European Polymer Journal 75 (2016) 46–55

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

The relevance of extensional rheology on electrospinning: the polyamide/iron chloride case

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ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form 6 November 2015
Accepted 4 December 2015
Available online 8 December 2015

Keywords:
Electrospinning
Capillary Breakup Extensional Rheometry
CaBER
PA6–$FeCl_3$ solution

ABSTRACT

The outcomes of the electrospinning of polyamide 6 (PA6) solutions in formic acid containing $FeCl_3$ are correlated with the extensional rheological behaviour of these fluids, which is investigated by the self-controlled capillary breakup of a filament. The rheological analysis enlightens a significant effect of the $FeCl_3$ content on the rheological behaviour, the viscous component becoming predominant over a certain salt content threshold. At this concentration, the electrospun fibres show the formation of severely inhomogeneous structures this indicating that an elastically dominated behaviour is necessary to yield defect-free fibres. Addition of $FeCl_3$ also decreases fibre crystallinity and fibres turn out to be completely amorphous above a critical concentration. Interestingly, this concentration coincides with the one at which the viscous component starts dominating the rheological behaviour.

1. Introduction

Conducting polymer nanofibres have gained great interest for several applications, ranging from electronics to chemical sensing, and promising developments are being widely suggested in the literature [1–3]. Currently, electrospinning is the only technique that allows the fabrication of continuous polymer nanofibres (i.e. strands with a diameter lower than 1 μm) with complex architectures [4,5]. Although this technique is rather easy to implement for most of synthetic polymers, the processing of conducting polymers is not straightforward, due to the relatively low solubility and the limited number of entanglements of these materials. A method to overcome this issue consists in the production of a polymer mat to act as template, where an *in situ* polymerisation of monomers may occur [6,7]. This strategy has been exploited by Granato and co-workers [6] to obtain nanofibres with an insulating core and a conducting shell starting from a polyamide 6 (PA6) solution containing iron(III) chloride ($FeCl_3$), which promotes the following polymerisation of pyrrole vapours onto the fibre surface.

Besides polymer processability, the major issue of the electrospinning technology concerns the control over the fibres morphology, as size and uniformity may significantly affects their performance [8]. A wide set of material and processing parameters can be varied to impart stability to the process, e.g. solution surface tension and electrical conductivity, applied voltage, flow rate or concentration of the polymer solution [9]. However, as in most case complex fluids are used, the literature suggests that the formation of non-uniform electrospun structures is mainly related to rheological aspects, which are often described in terms of heuristic concepts like 'spinnability' and 'stringiness' [10,11]. Indeed, electrospinning involves the formation, elongation and possible breakup of a liquid filament. All these phenomena occur in a free-surface elongational

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http://dx.doi.org/10.1016/j.eurpolymj.2015.12.003
0014-3057/

flow, during which the relative balance between capillary forces and fluid viscoelasticity of the polymer solution determines the extent of local capillary thinning and of homogeneous stress, thus leading to the different types of complex morphologies. Therefore, a rigorous approach can be considered which takes into account the degree of solution elasticity of the polymer solutions [12]. As spinning technologies mainly involve extensional rather than shear deformations [12], besides the traditional shear rheometry, extensional rheometry is a valuable technique to get reliable qualitative and quantitative information on fluid viscoelasticity in free surface elongational flows [10,13]. At present, the Capillary Breakup Extensional Rheometer (CaBER) is an accurate commercially available instrument to carry out reliable measures of viscoelastic properties of solutions.

In this context, the present work exploits the phenomenon of viscoelasto-capillary thinning in order to investigate the rheological behaviour of electrospinning solutions of PA6 and iron(III) chloride ($FeCl_3$) in formic acid and identify those parameters that allow the prediction of electrospun fibres morphology. This case study has been chosen as $FeCl_3$ is an oxidising agent which is widely known to promote polymerisation of many aromatic rings and heterocycles (e.g. pyrrole, thiophene, aniline) to afford semiconducting and conducting polymers [14]. Such kind of oxidative polymerisation of the aromatic monomers has been also demonstrated to occur *in situ* onto polymer films [15,16] and onto electrospun wire-shaped templates containing this oxidising salt [6,17]. However, when polyamide is used as template, the effect of $FeCl_3$ on the rheological properties of the polymer solution cannot be neglected, since the presence of the metal halide is known to strongly perturb or even prevent H-bonds formation between amide groups of polyamide backbones [18,19]. Further, the system is more complex than those adopted in the literature as references due to the simultaneous occurrence of a non-diluted regime of a low molecular weight polymer in a low viscosity solvent and the presence of a third component. Hence, it may constitute a challenging benchmark for theories developed for model fluids.

We demonstrate that the $FeCl_3$ concentration controls the rheological behaviour of the solution, which in turn influences the fibre morphology.

2. Experimental

2.1. Polymer solutions

PA6 in pellets (M_w = 10,000 g/mol), formic acid (puriss. p.a., ~98%, $\eta_s = 1.70$ mPa s, $k = 2$ mS/cm [20]) and iron(III) hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Sigma Aldrich. All reagents were used as received. PA6 (15 wt% with respect to formic acid) was dissolved in formic acid under magnetic stirring at room temperature. Then, iron(III) chloride hexahydrate was added at $FeCl_3$ concentrations ranging between 0 and 6.5 wt% with respect to formic acid, corresponding to stoichiometric amount ranging between 0 and 28.6 mol% with respect to amide functionalities. The solution was magnetically stirred until a homogeneous phase was obtained. Hydrate salt was preferred to anhydrous $FeCl_3$ as the latter is highly hygroscopic thus making handling and weighting not straightforward and solution moisture-sensitive. Freshly prepared solutions were used for electrospinning and CaBER measurements.

The critical overlap concentration c^* was evaluated according to the definition provided by Graessley [21] $c^* = 0.77/[\eta]$, where $[\eta]$ is the intrinsic viscosity of the polymer solution, which is related to the polymer molecular weight M_w via the Mark–Houwink–Sakurada equation $[\eta] = K_\eta M_w^a$, where K is a constant and a depends on the solvent quality. Considering a solution containing only PA6 and formic acid, $K = 22.6 \cdot 10^{-3}$ ml/g and $a = 0.82$ [22], and thus $c^* = 1.46\%$. In the studied system, the polymer concentration is far above c^* and even about the critical entanglement concentration c_e, which is typically found to be ten times above c^*. This implies that, despite the low M_w and solvent viscosity, the solution of 15 wt% PA6 in formic acid is expected to lead to successful fibre electrospinning [23].

2.2. Solution characterisation

2.2.1. Capillary Breakup Extensional Rheometry

Capillary Breakup Extensional Rheometry was adopted to investigate the extensional rheological properties of the solutions, by means of a commercially available HAAKE CaBER 1 (Thermo Fisher Scientific). In this device, a fluid is subjected to elasto-capillary self-thinning caused by an imposed step-stretch deformation and the evolution of the filament diameter is monitored as the slender thread undergoes necking and finally breaks [24]. This is pursued by placing a nearly cylindrical fluid sample between two cylindrical endplates (Fig. 1a), which are then rapidly separated by an imposed axial step-strain. On stretching, an elongated hourglass shaped liquid bridge forms between the plates; once the stretching has stopped, the capillary pressure causes a progressive thinning of the filament, in which a uniaxial extensional flow is produced (Fig. 1b). If the liquid thread reaches the breakup, two separated drops are left on the plates (Fig. 1c). During the test, the evolution of the thread midpoint diameter ($D_{mid}(t)$) is monitored by a near infra-red LASER diode assembly (Omron ZLA-4), allowing for observations about the overall extensional behaviour of the fluids as well as to extract rheological properties, if an appropriate constitutive equation is chosen to describe the fluid behaviour.

In this study, the temperature of the sample chamber was controlled by a cryostat (Thermo Scientific HAAKE DC10-K10) and it was set at 25 °C. The test conditions adopted to characterise all the solutions are listed in Table 1.