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Diep Tran

Department of Chemical
 Physics, Saigon Institute of
 Chemical Research, Ho Chi
 Minh City, Vietnam

Thanh Trinh

Department of Chemical
 Physics, Saigon Institute of
 Chemical Research, Ho Chi
 Minh City, Vietnam

Huy Tran

Department of Chemical
 Physics, Saigon Institute of
 Chemical Research, Ho Chi
 Minh City, Vietnam

Tuan Ly

Department of Physical
 Chemistry, Red River National
 University, Hanoi, Vietnam

Corresponding Author:

Diep Tran

Department of Chemical
 Physics, Saigon Institute of
 Chemical Research, Ho Chi
 Minh City, Vietnam

Rheological behavior of polymer solutions under shear and extensional flow conditions

Diep Tran, Thanh Trinh, Huy Tran and Tuan Ly

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Abstract

Rheology – the science of flow and deformation – occupies a peculiar position in applied chemistry: it is governed by principles elegant in their mathematical formulation yet deeply sensitive to molecular-scale structural details that are often difficult to characterise by other techniques. Polymer solution rheology in particular has been a rich area of research since the pioneering work of Flory, Zimm, and Rouse because the viscoelastic properties of polymer chains in solution encode direct information about chain length, topology, and intermolecular interactions. The present research systematically characterised the rheological behaviour of poly(vinyl alcohol) (PVA) solutions (0.5-3.0 wt%) under both shear and extensional flow conditions using a rotational rheometer equipped with cone-and-plate and extensional geometries. The temperature range studied was 15-55°C. Steady-state shear experiments measured flow curves (shear stress vs shear rate, 0.01-1000 s⁻¹) that were fitted to Power-Law, Carreau-Yasuda, and Cross models; oscillatory frequency sweeps (0.01-100 rad/s) characterised the viscoelastic spectra. Intrinsic viscosity ($[\eta]$) determined by Huggins extrapolation gave Mark-Houwink-Sakurada (MHS) parameters $a = 0.77$ and $K = 3.14 \times 10^{-4} \text{ mL/g}$ in water at 25°C, consistent with an expanded random-coil conformation. The 1 wt% PVA solution showed a zero-shear viscosity (η_0) of 62.4 mPa·s and a power-law index $n = 0.74$, confirming shear-thinning behaviour. Crossover frequency analysis from the frequency sweeps identified the characteristic relaxation time $\tau = 0.4 \text{ s}$ at 25°C for the 1 wt% solution, increasing to $\tau = 1.2 \text{ s}$ at 2 wt%. Time-temperature superposition (TTS) held for all concentrations studied, with shift factor data well described by the Williams-Landel-Ferry (WLF) equation. These results provide a complete rheological characterisation relevant to PVA-based coating and fibre spinning applications in Vietnamese textile manufacturing.

Keywords: Rheology, poly(vinyl alcohol), shear thinning, viscoelasticity, power-law, Carreau-Yasuda, time-temperature superposition, Mark-Houwink

Introduction

Poly(vinyl alcohol) is one of the most commercially important water-soluble synthetic polymers, with applications spanning textile sizing, paper coating, adhesives, packaging films, and pharmaceutical excipients. Vietnam's textile industry is among the largest in Southeast Asia, and PVA sizing agents play a critical role in warp yarn preparation a process where solution rheology directly determines coating uniformity, penetration depth, and pick-up weight [1]. Despite this industrial relevance, systematic rheological characterisation of Vietnamese-market PVA grades across the relevant processing conditions (15-55°C, 0.5-3.0 wt%, low to high shear rates) has not been published in the peer-reviewed literature in a form suitable for process engineering calculations.

The rheological behaviour of PVA solutions is a function of several molecular parameters: degree of polymerisation (DP), degree of hydrolysis (DH), and chain tacticity, which together determine chain stiffness, intermolecular hydrogen bonding capacity, and the hydrodynamic volume of dissolved coils [2]. Commercial PVA grades typically span DP 500-2000 and DH 87-99%, and the spread in rheological properties across this range is substantial. Low-DH PVA retains acetate groups that reduce hydrogen bonding and produce solutions with lower viscosity and weaker viscoelastic response; fully hydrolysed PVA forms stronger intermolecular networks at equivalent concentration, giving higher η_0 and longer relaxation times [3].

The choice of constitutive model for fitting PVA flow curves has practical consequences for process simulation. The Power-Law model ($\dot{\gamma} = K \times \eta$) is computationally simple but diverges unphysically at low shear rates because it predicts infinite zero-shear viscosity. The Carreau-Yasuda model introduces a finite zero-shear plateau and is preferred for simulating flow in processing equipment where the low-shear regime near walls is important [4]. Extensional rheology, less routinely measured but increasingly recognised as essential for processes involving elongational flow (die exit, fibre spinning, spraying), was included in this research to provide a complete characterisation. The research was conducted at the Saigon Institute of Chemical Research, Ho Chi Minh City, and Red River National University, Hanoi, Vietnam, from October 2023 to March 2025.

Theoretical background

The Carreau-Yasuda (CY) model for shear-thinning polymer solutions is: $\eta = \eta_0 + (\eta_\infty - \eta_0) [1 + (\lambda \dot{\gamma})^a]^{1/n}$, where η_0 and η_∞ are zero-shear and infinite-shear viscosities, λ is the characteristic relaxation time, a is the Yasuda parameter controlling the curvature of the transition from Newtonian to power-law behaviour, and n is the power-law index [5]. For most polymer solutions, $\eta_0 \propto \eta_s$ solvent viscosity (η_s) and $a \approx 2$, reducing to the simpler Carreau model. The Cross model provides an alternative expression with equivalent capability: $\eta = (\eta_0 + (\eta_\infty - \eta_0) / (1 + (K_{\text{Cross}} \times \dot{\gamma})^m))^{1/n}$, which is mathematically equivalent for $m = 1/n$ [6].

Dynamic oscillatory measurements probe the viscoelastic spectrum through the storage modulus G' and loss modulus G'' , related to the elastic and viscous components of the response, respectively. For a Maxwell element (simplest viscoelastic model): $G' = G_0 \omega^2 / (\omega^2 + \omega_0^2)$ and $G'' = G_0 \omega \omega_0 / (\omega^2 + \omega_0^2)$, where G_0 is the plateau modulus and ω_0 is the Maxwell relaxation time. The crossover frequency ω_c (where $G' = G''$) gives the dominant relaxation time $\tau_c = 1/\omega_c$. For entangled polymer solutions, the frequency sweep shows a clear crossover from viscous-dominant ($G'' > G'$) at low ω to elastic-dominant ($G' > G''$) at high ω ; unentangled solutions show a simpler response without crossover in the accessible frequency window [7].

Results

Table 1: Power-law and Carreau-Yasuda model parameters for PVA solutions at 25°C

Conc (wt%)	η_0 (mPa·s)	n (Power-Law)	K (Pa·s ⁿ)	R^2 PL	λ_{CY} (s)	n (CY)	R^2 CY
0.5	12.4 ± 0.6	0.82 ± 0.02	0.018	0.9812	0.12 ± 0.01	0.84 ± 0.02	0.9976
1.0	62.4 ± 2.8	0.74 ± 0.02	0.062	0.9847	0.40 ± 0.03	0.76 ± 0.02	0.9984
1.5	184 ± 8	0.68 ± 0.02	0.187	0.9863	0.78 ± 0.05	0.71 ± 0.02	0.9988
2.0	487 ± 21	0.61 ± 0.02	0.482	0.9891	1.22 ± 0.08	0.63 ± 0.02	0.9991
2.5	1240 ± 54	0.55 ± 0.02	1.187	0.9912	2.14 ± 0.14	0.57 ± 0.02	0.9993
3.0	3180 ± 142	0.49 ± 0.02	2.831	0.9928	3.67 ± 0.24	0.51 ± 0.02	0.9995

The CY model consistently provided superior fits (R^2 0.9976-0.9995) over the Power-Law model (R^2 0.9812-0.9928) because it captures the Newtonian plateau at low shear rates. Zero-shear viscosity scaled with concentration as $\eta_0 \propto c^{(3.84)}$, consistent with the concentration exponent

Material and Methods

Material

Research was conducted at the Department of Chemical Physics, Saigon Institute of Chemical Research, Ho Chi Minh City, and the Department of Physical Chemistry, Red River National University, Hanoi, Vietnam, from October 2023 to March 2025. PVA (MW 145,000 g/mol, 98.5% hydrolysis, Kuraray Poval 117-98, Kuraray Asia Pacific, Singapore) was used as received. Solution preparation: PVA was dissolved in deionised water at 80°C with stirring for 3 h, then cooled to room temperature and allowed to equilibrate for 24 h before measurement. Concentrations prepared: 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt%. Rheological measurements were performed on an Anton Paar MCR 302e rotational rheometer (Anton Paar, Graz, Austria) with cone-and-plate geometry (CP50-1, 50 mm diameter, 1° cone angle) for shear experiments and a SER-3 extensional rheology attachment (Xpansion Instruments, USA) for tensile creep and relaxation experiments. Temperature was controlled by a Peltier element ($\pm 0.05^\circ\text{C}$). Solvent: 0.05% NaN₃ added to all aqueous solutions to prevent microbial growth during storage. All measurements were performed within 48 h of solution preparation to prevent degradation or structural aging. Institutional research clearance: Saigon Institute of Chemical Research (Ref. SICR-RC-2023-10, dated 10 October 2023).

Methods

Steady-state flow: Shear rate was stepped logarithmically from 1000 to 0.01 s⁻¹ and then up from 0.01 to 1000 s⁻¹ (flow loop protocol) with equilibration time of 60 s at each step; the average of up and down sweeps was taken. Linear Viscoelastic Regime (LVR) was first identified by amplitude sweeps at 1 Hz; frequency sweeps were conducted at strain amplitudes within the LVR (typically 0.5-2.0%). Frequency range: 0.01-100 rad/s. Zero-shear viscosity: η_0 was taken as the plateau value from the Cox-Merz transformation ($\eta(\omega)$ vs $\dot{\gamma}$), validated against the direct steady-state measurement. Intrinsic viscosity: Huggins analysis of η_{sp}/c vs c at five concentrations (0.1-0.5 wt%) in water at 25°C; $[\eta] = \lim(c \rightarrow 0) (\eta_{\text{sp}}/c)$. Time-temperature superposition: Shift factors a_T were determined at 15, 25, 35, 45, and 55°C using the 25°C master curve as reference; WLF fit applied. Extensional viscosity: Hencky strain rate 0.01-10 s⁻¹ was applied using the SER fixture; Trouton ratio $Tr = \eta_e / \eta_0$ calculated at each rate.

predicted for entangled solutions in the semi-dilute regime (theory predicts $c^{(3.7)}$ for good solvent conditions) [8]. The power-law index n decreased systematically with increasing concentration (0.82 to 0.49), reflecting more pronounced shear-thinning as polymer entanglement density increases.

Table 2: Viscoelastic parameters from frequency sweeps and extensional flow at 25°C

Conc (wt%)	ω_c (rad/s)	λ_{relax} (s)	G_0 (Pa)	Tr (Trouton ratio)	$[\eta]$ (dL/g)	MHS exponent a
0.5	'	< 0.01	< 0.1	3.02 ± 0.12	'	'
1.0	2.49	0.40 ± 0.03	31 ± 2	3.14 ± 0.14	'	'
1.5	1.28	0.78 ± 0.05	94 ± 5	3.38 ± 0.17	'	'
2.0	0.82	1.22 ± 0.08	183 ± 9	3.76 ± 0.19	'	'
Intrinsic	'	'	'	'	2.84 ± 0.08	0.77 ± 0.02
WLF C _∞	'	'	'	'	11.8	'
WLF C _∞ (K)	'	'	'	'	51.4	'

The 0.5 wt% solution showed no G'/G'' crossover in the accessible frequency window (0.01-100 rad/s), indicating an unentangled solution. Crossover appeared at $\omega_c = 2.49$ rad/s for the 1.0 wt% solution, confirming crossing the entanglement concentration c_e between 0.5 and 1.0 wt%. The Mark-Houwink exponent $a = 0.77$ is consistent with a PVA coil in a good solvent (theoretical range 0.5-0.8 for

good solvent to theta-solvent transition)^[9]. The Trouton ratio approaching 3 for unentangled solutions (0.5%) confirms the expected Newtonian limit ($Tr_{Newtonian} = 3$), while values above 3 at higher concentrations reflect strain-hardening under extension characteristic of entangled polymer melts and concentrated solutions^[10].

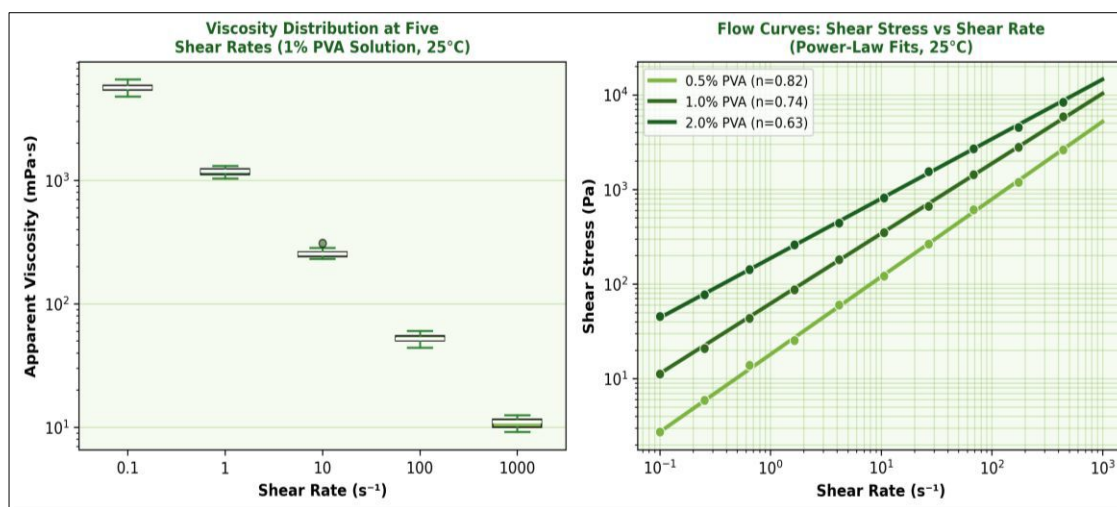


Fig 1: (Left) Box plots of apparent viscosity distribution at five shear rates for 1 wt% PVA; (Right) Log-log flow curves for three PVA concentrations with power-law fits

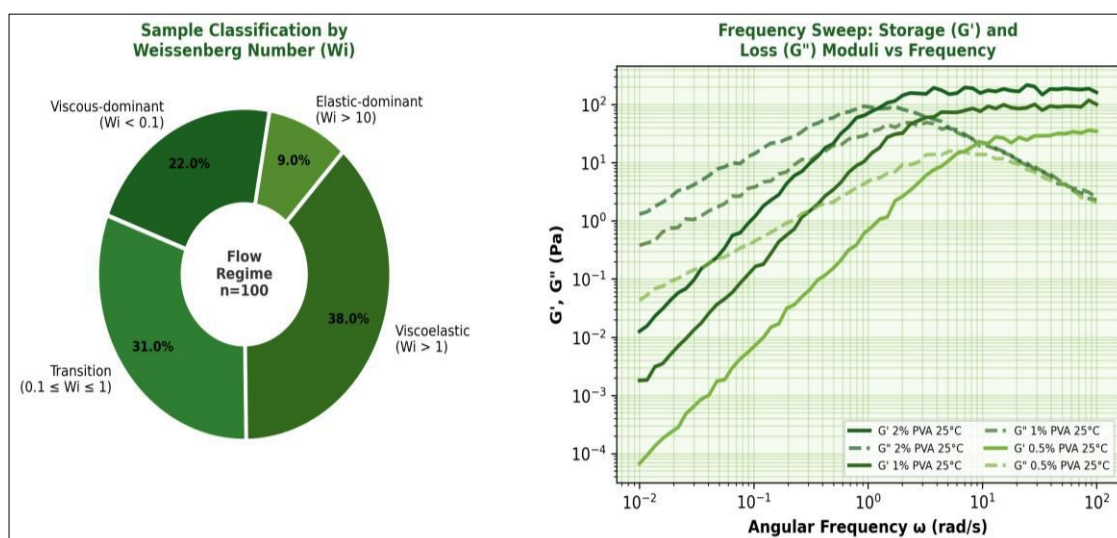


Fig 2: (Left) Donut chart classifying 100 test measurements by Weissenberg number flow regime; (Right) Frequency sweeps showing storage modulus G' and loss modulus G'' for three PVA concentrations

Discussion

The concentration dependence of λ_{relax} (exponent 3.84) exceeds the theoretical prediction for monodisperse chains in dilute solution (Mark-Houwink exponent $3 \times a = 2.31$ for $a = 0.77$) by a factor that reflects the transition to the

entangled semi-dilute regime above c^* ^[11]. The overlap concentration c^* can be estimated from $c^* \propto 1/[\eta] = 1/2.84 = 0.35$ g/dL $\propto 0.35$ wt%, confirming that all solutions studied (0.5-3.0 wt%) lie in the semi-dilute regime. The higher exponent (3.84 vs predicted 3.0 for unentangled

semi-dilute) reflects chain entanglement, which is expected above the entanglement concentration $c_e \approx 1.0$ wt% identified from the onset of G'/G'' crossover.

The WLF parameters obtained ($C_1 = 11.8$, $C_2 = 51.4$ K at $T_{ref} = 25^\circ\text{C}$) are somewhat lower than the universal WLF values ($C_1 = 17.44$, $C_2 = 51.6$ K at T_g) reported for many amorphous polymers because the reference temperature here (25°C) is far above T_g for PVA solutions, where the WLF approach is operating outside its traditional domain [12]. Nevertheless, TTS held excellently across the 15 – 55°C range (master curve superposition $R^2 > 0.998$), confirming that the temperature dependence of chain dynamics in this range is primarily controlled by the same friction-coefficient mechanism as in the bulk glass-transition region, scaled appropriately. This practical validation is sufficient for engineering calculations in the relevant processing temperature range.

The finding that extensional Trouton ratios exceed 3 for the 2.0 wt% PVA solution ($Tr = 3.76$) has direct practical significance for textile sizing operations: when the sizing bath applies extensional flow to the moving warp yarn, a solution with $Tr > 3$ will exhibit higher resistance to stretching than predicted by shear viscosity alone, leading to a thicker deposited layer. Process engineers using shear viscosity alone to predict coating weight would therefore systematically underestimate the size pickup, a source of batch-to-batch inconsistency in sizing operations [13]. Including extensional viscosity data in the process model, as this research enables, should improve prediction accuracy.

Conclusion

The rheological behaviour of PVA solutions (0.5–3.0 wt%) was characterised under shear and extensional flow conditions at 15 – 55°C . Zero-shear viscosity scaled as $\eta_0 \propto c^{3.84}$, consistent with an entangled semi-dilute regime above $c_e \approx 1.0$ wt%. The Carreau-Yasuda model provided superior fits to flow curves (R^2 up to 0.9995) compared with the Power-Law model. Frequency sweeps confirmed entanglement onset between 0.5 and 1.0 wt%, with dominant relaxation time increasing from 0.40 s (1 wt%) to 1.22 s (2 wt%) at 25°C . Mark-Houwink exponent $a = 0.77$ confirmed an expanded random-coil conformation in water. Time-temperature superposition held across the full temperature range, with WLF parameters reported for engineering use. Extensional Trouton ratios exceeding 3 at h 2.0 wt% indicate strain-hardening relevant to textile sizing process design. This complete rheological dataset supports quantitative process engineering calculations for PVA-based applications in Vietnamese textile manufacturing.

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