Fiber Spinning from Polymer Solutions

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ABSTRACT: The thinning of a cylinder of polymer solution in a volatile solvent is argued to be controlled by solvent diffusion through a dense polymer layer at the cylinder surface. That naturally leads to the exponential time dependence of cylinder radius that is observed in experiments using a fast camera, such as CaBER. The relaxation time is controlled by the thickness of the dense (and often glassy) polymer layer and the diffusion coefficient of solvent through that layer. If correct, this means that while CaBER is very useful for understanding fiber spinning, the relaxation time does not yield a measure of the extensional viscosity of polymer solutions in volatile solvents.

KEYWORDS: wet spinning, dry spinning, solvent evaporation, capillary breakup extensional rheometry, dripping on a substrate

Introduction

Cylindrical fibers are often spun from polymer solutions, with two broad categories of fiber spinning.[1] Dry spinning relies on evaporation of solvent to solidify the fiber,[2, 3] while wet spinning immerses the spun fiber into a nonsolvent for the polymer, in order to remove the solvent to solidify the fiber. In both cases, the only way for the solvent to leave the fiber is through the fiber surface, at radial position R. Whatever solvent molecules leave the fiber need to first diffuse to the fiber surface. As more solvent leaves, the polymer concentration at the fiber surface increases and the fiber radius decreases.[4] That naturally creates a concentration profile as a function of radial position in the fiber,[5] with the highest polymer volume fraction at the fiber surface, as seen in recent simulations [6] and in models of fiber spinning that include solvent evaporation.[7]

If the pure polymer had a glass transition temperature T_g below ambient temperature and did not crystallize, fiber spinning (either wet or dry) simply would not work, as the thinning of the fiber radius would continue until the fiber breaks. Hence fiber spinning from solution is done with polymers that have T_g above ambient. In this case the polymer concentration at the fiber surface can only increase until the surface concentration reaches ϕ_g, the polymer volume fraction with glass transition temperature coinciding with ambient temperature.[8] This solidification of the surface makes fiber spinning possible; the fiber then acts (from the outside) as a solid that can be easily handled to wind around rollers for stretching and calendering, etc. Such “skin” formation has been studied in detail with models[9-13] and clever proposed experiments[14] by Masao Doi and coworkers.

In this perspective, the consequences of the formation of a dense polymer layer at the fiber surface are considered. The dynamics of fiber thinning from polymer solutions with volatile solvents are argued to be controlled by solvent diffusion through the dense polymer layer at the surface, with no connection to the extensional viscosity of the polymer solution.

Fiber concentration profile and solvent escape

Whether formed by dry spinning or wet spinning, the concentration profiles of polymer and solvent inside the fiber are quite similar, shown schematically in Figure 1. There is a thin surface layer (of thickness δ) with $\phi > \phi_g$ that is effectively a solid shell of glassy polymer at the fiber surface.[15] Once formed, the exodus of remaining solvent in the fiber is limited by 1-dimensional diffusion of solvent through the glassy layer.[16, 17]

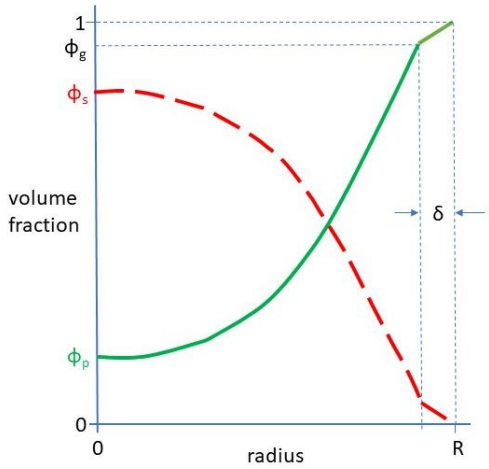


Figure 1. Schematic of the concentration profiles of polymer (in solid green) and solvent (in dashed red) during fiber spinning after the glassy layer of polymer has formed at the fiber surface. For polymer volume fraction $\phi > \phi_g$ the material is glassy and effectively solid, with thickness δ. Once formed, the glassy layer restricts further solvent from leaving the fiber. In dry spinning, this solvent diffusion is the rate-limiting step for solvent evaporation from the fiber surface. For wet spinning, a nearly identical concentration profile is formed, with diffusion through the glassy polymer layer limiting the solvent escape from the fiber into the surrounding non-solvent.

Usually both dry and wet fiber spinning are done with polymers that can crystallize and once the glassy layer is formed the fiber can be strongly stretched, promoting polymer crystallization and creating an anisotropic morphology that improves tenacity (tensile strength in the fiber direction). However, polymers are never fully crystalline, with many crystallites embedded in a continuous amorphous matrix of polymer and solvent[18] (solvent is excluded from the crystallites). The presence of crystallites slows solvent diffusion somewhat (by as much as a factor of 2 or 3)[19] since solvent molecules then need to take a longer path through the amorphous phase to reach the surface and evolve. However, that is a very weak effect compared with reaching the glass transition of the amorphous phase, which slows solvent diffusion by many orders of magnitude, with solvent diffusion coefficient in glassy polymers[20] of order 10^{-10} cm^2/s compared to solvent diffusion coefficients of order 10^{-5} cm^2/s in polymer solutions far above T_g.[21]

There is a natural time scale for solvent diffusion through the glassy polymer layer at the fiber surface.[9]

$$\tau = \frac{\delta^2}{2D} \tag{1}$$

D is an effective diffusion coefficient of solvent through the thin glassy layer (of thickness δ) at the fiber surface.[22] This limits the thinning of the fiber radius *R* to an exponential decay.[23]

$$R \sim \exp\left(-t/\tau\right) \tag{2}$$

Recently, devices that study such thinning of the fiber radius have been developed, using a fast camera.[24-31] Early work of Stelter, et al. focused on polymers with T_g far above ambient, such as polyacrylamide (including varying degrees of hydrolysis to acrylic acid) and xanthan in water.[30, 31]

Since such polymers cannot crystallize, the fibers eventually fail, but not before exhibiting a factor of three or more of the exponential thinning expected by Eq. 2 (see Figure 2).

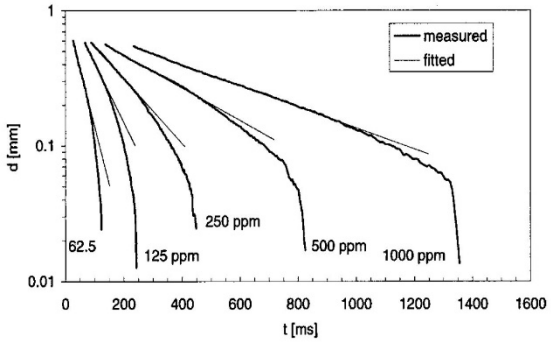
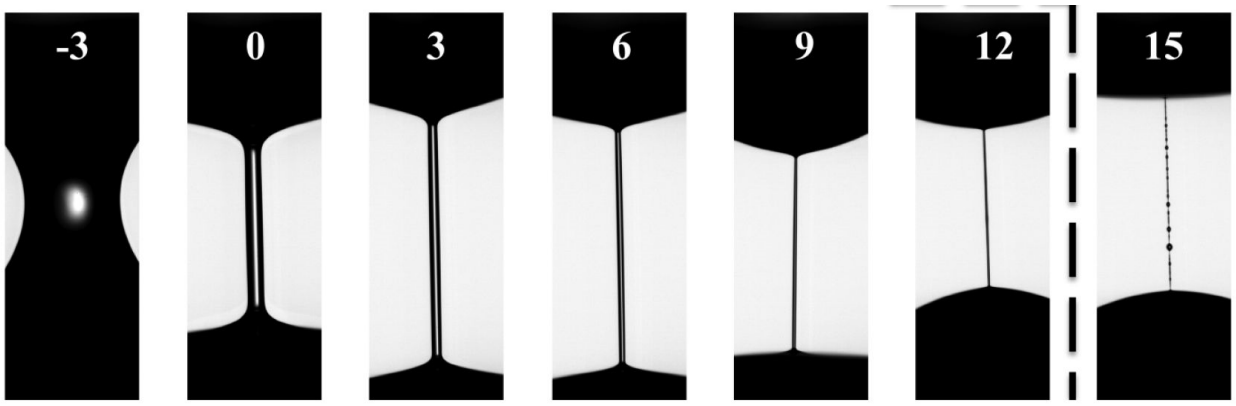


Figure 2. Time dependence of fiber diameter d = 2R for a 40% hydrolyzed polyacrylamide (M = 1.4 x 10^7 g/mol) in water.[30] Also shown as thin straight lines are fits to Eq. 2 that determine the relaxation time of Eq. 1. Despite all five concentrations being dilute solutions, the relaxation time increases with concentration, presumably because the thickness δ of the glassy layer increases with concentration. Since this polymer cannot crystallize, the fibers eventually fail. Reproduced from [30] with permission of the Society of Rheology.

In a very interesting study, Sousa, et al. compared polyacrylamide/water fibers surrounded by air (corresponding to dry spinning) with the same fibers surrounded by silicone oil.[26] Since significant amounts of water can partition into the silicone oil,[32] the polyacrylamide/water fibers surrounded by silicone oil correspond to wet spinning (silicone oil is a nonsolvent for polyacrylamide). The relaxation time for both dry and wet spinning of the same polymer show identical concentration dependences in dilute solution (ranging from 0.1 ms at 2 ppm to 100 ms at 1000 ppm), consistent with the rate of thinning being controlled by water diffusion through the glassy layer at the fiber surface.

Much recent work has focused on poly(ethylene oxide) (PEO) in water.[24-28] PEO has T_g far *below* ambient, so PEO can never form the glassy layer. The initial thinning accelerates rapidly, following $R \sim \left(t_p - t\right)^{2/3}$ as though the fiber was about to catastrophically fail.[24, 25, 27, 28] Such a 2/3 power law is even seen for glycerol/water mixtures with no polymer present.[27] However, once the polymer concentration gets sufficiently high at the fiber surface, evaporation of water becomes controlled by diffusion of water through the high concentration layer (with polymer volume fraction of order unity) and further decay of the fiber radius becomes slower, following the exponential of Eq. 2 (see Figure 3).



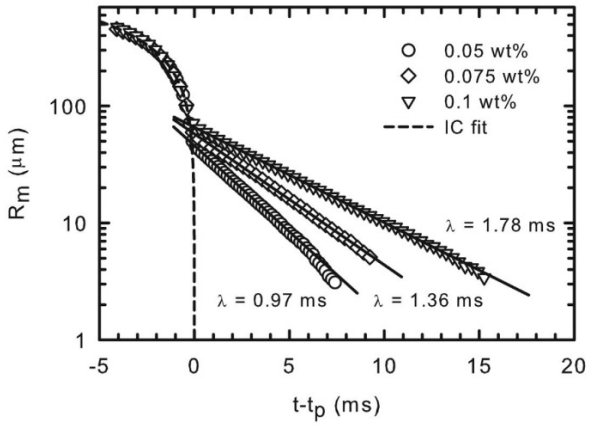


Figure 3. (top) The CaBER experiment on a 0.1 wt% PEO solution in water.[24] Numbers are the elapsed time (ms) since the high concentration layer was first formed at t_p. (bottom) Time dependence of fiber radius in three CaBER experiments on different dilute concentrations of PEO in water.[24] Initially, all three fibers thin identically, after which a high concentration polymer layer forms and each decay slows to an exponential decay. Note that $\tau = 2\lambda$ apparently depends on concentration in dilute solution! (also seen in Figure 2) Reproduced from [24] with permission of the Society of Rheology.

In the Capillary Breakup Extensional Rheometry (CaBER) experiment, after forming a fiber between fixtures (Figure 3 top) the radius of the fiber thins as a function of time. There are two regimes noted in this thinning (Figure 3 bottom). Roughly the first four milliseconds of data (with negative values of $t - t_p$) exhibit an accelerating decrease of radius, whereas beyond t_p, the data show 7 – 15 ms of exponential decay where the radius thins by more than an order of magnitude. One interpretation of t_p is that this is the time at which the polymer concentration at the fiber surface is high enough to limit evaporation,[15, 23] with relaxation time $\tau = 2\lambda$ increasing with the starting solution concentration, presumably because a thicker high concentration layer is formed. With $\tau = 2\lambda$ = 2 - 4 ms in the dilute PEO solutions of Figure 3, with D roughly 10^{-10} cm^2/s = 10^4 nm^2/s for water diffusing in very high concentration PEO solutions,[33] Eq. 1 estimates the thickness of the high concentration PEO layer at the surface of the fiber $\delta = \sqrt{2D\tau}$ = 6 – 9 nm. Rutledge[34] added large amounts of M = 10 kg/mol PEG (polyethylene glycol) to their dilute PEO solutions and this increases the relaxation time (for CaBER fibers that are uniform) to 0.3 s < τ < 1 s, yielding an order of magnitude thicker high concentration layer with $\delta = \sqrt{2D\tau}$ = 80 – 130 nm.

Another interpretation of the obvious exponential decay in Figures 2 and 3 is that this provides a measure of the extensional viscosity of the polymer solution inside the fiber. However, that idea seems strange for a number of reasons.

(1) Why would the relaxation time $\tau = 2\lambda$ increase with polymer concentration in *dilute* solution?[24, 25, 35] Bead-spring models with or without hydrodynamic interactions through

the solvent of course expect any polymer relaxation time in dilute solution to be independent of concentration.[8, 36-38]

(2) Trouton showed long ago that owing to the fact that the strain tensor had to be defined to be symmetric like the stress tensor, the extensional viscosity is 3 times the shear viscosity, known as Trouton's Rule.[38, 39] Measurements from the CaBER with volatile solvents that ignore solvent evaporation report nonsensical Trouton ratios as high as 10000 or more,[25, 28] meaning that the relaxation time $\tau = 2\lambda$ can be as much as 10000 times larger than *any* molecular relaxation time of the polymer in solution.

(3) Recent work used the CaBER to study a polymer solution that is 74% water, 25% glycerol and 1% PEO, by itself and with 10%, 20%, 30%, 40% glassy polystyrene particles that are 20 μm in diameter.[40] They report that while the initial accelerated thinning regime is logically slowed as particles are added, the long-time exponential decay is *independent of particle concentration*, strongly refuting this exponential decay being related to any polymer solution property inside the fiber.

Conclusions

We show herein that CaBER measurements with volatile solvents initially show a strong decay of fiber radius with time that increases the concentration of polymer at the fiber surface. With polymers having T_g above ambient, this concentration increase can lead to the formation of a glassy viscoelastic solid layer at the surface, after which further thinning of the fiber is controlled by solvent diffusion through the solid glassy layer, in order to evaporate at the surface and continue the capillary thinning. With polymers having T_g below ambient, the glassy layer cannot form but still a layer with high enough polymer concentration (with $\phi \approx 1$) can control solvent loss, as the solvent diffuses through that high concentration layer slowly. This process of thinning controlled by solvent diffusion has absolutely nothing whatsoever to do with the extensional viscosity of the viscoelastic fluid inside the fiber, which cannot even be estimated from such devices. The time scale extracted from CaBER at long times is the time scale for diffusion of solvent through the (often glassy) high concentration polymer layer at the fiber surface.

Fiber spinning from polymer solutions is a vital industrial process and the CaBER is a great way to study how long it takes to form the glassy layer (t_p in Figure 3) and the effective time scale τ for diffusion through that layer (Eqs. 1 and 2). It would be very interesting to see how t_p and τ change with choices of solvent, polymer and starting concentration. The expectation from this work is that t_p should decrease as solvent evaporation rate increases (solvent evaporation rates are typically in the range 10 – 500 kg/(m^{2}s) and of course correlate with vapor pressure).[41] Such a path forward could lead to a superior understanding of both dry and wet fiber spinning.

Similar extensional viscometers that stretch filaments are of course superb rheometers for molten polymers[42-44] and for polymer solutions in nonvolatile solvents (such as oligomers).[45] However, the expectation from this work is that filament stretching for polymer solutions with volatile solvents should not be interpreted as measuring any extensional rheology of the fluid inside the fiber, as resistance to stretching will be controlled by the high concentration polymer skin layer at the fiber surface, that may well be semicrystalline.

Acknowledgments

Support from the National Science Foundation under grants Chemistry-2203746 and DMR-2218775 is gratefully acknowledged. The author thanks Ole Hassager and Dimitris Vlassopoulos for very helpful comments on a preliminary version of this paper.

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