Electrospinning of liquid jets

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<u>Summary</u>: A very thin liquid jets can be obtained using electric fields. The electrically-driven bending instability of the jet enormously increases the jet elongation path and effectively leads to its tinning by very large ratios and can be used to produce nanofibres. The mechanism of electro-thinning of liquid jets, discovered almost one century ago, is yet not fully understood. In the following study detailed experimental data are collected for electrospinning of different liquids in the purpose to correlate these data with the existing models describing basic mechanisms responsible for the electrospinning.

INTRODUCTION

Slender axially symmetric liquid jets emerging from an orifice into passive gaseous environment play an important role in fluid mechanics as well as in many practical applications. The phenomena is characterized by an intrinsic capillary instability which under action of surface tension forces leads to disintegration of the jet into drops. It was found that high viscosity of the liquid as well as extensional stress reduce growth rate of the capillary instability. Further stabilization of the jet is possible for viscoelastic liquids [1], and led to maybe the most revolutionary application liquid jet spinning used to produce long and stable textile fibres. Mechanical spinning of fibres has its practical limits however, and only recently it appeared that further elongation of the liquid jet is possible by applying electrical field to enforce its controlled winding. This process is called electrospinning. It allowed for enormous increase of the spinning path, decreasing diameter of the created fibre several orders of magnitude, arriving to dimensions of hundreds or tens of nanometers. Unique mechanical properties of nanofibres activated wide interest in many fields of mechanics, physics, chemistry and material science.

Unfortunately, the control of electrospinning process relies mostly on empirical data up to now. Semi-analytical models present up to know are difficult to apply in practice as usually they are based on very limiting assumption concerning physics of the process [2]. Our experimental study is primary devoted to elucidate role of such basic parameters like liquid viscosity, surface tension, electric conductivity, reological properties as well as strength of the electric field on the electrospinning process. The aim of the present study is to obtain detailed experimental data on the process itself and to correlate these data with the existing models describing basic mechanisms responsible for the electrospinning.

The experimental setup consists of a pipette sustaining a pendant droplet, a high voltage DC source, a conducting mat for the nanofibres collection, and optical system for image acquisition. A bright field illumination using Fresnel lens is used in most cases. Three camera systems are used to collect transient parameters of the jet and measure details of the collected nanofibres: standard 25fps video camera (768x564 pixels), high-resolution PIV camera (1280x1024 pixels) and high speed (40500fps) Fastcam imaging system (256x256 pixels). As a working fluids mainly water-glycerol solutions and water-alcohol solution of poly(ethylene oxide) - (PEO) are used. By adding surfactant and sodium chloride surface tension and conductivity of the fluid is modified. In addition applicability of electrospinning to two commonly used polymer solution polyacrylonitrile (PAN) and chitin derivatives is tested. Several electrospinning jets emerging from parallel orifices are investigated to estimate possibility of creating boundless nanofibres. The high speed imaging system, as well as a double pulse laser with the PIV camera are used to evaluate local velocity of the jet during its tinning process. Details of geometry of the looping cone are recorded by the standard video camera. Structure of the product is analysed using microscopic system and the high-resolution camera. To estimate magnitude of the jet stretching forces, controlled air flow is used and its effect on the deformation of a segment of the jet analysed.

RESULTS

Typical form of the electrically charged jet of polymer solution is shown in Fig. 1a. The path of jet formed at the tip of a pendant droplet is characterised by three distinct segments. The first one, is a classical straight or slightly curved cylinder with typical length of several millimetres. Its length varies nearly linear with the electrical potential applied and depends on liquid properties (viscosity, surface tension). The second segment starts by sudden bending of the straight cylinder leading to development of a conical spiral. Its height and diameter at the bottom may reach size of several centimetres. The growth rate of the spiral diameter (envelope of the cone) depends on the electrical potential and fluid properties. Due to the electrical forces and stretching the fluid is accelerated reaching velocity of several m/s. After following several loops the conical shape becomes distracted, several difficult to characterise instabilities, small local looping or irregular large loops characterize last jet segments, which are finally collected on the metal electrode. The collected web is usually irregular in form, however by proper adjustment of the collector and the jet loop

inclination relatively regular, nearly parallel mesh of thin filaments was obtained. Diameter of the remaining segments of the jet can be as small as 50 - 100 nm, giving starching factor of more then thousand (Fig. 1b,c).



Figure 1. Electrospinning of polymer solution of poly(ethylene oxide): frame from high speed movie showing development of the bending instability (a); collected nanofibres web under optical microscope (b) and electron microscope (c).

To elucidate main mechanisms responsible for development of electro-bending instability electrified jets of glycerol solutions were used. It was found that despite of lack of viscoelasticity electrospinning of glycerol water solution (88%) is possible (Fig2a). The jet forms relatively long and well controllable spiral before it disintegrated into tiny droplets due to the capillary instability. However, the stretching factor is much smaller and amounts only about ten. By decreasing contents of water in glycerol electrospinning disappears, the relatively straight jet of highly viscous breaks up to many small droplets after passing path of several centimetres. It indicates importance of viscosity but also of an electrical conductivity for the development of the bending instability.

Mathematical description of the bending process given by Reneker et al [2] offers simple model describing relation between forces due to electrical charges, liquid viscoelasticity, surface tension and shearing. According to the model length of the rectilinear segment of the jet increases linearly with voltage, whereas angle of the spiralling cone decreases. The model appeared to work well for poly(ethylene-oxide) solution (Fig. 2b). Experiments performed for several other tested solutions could not confirmed validity of the model, giving even reversal relations (Fig. 2c). The model developed for small perturbations seems to overestimate role of viscoelastic forces compared with surface tension and viscous stresses.



Figure 2. Electrospinning of 88% glycerol solution (a); variation of the straight segment and angle of the spiral cone with electrical potential for poly(ethylene oxide) solution (b) and polyacrylonitrile (c).

CONCLUSIONS

Experimental investigation performed for several polymeric solutions and for glycerol solutions demonstrated possibility to stretch liquid jets in the electrical field into fractions of their initial diameter. Variety of jet paths are observed depending on material and electrical potential applied. It appears difficult to match observed characteristics with theoretical relations available in literature. Experiments demonstrated possibility to created boundless electrospinning jets, however long range electrostatic interaction was observed to hinder their alignment onto the collector grid.

References

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