

PARAMETRIC CONTROL OF MELTING GEL MORPHOLOGY AND CHEMISTRY VIA ELECTROSPRAY DEPOSITION

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ABSTRACT

Melting gels are a class of hybrid organic-inorganic, silica-based sol-gels which are solid below their glass transition temperatures, near room temperature, but show thermoplastic behavior when heated. While this phase change can be repeated multiple times, heating the gel past its consolidation temperature, typically above 130 °C, initiates an irreversible reaction that produces highly crosslinked glassy organic/inorganic materials via hydrolysis and polycondensation. This ability makes melting gels uniquely compatible with processing techniques inaccessible to other sol-gels. By properly tuning their properties, it should be possible to create protective coatings for electronics and anti-corrosive coatings for metals that are highly hydrophobic and insulating. However, melting gel consolidation reactions are highly dependent on charge interactions, raising the question of how these materials will respond to a processing technique, like electrospray deposition (ESD), which is dependent on charge delivery. In this study, we focus on the role that substrate temperature and charge polarity play on film morphology, consolidation chemistry, and surface properties when processing via ESD. Optical images, film thickness measurements, and FTIR were used to characterize the sprayed melting gel with the goal of developing a robust processing space for producing highly cross linked, hydrophobic, dielectric coatings.

Keywords: electrospray deposition, melting gel, FTIR

PhTES Phenyl triethoxysilane
DPhDES Diphenyl diethoxysilane

1. INTRODUCTION

Sol-gel processing is a low cost, low-temperature method for producing ceramic and hybrid organic-inorganic materials. In this technique, a colloidal solution or alkoxide precursor (“sol”) is used to generate a network of interconnected molecular chains and particles that can be consolidated by thermal treatment. First introduced by Matsuda et al. in 2001[1], melting gels are a unique class of sol-gel materials composed of oligomeric silsesquioxanes. They are solid at room temperature but are able to flow above their reversible glass transition temperature (“melt”) similar to other glassy materials. However, when the material is heated above its consolidation temperature (T_c), irreversible crosslinking takes place and a glassy hybrid 3D network is formed. After consolidation, these materials can be used for protection against corrosion, dielectric layers, hydrophobic coatings, and low temperature sealing glasses[2].

During synthesis of the melting gels, typically, mono- and di-substituted siloxanes derived from non-substituted tetraethyl orthosilicate (TEOS) are polycondensated to form an inorganic 3D backbone decorated with organic moieties. However, the functional groups remain unreacted, and the 3D network is incomplete, which allows for the “melting” behavior above the glass transition temperature. Molecular tuning of the composition of two or more precursors allows for control over macroscale properties such as the T_g and T_c . During consolidation, the alkoxy and hydroxyl groups react via

NOMENCLATURE

MTES Methyl triethoxysilane
DMDDES Dimethyl diethoxysilane

hydrolysis and polycondensation[3], though the pH of the reaction is critical to determining the dynamics of its mechanism.

The charge-dependent nature of consolidation raises the question of how these melting gels will interact with a technique like electrospray deposition (ESD) that depends on strong electric fields (~ 100 kV/m) to produce charged highly monodisperse droplets and deliver them to a grounded substrate. During this process, the initially sprayed droplets evaporate until they reach a balance between surface tension and surface charge. They then undergo a Coulomb explosion, which ejects smaller monodisperse droplets. The cycle of solvent evaporation and Coulomb explosion continues until a narrow dispersion of microdroplets deposits onto the grounded target[4]. Importantly, the heated substrate begins the process of consolidation as the material arrives. Therefore, ESD allows us to have high levels of control over the consolidation of nanoscale levels of melting gel, providing the ideal way to study the consolidation process.

Along with altering the chemistry of consolidation, ESD and charge injection will likely influence the morphology of the films. ESD has been observed to operate in three regimes for insulating polymers sprayed on conducting substrates depending on the temperature, and by extension, the fluid viscosity and thermal properties[5]. Near the glass transition temperature, in the charged melt regime, charges are unable to adequately dissipate as the film thickens, and the extreme growth can lead to fluid instabilities that create holes, which we have called Taylor-Bénard instabilities. Also, below the T_g , the self-limiting regime exists in some instances where a dry spray arrives at the substrate and trapped charges repel incoming particles. However, for this study, all sprays were undertaken well above the T_g which is known as the electrowetting regime. As material arrives, it spread laterally to allow for continued charge dissipation through the insulating polymer. This film spreads like a growing droplet with a thickness that increases nearly linearly with time. If films become too thick, they can shift to the charged melt regime and dewetting instabilities can also occur both on thin and thick films.

In this study, the interaction between ESD and melting gels is explored by observing the effects charge injection and thermal processing on both the physical morphology of films and the evolution of chemical structure during consolidation. To that end, several melting gel compositions were sprayed at various substrate temperatures and differing spray polarities. The resulting films were analyzed using filmetrics micro-reflectometry thickness measurements, water contact angle measurement, and Fourier-transform infrared spectroscopy.

2. MATERIALS AND METHODS

2.1 Materials

The alkoxide precursors used in this study were Methyl triethoxysilane (MTES) mixed with Dimethyl diethoxysilane (DMDES), or Phenyl triethoxysilane (PhTES) mixed with Diphenyl diethoxysilane (DPhDES). The ratios used in the synthesis of the melting gels are given in Table 1. These melting gels were prepared through the sol-gel process reported

previously[6, 7]. The initial mono-substituted precursor (PhTES, (Sigma Aldrich)) was mixed in an acidic solution at varying pH levels and stirred for 6 hours at 40°C, after which the di-substituted siloxane group (DPhDES, (Sigma Aldrich)) was added and the mixture stirred for 2 hours at 40°C. After formation of the gel overnight, the PhTES-DPhDES gels were thermally treated at 70°C for 24 hours and then at 110°C for another 24 hours. The PhTES-DPhDES melting gels were diluted for ESD using 2-butanone to reach a melting gel solids loading of 1 wt. %. The MTES-DMDES melting gels were prepared as follow: First, the water was mixed with hydrochloric acid (Fisher) and with half of the ethanol (Sigma Aldrich). Separately, the MTES was mixed with the other half of the ethanol. Then, the solution MTES (Gelest) and ethanol was added dropwise to the water solution under continuous stirring. The reaction vessel was sealed, and the mixture was stirred at room temperature for 3 hours. The molar ratios of MTES:EtOH:H₂O:HCl were 1:4:3:0.01. In the second step, the di-substituted alkoxide DMDES(Gelest) was diluted with ethanol in a molar ratio of DMDES:EtOH = 1:4. The DMDES-EtOH mixture was added dropwise to the first mixture. This resulting solution was kept under continuous stirring in the sealed reaction vessel at room temperature for two more hours. In the third step, ammonia (Sigma Aldrich) was added to the mixture, which was stirred for one more hour in the sealed container. The molar ratio of (MTES+DMDES):NH₃=1:0.01. The final solution was stirred for 48 hours at room temperature in an open container until gelation occurred. Ammonium chloride was formed as a byproduct during gelation. To remove this, 10 ml of dry acetone was added to the samples. The ammonium chloride was removed by filtration. Then the clear solution was stirred in an open beaker until all the acetone was evaporated. This was followed by a heat treatment at 70°C for 24 hours to remove any remaining acetone and ethanol, followed by another heat treatment at 110°C for removal of un-reacted water. The MTES-DMDES melting gels were diluted for ESD using 2-butanone to reach a melting gel solids loading of 1 wt. %.

Melting gels were electrosprayed onto ~ 320 μm thick, 0.25π in² silicon chips obtained by cutting 2" diameter silicon wafers (University Wafer, Inc., N/Ph) into quarters. These substrates were cleaned using standard solvents acetone (Sigma Aldrich) and isopropanol (Sigma Aldrich) to remove dust and impurities. They were then vacuum plasma treated in a Plasma Etch PE-25 plasma cleaning system for 10 minutes to remove unwanted hydrocarbons

<i>Composition (mol %)</i>	<i>pH</i>	<i>T_g (°C)</i>	<i>T_c (°C)</i>
87% PhTES, 13% DPhDES	1.5	28.54	126
87% PhTES, 13% DPhDES	2.5	29.88	135
70% MTES, 30% DMDES	< 2	-6.4	145

TABLE 1: MELTING GEL COMPOSITIONS

2.2 Methods

The electrospray system consisted of a Harvard, 70-2208 syringe pump, two Acopian, P012HA5M high voltage power supplies (positive sprays), and two Acopian N012HA5M high voltage supplies (negative sprays). A disposable 6-mL syringe (NORM-JECT®) containing the spray solution was fitted into the syringe pump and pumped through PTFE tubing and a stainless-steel needle (SAI Infusion, 20 gauge, 1.5" long) at a constant rate of 0.4 mL/hr. The solution is charged at the needle then passed through a weaker radial field produced by a steel focusing ring (2 cm inner diameter, 4 cm outer diameter, 3 mm thick) that provides additional Taylor cone stability. The chips were placed on a large silicon wafer atop a steel block and ceramic hot plate (Fisher Scientific) which were grounded to prevent charge accumulation. All tests were conducted with the needle tip located 6-cm above the silicon substrate and protruding 1-cm below the charged ring. This was done to allow for evaporation of all the solvent before reaching the target. All tests in this study were conducted at $\sim \pm 6.0 - 6.5$ kV, while the focusing ring was kept at $\sim \pm 3.0 - 3.5$ kV. Positive polarity sprays were conducted in a closed chamber (Electro-tech Systems Compact Temperature & Humidity Glove Box) that controlled humidity at 17-21% and ambient temperature at 24°C, while negative sprays were conducted in a downward duct fume hood (equipment) with similar ambient conditions. Melting gels were electrosprayed for 30 minutes at a range of temperatures (150-210 °C).

Film uniformity of consolidated melting gel films were measured on a Filmetrics micro-reflectometer by evaluating film thickness, roughness, and optical properties using the properties of silica. ATR FT-IR spectra were collected using a Nicolet I-S10 (Thermo Fisher Scientific) equipped with a Smart Orbit ATR to analyze the final chemical structure on the surface, identifying hydrogen bonding, bonding between solvent and melting gels, and determining whether solvent is fully eliminated from the final hybrid glass coating. To further examine surface properties, water contact angle measurements were done using an Attension T-200 Theta Optical Tensiometer (Biolin KSV) equipped with an LED light source and a 60fps camera. The contact angle was measured and calculated from optical images where droplets were placed in the center of the samples.

3. RESULTS AND DISCUSSION

3.1 Spray thickness and morphology

The general trend across different spray compositions, as illustrated in Figure 1, was that higher temperature sprays were thinner than low temperature, and negative sprays tended to be thinner than positive sprays. Focusing on temperature, this result is largely intuitive. As the temperature increases, the viscosity drops which allows the melting gel to spread more easily. However, this effect is manifested differently across compositions. For the methyl ($\text{pH} < 2$) system, sprays of both polarities clearly electrowet the substrate and tended to become thinner in a linear fashion with temperature. However, the phenyl spray, ($\text{pH} 1.5$) show higher thicknesses that drop off rapidly at

180°C and the sprays form islands on the substrate that grow as the temperature increases. While this may seem like a transition from a charged melt to electrowetting, all the experiments take place above the glass transition temperature of the melting gel. Therefore, we propose that the melting gel film dewets when it reaches the substrate due to its high hydrophobicity and surface adhesion. Accordingly, the change in thickness is simply due to the mobility of the gel overcoming the tendency to dewet.

Due to the instabilities seen in the phenyl melting gels, a polarity comparison was only drawn for the methyl sprays. It can be seen that the negative sprays are thinner than their positive counterparts on average by ~ 0.2 microns across temperature, making the negative 210 °C spray the thinnest of all the sprays. This effect is likely due to charge trapping mechanisms. Droplets are better able to trap negative charges during ESD allowing for more efficient charge dissipation which in turns allows for greater film spreading.

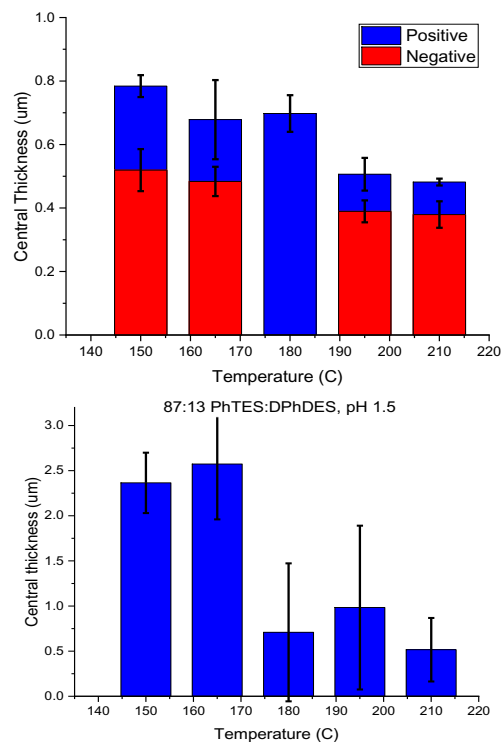


FIGURE 1: (TOP) 70:30 MTES:DMDDES, $\text{pH} < 2$ SPRAY THICKNESSES FOR POSITIVE AND NEGATIVE SPRAYS (BOTTOM) 87:13 PHTES:DPHDES, $\text{pH} 1.5$ SPRAY THICKNESSES FOR POSITIVE SPRAYS

3.2 Chemical Structure

Using FTIR data to analyze the chemical structure of consolidated films, it was found that higher temperature sprays generally had more of their functional groups reacted. The increase in internal energy influences the breakdown and formation of bonds in the silica network leading to films that generally have more complete 3D structure. For the phenyl substituted melting gel ($\text{pH} 1.5$), only positive sprays were

analyzed to look at the effect of temperature. From 150-180 °C, characteristic vibrations at higher wavenumbers $\bar{\nu} > 3200 \text{ cm}^{-1}$ indicate the presence of hydroxyl groups left over from siloxane precursors. For these same sprays (Figure 2) despite thermal treatment far above 2-butanone's boiling point for several hours, we also see the presence of ethoxy organic groups at lower wavenumbers indicating ethoxy groups which are coming from the partially unhydrolyzed MTES and DMDES along with some solvent that has become trapped during processing. These effects are much less pronounced between 195 – 210 °C, indicating better network formation due to the acceleration of the polycondensation reactions and more efficient solvent removal.

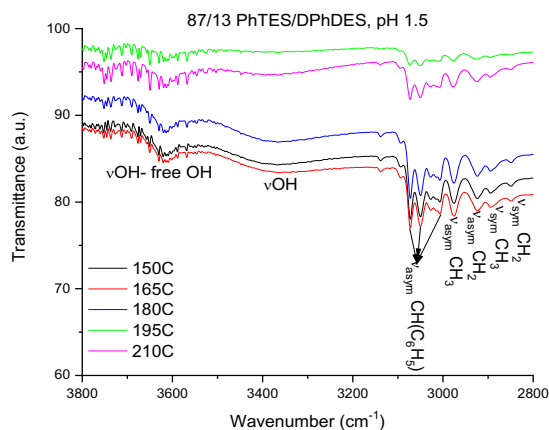


FIGURE 2: ATR FT-IR SPECTRA FOR POSITIVELY SPRAYED 87:13 PhTES:DPhDES, pH 1.5, 30 MINUTES AT DIFFERENT TEMPERATURES

For another phenyl melting gel synthesized at a pH of 2.5, sprays were analyzed across temperatures and polarity (Figure 3). For both polarities, it was seen that the highest temperature spray, 210 °C represented the best network formation, though the 165 °C negative spray produced surprisingly good results. For the positive spray, ethoxy groups are still present for all temperatures indicating that they are somehow protected by the positive polarity independent of temperature. On the other hand, sprays from 150 – 180 °C still have Si-OH bonds present, but these disappear at higher temperatures. There is also a transition at 195 °C where the low number of transverse Si-O-Si groups and shifted alkoxy peaks indicate that the alkoxy groups are starting to decompose. By 210 °C they have completely decomposed leading to a dense film with phenyl groups only bonded on the surface.

For the negative spray series, the effect of temperature can be seen in the elimination of the ethoxy groups Si-O-C in the higher temperature sprays, 185 – 210 °C. Si-C(C₆H₅) bonds at 1200 cm⁻¹, on the other hand, appear to be independent of temperature. Comparing the ratio of transverse Si-O-Si bonds to Si-C(C₆H₅) bonds can be used as a metric for 3D network formation (Figure 3). For the negative sprays, we can see that this ratio is relatively steady across temperatures, with the 165 and 210 °C sprays showing the highest 3D network formation.

Comparing both the positive and negative sprays, we can see that for the 150 – 180 °C positive spray, the results are similar to the negative sprays. However, for 190 °C, the ratio drops below 1 before increasing rapidly at 210 °C to form the most consolidated spray of all.

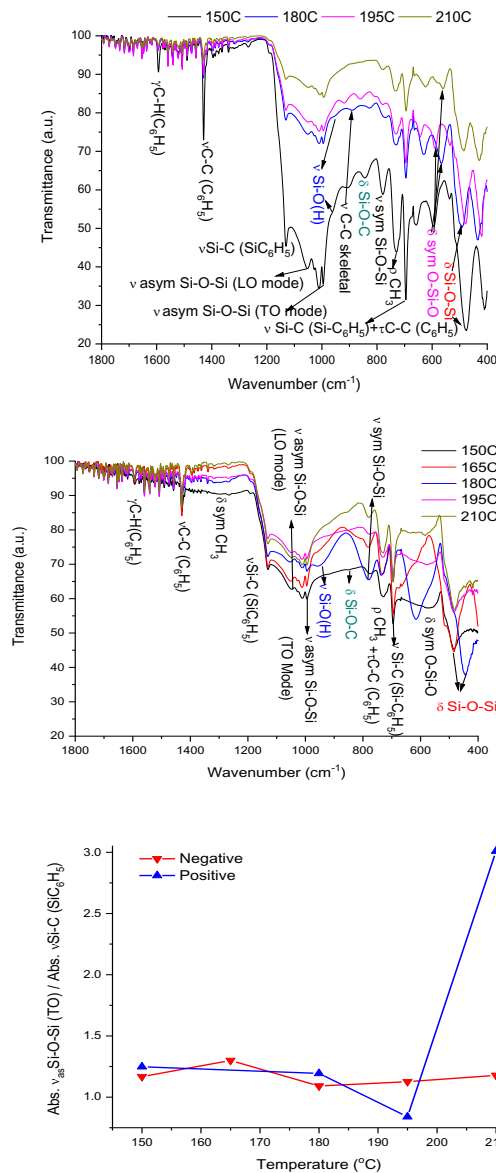


FIGURE 3: (TOP) ATR FT-IR SPECTRA FOR POSITIVELY (TOP) AND NEGATIVELY (MIDDLE) SPRAYED 87:13 PhTES:DPhDES, pH 2.5, 30 MINUTES AT DIFFERENT TEMPERATURES (BOTTOM) POLARITY COMPARISON OF RATIO OF TRANSVERSE Si-O-Si to C(SiC₆H₅) BONDS AS IT VARIES WITH SUBSTRATE TEMPERATURE

3.3 Contact Angle

Finally, the contact angle made by water droplets on the surface of the film was used to gauge hydrophobicity and provide insight on surface properties like surface tension. For the pH 2.5

phenyl spray it was found that films across temperatures and spray polarities were generally hydrophobic, with negative sprays being consistently more hydrophobic than positive sprays. Positive sprays all had contact angles below 95 °, while negative sprays all had contact angles above 97 °. The 165 °C negative spray was the most hydrophobic of all with a contact angle of 106 °. Although there is not a clear trend with temperature, these results align with the FTIR data which shows a reduction in polar groups for the 165 °C film. While the dewetting behavior of the phenyl gels somewhat obscures these results because the instabilities create surface roughness that can contribute to the hydrophobicity, the coincidence with the FTIR data indicates this is not a spurious result.

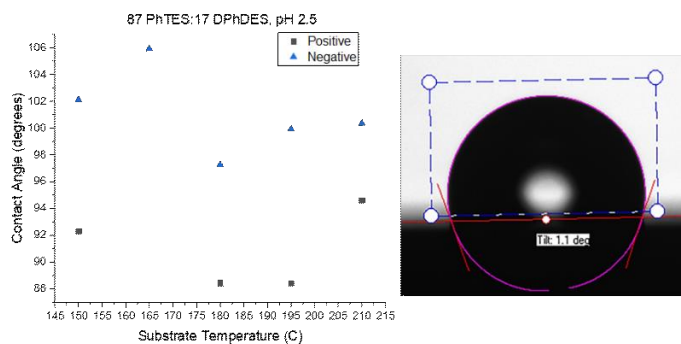


FIGURE 4: (LEFT) CONTACT ANGLES MEASURED ON 30-MINUTE SPRAYS OF 87:13 PHTES:DPHDES, pH 2.5 (RIGHT) OPTICAL IMAGES OF WATER DROPLET ON THE SURFACE OF PHENYL MELTING GEL NEGATIVELY SPRAYED AT 165 °C

Property	Result
Thickness	Higher temperature sprays are thinner than lower temperature, and negative sprays are thinner than positive
Morphology	Increased mobility in higher temperature sprays overcomes the tendency for sprays to dewet
Chemical Structure	The most complete consolidation for pH 2.5 phenyl spray occurs at 210 °C positive spray
Contact Angle	The negative sprays are more hydrophobic than the positive

TABLE 2: SUMMARY OF RESULTS

4. CONCLUSION

This parametric study of melting gels processed via ESD has demonstrated preliminary trends addressing the impact of temperature and charge injection on the consolidation of micro/nanoscale melting gels. By exploring this parameter space, we are better able to control the coatings produced by ESD which will allow us to optimize them for specialized

applications. For example, for corrosion protection, uniform, well cross-linked, relatively soft, and hydrophobic thin film is desired. However, this research is not limited to a single application, and exploring the fundamental properties of melting gels will allow for broad use.

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