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Volatile dripping onto substrate (vDoS) extensional rheology of viscoelastic polymer solutions

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ABSTRACT

Extensional flow properties of volatile polymer solutions govern many industrially-relevant coating processes, but existing instrumentation lacks the environmental control necessary to control evaporation. To mitigate evaporation during volatile dripping-onto-substrate (vDoS) extensional rheology measurements, we developed a chamber to enclose the sample in an environment saturated with solvent vapor. We validated the vDoS device by measuring a model high molecular weight polyethylene oxide (PEO) in various organic solvents both inside and outside of the chamber. Evaporation substantially increased the extensional relaxation time λ_E for PEO in volatile solvents like dichloromethane (DCM) and chloroform. PEO/chloroform solutions displayed an over 20-fold increase in λ_E due to the formation of an evaporation-induced surface film; evaporation studies confirmed surface features and skin formation reminiscent of buckling instabilities commonly observed during drying in polymer solutions. Finally, the relaxation times of semi-dilute PEO/chloroform solutions were measured with environmental control, where λ_E scaled with concentration by the exponent $m=0.62$. These measurements validate the vDoS device by confirming that chloroform is a good solvent for PEO, with a Flory exponent of $\nu=0.54$. Our results demonstrate the first environmental control of evaporation during DoS extensional rheology, and provide guidelines establishing when environmental control is necessary to obtain accurate rheological parameters.

Introduction

Extensional flows play an important role in the transfer,¹ deposition, and breakup of low-viscosity volatile fluids in industrial processes from coating^{2,3} and inkjet printing^{4,5} to fuel injection.⁶ Complex flows like forward roll coating³ and spraying^{7,8} generate droplets via the extension and breakup of filaments. Volatile organic solvents are often used in these industrial processes to dissolve formulation components and enable facile drying of coatings once deposited.^{9–11} In addition to the applied processing parameters, the fluid viscoelasticity and corresponding extensional rheological properties dictate the fraction of fluid that breaks up into droplets, the timescales for breakup, and the droplet size distribution.⁷ These rheological parameters can thus be used to quantify the coatability and sprayability of macromolecular solutions,^{12–14} which when paired with the rate of solvent evaporation, largely dictate the coating quality.¹⁵ Although properties like shear viscosity (η) play a role in governing these flows, counterparts like extensional viscosity (η_E) determine the final breakup of fluid droplets. Additionally, the extensional viscosity in dilute polymer solutions is often orders of magnitude larger than the shear viscosity,^{2,16} a property which can be detrimental in coating and printing applications. As extensional flows impart deformations that disrupt the structure of complex fluid elements like polymer coils more substantially than in the analogous shear flows,^{17,18} extensional rheology may also be more indicative of performance in coating processes for low-viscosity fluids. The prevalence of extensional flow in industrial processes and its strong impact on polymer conformation thus makes extensional rheology particularly useful in measuring fundamental material properties of complex fluids and in guiding sample formulation prior to scale-up.

Rheological parameters like extensional viscosity and relaxation time (λ_E) that are useful in characterizing these flows cannot be predicted by shear behavior alone.^{2,19} While uniaxial extensional flow can be generated by a microfluidic device²⁰ or a jet,^{16,21} both of these techniques use custom-fabricated devices, requiring *a priori* knowledge of material properties of the fluid like extensional viscosity to determine the extension rates that occur. The extension rate of a fluid in a microfluidic device or a jet is dependent on the size of the custom-built channel or nozzle,^{21,22} so extraction of material properties can be a complicated, iterative process. Furthermore, these techniques often produce mixed shear and extensional flows, which makes distinguishing the specific impact of extensional forces challenging.

A technique to generate a more well-defined extensional flow in low-viscosity fluids is capillary-driven thinning and breakup of a stretched liquid bridge. Here, a liquid bridge self-thins and breaks up in the absence of active external forces.^{22,23} Depending on the balance of inertial, viscous, elastic, and capillary forces on the thinning liquid bridge, the minimum radius of the liquid bridge, R , evolves in time following scaling laws corresponding to a range of flow regimes. The dimensionless Ohnesorge

number, Oh , describes the balance of viscous to inertial and surface tension forces, given by:

$$Oh = \frac{\eta}{\sqrt{\rho\sigma R_0}} \quad (1)$$

where η , ρ , and σ are the solution viscosity, density and surface tension respectively, and R_0 is the initial radius of the liquid bridge, typically the radius of the nozzle or plates used to generate the bridge. For low-viscosity fluids ($Oh < 1$), thinning is expressed as a balance between inertial and capillary forces, known as inertio-capillary (IC) thinning. When $Oh > 1$, viscous forces become important and visco-capillary (VC) thinning occurs. For fluids with significant elasticity such as polymer solutions, elastic forces can begin to dominate over inertial and viscous forces during thinning, causing a transition into the elasto-capillary (EC) regime. Expressions that mathematically describe the thinning phenomena in each regime can subsequently be used to extract a range of rheological and processing parameters, like the extensional relaxation time λ_E or the “breakup” or pinch-off time at which the filament ruptures, t_b .^{224–26}

Mathematical descriptions of capillary self-thinning phenomena depend on assumptions of fixed endpoints, homogeneous composition of the liquid bridge, and steady thinning unperturbed by oscillations of the free surface. The unstable liquid bridge is typically formed in an instrument like the Capillary Breakup Extensional Rheometer (CaBER)^{27–29} via the rapid separation of two plates. However, low-viscosity samples often thin on timescales similar to the time required for plate separation, preventing formation of a self-thinning liquid bridge.³⁰ Furthermore, rapid plate separation can cause severe inertial effects,^{2,16,31,32} which are exacerbated by the low surface tensions associated with solutions formed in organic solvents. Evaporation is a further concern in measuring volatile systems,^{5,33} given that the CaBER plates are not well-sealed to the ambient environment. While custom-built CaBER instruments have introduced chambers with better sealing for temperature control,^{34,35} no attempts have been made to utilize these chambers for control of evaporation.

An alternative to CaBER is the recently-developed dripping-onto-substrate (DoS) rheometry technique.^{23,32} In the DoS method, the unstable liquid bridge is generated via the slow dripping of a single droplet onto a substrate. This technique enables measurement of complex fluids in small volumes ($\sim 10 \mu\text{L}$), reducing use of expensive sample components, mitigating pre-deformation, and minimizing inertial effects, which allows for the measurement of low surface-tension, low-viscosity systems. By directly mounting the syringe above the substrate,³⁶ contact between the sample and excess tubing used in the standard DoS instrumentation^{23,32} can be eliminated, preventing leaching issues from the use of organic solvents and further reducing sample volume. However, the small volume and high surface area-to-volume ratio of the drop exacerbates evaporation effects in volatile systems, and current DoS instrumentation to-date has not employed environmental control.^{5,23,36,37}

While most DoS experiments to-date focus on aqueous systems, recent work demonstrates use of the DoS technique to measure complex fluids in solvents with moderate boiling points ($T_{BP} \approx 80^\circ\text{C}$) like methyl ethyl ketone⁵ and ethyl acetate.³⁸ These studies attempted to limit evaporation by performing trials quickly to minimize the time that the sample contacts the air. However, neither work quantified or estimated evaporation effects, and even if this type of approach was successful in reducing evaporation for these particular systems, this method can likely be used only for complex fluids dissolved in moderately volatile solvents. As the evaporation rate is a central consideration in selecting processing parameters for coating processes incorporating volatile solvents,^{39,40} these volatile coatings can only be studied by controlling evaporation to the environment. Furthermore, without a method of true environmental control, the effect of evaporation on extension cannot be easily separated from the effect of flow rate. Previous work with CaBER by Sousa and coworkers^{33,41} incorporates true environmental control by suspending the aqueous samples in an oil bath, but this method introduces an oil-water interface which further affects liquid bridge thinning⁴² and is furthermore unsuitable for samples miscible in oil.

As such, capillary thinning of dilute polymer solutions has yet to be characterized in a geometry with a free surface at which the rate of evaporation can be controlled, so capillary thinning extensional rheometry has largely been limited to studying solvents with relatively high boiling points ($\sim 80^\circ\text{C}$ and above). In addition, there has been no study of the coupling effects of evaporation and extension in such systems. Evaporation can concentrate the sample or cause surface inhomogeneities like films, similar to those observed in electro-spinning^{43,44} and in sessile drops,^{45,46} which would affect the thinning behavior of the liquid bridge even in the dilute regime.

To accurately measure dripping-onto-substrate (DoS) extensional rheology in complex fluids dissolved in volatile organic solvents for the first time, we developed a direct-mount DoS device,³⁶ which was further adapted to enclose the liquid bridge in an environmental control chamber to minimize evaporation. To validate the instrument and examine evaporative effects, a high-molecular weight polyethylene oxide (PEO, $M_w = 10^6 \text{ g/mol}$) sample was examined in solvents of varying quality and volatility. PEO was selected as a model system due to its extensive characterization in dilute and semi-dilute aqueous solutions via capillary thinning methods (CaBER and DoS).^{22,347–50} Here, the elasto-capillary (EC) thinning behavior^{22,348–50} of PEO was compared in the freely-evaporating vs. environmentally-controlled configurations of the instrument. Using a combination of DoS, surface tension measurements, and evaporation studies, we demonstrate the utility of the volatile DoS (vDoS) instrument for measuring accurate extensional rheology of polymers dissolved in highly volatile solvents. In addition

to identifying concentration changes induced by evaporation, these studies also reveal surface film formation in particular solutions during evaporation at ambient conditions. By assessing the impact of solvent evaporation on extension, we validate our technique for volatile DoS (vDoS) and establish guidelines for when environmental control during DoS extensional rheology is required for accurate measurements.

Results

vDoS environmental chamber development

A dripping-onto-substrate device consists of a dispensing system to extrude the drop which forms the liquid bridge and an imaging system to precisely measure the thinning profile of the bridge at high speed (Figure 1).

Figure 1. Schematic of the volatile DoS (vDoS) instrument with sacrificial solvent reservoir and environmental control chamber, adapted from Lauser et al.³⁶; see SI.2. To perform DoS measurements, the syringe pump is used to extrude a droplet from a needle with radius R_0 , which then forms a liquid bridge with height h upon contact with the substrate. A high-speed camera captures the evolution of the liquid bridge minimum radius R as the bridge thins in time. The environmental control chamber provides an atmosphere enriched in solvent vapor around the drop to prevent evaporation during this thinning process.

The DoS instrument used here consists of a 2600 lumen light source, a Chronos 1.4 high-speed camera capable of recording 38,000 frames per second, a syringe pump, and a syringe with a nozzle of outer radius R_0 . This syringe is mounted directly above the substrate, rather than using tubing as in other DoS instruments,⁴⁸ to minimize pre-deformation³⁶ and eliminate leaching of compounds from the tubing due to incompatibility with solvents used. To form the liquid bridge, the syringe pump is used to extrude a drop nearly until the point of contact with the substrate at a very low flow rate, typically below 0.1 mL/hr. To minimize fluid oscillations resulting from pump vibrations in this “direct mount” approach, the pump is subsequently turned off, and the pendant drop and substrate are brought into contact to form the liquid bridge.³⁶

To provide an atmosphere enriched in solvent vapor around the drop, a glass chamber was modified by adding a self-healing septum to the top, silicone sealant to the lid, and longer screws to attach the clamps for the lid and serve as internal fasteners. A custom platform was designed to fit inside of the chamber, 3D printed in nylon, and attached to new screws on the inside to support a miniature lab jack above the solvent reservoir. To make measurements with this instrument for volatile DoS (vDoS) (Figure 1), the environmental control chamber is placed beneath the syringe pump on anti-vibration slats to minimize mechanical interference, with the needle aligned to the septum on the top. After filling the reservoir with solvent, the chamber atmosphere is allowed to saturate with solvent vapor for ≥ 45 minutes prior to performing vDoS measurements. Evaporation studies (SI.10) on 3 mg/mL PEO in four solvents confirm that 45 minutes is sufficient to mitigate evaporation for timescales longer than required to perform the DoS measurement (SI.10).

Validation of vDoS device with PEO in various solvents

Capillary thinning and evaporation measurements of PEO in solvents of different quality and volatility demonstrate that the environmental control chamber is highly effective in limiting evaporation (Figure 2). Solvent quality was estimated via relative energy density (RED) values calculated from Hansen solubility parameters,⁵¹ where smaller values indicate better solvent quality; here, $RED \leq 1$ for each solvent with PEO, indicating good solvent quality. Chosen solvents include chloroform, dichloromethane (DCM), water, and N-methylformamide (NMF), with boiling points ranging from 40-183 °C (Table 1). Figure 2 shows representative vDoS trials and fits when the drop is enclosed inside of the chamber (● symbol) and when the drop is exposed to ambient conditions (□ symbol, ~23 °C, 40% relative humidity); 2D images during thinning in the closed configuration are shown inset for solutions experiencing the least (PEO/NMF) and most significant (PEO/chloroform)

evaporation effects. For raw data from all trials and reproducibility, see [SI.11](#). Representative radial evolution profiles are nearly identical between the open and closed configurations for water and NMF, the two least volatile solvents (Figure 2a,b); however, significant deviations in the thinning profiles are observed for PEO in DCM and chloroform (Figure 2c,d), where trials performed without environmental control show substantially longer extensional relaxation times (λ_E) and filament lifetimes (t_b).

Figure 2. Representative vDoS capillary thinning measurements of 3 mg/mL PEO in: a) water, b) NMF, c) DCM, and d) chloroform. Insets in b) and d) show 2D images of the thinning inside of the chamber at (from L to R) $R/R^* = 1$ (onset of EC regime), 0.7, 0.4 and 0.1. (a,b) As expected, no statistically significant difference in λ_E is observed for low volatility solvents (water, NMF); see Table 1. (c,d) In more volatile solvents (chloroform, DCM), pronounced differences in the thinning profiles and λ_E result between trials taken inside vs. outside the environmental control chamber.

All PEO solutions measured with environmental control display two distinct flow regimes; conversely, freely evaporating PEO/chloroform shows a broad transition between the flow behavior at early times and at long times. Given the low solvent viscosities and low PEO content (3 mg/mL), PEO solutions are expected to initially display inertio-capillary (IC) thinning ($Oh < 1$, Eqn. 1) prior to transitioning to an elastocapillary (EC) regime. The IC regime is governed by the Rayleigh time²⁵² ($t_R = \sqrt{\rho R_0^3 / \sigma}$) for a fluid with density ρ and surface tension σ . The evolution of the minimum radius R from its initial value R_0 during IC thinning is described by Equation 2:²²⁴²⁵⁵³

$$\frac{R}{R_0} = \alpha \left(\frac{t_c - t}{t_R} \right)^{\frac{2}{3}} \quad (2)$$

where α is a constant and t_c is a critical time corresponding to filament rupture, or in this case, a transition to EC thinning. Note that in Figure 2, t_c is fixed to zero and R is instead normalized to R^* , the radius at the onset of EC thinning, to enable straightforward comparison between solutions. In the initial flow regime ($t < 0$ in Figure 2), PEO self-thins in all solvents following a power law scaling at or near the characteristic value of $n = 2/3$ for IC thinning (Eq. 2). In the worst solvent (water), $n = 0.66 \pm 0.03$, whereas n increases slightly for PEO in the three better solvents ($n = 0.70$ - 0.74 , Table 1). With increasing Oh , the power law scaling of $n = 2/3$ for IC thinning increases, eventually reaching $n = 1$ for viscocapillary (VC) thinning ($Oh > 1$).²⁵⁴ For PEO in the three better solvents, n increases with solvent (and likely solution) viscosity, reflecting an increasing Oh .

Following the initial IC regime, pronounced EC thinning occurs in all PEO solutions measured both with and without environmental control. The EC regime is defined by the extensional relaxation time of the polymer chains in solution, λ_E . When this relaxation can be described reasonably well by a single exponential decay function,²²⁶⁵⁵ the liquid bridge thins as:

$$\frac{R}{R_0} \approx \left(\frac{GR_0}{2\sigma} \right)^{\frac{1}{3}} \exp\left(\frac{-t}{3\lambda_E} \right) \quad (3)$$

where G is the elastic modulus. Here, $(GR_0/2\sigma)^{1/3}$ is treated as a fitting constant, as is commonly done.²³³⁶

The extracted extensional relaxation times λ_E for PEO solutions in water are statistically similar for measurements taken inside and outside of the environmental control chamber (Figure 2a, Tables 1, S1), and are in quantitative agreement with previously published DoS results.²³³⁶ These prior studies did not incorporate environmental control, suggesting that ambient conditions are sufficient for measuring dilute aqueous polymers via DoS. Likewise, no statistically significant differences are observed between open and closed trials for solutions in NMF (Figure 2b, SI.3), a solvent with lower volatility than water (Table 1). Following Eqn. 3, the shallower slope in the fit region for PEO/NMF vs. PEO/water indicates that PEO in NMF exhibits longer relaxation times ($\lambda_E = 3.9 \pm 0.4$ ms vs. 2.9 ± 0.3 ms, respectively). The longer λ_E in NMF is likely due to both its higher viscosity and better solvent quality for PEO (lower RED value, Table 1).

However, when PEO is dissolved in more volatile solvents like chloroform and DCM, strong differences in extensional flow parameters are observed due to evaporation at ambient conditions. When PEO is dissolved in DCM, the filament lifetime t_b , or the time at which the filament breaks up, increases by roughly 40% when capillary thinning is performed outside of the chamber (Figure 2c). The resulting relaxation time is also 40% longer for trials measured in ambient conditions than for those extracted from analogous measurements incorporating environmental control ($\lambda_E = 4.7 \pm 1.2$ ms vs. 3.4 ± 0.2 ms), likely due to the higher solution concentration that results from solvent evaporation. The wider uncertainty associated with λ_E for trials outside of the chamber stems from large variation in the radial decay profiles between repeated trials (see SI.11); this variation is likely driven by non-uniform evaporative effects during thinning due to the lack of controlled environment (see Discussion, SI.8).

Evaporative effects during thinning are most significant for PEO in chloroform (Figure 2d), where both the average filament lifetime and average extensional relaxation time are over ten-fold longer for PEO in chloroform measured without vs. with environmental control (Table 1). The uncertainty in the extracted value of λ_E for trials outside of the chamber is nearly as large as λ_E itself, stemming from the drastically different thinning profiles obtained across trials (see SI.11). Notably, the trials recorded inside of the chamber exhibit highly reproducible thinning (SI.11). As such, uncertainties in λ_E for all trials conducted inside of the chamber are $\leq 10\%$ of λ_E . Furthermore, 2D images during thinning inside of the environmental control chamber follow the same progression for both PEO/NMF and PEO/chloroform (Figure 2 insets), suggesting that undesirable evaporative effects during thinning are successfully mitigated by use of the chamber - SI.8 shows differences in the 2D images during measurements performed outside of the chamber when evaporation is significant.

Interestingly, evaporative effects are substantially more pronounced in chloroform vs. DCM (20x vs. 1.4x increase in λ_E), despite the fact that DCM has a boiling point over 20 °C larger than chloroform (Table 1). Chloroform and DCM have nearly identical surface tensions (Table 1), suggesting that these differences are not driven by solvent surface tension. However, the average extensional relaxation time is $\sim 30\%$ longer in chloroform vs. DCM ($\lambda_E = 4.4 \pm 0.3$ ms vs. 3.4 ± 0.2 ms, respectively). Given that DCM and chloroform are good solvents for PEO and that λ_E directly scales with the solvent viscosity η_S ,⁵⁶ this difference is likely attributable to differences in η_S , which is $\sim 30\%$ higher in chloroform than in DCM (0.54 vs. 0.41 mPa·s, respectively). While chloroform and DCM are of similar quality for PEO, RED values (Table 1) and experiments⁵⁷⁵⁸ at this PEO molecular weight suggest that DCM is a slightly better solvent. Thus, we hypothesize that this apparent discrepancy in magnitude of evaporation effects and solvent volatility may result because of reduced PEO mobility in chloroform due to higher η_S , slightly poorer solvent quality, or a combination of both, to be explored further below.

Table 1. Average λ_E and n values for 3 mg/mL PEO solutions; ‘open’ indicates no environmental control whereas ‘closed’ occurs with the chamber sealed. Open and closed λ_E values are statistically similar for water and NMF, whereas chloroform and DCM solutions exhibit longer λ_E with the chamber open. Chloroform and DCM are more volatile (higher vapor pressures P_{vap} and lower boiling points T_{BP}), less viscous (η_S), and form lower surface tension ($\sigma_{solution}$) solutions than water and NMF. All three organic solvents are predicted to be better solvents than water for PEO, given relative energy density (RED) values calculated from Hansen solubility parameters (SI.6).

solvent	λ_{closed} [ms]	λ_{open} [ms]	n_{closed}	P_{vap} [bar]	T_{BP} [°C]	η_S [mPa·s]	$\sigma_{solution}$ [mN/m]	RED
water	2.87 ± 0.29	3.04 ± 0.24	0.66 ± 0.03	$3.2 \cdot 10^{-2}$	100	0.89	62 ± 1	1.03
NMF	3.94 ± 0.37	3.96 ± 0.43	0.74 ± 0.02	$3.4 \cdot 10^{-4}$	183	1.68	37 ± 1	0.74
DCM	3.35 ± 0.17	4.65 ± 1.25	0.70 ± 0.01	$5.7 \cdot 10^{-1}$	40	0.41	25 ± 2	0.67
chloroform	4.41 ± 0.27	93.2 ± 79.2	0.72 ± 0.01	$2.6 \cdot 10^{-1}$	61	0.54	29 ± 1	0.82

Concentration scaling in chloroform

As chloroform solutions display the most drastic evaporation effects, the extensional relaxation times of PEO/chloroform solutions were measured at a number of concentrations in the dilute and semi-dilute regimes to confirm that evaporation is sufficiently mitigated by the chamber. These measurements enable the solvent quality of chloroform to be determined via known scalings between concentration and λ_E , providing an additional metric by which to validate the environmental control capabilities of the vDoS sample environment. For semi-dilute, unentangled polymer solutions (SI.7, λ_E is predicted to scale as:⁵⁶

$$\lambda_E \approx \frac{\eta_s b^3}{kT} N^2 \phi^{(2-3\nu)/(3\nu-1)} \quad (4)$$

where N is the degree of polymerization, ϕ is the volume fraction of polymer, b is the statistical segment length,⁵⁹ kT is the thermal energy, and ν is the Flory exponent⁶⁰ with values from 0.5 (theta solvent) to 0.588 (good solvent).

As ϕ scales with the concentration c , solvent quality can be measured according to this prediction by fitting the average relaxation times to a power law $\lambda_E = Ac^m$, where $m = \frac{2-3\nu}{3\nu-1}$ and ranges from 0.31 (good solvent) to 1 (theta solvent). Here, the critical overlap concentration c^* marking the nominal onset of the semi-dilute regime was estimated using the intrinsic viscosity $[\eta]$ calculated from the Mark-Houwink-Sakurada equation, where $c^* \approx \frac{1}{[\eta]}$ (SI.7). As shown in Figure 3, for PEO in chloroform, $m = 0.62$, corresponding to a Flory exponent of $\nu = 0.54$. This finding is consistent with better solvation in chloroform than in water, where over a comparable concentration range, water is a theta solvent ($m = 1$, $\nu = 0.5$).⁴⁹ However, chloroform is still far from the ideal good solvent ($m = 0.31$, $\nu = 0.588$), which combined with its high vapor pressure may lead to enhanced evaporation effects and film formation on the free surface of the liquid bridge, causing dramatic differences between extensional relaxation times observed with and without environmental control.

Figure 3. Relaxation times for semi-dilute PEO/chloroform solutions scale with concentration as $\lambda_E \propto c^{0.62}$. Error bars reflect standard deviation in trials for a single concentration, whereas the grey area reflects 95% confidence intervals for the fit to average values.

We note that in Figure 3, m is fit including one point in the dilute regime, as c^* is an estimate and changes in scaling of λ_E with concentration do not always align perfectly with c^* .^{23,49} If only the four points above c^* are used to determine ν , a similar result is obtained ($\nu = 0.55$). Notably, dilute aqueous PEO scales similarly to the semi-dilute PEO/chloroform here, as $\lambda_E \propto c^{0.65}$ ($\nu = 0.535$). Although the scaling in Equation 4 is derived from a blob theory for semi-dilute, unentangled polymer solutions,⁵⁶ the stretching of polymer chains from extensional flow can lead to screening of excluded volume interactions,⁴⁹ potentially increasing the value of m (lowering ν) regardless of solvent quality for sufficiently stretched chains. Another consequence of these stretch-induced polymer chain interactions is that polymer solutions considered dilute based on their equilibrium conformation may significantly overlap, such that their relaxation times still scale according to the semi-dilute theory shown in Equation 4.^{23,47,49} However, regardless of whether the concentration scaling for PEO/chloroform ($\nu = 0.54$) is compared to aqueous dilute PEO ($\nu = 0.535$) or aqueous semi-dilute PEO ($\nu = 0.5$), chloroform is always the better solvent.

Surface effects in free chloroform evaporation

To further explore evaporative and free surface effects, we consider two possibilities: 1) that evaporation occurs homogeneously, where the sample uniformly concentrates with evaporation, or 2) inhomogeneously, where the polymer concentrates at the drop

surface and forms a viscoelastic film. Both homogeneous and inhomogeneous evaporation effects would increase the observed relaxation time. However, as chloroform is less volatile than DCM but exhibits more severe evaporation effects, a homogeneous increase in PEO concentration proportional to the solvent evaporation rate is insufficient to fully explain the order-of-magnitude difference in λ_E for trials in chloroform compared to DCM outside of the chamber. However, formation of a surface film or surface inhomogeneities during evaporation in dilute PEO/chloroform solutions could better explain these observations.

Time lapse videos during evaporation capture droplet surface features and surface tension evolution, confirming the formation of surface inhomogeneities in evaporating PEO/chloroform; for images showing film formation during DoS, see SI.8. The extracted value of the surface tension during evaporation outside of the chamber decreases continuously in time, but by only 10% in the first 35 s of evaporation (Figure S5). However, the 2D images shows clear evidence of a PEO surface film forming and contracting as solvent evaporates and the drop shrinks (Figure 4a). Notably, the formation of a surface film is evident from the start of the video ($t = 0$ s), suggesting that evaporative effects begin before the drop is fully formed. The wrinkling of the surface of the pendant drop is consistent with a buckling instability observed in the evaporation of sessile drops.^{45,46} Analogous time lapse images taken with the chamber closed show no evidence of surface film formation (Figure 4b), and virtually no change in surface tension is observed in time (SI.9).

Figure 4. Freely evaporating PEO/chloroform (3 mg/mL) forms a central dimple with radiating wrinkles, distorting the transmitted light. These irregularities are consistent with formation and buckling of a surface skin, as seen in sessile drops of evaporating polymer solutions.^{45,46}

Surface film formation is governed by a Péclet number $Pe = \frac{R_0 J}{D}$,⁴⁶ where R_0 is the initial drop or bridge size, J is the evaporative flux of solvent per unit area, and D is the polymer diffusivity in the solvent. Film formation in PEO/chloroform indicates a higher Péclet number than in PEO/DCM, as the evaporative flux of solvent pushing the polymer toward the droplet free surface outpaces polymer diffusion away from the surface. Without environmental control, J for dilute solutions is primarily determined by the solvent vapor pressure, confirmed by the faster drop evaporation times observed in PEO/DCM vs. PEO/chloroform (SI.10), suggesting that $J_{DCM} > J_{chloroform}$. As the initial drop sizes are equal, PEO diffusion from the surface must then be slower in chloroform than in DCM. Slower diffusion in chloroform is consistent with the slightly lower solvent quality of chloroform^{57,58} and reduced PEO mobility in chloroform due to higher η_s .

Discussion

The vDoS methodology presents the first environmental control to reduce evaporation in dripping-onto-substrate extensional rheology measurements of low-viscosity, volatile fluids. Aside from the use of an oil bath,³³ suitable only for immiscible samples, previous capillary thinning extensional rheology measurements of volatile systems rely on reducing measurement time to reduce evaporation.^{53,8} Thus in neither case can the severity of evaporation effects be quantified. Furthermore, while evaporation may be exacerbated by the small droplet volume in DoS measurements, comparative measurements of PEO/chloroform using CaBER (SI.13), which requires a larger volume of sample and has a smaller surface area to volume ratio, still show significant lengthening of the thinning process due to evaporation. Additionally, the step-strain required to form the liquid bridge in CaBER is unsuitable for measuring these low viscosity, low surface tension solutions, as clear oscillations

during thinning are observed in many CaBER trials (Figure S11). Therefore, surface film formation makes measuring the extensional rheology of polymer solutions in solvents like chloroform nearly impossible without environmental control.

Using the vDoS technique, extensional relaxation times for PEO in various solvents were measured to quantify evaporation effects. While solutions in both DCM and chloroform exhibited significant evaporation outside the environmental control chamber, chloroform solutions exhibited drastically larger evaporative effects, with an average increase in λ_E of 2000% for chloroform solutions compared to 40% for DCM solutions. These dramatic differences in evaporation in chloroform solutions were attributed to surface film formation, visually confirmed with additional DoS measurements (SI.8) and from time lapse videos during evaporation. Given the lower vapor pressure of chloroform vs. DCM, these results suggest that evaporation effects are a function of solvent quality and viscosity in addition to solvent volatility.

In open DoS measurements of PEO/chloroform, large deviations in the breakup and relaxation times, t_b and λ_E were observed, corresponding to a bimodal distribution of radial decay profiles (SI.11). One set of profiles exhibited λ_E values roughly double that of the trials taken inside of the chamber; in the other set, λ_E was more than an order of magnitude larger. To rationalize these results, we postulate two regimes of film formation. In the first regime, the film begins to form near the bottom of the pendant drop based on the greater curvature there, and near the interface with the needle, but does not yet enclose the entire drop. When capillary thinning is initiated by making contact between drop and substrate, the film may not coincide with the neck of the liquid bridge as it thins, and therefore may not substantially resist thinning. In the second regime, the film covers the entire drop, so the elasticity of the surface skin becomes the primary force resisting thinning. In this event, the radial decay of the liquid bridge slows down dramatically. The speed of film formation can be related to a critical Péclet number at which a film forms $Pe = \frac{R_0 J}{D}$.⁴⁶ This critical Péclet number can also be defined in terms of the initial solute concentration ϕ_0 and the critical concentration for film formation ϕ_g as $\frac{\phi_g - \phi_0}{1 - (\phi_0)\phi_0}$.⁴⁶ Given that drops of each PEO solution have the same initial size and concentration, and that evaporative flux is higher for DCM solutions than for chloroform solutions (SI.10), the formation of the film in chloroform solutions indicates slower diffusion of PEO, or a lower critical concentration of film formation. Because of the higher viscosity of chloroform, and the slightly lower quality of chloroform than DCM for high-molecular weight PEO,^{57,58} both lower mobility and lower solvent quality of PEO in chloroform are likely to play a role in the formation of the surface film.

While evaporation may not be a major concern for ambient, short timescale DoS measurements in solvents less volatile than water, the impact of evaporation on these measurements in volatile solvents cannot be predicted precisely either without knowing properties like the solvent quality, polymer diffusivity, and evaporative flux, or without explicitly controlling for evaporation phenomena. In addition to enabling measurement of volatile organic solutions, evaporative control is likely desirable for measuring solutions in relatively non-volatile solvents at elevated temperatures or for extended times, especially if these solvents do not dissolve their solutes well. Therefore, the vDoS technique provides an important new tool for measuring the extensional rheology of low-viscosity volatile systems, and for detecting and quantifying evaporation effects on the measured rheological parameters.

Methods

Materials

Polyethylene oxide ($M_w = 10^6$ g/mol, DP=22700) was purchased from Beantown Chemical. ACS-grade chloroform (Fisher Scientific), ACS-grade dichloromethane (DCM, Macron Chemical), 99% N-methylformamide (NMF, Sigma-Aldrich), and high performance liquid chromatography (HPLC)-grade water (Fisher Scientific) were used as-received. Solutions were prepared by dissolving powder in warm solvent, and shaking at 4 °C for 24 hrs. Low concentration PEO/chloroform solutions were prepared by dilution from a 3 mg/mL stock solution.

Dripping-onto-substrate (DoS) measurements

“Open” configuration trials were performed without the environmental control chamber shown in Figure 1. The approximate aspect ratio $\frac{h}{2R_0}$ was adjusted to ~ 1.4 , with R_0 fixed to 0.82 mm. While results for aqueous polymer solutions are nearly independent of syringe pump flow rate below 0.5 mL/hr,²³ trials conducted using the ‘direct mount’ approach (Figure 1) with the pump on exhibited inertially-driven oscillations on the liquid bridge surface (SI.4).³⁰ To remedy this problem, the pump is turned off prior to drop contact with the substrate and the stage is slowly moved to contact the drop, as previously described.³⁶

For all “closed” vDoS measurements in the chamber, the reservoir was filled with 100 mL solvent. Before sealing the chamber, the aspect ratio ($\frac{h}{2R_0}$) between the needle and substrate is adjusted using the camera. The aspect ratio was ~ 1.4 for all vDoS trials, with R_0 fixed to 0.82 mm. The chamber atmosphere was allowed to saturate with solvent vapor for 45 minutes before drop extrusion. This equilibration period was standardized across solvents for comparison purposes; however, longer equilibration periods reduced evaporation rates further (SI.10), enabling evaporation effects to be tuned. Evaporation rates were quantified via time-lapse videos of evaporating pendant drops, taken after the equilibration period (SI.10). The syringe was then

filled with sample and lowered to pierce the septum. As the stage could not be moved to meet the drop while in the chamber, the needle was instead slowly depressed to initiate substrate contact. This mode of operation was least prone to introducing surface oscillations of the liquid bridge,³⁰ likely due to mechanical dampening from the septum.

High-speed videos of the filament radial decay were recorded for all trials (open and closed configurations) at 11,800 fps, with a spatial resolution of 288 by 326 pixels. Individual frames were thresholded in ImageJ and analyzed in Matlab to extract values of the minimum radius in time; see SI.1 for more details. Extracted radii were normalized to the radius at the transition between IC and EC regimes, R^* . Despite the lower surface tension in the selected volatile solvents (Table 1), contributions from gravitational sagging are unimportant in the analyzed thinning processes; see SI.5 for Bond number calculations.

Parameter fitting, solvent quality analysis, and statistics

Extensional relaxation times were determined by fitting the elasto-capillary regime data to Equation 3 following a binning procedure; see SI.1 for details. Uncertainty is reported as the standard deviation of λ_E between trials, which was much larger than the fit uncertainties. Surface tension values were extracted from the pendant drop shape using an ImageJ plugin.⁶¹

Solvent quality was estimated using values of the relative energy density (RED) calculated from Hansen solubility parameters,⁵¹ where smaller values correspond to better solvents, and values larger than unity indicate poor solvent quality. Solvents were thus selected based on an RED value of ≤ 1 for the solvent and PEO. To determine the onset of the semi-dilute regime, the critical overlap concentration c^* was estimated for PEO in water ($c^* = 1.7$ mg/mL) and chloroform ($c^* = 1.0$ mg/mL) were estimated using intrinsic viscosity $[\eta]$ from the Mark-Houwink-Sakurada equation as $c^* \approx \frac{1}{[\eta]} = \frac{1}{KM_W^a}$. The values of K and a for PEO in chloroform were estimated based on published values of intrinsic viscosity of PEO in chloroform (see SI.7).^{62–64}

To assess if statistically significant differences resulted between freely evaporating and evaporation-controlled DoS measurements, two-sample, one-tailed Student's t -tests (assuming unequal variances) were performed, where values of λ_E were compared in the open and closed configuration. The null hypothesis was that the mean λ_E values were equal. As evaporation effects increase the timescales for thinning, the alternative hypothesis was that $\lambda_{open} > \lambda_{closed}$. Differences were determined to be statistically significant at the 95% confidence level based on p -values (see SI.3).

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Author contributions statement

B.P.R. performed all experiments, and analyzed data with assistance from M.A.C. B.P.R. and M.A.C. wrote the manuscript. All authors reviewed the manuscript.

Additional information

The authors declare no competing interests.

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