 1144 Pa just 1 wt% NaOH and to ~ 155 Pa at 10 wt% NaOH, corresponding to a reduction of more than 95%. Unlike PEG, NaOH significantly affected almost all amplitude-sweep parameters ($p < 0.05$). Both the yield strain (γ_f^*) and γ_{LVE}^* increased markedly with NaOH concentration, indicating that the weakened networks could sustain larger deformations before yielding, while τ_f^* decreased progressively, suggesting a substantial loss of structural integrity. Interestingly, S' remained stable and comparable to

the PEG-modified systems at low-to-moderate alkali concentrations (1–5 wt%) but became progressively less negative at higher NaOH contents (9–10 wt%). This shift suggested a transition towards a more compliant and weakly-connected network. The energy parameters exhibited a non-monotonic response; U_c^* increased up to 9 wt% NaOH before decreasing at 10 wt%, whereas W_d showed a similar but statistically non-significant trend. These observations suggested that alkali-induced weakening was accompanied by increased network deformability prior to extensive structural disruption at high NaOH concentrations.

The combined PEG-NaOH suspension exhibited a substantially weakened network, with G'_0 reduced to ~ 323 Pa and τ_f^* to ~ 12 Pa. Nevertheless, both values remained higher than those of corresponding high-NaOH suspensions ($C_6P_0N_9$ and $C_6P_0N_{10}$), indicating that PEG partially moderated NaOH-induced network disruption. The γ_{LVE}^* increased to $\sim 1.06\%$, indicating a highly deformable structure, while S' (≈ -0.91) remained comparable to the highly alkaline formulations. Interestingly, the combined suspension exhibited the highest recoverable elastic energy density ($U_c^* \sim 18$ mJ/m³) despite its relatively low stiffness, whereas W_d (~ 3.4 J/m³) remained comparatively low.

Independent pH adjustment produced statistically significant changes in all parameters ($p < 0.05$), although the magnitude of variation remained smaller than that observed for NaOH addition. The G'_0 varied non-monotonically, with relatively high values at pH 3 (~ 2390 Pa) and pH 8 (~ 2430 Pa), and lower values at pH 5 and 10 (**Fig. 5(c)**). Similarly, τ_f^* decreased from ~ 53 Pa at pH 3 to ~ 28 Pa at pH 10, indicating a gradual reduction in network strength with increasing alkalinity.

Both γ_{LVE}^* and γ_f^* increased with pH, suggesting progressively greater deformability, while S' became more negative, indicating a slightly sharper structural breakdown following the onset of nonlinear deformation. The energy parameters also showed non-monotonic behaviour, with higher values of acidic conditions and lower values at pH 10.

Table 2. Summary of parameters derived from amplitude-sweep data. One-way ANOVA results are provided in Table S7. Parameters without a standard deviation rounded to zero at two decimal places.

Studied Parameter	Sample Code	G'_0 (Pa)	γ_{LVE}^* (%)	S'	γ_f^* (%)	τ_f^* (Pa)	U_C^* (mJ/m ³)	W_d (J/m ³)
CNF	C ₂ P ₀ N ₀	89.97±3.89	0.17±0.21	-0.51±0.21	24.95±6.06	3.65±0.40	0.22±0.31	2.11±0.70
Concentration	C ₄ P ₀ N ₀	1131.25±59.62	0.19±0.01	-0.73±0.01	9.36±0.25	23.62±1.61	1.94±0.18	5.02±0.43
	C ₆ P ₀ N ₀	3386.30±95.52	0.18	-0.72	11.09±0.88	70.97±2.97	5.22±0.39	17.90±2.37
	C ₇ P ₀ N ₀	5018.47±199.14	0.17	-0.74±0.02	9.09±1.59	96.17±9.41	7.44±0.60	19.85±5.03
PEG	C ₆ P ₁ N ₀	2024.44±37.31	0.22	-0.80±0.03	9.25±0.19	40.51±1.25	4.76±0.70	8.52±0.41
Concentration	C ₆ P ₃ N ₀	1903.19±156.67	0.22	-0.83±0.03	7.06±0.46	34.55±2.59	4.50±0.46	5.48±0.74
	C ₆ P ₅ N ₀	1619.99±30.28	0.21	-0.80±0.04	6.83±0.85	28.66±1.59	3.68±0.26	4.45±0.82
	C ₆ P ₁₀ N ₀	939.68±47.55	0.22	-0.80±0.03	5.88±0.40	32.07±1.81	4.65±0.33	4.29±0.52
NaOH	C ₆ P ₀ N ₁	1144.13±21.47	0.26±0.02	-0.81±0.02	8.92±1.93	23.78±2.54	3.75±0.44	4.87±1.58
Concentration	C ₆ P ₀ N ₅	714.36±28.79	0.47	-0.81±0.04	14.24±2.01	21.60±1.44	7.86±0.16	7.01±1.43
	C ₆ P ₀ N ₉	189.14±7.77	0.94±0.02	-0.77	26.22±1.24	9.10±0.40	8.51±0.42	5.46±0.50
	C ₆ P ₀ N ₁₀	154.51±6.54	0.79±0.07	-0.73±0.02	27.38±1.63	7.76±0.43	4.78±1.08	4.86±0.56
pH	C ₆ pH ₃	2389.91±142.70	0.20	-0.74±0.03	16.64±7.33	52.75±10.03	4.71±0.11	20.97±11.83
	C ₆ pH ₅	2016.73±23.22	0.20±0.01	-0.81±0.01	9.60±3.01	36.40±4.42	4.10±0.52	8.14±3.61
	C ₆ pH ₈	2429.96±65.25	0.22±0.01	-0.85±0.02	7.51±0.72	41.54±2.95	5.94±0.86	7.11±1.23
	C ₆ pH ₁₀	1872.73±90.88	0.23±0.01	-0.89±0.01	5.22±0.58	28.11±2.23	4.79±0.52	3.33±0.53
Combined PEG NaOH	C ₆ P ₁ N ₉	322.59±18.24	1.06±0.03	-0.91±0.01	12.14±2.12	12.36±0.87	18.14±3.39	3.39

Discussion

The results from steady shear, frequency sweep, and amplitude sweep suggested that the rheological behaviour of concentrated CNF suspensions was primarily governed by the degree of fibrillar network connectivity. In concentrated suspensions, CNFs form a percolated structure through physical entanglement and hydrogen-bond-mediated contacts (Alves et al., 2024; Wattana et al., 2025). The density and strength of these contacts determine the ability of the network to resist flow, store elastic energy, and sustain stress under deformation. Consequently, parameters associated with flow resistance (viscosity and τ_y), linear viscoelasticity (G'_{LF} and G'_0), and nonlinear yielding (τ_f^* and U_C^*) exhibited consistent trends throughout this study because they represented different manifestations of the same underlying structural feature, which was network connectivity.

Increasing CNF concentration increased fibril crowding and the number of effective inter-fibrillar contacts, producing simultaneous increases in viscosity, yield stress, viscoelastic stiffness, oscillatory yield stress, and energy storage capacity. The similarity between the concentration-scaling relationships obtained from steady-shear and oscillatory measurements further suggested that both flow initiation and nonlinear yielding were governed by a common connectivity-controlled mechanism. Despite the

substantial increase in network strength, the weak frequency dependence of G' and G'' and the relatively stable strain-sensitivity behaviour may be explained by the increase in concentration which primarily strengthened the existing network rather than altering its fundamental deformation pathway. These observations were consistent with previous descriptions of concentrated CNF suspensions as physically percolated fibrillar gels in which rheological behaviour was controlled by fibril overlap, entanglement, and reversible hydrogen-bond-mediated contacts (Albornoz-Palma et al., 2022; Alves et al., 2024; Miao et al., 2024; O'Banion & Shams Es-haghi, 2023).

PEG and NaOH modified the CNF network through markedly different mechanisms. PEG produced a saturation-type response, where most rheological changes occurred upon initial addition, and only limited further changes were observed at higher concentrations. The simultaneous reduction in viscosity, yield stress, G'_{LF} , G'_0 , and τ_f^* suggested that PEG weakened the strength of inter-fibrillar contacts. However, the relatively unchanged relaxation behaviour, strain sensitivity, and deformation characteristics suggested that PEG did not substantially alter the overall network structure or connectivity density. This behaviour was consistent with PEG acting primarily as a surface-interaction modifier through hydroxy-group screening, hydration-layer modification, or steric interference, thereby reducing contact strength without disrupting the percolated fibrillar structure. Similar behaviour was reported in cellulose-PEG systems, where PEG influenced rheology through surface-associated interactions rather than large structural reorganisation (Beuguel et al., 2018; Yazdani et al., 2021).

In contrast, NaOH induced much larger changes in both linear and nonlinear rheological behaviour. The simultaneous reduction in all studied rheological parameters may reflect that NaOH affected not only the strength of inter-fibrillar contacts but also the effective connectivity of the fibrillar network. These changes were consistent with alkali-induced swelling, weakening of hydrogen-bond-mediated contacts, and structural rearrangement of the cellulose fibrils, as reported previously (Budtova & Navard, 2016; Reyes et al., 2022; Žepič et al., 2022). The amplitude-sweep results further suggested that low-to-intermediate NaOH concentrations promoted network mobility and deformability before the extensive loss of connectivity observed at higher alkalinity.

The combined PEG-NaOH formulation further emphasised the dominant role of alkali-induced structural modification. While the rheological response remained largely controlled by NaOH, the higher modulus and energy-storage capacity relative to the corresponding highly alkaline NaOH-only suspensions suggested that PEG partially moderated the loss of connectivity. This observation may reflect that local fibril interactions could still contribute to network stability even after substantial alkali-induced weakening (O'Banion & Shams Es-haghi, 2023; Yazdani et al., 2021).

The comparatively modest effects of pH adjustment may indicate that protonation-deprotonation and the associated electrostatic interactions alone were insufficient to induce major structural changes in the concentrated CNF network. Previous studies on charged CNF systems have shown that pH and ionic conditions can alter aggregation, viscosity, and yield stress by changing electrostatic repulsion and fibril

association (Wattana et al., 2025). However, in this study, the rheology results suggested that pH primarily modified interaction strength through changes in surface charge and electrostatic repulsion, while fibril crowding, physical entanglement, and network connectivity remained largely preserved. Some aspects of the present results differ from behaviour reported for dilute, highly charged, or chemically modified nanocellulose systems. In particular, the absence of pronounced multi-regime flow transitions, the relatively limited changes in relaxation behaviour, and the persistence of weak-gel characteristics across most formulations contrasted with studies where polymer addition, ionic conditions, or surface charge produced more extensive rheological transformations (Beuguel et al., 2018; Wattana et al., 2025). These differences likely arose from the highly concentrated nature of the present suspensions. In dilute suspensions, rheology is strongly influenced by individual fibril mobility and electrostatic interactions, whereas the present suspensions were dominated by fibril crowding, physical entanglement, and constrained collective motion. Under these conditions, additives such as PEG likely just modified local interactions strength, while NaOH altered network connectivity likely through swelling-induced disruption, and pH adjusted electrostatic interactions without fundamentally changing the network architecture. This can explain why the suspensions retained weak-gel characteristics across most formulations despite substantial reductions in stiffness and yield stress. From a processing perspective, PEG-induced behaviour may be advantageous in coating, casting, and printing operations where improved flowability is required without substantial loss of post-deposition structural integrity. While NaOH would be expected to facilitate pumping, mixing, and spreading operations, although the accompanying loss of network stiffness and structural integrity may reduce shape retention following deposition. The comparatively modest effects of pH adjustment suggested that electrostatic regulation alone may provide a means of fine-tuning rheological properties.

Conclusion

This study successfully achieved its objective of establishing a quantitative rheological framework of concentrated CNF suspensions by evaluating the effects of CNF concentration, PEG, NaOH, and pH on flow behaviour, viscoelasticity, yielding, and nonlinear deformability. The results consistently showed that CNF concentration and NaOH addition were the dominant factors governing suspension's rheology, while PEG and pH primarily acted as secondary modifiers of network strength. Statistical analysis further confirmed these trends across both steady-shear and oscillatory rheological parameters. The results reflected that concentrated CNF rheology was governed by the balance between fibril connectivity, interaction strength, swelling, and network deformability. Increasing CNF concentration strengthened the percolated fibrillar network and enhanced resistance to flow and yielding, whereas PEG and NaOH modified the network through fundamentally different mechanisms. PEG primarily altered local inter-fibrillar interactions and produced a saturation-type response, while NaOH induced substantial structural modification likely through swelling and disruption of hydrogen-bond-mediated

connectivity. Consequently, the rheological properties could be systematically tuned across a broad range of stiffness, flowability, and deformability relevant to concentrated cellulose processing systems. Despite the comprehensive rheological characterisation achieved under controlled laboratory conditions, several limitations remain. In particular, the proposed PEG–NaOH interaction mechanisms were interpreted from rheological behaviour and would benefit from complementary microstructural and spectroscopic characterisation. Future work should also establish direct links between suspension's rheology, processing behaviour, structural evolution, and the properties of the resulting cellulose-based materials.

This work provided a mechanistic understanding of how concentration, alkalinity, and polymer additives govern the rheological behaviour of concentrated CNF suspensions. These findings contributed to the rational design of cellulose-based formulations and provided a foundation for optimising coating, printing, casting, and other scalable manufacturing processes involving concentrated CNF systems.

Statements and Declarations

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Competing Interests

The authors declare no conflict of interest. The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

Study's conception and design, writing the draft of the manuscript, methodology, data collection, formal analysis, and data curation were done by Shadi G. Mehmandoust Olya and were reviewed and supervised by Thomas Rainey. All authors read and approved the final manuscript.

Data Availability

The datasets generated and analysed during the current study are available from the corresponding author on reasonable request. Raw rheological data and processed datasets are stored in institutional repositories and laboratory records.

Ethical Approval

Not applicable. The research is not covered by any regulation, and formal ethical approval is not required.

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