In-air Polymerization and Crosslinking of Monomers during Electrospray Deposition

Catherine J. Nachtigal*, Michael J. Grzenda, and Jonathan P. Singer

Abstract Electrospray deposition (ESD) is a coating technique in which a solution is passed through a charged capillary, causing the solution to disperse into child droplets through a series of Coulomb fissions until the droplets reach a grounded target. This process is advantageous due to its ability to create nanostructured self-limiting electrospray deposition (SLED) coatings with certain solutions. A large disadvantage is its use of a large amount of solvent. This is wasteful and causes sprays to take a long time to deposit a film. To alleviate this, this study focuses on spraying monomers, which can be sprayed at a much higher weight percentage than their corresponding polymers, blended with a photoactivated polymerizing agent and crosslinker under ultraviolet light to create polymers mid-spray. It was found that the spray, using methyl methacrylate as the monomer, deposited a film consisting of oligomeric polymers that could be optionally crosslinked.

Key words Electrospray deposition, self-limiting electrospray deposition, thin-film, monomer, polymer, crosslink, polymerization, efficiency.

1 Introduction

Electrospray deposition is a promising coating technique that has several advantages in its method of deposition, including its ability to create complex nanotextured coatings, ability to adjust solutions and their corresponding spray morphologies, ability to create SLED coatings due to the build-up of charge in the sprayed film, and its ability to be completed in any environment as well as an ambient environment [1, 2, 3]. This versatile process has several applications, ranging from use in biomedical engineering and pharmacological settings, to sensors and other complex nanotechnology [4, 5, 6].

This process involves spraying a solution by passing it through a conductive capillary and applying a voltage to it, resulting in the formation of a Taylor cone as the solution is drawn out through a build-up of charge. At a critical voltage, the solution then begins to disperse into child droplets repeatedly through a series of Coulomb fissions until there is an equilibrium between the surface tension and charge of the droplet [7, 8, 9]. The droplets produced during ESD have been correlated with several properties and is found as:

$$d = \alpha(\frac{Q^3 \varepsilon_0 \rho}{\pi^4 \sigma \gamma})^{\frac{1}{6}} + d_0$$

Where α is a constant related to the fluid's dielectric permittivity, ρ is the density, γ is the surface tension, σ is the electrical conductivity, Q is the flow rate, ε_0 is the permittivity of free space, and d_o is a small droplet diameter only significant at low flow rates [10].

Efficiency is an important element of making sure that any method of manufacturing is feasible on a large scale. Several studies have been completed in order to increase the efficiency of ESD and its deposition onto given targets. This includes but is not limited to attempts to increase the spray efficiency of solutions on to nonconductive surfaces, as well as controlling the areas in which the sprays are being deposited [11, 12]. Though these studies have taken a large step in making the process scalable, no studies have focused on a key aspect of efficiency – the weight percentage (wt%) of solute that can be loaded into and sprayed using ESD. It has been found that the stability of these sprays is greatly affected by the viscosity of the solution, and an increase in the wt% of polymers in particular has a large effect on the viscosity of the solution [13]. Usually, sprays previously completed using polymers could

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only handle at most 8.2 wt% polymers in the solution [14]. This necessity to use a large amount of solvent to spray a small amount of solute forces sprays to not only be wasteful and not environmentally friendly, but it also causes them to take a long time in order to deposit a given film thickness. The process of ESD requires the use of a high voltage power supply in order to cause a build-up of charge in the solution to create the spray. This means that the longer that a spray needs to run, the more power consumed solely by the usage of the high voltage power supply, as well as power used by the syringe pump or other devices used to feed the solution into the capillary, any ventilation equipment used such as ventilation, and other devices required for the operation of an ESD system.

This study focused on determining a method of ESD that would allow polymers to be sprayed at a higher wt% in order to avoid these drawbacks of the process. To combat this, monomers were sprayed in place of their polymer counterparts. In order to transition these monomers into polymers, first a photinitiated polymerizing agent was loaded into the solution, which was a mix of the monomer at a high wt% in a sprayable solvent. Then, a crosslinking agent was loaded in as well in order to create a complex connected nanostructure. Following the spray of this solution under ultraviolet light, the photoinitiator (PI) would cause the monomers to polymerize into polymer chains mid-spray, and these chains would then (optionally) crosslink, depositing a polymer formation onto the desired spray substrate. In order to determine if the deposited film was truly polymers, gel permeation chromatography and differential scanning calorimetry were used to determine the molecular weight of the film deposited. A scanning electron microscope (SEM) was also used to determine the morphology of the films, and microscopic reflectometry was used to measure the thickness of the film over time in order to determine if the spray was SLED.

2 Experimental

Solutions

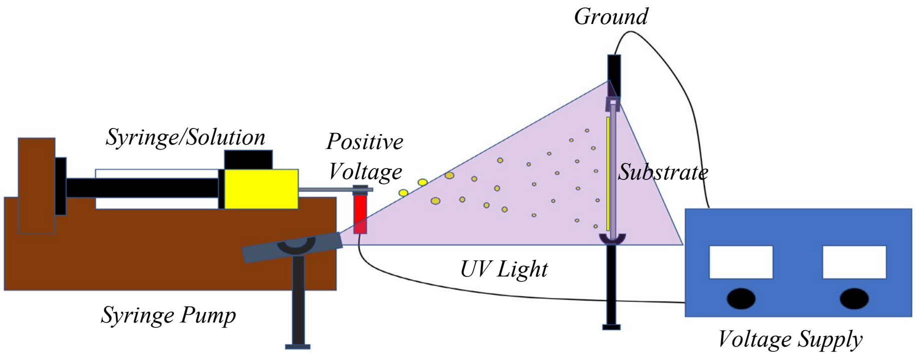
Acrylic acid, vinyl pyrrolidone, polyethylene glycol diacrylate, bis-acrylamide, and phenylbis phosphine oxide were obtained from Sigma Aldrich and used as received. Methyl methacrylate (min 99.5%) was obtained from Polysciences, Inc. and used as received. Ethanol (Koptec, 200 proof pure ethanol) and methyl ether ketone (Sigma Aldrich, ACS Reagent, >= 99.0%) were used as the carrier solvents for the ESD solutions. Acrylic acid (AA) and vinyl pyrrolidone (VP) were blended with ethanol individually in order to test their maximum weight loading when electrosprayed. Methyl methacrylate (MMA) was blended with methyl ether ketone (MEK) in order to determine the maximum weight loading when electrosprayed. Phenylbis phosphine oxide (PI) was loaded into each monomer or monomer and solvent blend in order to determine polymerization rate and minimum PI loading amount in each blend. Polyethylene glycol diacrylate (PEGDA) and bis-acrylamide (BIS) were individually blended with each monomer, solvent, and PI blend in order to determine the minimum crosslinker loading amount in each blend.

Solution Formulation

To determine the minimum PI needed for each solution in order to successfully polymerize the monomer, first MMA was blended with PI in 100:1, 100:5, 100:10, 100:15, and 100:20 ratios and placed in droplets under a direct UV lamp for a period of time of 30 seconds, 1, 3, 5, 10, 20, or 30 minutes. Polymerization was determined when a thin film formed over the droplet during the given period of time. For all other monomer solutions, the minimum PI needed was determined by first determining the maximum monomer loading in solvent that was capable of ESD, then determining the minimum PI needed to polymerize the spray. Polymerization was determined by either surface appearance or by heating the sprayed substrate and observing the melting point. The maximum monomer loading in solvent was determined by loading either the monomer or the monomer and PI blend into its soluble solvent and using ESD and determining the maximum monomer amount that could successfully undergo ESD and produce a stable spray. The minimum crosslinker loading in each blend was determined by loading either BIS or PEGDA into the blend and then using the blend in ESD. The sprayed wafer was then treated with a droplet of the solution's solvent, and dissolution would indicate that the solution had not crosslinked and more crosslinker was necessary.

Electrospray Set-up

Figure 1 Schematic of experimental ESD set-up.



The set-up of this ESD process consisted of the use of a syringe pump, syringes, silicon wafers, a high voltage power supply, a wafer holder, a UV light, and a ring stand to hold the UV light in place, as displayed in Figure 1. For sprayed on 3D objects, the silicon wafer and wafer holder would be replaced with a 3D object, such as a brass hedgehog or silver-coated plastic anchor charm, and a tin/lead soldering wire to hold the object in place and serve as a conductive piece to apply the ground charge to. The syringe (5 mL NORM-JECT®) was loaded with the given solution and placed in the syringe pump (KD Scientific Syringe Pump 780-100) at a desired flow rate. The wafer or 3D object were placed directly in front of the syringe needle and in the case of the wafer it would be secured in the wafer holder. A high voltage power supply (Gamma High Voltage Research, HV Power Supply ES30P – 5W/DAM) was connected to the system with the positive voltage wire attached to the needle on the syringe and the grounded wire attached to the wafer or 3D object's securing soldering wire. Silicon wafers and 3D objects were cleaned and degreased with acetone and ethanol before each spray. The UV light (Dymax Model PC-3) was secured using a ring stand and a clamp to point directly at the spray path as well as the substrate during the ESD process at a distance of 8 cm.

Spray Conditions

All sprays were sprayed in the Taylor-cone jet regime in this study. Each spray was completed in ambient 23-54% relative humidity. The positive voltage for each was set between 4.5-8.0 kV in order to produce a stable spray and a Taylor cone. The spray distance for each spray was constant at 8 cm between the tip of the syringe needle and the silicon wafer or 3D object. Each spray was conducted at room temperature, ranging from 18-23 °C under a fume hood. All silicon wafer samples were sprayed at 0.25 mL/hr or 0.5 mL/hr. For each time series, each spray was completed for either 10, 50, or 90 minutes. For each spray solution test, each spray was completed for 5 minutes.

Sample Analysis

The thickness of each sample was measured using microscopic reflectometry using a Filmetrics microscope model F40-EXR with custom translation stage. Prior to thickness measurement, each sample was smoothed at 125 °C on a hot plate for 5-20 seconds. The sample central thickness was determined by measuring the thickness of the sample across the diameter of the spray spot on the substrate at 100 points equally spaced across and taking the mean and standard deviation of the center centimeter. The data was processed using a MATLAB program to determine the central thickness from these points. The morphologies of these spray films were characterized using a Zeiss Sigma Field Emission Scanning Electron Microscope (SEM) and a normal microscope. The glass transition temperature of the film samples was determined using a TA Instruments Q1000 differential scanning calorimeter (DSC). The molecular weight of the film samples was determined using gel permeation chromatography using an Agilent 1260 Infinity II.

3 Results and Discussion

Spray Conditions and Formulation

Figure 2 MMA and PI blends droplet post UV light exposure in (a) 100:1 for 20 min, (b) 100:10 for 1 min, and (c) 100:20 for 1 min MMA:PI ratios.

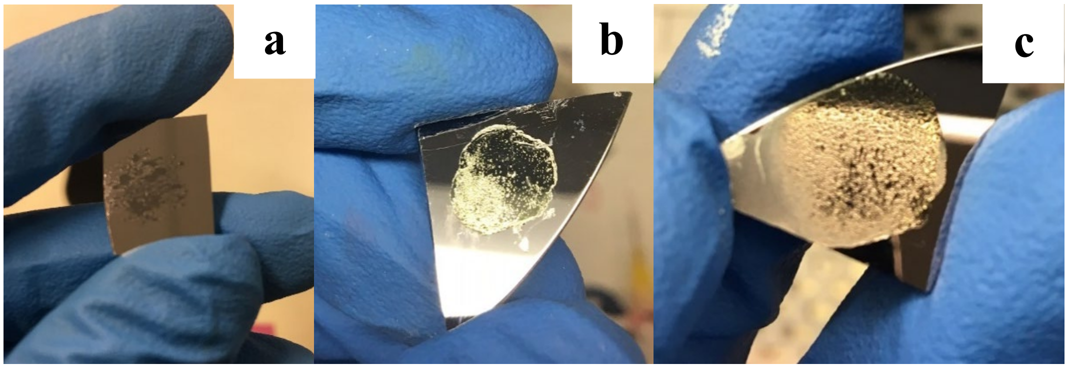


Figure 2 (a-c) shows each MMA:PI blend droplet after being exposed to direct UV light. The sample shown in Figure 2 (b) was able to form a solid film over the surface of the droplet in the 1 m light exposure, while the sample shown in Figure 2 (a) was unable to form a film even with 20 min of UV light exposure. Similar results were found for MMA:PI ratios under 100:10 as in Figure 2 (a), making the 100:10 ratio the minimum amount of PI needed in order to polymerize the MMA in a reasonable amount of time, making it likely that the much smaller (~3 orders of magnitude) spray droplets would be able to sufficiently polymerize mid-spray.

Figure 3 1:1 (10% PI in MMA):(MEK) ESD samples sprayed at 0.5 mL/hr for 5 minutes at 5.5 kV (a) Silicon wafer spray spot with UV light pointed at silicon wafer. (b) Sample in (a) examined under 5x microscope objective. (c) Silicon wafer spray spot with UV light pointed with spray path. (d) Sample in (c) examined under 5x microscope objective.

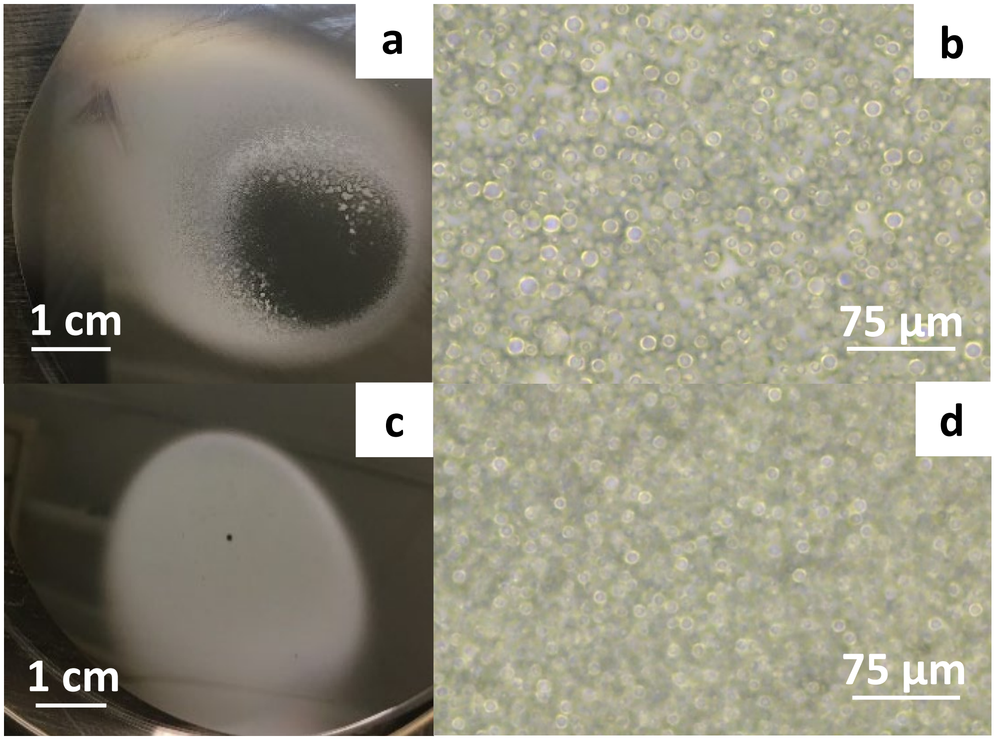
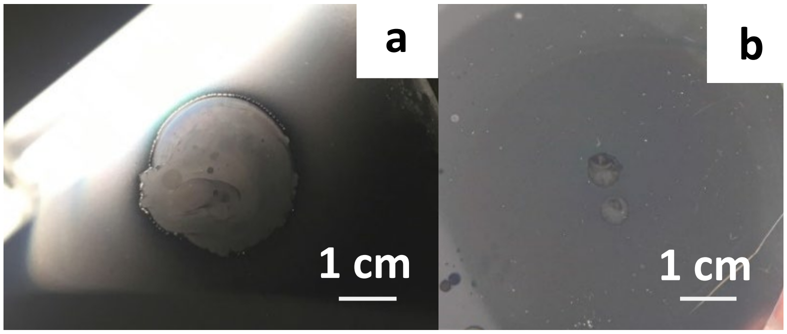


Figure 3 (a-d) demonstrates the necessity of deliberate selection of the UV light path when polymerizing the MMA MEK PI blended solution. As shown in Figure 3 (a), when the UV light does not point through the spray path the solution is unable to properly polymerize and create a powdery film as seen in Figure 3 (c) that is more consistent with a polymer. This blend was determined and used to find the best UV light set-up as it was the maximum amount of monomer in solvent that was able to spray in a stable manner and form a stable Taylor cone.

Figure 4 (a) 50% MEK, 41% MMA, 5% PI, and 4% PEGDA and (b) 50% MEK, 43% MMA, 5% PI, 2% PEGDA ESD films with MEK droplet applied to film post-spray.



This solution, containing 50% MEK, 45% MMA, and 5% PI was then crosslinked using BIS and PEGDA. For each of these blends, the crosslinker replaced a portion of the MMA in the blend to determine how much crosslinker was needed to sufficiently crosslink the polymerized monomer. When sprayed, the minimum amount of PEGDA needed in order to crosslink the solution was 4% PEGDA with 50% MEK, 41% MMA, and 5% PI, while the minimum amount of BIS needed in order to crosslink was more than what could be dissolved into the solution. Crosslinking in the case of PEGDA was determined by placing a droplet of MEK on the sprayed film. Upon dissolution, it was determined that the film had not been able to crosslink, while a lack of dissolution indicated the film had crosslinked, as displayed in Figure 4.

Electrospray Thickness and Morphology

Figure 5 50% MEK, 45% MMA, and 5% PI solution ESD film thickness over time. Each spray was completed at 0.25 mL/hr with a positive voltage of 6.5-8.0 kV and sprayed on to a silicon wafer. Each individual series was completed at the same humidity, with the humidity for the series ranging from 26-46%.

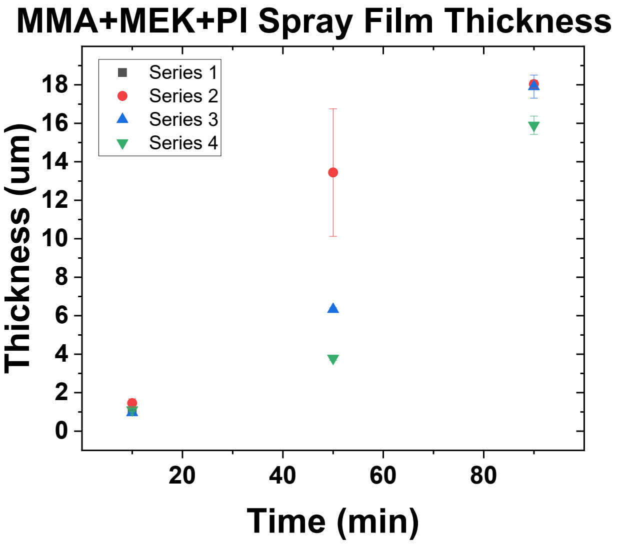


Figure 5 shows the evolution of the thickness of the film over time in order to determine the SLED properties of the film. As shown, the thickness increases nearly linearly over time and does not asymptote as the time increases. This data indicates that the spray is not strongly SLED. This data, however, is inconsistent with the observation that the spray spots were increasing in size significantly over time, indicating that the spray was spreading out over time and that the film's charge was deflecting further spray. As this film was determined to be an oligomer, it makes sense that it had difficulty displaying SLED characteristics, though it may be possible to enhance its SLED properties further through loading in additional materials or through better polymerization of the particle surfaces.

Figure 6 Sprayed 3D anchor charm. (a) Front side facing spray needle. (b) back side facing away from spray needle. Coated with 50% MEK, 45% MMA, 5% PI for 30 minutes at 0.25 mL/hr and 7.0 kV.

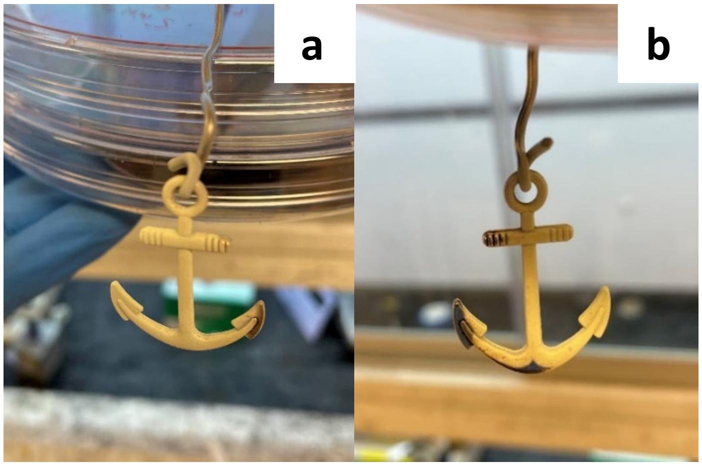


Figure 6 shows a 3D anchor nearly-completely coated in a spray film. Though the back of the anchor does not face the spray needle at all and the electric field would not favor the spray to go to the back of the anchor, it does so likely because the charge formation in the film on the front of the anchor begins to deflect further spray towards the back of the anchor, making the spray, at least to some extent, SLED.

Figure 7 SEM image of 50% MEK, 45% MMA, and 5% PI spray completed at 0.25 mL/hr for 10 minutes.

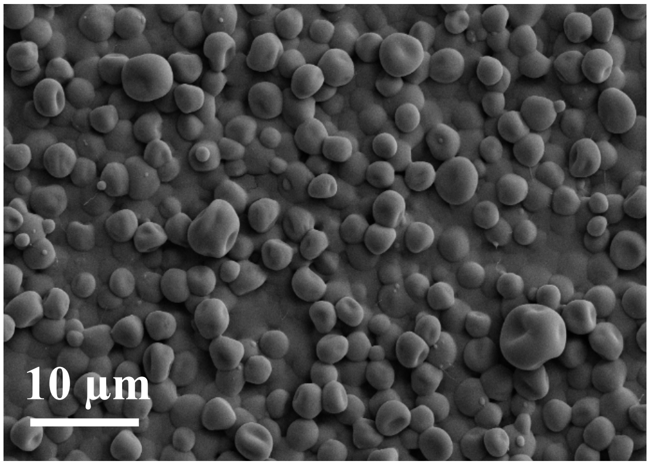


Figure 7 shows the spray morphology of the standard spray sample, showing a density gradient in the droplets formed and deposited on the silicon wafer.

Polymeric Analysis

Figure 8 DSC results from 50% MEK, 45% MMA, and 5% PI sample sprayed for 50 minutes.

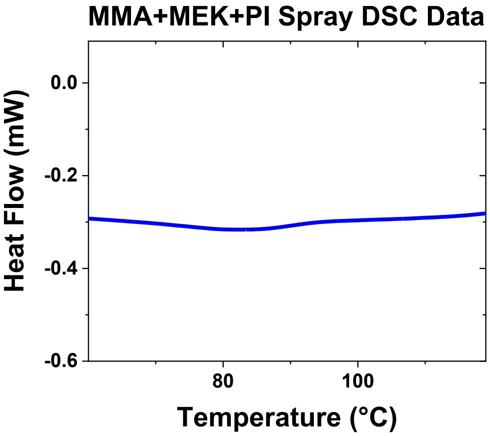


Figure 8 shows the DSC results for the standard sample in this study. This dip in the graph shows a low glass transition temperature (Tg) of approximately 90 °C. Alongside this study, a gel permeation chromatography (GPC) study was completed in order to determine the molecular weight (MW) of the film. This data found that the polymer was below the 2 kDa detection threshold. Taken together, the results of the GPC and DSC studies show that the film contained an oligomeric polymer, or a polymer with a low MW.

As the GPC and DSC studies confirm, the studied process of using UV light to polymerize and crosslink a monomer mid-spray was able to successfully convert the given monomer into a polymer. The spray behavior of varying SLED abilities, though troublesome to need to control humidity in order to maintain a SLED spray, is consistent with the spray properties of low MW polymers, as these have been shown to vary significantly with varying humidity as well [12]. Future work will look to increase the MW of the sprayed polymer for more reliable results through use of more-optimized initiators. Despite this, these results indicate that this method can be useful in circumventing the issue of requiring a low wt% of solids to produce a stable electrospray sample consisting of polymers. This allows the sprays to be completed in a much shorter period of time, as they can be sprayed at moderate flow rates with a large wt%, and also waste less monomers. Because of the necessity for smaller droplets though and a high surface area to completely polymerize the droplets under UV light, the flow rate cannot be set as high as other polymer sprays. Higher flow rates in this study were also found to make the Taylor cone unstable, making a more moderate flow rate necessary for proper spray deposition. Even with the sprays being completed at about half of the flow rate as their polymer counterpart sprays, the deposition rate is still up to an order of magnitude higher because of the high wt% loading, making this process still a significant optimization of the standard polymer ESD process.

5 Conclusion

This new method of utilizing in-air polymerization and crosslinking during ESD to deposit polymers using an exceptionally low wt% of solvents can be extremely promising in the industrial use and scale-up capabilities of ESD. Studies have found ways to scale-up the ESD process to make it more feasible in a manufacturing environment, but few have done so in a way to improve efficiency to make the process affordable enough to make it a candidate in thin-film deposition in an industrial setting [16]. Because of the SLED capabilities that these films could display with future development, this method is even more promising in industrial use as the spray target and spray capillary do not have to be moved to coat the entire surface evenly, making high-quality automated ESD coatings possible. Moreover, this method has the potential to be applied to several different polymers beyond MMA, making it possible to become a standard in efficiently coating with polymers using ESD. It was found to work with vinyl pyrrolidone and acrylic acid, though not as efficiently as MMA, further justifying the need to study this method more to determine its possible uses and applications. These polymers can likewise be optionally crosslinked through loading in crosslinkers, adding in an additional capability of this spray method. Most importantly, beyond the scope of an industrial setting, this method greatly reduces the environmental impact of spray coatings by using fewer toxic solvents, which have been shown to have significant negative health effects in people [17]. Overall, this process provides a less wasteful, more efficient, and more environmentally friendly way to utilize ESD in polymer thin-film deposition that has the capability to be scaled-up to industrial settings.

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