Polymer Films with Electrospray Deposition, model and experiment

Ivo B. Rietveld,*, 1 Kei Kobayashi,2 Hirofumi Yamada,1 Kazumi Matsushige1

1Department of Electronic Science and Engineering, Kyoto University, Kyoto, 615-8510 Japan
2International Innovation Center, Kyoto University, Kyoto, 615-8520 Japan
rietveld@piezo.kuee.kyoto-u.ac.jp

Introduction

Electrospray is the dispersion of a liquid under the influence of a high electric field. Fields are generally in the order of 1 kV/cm and droplets have a diameter in the order of 1 μm. Small particles can be produced by dissolving compounds in the sprayed liquid; the liquid evaporates and a nanosized particle results. Under the proper conditions, particles with well-controlled shapes and monodisperse size distributions can be obtained [1].

The electrospray technique is becoming more and more popular to process nanoparticles, fibers, and thin films, with polymer films obtaining much attention. Because the technique is relatively new, conditions to control polymer film morphology are not well understood and most research is limited to the study of film formation as a function of a series of separate parameters. Here an approach will be presented which aims to limit the variables to a few important ones and to incorporate the remaining ones as acting through the working variables. It is the intention to be able to predict and control film morphologies, if solvent and solute properties are known.

The approach consists of the construction of a model, based on droplet evaporation, which calculates the state of an electrosprayed droplet at impact on the substrate. Morphologies of poly(vinylidene fluoride) films have been compared with the results of the model. It will be shown that the state of the droplet at impact forms the basis for a framework to predict the film morphologies.

Experimental

Films of poly(vinylidene fluoride) (PVDF) have been made with an in house constructed electrospray chamber. A detailed description of the spray geometry can be found in ref. [2]. PVDF was dissolved in DMF and deposited on silicon wafer at 40°C under a nitrogen atmosphere. Selected spray conditions are shown in **Table 1.** Q is the flow rate, I the current during the spray and d the droplet diameter. The concentration of the solution was 0.25 wt%. An additional series of films was prepared with a number of solutions with varying concentration and a flow rate of 3 μl/min.

Table 1. Spray conditions

Q (μl/min)	I (nA)	d (μm)
1.2	27	1.7
2.5	50	2.3
3.0	21	3.4
4.0	25	3.9
6.0	26	5.0

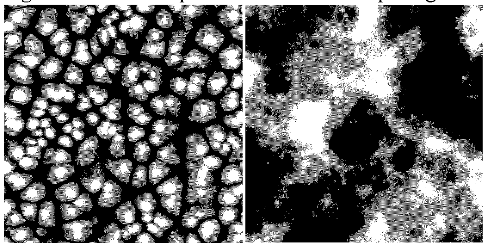
The films have been studied with AFM (JEOL SPM 4200). 25× 25 μm^2 images of the films have been made and where possible the roughness average of the films has been determined.

In addition to the experiments, a model has been developed with the following features. Droplet size is calculated with the flow rate and the current during the electrospray process [1]; the droplet sizes can be found in **Table 1**. Droplet evaporation is evaluated as a function of time, which is converted to the spray distance between the nozzle and the substrate. Various properties of the droplet at impact are determined, such as its viscosity, its velocity, the shear stress on the droplet and its shear rate. Moreover, the average surface on the substrate for a single droplet has been determined.

Results and discussion

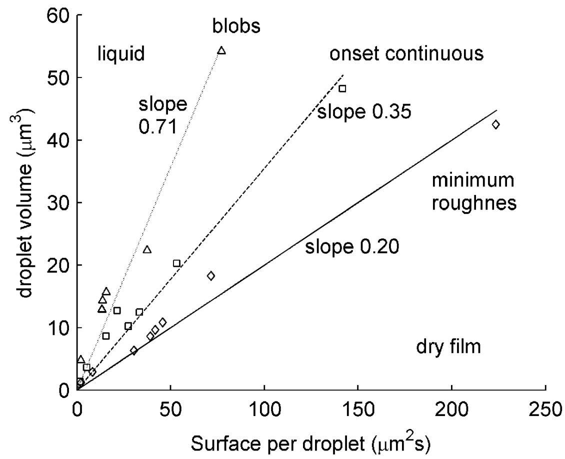
Two examples of PVDF film morphologies are shown in **Figure 1**. The left film, consisting of blobs, is made with relatively wet deposition; the right film is made with a drier deposit, but it still flows well enough to form continuous film. Droplet size, as given in **Table 1**, and spray distance are important parameters in the model, because these determine the amount of evaporation before droplet impact on the surface occurs. From the experiments, it follows that the concentration variation does not affect the polymer film morphology; it only affects the roughness of the film. On the other hand, the droplet size and spray distance affect the film morphology very strongly.

Figure 1. Two examples of PVDF film morphologies



With use of the model, the droplet volume at impact can be plotted against the available surface for the droplet on the substrate. This plot is shown in **Figure 2**. Different morphologies are indicated in the figure, liquid, blobs, onset continuous, minimum roughness, and dry film. There is a clear dependence of the morphologies on the growth rate, which is represented by the straight lines in **Figure 2**. Morphology regions, defined by certain growth rates, depend on specific factors that determine the appearance of the film. For example, the film on the right side in **Figure 1** is entirely determined by the shear rate of the droplet. This region is defined by the line with a slope of 0.20 μm/s down to the x-axis. The model calculates the shear rate, which can be related to the roughness averages of the films with a simple power law. Due to the high viscosity of polymers, this morphology region is so extended. For the blobs morphology, it is likely that the surface tension plays an important role, but this is more difficult to determine, because the surface tension is not part of the model.

Figure 2. Mapping of the film morphology on growth rate.



Conclusions

The morphology of electrospray deposited film can be predicted with the growth rate of the film. With use of the developed model, many droplet properties at impact can be calculated and compared with polymer films. For a particular growth rate region, the morphology is generally determined by a few important parameters only. For polymers, the regime that is solely determined by the shear rate is relatively large, due to the high viscosity of polymer solutions. This approach can also be applied to electrospray deposition of compounds other than polymers.

References

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