Correlations between electrospinnability and physical gelation

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Abstract

Fiber formation by electrospinning is investigated for polymer solutions capable of physical gelation. It is shown that close to the gelation threshold, the combination of thermoreversible junctions and chain entanglements help to stabilize the liquid jet and overcome capillary forces thus giving micro/nano fibers. The effect of cooling time and dissolution temperature besides polymer concentration and molecular weight is clearly demonstrated for polyvinyl alcohol/water and polyvinyl chloride/THF solutions. Finally, the relationship between solvent quality, chain entanglements and poly(vinyl chloride) fiber formation is unequivocally illustrated.
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1. Introduction

In the past decade, electrostatic processing has been routinely employed to obtain ultra-fine fibers [1–3]. The process consists of applying a high voltage to inject charge into a polymer solution of adequate concentration. As the voltage is increased, the drop of liquid presented at the tip of the syringe is attracted to the ground electrode thereby forming a Taylor cone. Above a critical voltage, the electrical energy, a consequence of the injected charge overcomes the surface tension and a continuous jet of liquid is ejected from the Taylor cone and accelerates towards the target electrode. Ultra fine fibers are deposited on the collector due to evaporation of solvent en route. This technique has been employed to numerous polymer/solvent systems to obtain fiber diameters ranging from tens of nanometers to microns. A vast majority of studies reported in the literature concentrate on applications of electrospun fibers [4–9]. However, fundamental understanding of the

electrospinning process is limited. Only recently has there been a concerted push to gain deeper insights into the electrospinning process. For example, a number of efforts have concentrated on modeling the whipping instability and fiber diameter [10–17]. However, there has been a lack of knowledge with regards to fiber formation and its relationship to the polymer solution properties. Recently, McKee et al. investigated the solution properties, in particular, the viscosities of linear and branched polyesters, and proposed that fiber formation occurs at the entanglement concentration [18]. Over the past year, we have particularly interested in the effect of polymer solution properties on fiber initiation/formation or 'electrospinnability' (spinnability in electrostatic processing). In this regard we have demonstrated a clear link between chain entanglements in the polymer solution and electrospinnability [19]. In particular, we presented a semi-empirical methodology to a priori predict the transition from electrospraying to electrospinning (or beads to fiber+beads) in good solvents. Additionally, we were also able to predict the transition from fiber+beads to solely fibers (complete fiber formation). The salient features of the approach are described below.

To facilitate predictions from electrospraying (beads) to electrospinning (fibers), as part of our model, we have defined the solution entanglement number $(n_e)_{soln}$, as the ratio of the polymer weight average molecular weight (M_w) to the entanglement molecular weight in solution, $(M_e)_{soln}$.

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$$(n_{\mathrm{e}})_{\mathrm{soln}} = \frac{M_{\mathrm{w}}}{(M_{\mathrm{e}})_{\mathrm{soln}}} = \frac{\phi M_{\mathrm{w}}}{M_{\mathrm{e}}} \qquad (1)$$

Here, M_{e} is the entanglement molecular weight in the melt and ϕ is the polymer volume fraction. Note that M_{e} is generally a function of chain topology or geometry and ϕ accounts for the dilution effect due to presence of solvent. Using the results from polymer solution rheology, a correlation was established between fiber initiation (spray to spin transition) and the upturn in zero shear viscosity/M_{w} plot. Thus in terms of the entanglements, fiber formation is initiated at $(n_{\mathrm{e}})_{\mathrm{soln}} \sim 2$ (or # of entanglements per chain ~ 1). The veracity of this correlation was demonstrated by comparing the predicted polymer concentrations with experimental observations for a number of polymer/solvent systems [19]. The applicability of this approach is clear since a wide range of systems were tested including those involving strong polymer–solvent hydrogen bonding (PEO/water and PVP/ethanol). McKee et al. [18] have reported a similar approach where they employed the entanglement concentration obtained using solution viscosity data, to explain the spray to spin concentration for linear and branched polyesters. With the use of $(n_{\mathrm{e}})_{\mathrm{soln}}$ (or # entanglements per chain), our approach allows a priori prediction of polymer concentration for electrospinnability without having to measure solution viscosities.

Besides fiber initiation, it was demonstrated that the critical concentration for complete fiber formation (no beads or beaded fibers) corresponds to $(n_{\mathrm{e}})_{\mathrm{soln}} = 3.5$ (average of 3–4), i.e. the number of entanglements per chain ~ 2.5 (average of 2–3). Based on the results of Schreiber et al. [20] and Hayahara et al. [21] obtained for conventional dry spinning, we believe this corresponds to the formation of an elastically deformable network under the influence of an elongational flow field. An advantage of our approach is that the only parameter required for the predictions is M_{e}. Thus, for a given polymer, the spray to spin transition and complete fiber formation (electrospinnability) can be calculated for any concentration/molecular weight space. Note that an underlying assumption of our approach is that chain entanglements are solely responsible for both the upturn in solution viscosity and the formation of the elastic network under the influence of an elongational strain. Therefore, the approach is valid only for the good solvent case where polymer–polymer interactions are negligible.

However, in systems where strong interactions such as hydrogen or ionic bonding are present, polymer–polymer interactions may not be negligible. Increased inter-chain interactions in these systems may serve to stabilize the physical (chain) entanglements by retarding chain disentanglement or forming additional junction points which may facilitate fiber formation at concentrations lower than predicted by Eq. (1). Other factors such as liquid–liquid (L–L) microphase separation [22] in conjunction with vitrification and/or solid–liquid (S–L) phase separation (crystallization) can also serve a similar purpose by creating

additional junction points, thereby lowering the concentration threshold for fiber formation. In these systems, the upturn in solution viscosity could be due to the combination of various factors; namely chain entanglements, polymer–polymer interactions and phase separation (L–L, S–L).

In previous work from our laboratory, Kenawy et al. [22] have described a classical system where we believe both L–L and S–L phase separation assists fiber formation. Electrospun mats of ethylene vinyl alcohol copolymers containing 56–71 wt% vinyl alcohol were obtained by electrospinning from rubbing alcohol (70% 2-propanol/30% water, vol:vol). Due to copolymer crystallinity, application of heat (80 °C) was a prerequisite to completely dissolve the copolymer. Upon cooling to room temperature, electrospinning results in EVOH fibers. However, polymer precipitation was always observed, but not until several hours after cooling the solution to room temperature. Since precipitation of EVOH is kinetically quite slow, fiber formation was quite extensive prior to precipitation. Previously, we had speculated that the thermodynamic instability resulting from proximity to liquid–liquid phase separation (upper critical solution temperature or UCST) might be promoting the electrospinning process and subsequent fiber formation [23]. Of course, an additional driving force could be solid/liquid phase separation (crystallization) or a combination of the two (crystallization + UCST). The microscopic crystallites or 'embryonic nucleation sites' comprising of fringed micelles or chain folded crystals can easily serve as junction points where several different polymer chains, come together. The entanglement approach described in our most recent work is clearly not adequate for this type of system. In contrast to the dynamic nature of the physical entanglements, i.e. entanglements formed by crossing over (or knotting), the crystallite junctions are essentially semi-permanent (dissolves at crystallite T_{m}). Clearly, a combination of the microcrystalline junctions with physical entanglements can facilitate fiber formation.

Additionally, in the course of electrospinning studies, we have frequently observed that some polymer solutions form physical gels quite unlike the precipitation observed for EVOH systems. For example, poly(vinylidene fluoride) (PVDF)/dimethyl formamide (DMF) solutions are prone to form physical gels on cooling to room temperature within a few hours, particularly at high polymer concentrations [24]. The solution can regain its fluidity upon reheating the PVDF/DMF gel. Another system which behaves in a similar manner is completely hydrolyzed ($>99\%$) poly(vinyl alcohol) (PVA)/water [25]. Both systems required application of heat to completely dissolve the semicrystalline polymers (PVDF, PVA). Upon cooling to room temperature, the solutions undergo thermoreversible gelation, quite unlike EVOH (in 2-propanol/water), where precipitation is observed. Interestingly, despite the differences in the final morphology of the solutions (gelation versus precipitation) the mechanisms are quite similar. Therefore, it is possible that mechanisms that promote physical gelation also aid in