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. Control over these instability events is important in polymer particle production by ES (e.g. pharmaceutical), as particle functionality 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 N₂ 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>
<thead>
<tr>
<th>Scenario</th>
<th>Mechanism</th>
<th>Collected morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Coulomb fission</td>
<td>non-filamented, with progenies</td>
</tr>
<tr>
<td>B</td>
<td>Coulombic instability with or without fission</td>
<td>filamented, with or without progenies</td>
</tr>
<tr>
<td>C</td>
<td>Early shell formation</td>
<td>non-filamented without progenies</td>
</tr>
<tr>
<td>D</td>
<td>Incomplete jet breakup</td>
<td>fibers or beaded fibers</td>
</tr>
</tbody>
</table>

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).

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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.