Ionogel Thin Films as Compatibilizing Pretreatments for Electrospray Deposition

Tejasvi Venkat[1], Hannah Mow[2], Emily Li[3], Weronika Wasniowska[4], Ayman Rouf[2], Noah M. McAllister[2], Zainab Al-Jaleel[2], Jonathan P. Singer[1,2,4,]*

[1] Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA.

[2] Department of Mechanical and Aerospace Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA.

[3] Department of Electrical and Computer Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA.

[4] Department of Biomedical Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA.

**Corresponding Author Email: jonathan.singer@rutgers.edu*

Supplementary Information

Chitosan Preliminary Study

A preliminary study was conducted to determine the efficacy of hydrophilic thin films as a pretreatment for incompatible surfaces. Chitosan was selected as a biosourceable, hydrophilic polymer that was not water soluble (it is only soluble in aqueous acid) and thus would resist delamination due to ambient humidity. To investigate the effect of chitosan film thickness on SLED, multiple concentrations of chitosan solution were prepared by dissolving chitosan powder (low molecular weight, Sigma Aldrich, 448869) in 0.5M acetic acid (Sigma Aldrich). After dipping, a drying step was applied at 60° C for 10 minutes.

Thickness of chitosan films was determined by optical reflectometry of the films deposited on silicon wafers. Here we are assuming that dip coated samples deposited on either quartz or silicon will have the same thickness. Further, this thickness was confirmed by contact profilometry of scratched films on quartz.

Dipped samples were placed on a silicon wafer on a metal grounding plate and connected from the dipped surface to the wafer with conductive carbon tape. Spraying was then conducted for 30 minutes on flat samples or 3-6 h on 3D samples in either a dry or wet environmental chamber at room temperature and atmospheric pressure with one dry case (RH=20%), which led to no detectable film, and a range of elevated cases (RH=45%-60%). Due to the relative difficulty in stabilizing a specific value of high humidity, the humid cases sometimes varied during an experiment.

A modified version of the mechanical cross-sectioning method developed in our previous work[1] was used to obtain the sprayed PS thickness over the CS thin film on the quartz samples. As a destructive method, it required a preparation process for the quartz substrate which was done by scribing one side of the sample before dip coating. Then, the cutting step for the sample was done after finishing the ESD. The blue PS film was imaged by a Leica DM2700 optical microscope and measured in ImageJ.31 Due to inconsistent fracture surfaces of quartz, undamaged regions were then selected for thickness measurements.

PS thickness versus chitosan thickness is plotted in Figure S1a. It can be seen that the presence of chitosan in high humidity allows for some SLED coating, but only after a film >1 μm is deposited.

This can be applied to 3D surfaces, as shown in Figure S1b, but has the disadvantages of (1) requiring high humidity, which is detrimental to the charge buildup that allows SLED, (2) requiring hydrophilic layers commensurate with the SLED coating thickness, and (3) often requiring plasma treatment. Still, this result indicates that many more commodity materials can be used for pretreatment. As one example, common sugar[†] can be readily coated in humid environments (Figure S1c).

Sapphire Wafer Ionogel Pretreatment Details

Details of dipcoat process for samples A-G, whose film thicknesses listed in Column B correspond to those referenced in Figure 2. Dipcoating occurred in a climate controlled room held at ~21 ºC.

Sample	Film Thickness (μm)	Concentration of 30:70 IL:BCP Ionogel Solution (wt%)	Withdraw Rate (mm/s)	Relative Humidity (% ±5)	Days Stored Before Film Measured	Days Stored Before Sprayed
A	0.10	10	0.1	50	1	1
B	0.11	10	0.1	50	1	1
C	0.12	10	0.1	50	1	1
D	0.26	10	0.1	60	1	2
E	0.70	30	0.05	40	1	1
F	2.15	30	0.005	60	3	3
G	2.62	30	0.005	60	3	3

Samples were dipped and stored in ambient temperature and humidity.

[†] But, regrettably, not chocolate.

Other Figures

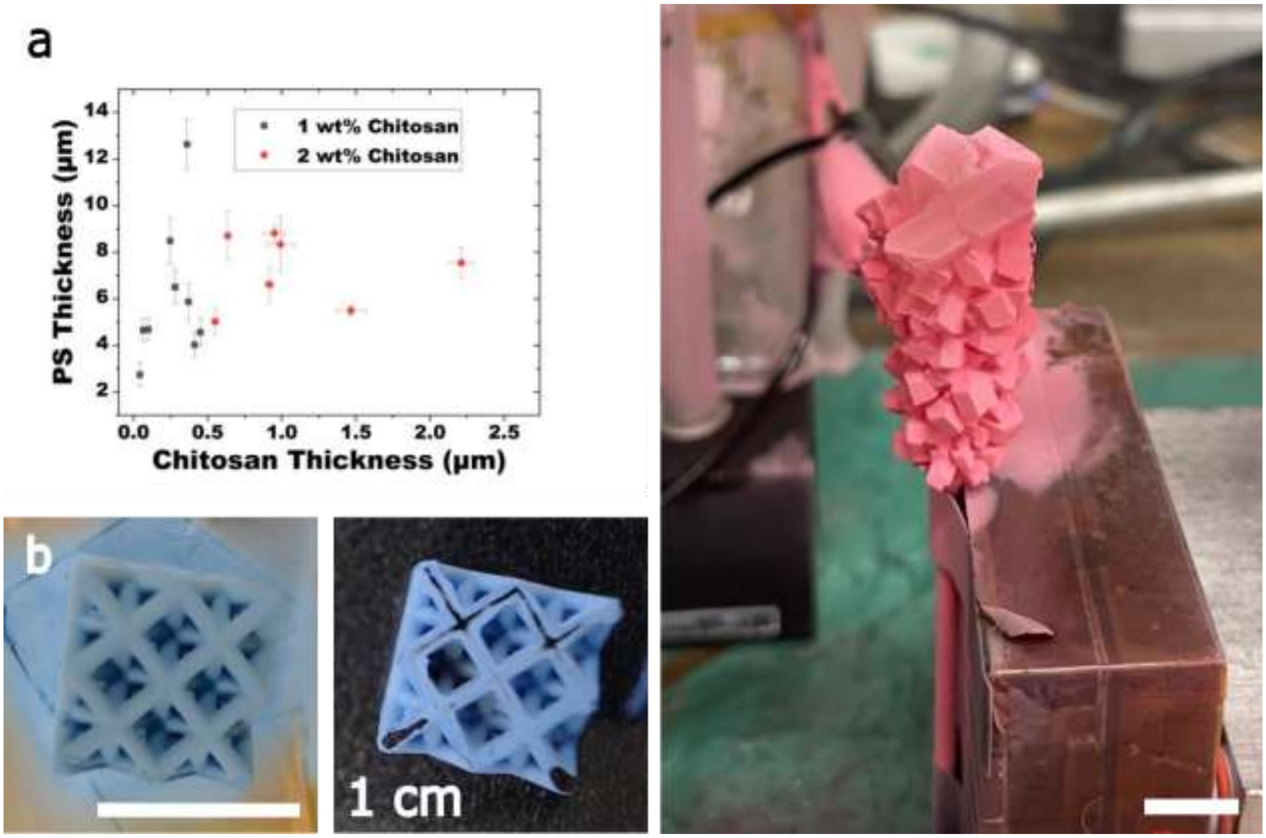

Fig. S1 *(a) Cross-sectionally measured polystyrene porous thicknesses as measured as a function of reflectometry-measured chitosan thicknesses as deposited from different concentrations of 0.5 M solution. (b) A urethane lattice electrosprayed with 1% PS in MEK + trace Oil Blue after dip coating in chitosan solution shown from the top (left) and bottom (right). (c) A sugar "rock candy" and wood stick electrosprayed with 1% PS in MEK + trace Oil Red without further treatment. All samples were sprayed at 45-60% RH. All bars represent 1 cm.*

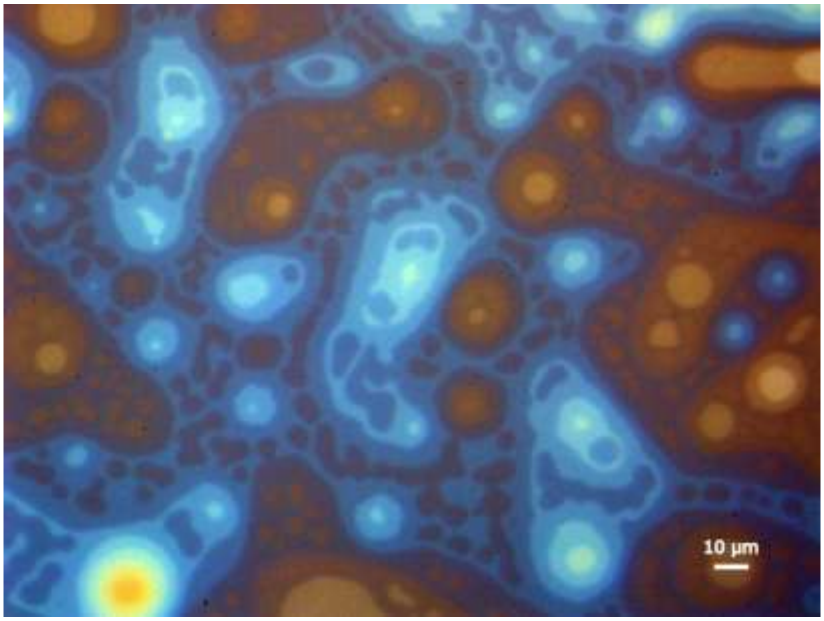

Fig. S2 *Ionogel thin film around 100 nm thick imaged through bright field microscopy at 50x. Each step in color represents a step of ~10 nm due to a block copolymer lamella.*

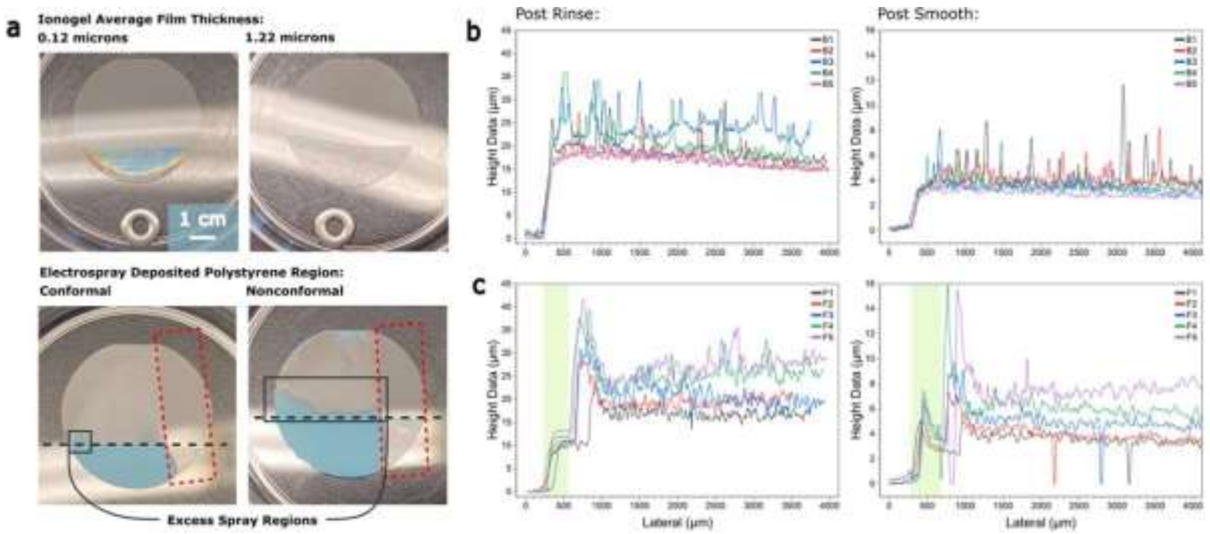

Fig. S3 *(a) (Top) Sapphire wafers with partial ionogel films. (Bottom) Same wafers sprayed with 1% PS in MEK + trace Oil Blue dye at 0.5 mL/h for 60 minutes. (b,c) Thickness plots of porous PS coated regions with ionogel removed, starting from uncoated middle of wafer to coated bottom for (b) sample B – 0.11 micron thick film, and (c) sample F – 2.15 micron thick film, with overspray region highlighted in green. The left plots are unsmoothed, and the right plots are acetone vapor smoothed, illustrating the greater variation in the thicker ionogel coating.*

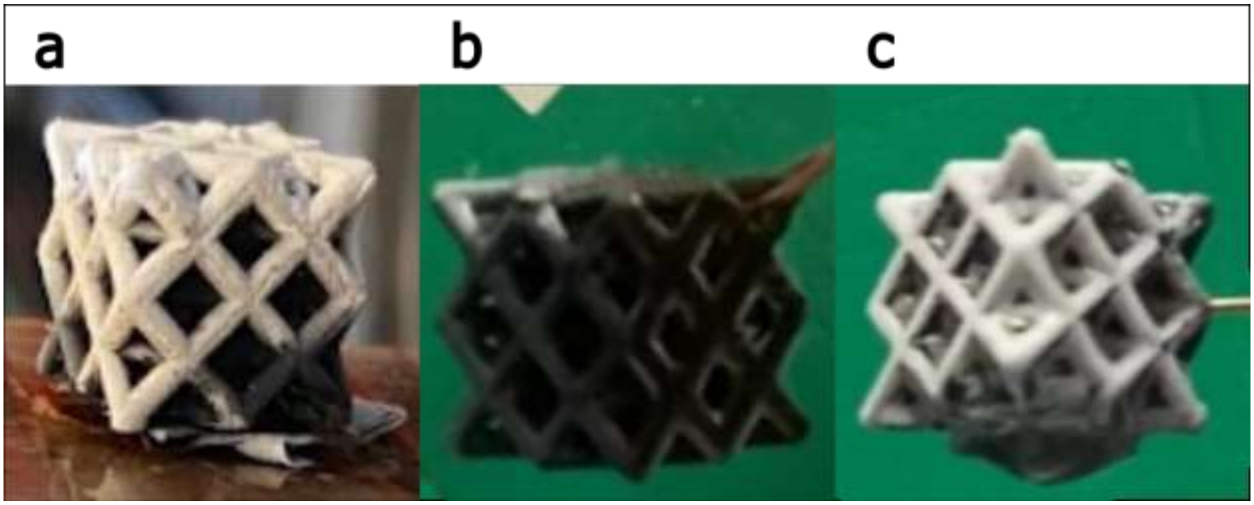

Fig. S4 *(a) Urethane lattice dipped in 10 wt% IG in water sprayed with 1% PS in MEK at 0.3 mL/h for 60 minutes (a) immediately after ESD: porous particle deposition produces "white" scattering (b) over 24 hours after ESD: ionogel rises through particle pores via capillary action turning surface “transparent” (c) after ethanol rinse: ionogel is replaced by ethanol, which evaporates, leaving behind only the porous particle coating and reverting surface to “white” scattering.*

Fig. S5 *Decreasing concentrations of 70:30 IL:BCP in DI water with which thermoplastic figurines were dip-coated for film formation. Electrosprayed with 1% PS in MEK + trace Oil Red dye at 0.3 mL/h until fully coated or coated region stops growing. (a) 10 wt% ionogel – partial coat, (b) 7.1 wt% - partial coat, (c) 3.3 wt% – full coat. All scale bars represent 1 cm.*

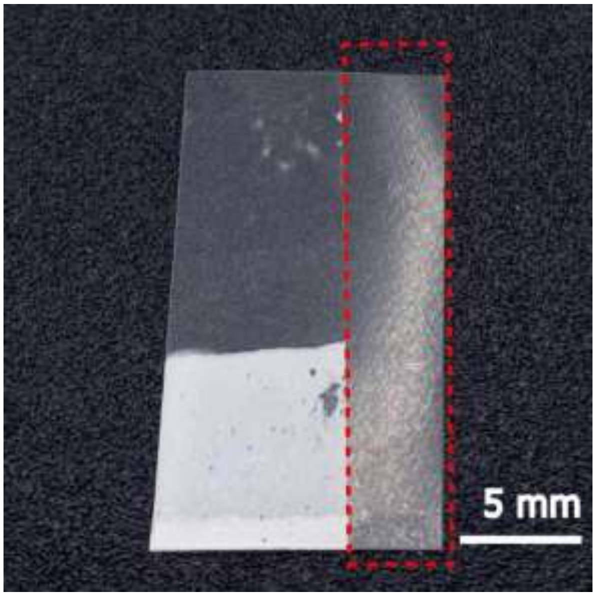

Fig. S6 *Polyethylene shrink wrap half-dipped in 10 wt% ionogel solution at a withdraw rate of 0.1 mm/s and sprayed with 1% PS in MEK at 0.5mL/h for 60 minutes. The dotted red box indicates the position of the grounding carbon tape.*

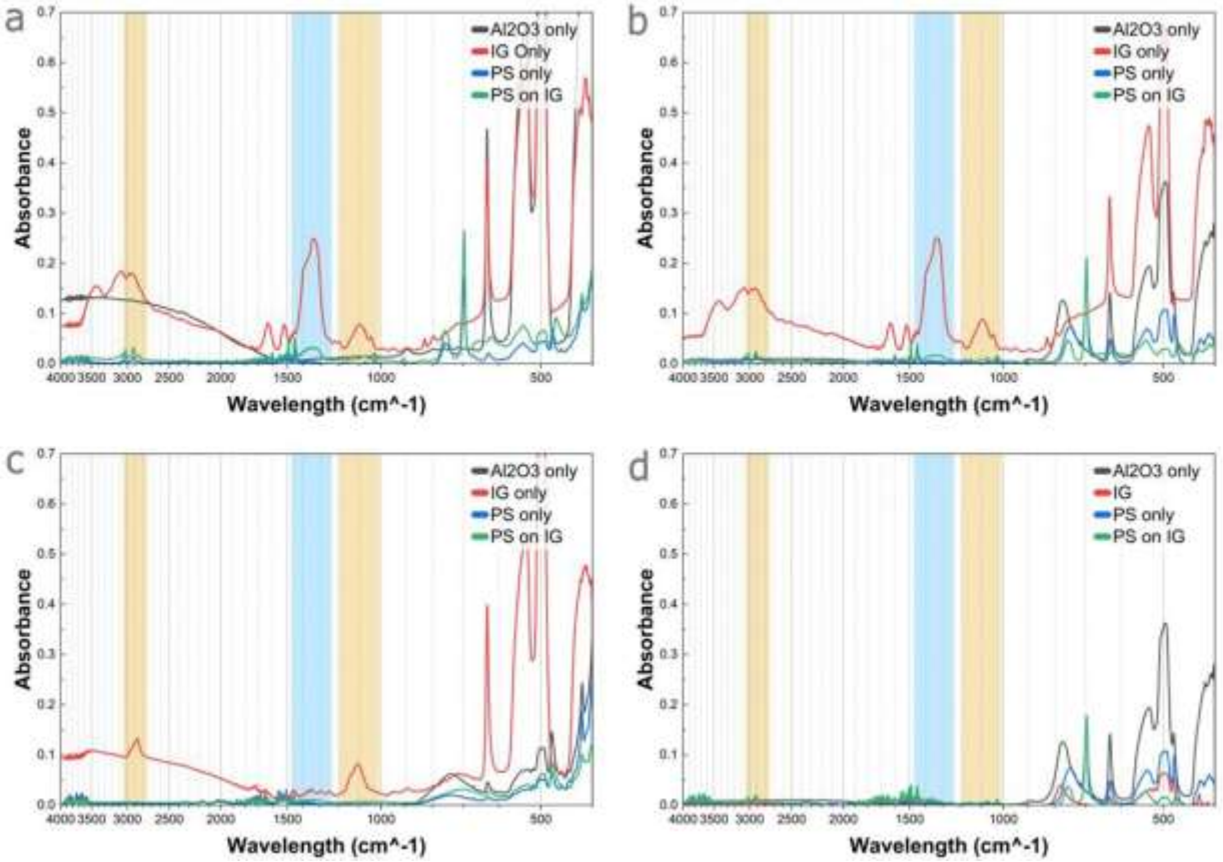

Fig. S7 *FTIR Spectra for no coat/film region (black), film only region (red), coat only region (blue), and film+coat region (green) of (a) pre-heat treatment, (b) pre-rinse treatment (c) post-heat treatment: baking at 75°C for 1 hour, (d) post-rinse treatment: dipping in ethanol for 20-40 seconds. Blue region indicates EAN peaks: present in pre- spectra, absent in post- spectra, and yellow regions indicate Pluronic peaks: present in pre- spectra and post-heat spectra, absent in post-rinse spectra. Results show solvent removal of ionogel with heat treatment and full removal of ionogel with rinse treatment.*

References

1. N. M. McAllister, R. A. Green-Warren, M. Arkhipov, J.-H. Lee, A. A. Pelegri and J. P. Singer, *Engineering Reports*, 2024, **6**, e12830.