Polymer particle formation by electrospray drying

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Electrospray (ES) atomization can be used to form small, uniformly sized droplets when operating in stable cone-jet mode. In the spray, the droplets go through electrocapillary (or Coulombic) instability upon solvent evaporation, as the droplet diameter decreases below the Rayleigh instability diameter (Fernández de la Mora, 2007). During Coulombic instability events the droplets emit nanojets which can either disintegrate into smaller droplets (progenies) or, in the case of viscoelastic polymer solutions, "freeze", resulting in a variety of particle shapes. Contol over these instability events is important in polymer particle production by ES (e.g. pharmaceutical), as particle funcionality often depends on particle shape and size distribution.

In this work we focus on the mechanisms that lead to polymeric structures during Coulombic instabilities in electrosprays. We study how polymer molecular weight and polymer concentration affect the particle morphology, for different polymers and solvents. We identify an additional factor, the ambient relative humidity (RH), which has often been overlooked in the ES literature. We have electrosprayed water insoluble polymers PMMA, PS, EC in volatile solvents MEK, and DCM. We show that a solvent-saturated N_2 co-flow around the ES needle is needed to suppress solvent evaporation from the liquid meniscus (Taylor cone).

Most of our results fit into one of the possible scenarios shown in Table 1, depending mainly on the viscoelasticity of the electrosprayed solution (also studied by Almería *et al*, 2010).

Table 1. Particle formation scenarios encountered in ES as solution's viscoelasticity increases

Scenario	Mechanism	collected morphology
A	Coulomb fission	non-filamented, with progenies
B	Coulombic instability with or without fission	filamented, with or without progenies
C	early shell formation	non-filamented without progenies
D	incomplete jet breakup	fibers or beaded fibers

We have discovered additional particle morphologies formed during Coulombic instability events, which do not fit into the current paradigm of polymer particle formation by ES. These are particles with strongly elongated or dumbbell shapes. Though not previously described in the ES literature, similar shapes have been found in sol-gel ES experiments (Li *et al*, 2007). We provide possible formation mechanisms (fluid dynamic qualitative model) of these shapes.

The presence of ambient relative humidity results in polymer precipitation before the first Coulombic instability, leading to non-filamented particles, often with a shell structure (Figure 1). In the high molecular weight cases (at sufficiently high polymer concentration) the particles show porous surface, which is caused by water templating, similarly to breath figure formation (Zheng *et al*, 2012).

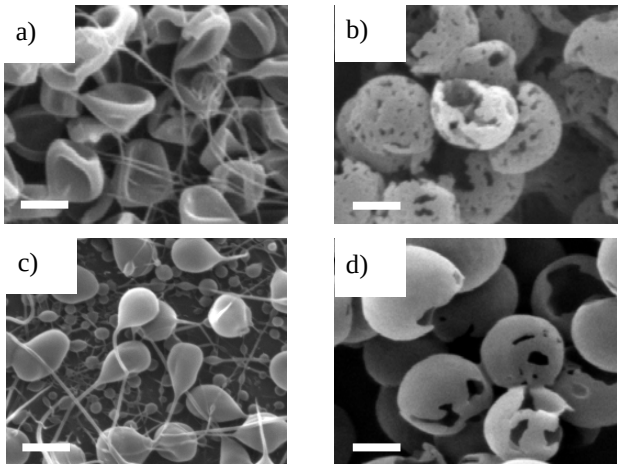

Figure 1. Example microstructures collected from 1% w/v PS–MEK solution at (a), (c) low RH (<10%), and (b), (d) high RH (~60%), for PS molecular weights (a,b) 350 kDa, (c,d) 35 kDa; scale bar: 1 µm.

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