

Morphologies of polymeric particles formed during electrocapillary instability of electrospray microdroplets

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Keywords: electrospray, Coulomb explosion, polymers, evaporation.

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In electrosprays of polymer solutions interesting particle shapes can be obtained when electrospray droplets undergo electrocapillary instability. Also called a Coulombic instability or Coulomb explosion (Ferdández de la Mora, 2007), an electrocapillary instability occurs to an electrically charged droplet while drying and shrinking, at the moment when the (outward) electrostatic stresses on the droplet surface exceed the (inward) capillary tension stresses which try to hold the droplet together. Droplets undergoing instability develop one or two nanojets, which can either (i) break up spontaneously into smaller progeny droplets, or (ii) freeze to solid form, in the case when the droplet contains condensable solids, resulting in filamented particles. Though in some technological fields spherical particles are required (e.g. pharma), shapes with different aspect ratio may also be desirable, such as filamented particles for use as micromotors (Liu *et al*, 2015). However, the conditions leading to solid phase formation in the nanojets formed during such instabilities are not theoretically well understood.

In the present work we aim to experimentally characterize the different shapes that can be obtained, and to suggest possible fluid mechanical mechanisms responsible for the formation of the different particle shapes observed. We have electrosprayed solutions of different water insoluble polymers in various volatile solvents. We have identified different particle morphologies, such as filamented and non-filamented particles with or without progeny particles (derived from the drying of progeny droplets), and shapes not previously described in the electrospray literature: dumbbell and intensively elongated shapes (see some examples in Figures 1 and 2).

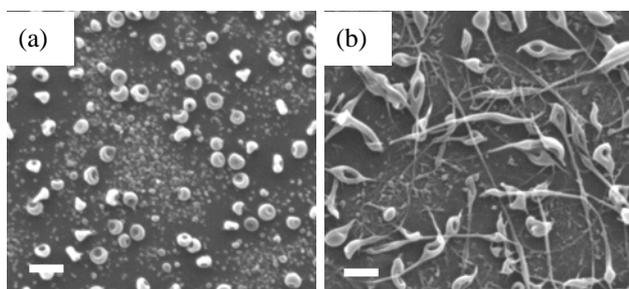


Figure 1. Microstructures collected from 0.2% w/v PMMA – MEK solutions, (a) 15 kDa PMMA, (b) 350 kDa PMMA; scale bar: 1 μ m

In some samples we find significant differences in particle shape at different spray radial locations, i.e. in the central region vs. the periphery of the collection pattern (Figure 2).

We hypothesize various formation pathways (fluid dynamic qualitative model) resulting in the different shapes.

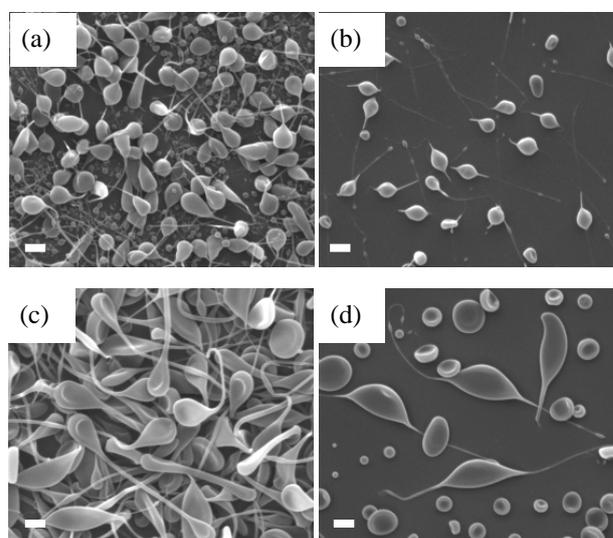


Figure 2. Microstructure collected from 35 kDa PS solutions in center (a,c) vs. periphery (b,d) of the film, (a,b) 1% w/v PS in butanone, (c,d) 5% w/v PS in DCM; scale bar: 1 μ m.

This work has been supported by the Spanish MINECO under grants DPI2015-68969-P and DPI2012-35687, and the Catalan government under grant 2014 SGR 1640.

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