Micro-particle Entrainment From Density Mismatching Mixture by Dip Coating Process

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MICRO-PARTICLE ENTRAINMENT FROM DENSITY MISMATCHING MIXTURE

BY DIP COATING PROCESS

By

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Solid particle transfer is a vital process for many applications such as painting, coating, materials joining, meta-surface, bio-medical applications etc. Different solid transfer techniques including welding, spray coating, roll coating etc. are available for delivering solid particles on simple structures. However, those techniques cannot effectively deliver particles to complex structures. In this thesis work, the research objective is to develop a high throughput and economical material transfer technique for complex architecture with low volumetric flux.

In first part, the particle concentration of pseudo suspension was investigated in dip coating process from density mismatching mixture. The solid particles concentration was varied from \( \phi_p = 20\% \) to \( \phi_p = 50\% \) and the suspension viscosity was measured through Anton Paar MCR 302 rheometer and it was observed that suspension rheology varied from Newtonian behavior in high concentration (\( \phi_p = 50\% \)) of solid particles and coating thickness as well as surface coverage become independent of the suspension viscosity on this concentration. The binder volume fraction is also varied ranging from \( \phi_b = 2.5\% \) to \( \phi_b = 10.5\% \) mostly to understand the
effect of binder on the particle entrainment behavior. It was observed that increasing the binder volume fraction \((\phi_b = 6.5\% \text{ to } \phi_b = 10.5\%)\) while the solid loading is constant \((\phi_p = 35\%)\), high surface coverage over 90% and uniform coating thickness can be achieved which demonstrated an optimum composition for efficient solid transfer process. Also, at zero particle regime, particle entrainment was resulted at very low capillary number below the threshold value.

In second phase, the binder influence and its working mechanism was described to understand its effect of particle entrainment. To show that the particle concentration was remained constant \((\phi_p = 10\%)\) and binder PMMA was varied on molecular weight \((15K, 120K \text{ and } 350K \text{ g/mole})\) as well as its mass loading. Binder at liquid carrier system (LCS) forms a dilute condition at low viscosity \((\leq 2 \text{ mPa.s})\) and high MW \((120K \text{ and } 350K \text{ g/mole})\) which considers the small particles entertainment for its thin polymer layer and high evaporation rate. However, at high viscosity of 15K PMMA \((4 \text{ and } 6 \text{ mPa.s})\), the LCS mixture acts as a concentrated gel-like solution and the particle accumulation follows the distribution like the bulk powder distribution. This behavior can be incorporated on particle sorting process and high-throughput material transfer for material joining process on porous structures.
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CHAPTER 1

INTRODUCTION

Solution derived material transfer or particle deposition in the form of thin (<5 µm) film, is gaining attentions for miniaturization, system integration, and complex design through optimization. Material transfer in the form of coating has widespread applications on radio frequency identification [1], e-paper [2], organic photovoltaics [3], batteries [4], fuel cells [5], sensors [6], microfluidics [7, 8], and supercapacitors [9, 10]. Coating process has different methodology due to the environmental conditions like atmospheric or vacuum conditions. Metal deposition for making thin and uniform layers requires low or high vacuum conditions and physical vapor deposition [11, 12], chemical vapor deposition [13, 14] or plasma sputtering [15, 16] are popular techniques for these metallic coatings. In contrast, solution derived, or sol-gel coatings require atmospheric conditions, and it can be directly deposited on the substrate where the solution volatilizes making a dried thin film [17, 18].

Sol-gel techniques [19] like dip coating, spin coating, and roll coating are common processes used for different electronic applications. Spray, spin or roll coatings have some drawbacks with their operation procedure including uncontrollable thickness on roll coating, uneven spraying, sagging, spluttering on spray coating and uncoated areas on spin coating. Solid transfer techniques like welding, spray coating, roll coating etc. are available for delivering solid particles on simple structures. However, those techniques cannot effectively deliver particles to complex structures. In contrast, dip coating provides uniform coating on different substrates or porous complex architectures [20]. Dipping into homogeneous density-matching solutions having micron particles, are popular interest for its applications on surface passivation [21], selective activation of surface energy [22], thermal barrier, antifouling, surface filtration [23] and meta-
Surface wave absorption or manipulation [24]. Dip coating can also transfer particles in complex geometry like porous solid structure. It can also be used for tissue scaffold fabrication [25], oil/water separation [26], surface protection [27-29] and flexible electronics isolation [30].

Liquid film thickness by dip coating is proposed by Landau, Levich [31], and Derjaguin in 1942 for Newtonian fluid using the LLD equation, \( h = 0.94l_{c}Ca^{2/3} \). This liquid thickness depends on both fluid properties (i.e., surface tension \( \gamma \), density \( \rho \), viscosity \( \eta_0 \)) and process parameters (i.e., withdrawal velocity \( U \)). This equation is applicable for \( Ca < 10^{-2} \), where capillary number, \( Ca \) is a dimensionless number and \( Ca = \frac{\eta_0 U}{\gamma} \). This equation is later modified in different experimental conditions and expanded for cylindrical geometries like wires, ropes, fibers or tubes. Solid particles in a liquid carrier system (LCS) act as an obstacle to Newtonian behavior and it demonstrates complex rheological behavior which has received attention since 1906 by Einstein [32, 33]. Einstein first provided an expression to describe the viscosity of suspension with low concentration of particles. This expression is later modified considering the suspension properties (i.e., particle concentration) and process parameters (i.e., high and low shear rates).

Micro-scale large inorganic hard solid particles have reduced surface area and higher density. When these large inorganic particles are added to the LCS, it creates a negatively buoyant mixture due to the high particle to liquid density ratio and it creates a phase separated mixture with LCS. Therefore, external kinetic energy is required to ensure the uniform dispersion of particles to the mixture which acts as a pseudo suspension. The entrainment through dip coating using neutrally buoyant particles suspension has been studied before. Gans et al. used polystyrene particles (20, 40 70, 125 \( \mu \)m radius) in a homogeneous density matching mixture in highly densed and viscous silicon oil to investigate the volume fraction of particles on
entrainment by dip coating without evaporation. Palma et al. experimented monodisperse 80, 145 or 550 µm dia. polystyrene particles in a liquid mixture of PEGPG (poly(ethylene glycol-\text{-}ran-propylene glycol)\text{-}monobutyl-ether) water solution and zinc chloride to study the dependence of withdrawal velocity, particle size and volume fraction on the entrainment from neutrally buoyant mixture by dip coating process. [34, 35]. Due to the complex nature of suspension and inorganic hard solid large polydisperse particles (>1 µm) with high solid loading, dip coating from density mismatched mixture with large polydisperse particles is not fully investigated in previous literatures.

In this thesis work, the objective is to develop a high throughput and economical material transfer technique, particularly dip coating, for complex architecture with low volumetric flux. To achieve this objective, solid microparticles from density mismatching mixture are transferred on the substrate in an optimum way, then the fabricated thin film has been characterized and finally the influence of process parameters (i.e., withdrawal velocity \(U\)) and suspension properties (i.e., solid loading, polymer loading in LCS, polymer MW in LCS). Furthermore, the transferred mechanism of this research with dip coating is compared with the existing literature of neutrally buoyant suspension.

Noteworthy, chapters 2 to 4 are included as research articles, and they are presented as it is on the journal paper. Chapter 2 is published in a reputed journal named Journal of Micro and Nano-Manufacturing (DOI: 10.1115/1.4051260) and chapter 3 is published in a reputed journal named Scientific Reports (DOI: 10.1038/s41598-022-14162-5). Chapter 4 is in the submission stage in a journal.
CHAPTER 2

DIP COATING FROM DENSITY MISMATCHING MIXTURE

Abstract:

Solid transfer technology from mixtures is gaining ever-increasing attention from materials scientists and production engineers due to their high potential in near net-shaped production of cost-effective engineering components. Dip coating, a wet deposition method, is an effective and straightforward way of thin-film/layers formation. The dipping mixtures are often embedded with inorganic fillers, nanoparticles, or clusters ($d<30$ nm) that produce a thin film ranging from $nm$ to couple microns. An increase in the volume of solid transfer by the dipping process can open-up a novel 3D near-net-shape production. However, adding larger inorganic particle size ($>1\mu m$) or adding a higher solid fraction will increase the solid transfer but may result in a multi-phase heterogeneous mixture. In this work, the physical mechanism of an increased volume of solid transfer with a larger spherical particle size ($>5$ $\mu m$) is investigated. Polymer-based glue and evaporating solvent are mixed to construct the liquid carrier system (LCS) for large inorganic hard particles. Moderate volume fraction of inorganic particles ($20\% < \phi_p < 50\%$) are added into the LCS solution as solid loading. Three levels of binder volume fraction are considered simultaneously to investigate the effect of the solid transfer. Cylindrical AISI 304 steel wire with dia. 0.81 mm is used as the substrate for dipping and coating. The coating thickness, weight, and the surface packing coverage by the particles are measured in our lab. The results presented the influence of volume fraction of inorganic particle and glue composition on the solid transfer from the heterogeneous mixture.

Keyword: Dip coating, particle transfer, liquid carrier system, density mismatching mixture.
Introduction:

Solution derived material transfer, or deposition in the form of thin (<5 µm) film is of great interest due to the drive for miniaturization, system integration, and complex design through optimization. The purpose of the generated coating has widespread application for decoration, protection, and functionality [36]. Recent applications of coating technology was found on radio frequency identification [1], e-paper [2], organic photovoltaics [3], batteries [4], fuel cells [5], sensors [6], microfluidics [7, 8] and supercapacitors [9, 10]. The solution/liquid carrier may contain the material as suspension (direct transfer) or as precursor chemicals (ionic transfer). Common transferrable are either organic (polymer chain from the solution) or inorganic nanoparticles (ceramics or metal oxides). The generated film thickness ranges from nm to a couple of micrometers. The resultant liquid carrier system (LCS) can be in various forms, i.e., solution, slurry, suspension, or heterogeneous mixture.

Various coating methods are available for its enormous applications and necessities in different fields of atmospheric to vacuum conditions. Vacuum deposition techniques like physical vapor deposition [11, 12], chemical vapor deposition [14, 37], or plasma sputtering [15, 16] methods are generally applied for thin and uniform deposition of metallic layers in low or high vacuum conditions. In contrast, solution or sol-gel coating methods can be applied in atmospheric conditions. It requires a target material (solid or liquid) and a binder, which are dissolved in a homogeneous solution. Sol-gel can be directly deposited on the substrate where the solution evaporates and makes a dried thin film [17, 18].

Among all the solution or sol-gel [19] techniques, dip coating, spin coating, spray coating, and roll coating are simple to use in different electronic applications. Spray coating requires a spray gun that sprays viscous or non-viscous liquid coatings on different sizes of surfaces. The coating
surface needs to be accessible to the spray gun, which may restrict this process to the internal surface, including porous architecture. Besides, uneven spraying, sagging, spluttering on spray coating may occur. Spin coating is applied in the center of the substrate and then flourish at high centrifugal force. The process is suitable for symmetric surfaces, and a special vise may need to be designed for the rotating object. However, swirl patterns and uncoated areas are often observed in the spin coating process. Paint rollers are required for roll coating over a large and often flat surface area. Like the spray gun, the roller needs to access the substrate and can become labor or capital intensive technique. However, dip coating, often known as dipping lacquers, can provide a high-quality uniform coating on different size or shaped substrates or large surface areas, including porous architecture.

Evaporation based dip coating or dipping lacquers is the simplest and probably the most economical and commercially applied method for the film fabrication process [27, 38]. Dip coating of colloids [39], sol-gels [17, 19], or suspensions [34, 35] are previously reported where positively or neutrally buoyant solid particles were applied for making the homogeneous mixture. Particles are entrained on the substrate, and evaporation of the volatile compound (solvent) leaves a dried film as a coating. The dip-coating functionality is often achieved via liquid phase epitaxy or self-assembled monolayer (SAM). The uniform film thickness from this technique can range from a few angstroms to a couple of microns. However, high volume solid transfer by the LCS through the dipping process can open-up novel techniques for the 3D near-net-shape production process via sintering, robocasting, additive manufacturing, or material joining [20]. For example, larger inorganic micro-scale particles (>1 µm) are commonly used in manufacturing industries (e.g., brazing powder, metal filler, and powder particles). Their substantial delivery in hard-to-reach places (i.e., porous structure, inner surface in thin holes) is
often a functional requirement. The micro-scale inorganic particles have reduced surface area compared to nanoparticles, and their higher density makes them prone to sedimentation in most the liquid carrier system. As a result, they create a mismatch in density with LCS and produce negatively buoyant mixtures defined as a heterogeneous mixture. Dip coating with such a heterogeneous mixture has not been studied before.

In this paper, the inorganic particle transfers process on a cylindrical metal substrate from a heterogeneous mixture using the dipping lacquers process is studied. The liquid carrier system (LCS) is designed with a binder and evaporating solvent to make a homogeneous solution. Spherical shape brazing powder is considered as the coating material, which is added in the LCS to make the dipping mixture. External kinetic energy is required to maintain the stability (sedimentation) and the rheological properties of the multi-phase heterogeneous LCS. A magnetic stirrer provides a continuous stirring, which suspends the denser micro-particle and distributes them in the mixture. The thin metal rod is dipped into the pseudo suspension, and particles are entrained on the substrate by balancing the capillary rise and viscous drag. The coating thickness, coating weight, and the surface packing coverage by the particles are measured in our lab. The results are analyzed to find the influence of volume fraction of inorganic particle and glue composition on the solid transfer from the heterogeneous mixture. This research can help understand the high-volume solid transfer technique and the knowledge can be used to develop novel manufacturing processes.

**Materials and methods:**

The heterogeneous dipping mixture in this paper has three main components (i) solute (ii) solvent, and (iii) particles. The solute and the solvent create the homogeneous LCS, which helps to deliver the particle on the substrate.
**Solute/Binder:** Polymethyl methacrylate (PMMA; Mw~15,000; Sigma Aldrich) is considered as the binder. It is a popular transparent acrylic resin commonly known as plexiglass. This amorphous thermoplastic demonstrates satisfactory gap-filling properties, excellent thermal stability (flash point >250°C) and tensile strength (72 MPa), low density (~1.17 g/cm³), relatively harmless non-explosive and non-flammable material. The popular aphorism of “like-dissolve-like” governs its solubility [40].

**Solvent:** Toluene, chloroform, butanone (MEK), and Dioxolane are some common solvents for PMMA. Among them, 1,3-dioxolane has a favorable toxicity profile, low density (~1.06 g/cm³), and an excellent evaporation rate. This cyclic acetal facilitates polymerization of PMMA, has an intermediate polarity (dielectric constant = 7.13), and vapor pressure 70 mmHg (20 °C). The solvent is acquired from Sigma Aldrich.

**Inorganic Particles:** Brazing powder (Nicrobraz 51; Wall Colmonoy company, Ohio) is considered as the solid particles. They are commonly used to join similar or dissimilar materials using various solid-state joining processes (e.g., diffusion bonding, transient liquid phase bonding, and brazing). The powders are usually hard spherical particles with an average diameter of φ ≈ 44 microns (Mesh 325). The particles are sieved with Gilson Performer III shaker through Stainless Steel 635 Mesh (20 µm) in our lab to reduce polydispersity and are analyzed using SEM as shown in Figure 1. The samples are attached to a cylindrical mount with carbon adhesive tape during SEM imaging. Images are obtained in an Electron High Tension (EHT) value of 2.00 kV, and the magnification was 800 X. The SEM images are analyzed through ImageJ software (NIH, USA). The images are at first converted to an 8-bit image and calibrated to a 10 µm scale bar. The measurements are done through the calibrated scale bar. For size distribution, 163 particles from SEM images are measured, and the particle size distribution is
plotted using Origin50 software, as shown in Table 1 and Figure 1. The average particle diameter is 5.69 µm, and most of the particles range from 2.5 to 6.5 microns.

Table 1: Properties of Nicrobraz 51 powder.

<table>
<thead>
<tr>
<th>Specification</th>
<th>AWS A5.8: BNi-12; ISO: Ni 720</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Cr 25%; P 10%; Ni 65%</td>
</tr>
<tr>
<td>Particle shape and size</td>
<td>Spherical, Avg 5.69 µm (min: 1.25 µm and max: 19.9 µm)</td>
</tr>
<tr>
<td>Density</td>
<td>0.285 lb/in³</td>
</tr>
</tbody>
</table>

Figure 1: SEM Micrograph of inorganic particles (Nicrobraz 51) and its size distribution after sieving (10 µm bar).

**Heterogeneous mixture preparation:** Adding the binder in the solvent at a different ratio and stirring it with the help of a magnetic stirrer at room temperature (25°C) and 500 rpm for 4hrs will create a homogeneous liquid carrier solution (LCS). The insoluble solid particles are then added with the LCS at a different volume fraction and are kept for 30 minutes while the magnetic stirrer was moving at minimal suspending speed. As the solution density has a major difference from the particle density, it makes a negative buoyant suspension with particles in a
heterogeneous mixture. The solid loading volume fraction for particles is kept below 60% for avoiding high yield stress (jammed state) due to random close packing (RCP) [41]. The preparation flow diagram of the heterogeneous mixture is shown in Figure 2, and the prepared mixture is pictured in Figure 3.

Figure 2: Heterogeneous dipping mixture preparation.

**Metal rods as substrate:** Rods are mechanical structures with one-dimension much larger than the other two, e.g., wire, ropes. Metal wire or rods will be used as the substrate for transferring the particles. Metal wire or rods are a readily available form of material with a wire size ranges from a tiny wire of 0.2 mm in dia. to cables of 13 cm in dia. or more. Almost all metals, including zirconium and tungsten [42], or bio-degradable Mg [43] can be formed into a wire. Stainless Steel AISI 304 (procured from ClampTite LLC) with 0.81 mm diameter is used as a substrate. The wire to particle diameter ratio >300 for which the curvature of the wire can be assumed as a 2D surface with respect to the particle diameter. Sample metal rods are cut in 8 cm length specimens and are sequentially polished by emery papers from 800 to 1200grit. Samples are cleaned in the ultrasound bath with acetone for 10 minutes at 50 ºC, which will remove any
surface contaminant and passive film. They are rinsed with distilled water and dried at a 60 °C oven temperature for 10 minutes to remove the water films rested after rinsing.

![Image of polymeric solution, phase-separated mixture, and stirred heterogeneous mixture]

Figure 3: (a) Polymeric solution (b) phase-separated mixture and (c) stirred heterogeneous mixture.

**Dipping setup:** An in-house dipping station is prepared in our lab with a Z-axis stage controlled with a Flashcut CNC controller using G-code. A high precision bipolar stepper motor (SANYO) connected with a computer is used to control the dipping speed within a ±2% precision. The metal substrate is attached to a fixed support saddle with a reference, and the stepper motor translates the wire surface. The metal substrate is immersed into the ‘pseudo’ suspension or mixture at a constant speed of U=10 mm/s, maintains a constant dwelling time of 5 sec, and then retracts at the same hoisting speed. The dipping station's schematic is shown in Figure 4, placed at a room temperature of 25°C and atmospheric pressure with a relative humidity of 20%. The low relative humidity facilitates the evaporation of the solvent from the meniscus. The mixture height is kept at 1 inch, and the dipping length was 0.6 inches during the
whole experiment. The remaining height is used to accommodate the magnetic stirrer height and clearance between the dipped substrate and the stirrer.

![Diagram of the dipping setup](image)

**Figure 4: Schematic diagram of the dipping setup.**

**Characterization:** Microbraz 51 microparticles are prone to sedimentation due to their reduced surface area and higher density. The heteronomous mixture is stirred at the minimum rotational speed to make it a complete off-bottom mixture and minimize the turbulence and eddies. Such stirring RPM is often defined as minimum suspended speed [44] in mechanical agitation of an industrial process for which no solids rest on the vessel base for longer than 1–2 sec. Both powder loading and the binder volume fraction determines the stirring energy required for bulk motion and the RPM requirement. In this experiment, an oval shape Teflon stir bar with the major and minor axis dimensions as 0.6 inches and 0.25 inches is used to stir the mixture between 500-700 RPM. Higher lifting energy will be exerted on the mixture near the pellet at the bottom compared to the top of the dipping vessel. This will result in some gradient distribution of powder particles, which may cause some variation of coating thickness. Thus, the coating thickness and coverage are measured as a weighted average in this paper.
Three samples rod are prepared and dipped for each experiment conducted here to ensure statistical significance. After dip coating, the dipped substrate's surface is divided into three regions: top, middle, and bottom at an equal length of 0.2 inches for measurement. The morphological analysis of the coated substrate is carried out in those three regions. A Keyence VHX 7000 digital microscope is used to measure the coating thickness and coating coverage on the substrate.

**Coating thickness measurement:** The coating thicknesses are determined by measuring the cross-section of the coated sample in the three regions (top, middle, and bottom). The cross-sectional measurement is performed following the metallographic sample preparation and analysis of the coated substrate with the help of the resin casting process. Epoxy resin and Epoxy hardener are mixed in a 5:1 ratio and stirred carefully for 10 minutes to form no bubbles. The epoxy is then poured on the coated substrate, which is cured for 24 hours. After the solidification, it is cut and then polished in a rotating disk using emery paper grit 60, 120, 800, and 1200. Finally, the visible cross-section of the coated substrate is analyzed through the digital microscope for coating thickness. The thickness is measured at multiple locations along the perimeter, and a weighted average technique is applied to determine the final coating thickness. The weight is determined as the ratio of covered and uncovered length along the perimeter of the cross-section. After each measurement, the epoxy casted substrate is cut and polished with emery paper to get a new location along the substrate length. In this way, the cross-sectional coating thickness of each substrate is measured in six different locations (0.1 inches apart) to investigate their spatial distribution.

**Surface coverage measurement:** After dipping, the coated film characterization is carried out by digital microscopy (VHX 7000). For calculating the surface packing coverage, the
particle covered areas are measured using ImageJ software. The images are converted to an 8-bit image in this software and are calibrated to a 3µm scale bar for the measurements. The micrographs are cropped into a rectangular shaped image, and the particle covered area is measured using contours in the ImageJ software. The ratio of the particle covered areas and the rectangular cropped area provides the surface packing coverage. For statistical significance, five cropped images are analyzed for each specimen at three locations (bottom, middle, and upper layer), and results are shown in the result section.

**Results and Discussion:**

A workable range of volume fraction has been determined first to investigate their effect on solid transfer and coating characteristics. Adding polymer binder and immiscible particles to any liquids modify its physical properties, i.e., density, viscoelasticity. LCS is a particle bearing liquid and can display complex rheological behavior considering the volume fraction of its content. Added particles will act as obstacles to the fluid flow, increasing the flow resistance or the viscosity, which may result in shear thickening behavior. Similarly, adding binder will also increase the viscosity facilitating shear-thickening but may help adhere the particles on the substrate. Persistent shear-thickening inevitably leads to some attraction between the particles, and soon the mixture becomes unfit for dipping and becomes jammed. Jamming volume fraction for monodisperse sub-micron spherical particles ($\phi_{p,max}$) can range from 0.52 to 0.74 with some staking scheme. However, their random close packing (RCP) density is about 0.64, which may increase up to ~0.74 for polydisperse particles [41]. A wide range of volume fraction for binder and particles have been reported in the literature, where the volume fraction is used as an adjustment tool for density matching suspension. A density matching mixture is prepared with PEGPG (poly(ethylene glycol-ran-propylene glycol)-monobutyl-ether) and neutrally buoyant
spherical polystyrene particles of mean diameter 80, 145, or 550μm [35]. The viscosity of the mixture is controlled by adjusting the volume fraction of the binder between 4 wt% to 45.5 wt% and the volume fraction of the particle between 10% to 50%. Similar non-Brownian polystyrene micro-particle (d=20, 40, 70, 125 μm) is used [34] in silicone oil carrier with a volume fraction of 10% to 41% to study the effect of particle size and the coating layer. Smaller microparticles are also reported (d=1.1μm polystyrene volume fraction of 0.9-35% and d=2μm silica volume fraction of 5-27%) to form self-assembled monolayers (SAM) [45]. Sub-micron particles have also been studied for dip coating application, usually with smaller volume fractions. For example, gold nano-particle (d~12 nm) suspended in the water is studied in the range of 0.01-0.3% vol fraction [46]. Unlike microparticles, the electrostatic force and van der Waals forces become prominent in submicron size particles due to their possession of a large specific surface. To avoid the agglomeration between nano-particles, a dispersant is often added to the mixture. However, for larger particles (>1μm) the specific surface area is reduced, which makes them non-interacting and non-agglomerating spherical solid particles in the liquid matrix (non-Brownian regime) [47, 48]. Thus, no dispersant is used in our mixture. In this paper, three levels of particle volume fraction (LP) as 20%, 35%, and 50% are investigated. Similarly, three-level of binder volume fraction (LB) as 3%, 7.5% and 12% and three levels of solvent volume fraction (LS) as 45%, 58% and 72% is considered. To prepare the mixture, the particle volume fraction is kept fixed (LP = φp), while binder and solvent volume fraction is normalized, and the % volume fraction is shown in Table 2.
Table 2: Composition of heterogeneous mixture binder, powder, and solvent.

<table>
<thead>
<tr>
<th>Mixture Composition*</th>
<th>Component Volume Fraction Level</th>
<th>Normalized Volume Fraction %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binder Level, $L_b$</td>
<td>Powder Level, $L_p$</td>
</tr>
<tr>
<td>000</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>012</td>
<td>3</td>
<td>35</td>
</tr>
<tr>
<td>101</td>
<td>7.5</td>
<td>20</td>
</tr>
<tr>
<td>202</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>021</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>110</td>
<td>7.5</td>
<td>35</td>
</tr>
<tr>
<td>122</td>
<td>7.5</td>
<td>50</td>
</tr>
<tr>
<td>211</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>220</td>
<td>12</td>
<td>50</td>
</tr>
</tbody>
</table>

*0=Low, 1= Medium and 2= High

Figure 5: Viscosity vs shear strain rate for (a) LCS solution and (b) particle laden mixture.

To determine the impact of binder, solvent and particles, the viscosity is measured for a range of shear rate (0.2 to 1000 s$^{-1}$) as shown in Figure 5. The binder solution (i.e., LCS) is prepared by stirring and mixing the solute (PMMA) and the solvents ($1,3$ Dioxolane) at different ratios. The binder PMMA has the polar ester group located as a pendant in the non-polar hydrocarbon backbone, which lays as an interlaced coil. As a result, the location of the carbonyl group in the chain is not entirely accessible, and polarity is implicit. Smaller solvent molecules diffused in the glassy state of binder polymer and increase the mobility of PMMA, creating a homogenous and
transparent solution. However, the dissolution of PMMA may require a couple of hours following the diffusion of the solvent. The viscosity of the LCS will increase with a higher percentage of PMMA due to the saturation of polar bonding between the solute and solvent molecule. The change in rheological properties, i.e., viscosities and shear stress, can be observed in Figure 5(a). For example, the composition ‘012’ without particle has the lowest volume fraction of the binder (4%), which shows the lowest apparent viscosity. Whereas composition ‘220’ without particle has the highest volume fraction (~21%) and the viscosity of all compositions considered here.

The presence of non-Brownian (>1μm) solid spherical particles (SP) in the LCS solution will reduce its flowability due to the frictional contact. The rheological window can shift based on the parameter (i.e., shear rate, \( \dot{\gamma} \) or particle size, \( d \)) of the mixture. For example, with a low particle volume fraction (20%<\( \phi \)), the viscosity \( \eta \) of the mixture may remain in the Newtonian regime for a low shear rate, \( \dot{\gamma} \) [49]. With increased volume fraction (\( \phi > 20\% \)) of micro-spheres, the LCPS mixture may demonstrate pseudoplastic behavior and even may reach to the jamming density. From the viscosity plot in Figure 5(b), it can be observed that adding particles significantly increases the viscosity of the mixture. At the lowest volume fraction of particles (20%), the viscosity decreases with an increase in binder fraction. However, such a trend was not consistent for the higher volume fraction of particles (35% and 50%). For example, viscosity increases from 012 to 211 and to 122 compositions. This increment can be attributed to the reduced interstitial spacing between particles and the binder fraction. In contrast, the highest viscosity is observed in 110, 220, and 021 compositions which can be primarily attributed to the friction between particles due to the reduced interstitial spacing among them.
**Qualitative Observations:** Once the substrate is dipped inside the heterogeneous mixture, the liquid carrier with inorganic particles adheres to the solid substrate surface due to the intermolecular force between the mixture and the solid substrate surface. During the withdrawal of the substrate, the mixture velocity is directed downward, and a layer is entrained. The balance between the viscous drag, and the capillary rise determines the film thickness [50]. Figure 5 illustrates the mechanism of the dip-coating process. The evaporation, during dip coating, occurs when the whole substrate is outside the heterogeneous mixture. The convective flux on particles generates from the solvent evaporation and the capillary rise during the dipping process [46, 51, 52]. The particle transfer mechanism is expressed with the formation of three areas [53], namely, (i) deposition area, (ii) assembling area, and (iii) collection area, as schematically showed in Figure 4. The deposition area represents a dry region where the particles are entrapped or attached to the substrate with the help of binders following single-layer or multilayer or a random dispersion of the particles. The solvent, embedded in thin-film, tends to evaporate in the assembling area as shown in Figure 5. In the collection area, the volumetric density of inorganic particles is higher than the rest of the mixture due to the continuous flux of particles formed by the convective forces in the heterogeneous mixture.
The entrapment of particles on the substrate is governed by the capillary rise and viscous drag, which is counterbalanced by the evaporation of the solvent used in the heterogeneous mixture. Withdrawal speed is reported as a significant parameter in dip coating for coating thickness and its uniformity [50, 54]. A wide range of withdrawal speed has been investigated in the literature ranging from 1 to 50 mm/s. At lower withdrawal speed, convective flux is suppressed by the evaporation of the solvent as the influx of particles is limited. At a higher withdrawal speed, the capillary number is increased, causing larger convective flux, and a larger volume of material will travel with the withdrawing substrate due to visco-inertia. The balance between the evaporation and the gravity may cause unstationary thickness of the entrained mixture (expulsion of the droplet). We observed periodic change in thickness as drop expulsion with higher (>10 mm/s) withdrawal speed in this experiment. At lower withdrawal speed, few particles are
entrained following random distribution on the substrate. Thus, to achieve measurable outcomes, 10 mm/s withdrawal speed, and 20% relative humidity (RH) is considered in this paper.

![Figure 7](image)

Figure 7: Picture observations after the withdrawal of the substrate with the different volume fraction of powder, $\phi_p = 20\%, 35\%, \text{and} 50\%$ (from left to right) and with low to high (top to bottom) glue concentration. The orange and blue scale bar is 100 $\mu$m.
After dipping, the substrates are analyzed under the microscope, which are shown in Figure 6. With a low volume of binder ($\phi_p = 5\%$) and powder ($\phi_p = 20\%$), the 10 mm/s withdrawal velocity resulted in a coating film with very few particles. When the substrate is withdrawn from the mixture, a polymeric layer of the glue is formed as a liquid film. With a low volume fraction of particles, this polymeric layer gets an insufficient amount of particles from the meniscus to adhere to the substrate. As a result, a few clusters of particles on the substrate are observed with some irregular arrangement for this low volume fraction mixture. Due to the low binder concentration, the liquid film thickness remains very low, and it captures very few particles from the meniscus. However, with the same amount of particles and increased binder, the entrapment of the particle on the substrate is improved, as shown in Figure 7.

When the volume fraction of particles in the heterogeneous mixture increases, more inorganic particles were entrained in the film with a regular pattern. The volume fraction ($\phi_p = 35\%$) being moderate, we observed the particle distribution in the film remained heterogeneous with some regions covered by a cluster of particles. This heterogeneous coating regime provides diverse properties in different coating zone, which is not desirable for practical applications. We also observed this coating regime by changing only the concentration of the binder for the same amount of particles. As we increased the binder concentration, a high viscous layer of the binder is developed on the substrate, increasing the liquid film thickness as plotted in Figure 7 and reported in Table 3. This polymeric layer entrapped more powder from the meniscus forming high contact area of particles. The high-volume fraction ($\phi_p$) of inorganic particles in the mixture influences particle concentration on the coated film. With $\phi_p = 50\%$, a uniformly distributed coating of particles was obtained, covering almost the full substrate surface area. This coating may form single or multilayer or both with random dispersion of particle assembly.
Our observation is consistent with the three coating regimes described by Gans et al. [34] for the dip coating of suspensions with spherical density matching micro-particles. As the coated area is mostly covered with liquid only, this regime can be referred to as a liquid regime. The medium volume fraction of binder and particle (second column of Figure 7) matches the definition of the heterogeneous coating regime. The high volume fraction column can be referred to as an effective viscosity regime. With a higher volume fraction of binder, we observed multilayer coating with full coverage. The quantitative result presented in Table 3 shows the coating thickness and surface coverage measurement at different compositions of the heterogeneous mixture. The coating thickness and substrate coverage increase with a high concentration of binder and powder. The depth of the coated layer is also measured with the image stacking technique, which is presented as a color-coded depth distribution in Figure 9. The maximum coating thickness measured from these color-coded images are also presented in Table 3. The maximum coating thickness for 000 compositions is reported as lower (10.37 µm vs. 7.96 µm) than the average cross-sectional coating thickness. This is due to the presence of a low number of smaller particles and limited imaging locations. The dry weight of the substrate before and after the coating is also measured, which is also shown in Table 3. As the volume fraction of binder and powder increases, the weight of the coating also increases. However, it should be noted that due to the quick evaporation of the solvent, only the binder and particles are accounted for in the measured weight.
Table 3: Coating thickness, maximum thickness, weight, and surface coverage on the different volume fraction of powder and binder

<table>
<thead>
<tr>
<th>Mixture Composition</th>
<th>Avg. Cross-sectional Coating Thickness (μm)</th>
<th>Maximum Coating Thickness (μm)</th>
<th>Avg. Coating Weight (mg)</th>
<th>Avg. Surface coverage by particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>10.37</td>
<td>7.96*</td>
<td>0.17</td>
<td>18%</td>
</tr>
<tr>
<td>101</td>
<td>11.46</td>
<td>11.87</td>
<td>0.23</td>
<td>25%</td>
</tr>
<tr>
<td>202</td>
<td>9.94</td>
<td>14.85</td>
<td>0.3</td>
<td>72%</td>
</tr>
<tr>
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<td>14.23</td>
<td>23.73</td>
<td>0.67</td>
<td>72%</td>
</tr>
<tr>
<td>110</td>
<td>18.23</td>
<td>28.6</td>
<td>1.57</td>
<td>93%</td>
</tr>
<tr>
<td>211</td>
<td>19.94</td>
<td>34.45</td>
<td>1.6</td>
<td>97%</td>
</tr>
<tr>
<td>021</td>
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<td>37.26</td>
<td>3.2</td>
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</tr>
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<td>122</td>
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</tr>
<tr>
<td>220</td>
<td>36.57</td>
<td>47.78</td>
<td>6.8</td>
<td>100%</td>
</tr>
</tbody>
</table>

Figure 8: Average surface coverage distribution on different glue and powder concentration
Figure 9: Color map distribution of particles and their z-height using image stacking from the mixture composition.
Figure 10: Cross-sectional pictures at the bottom location after the withdrawal of the substrate with a different volume fraction of powder, $\phi_p = 20\%$, $35\%$, and $50\%$ (from left to right) and with low to high (top to bottom) binder concentration. The red scale bar is $100 \mu m$.

To investigate the effect of gravity on the coating thickness, the cross-section of each specimen is taken 0.1 inches apart, as explained in the methodology section. Figure 9 represents the coating thickness of the substrates at a 0.1-inch location from the bottom of the substrate length for different compositions of a heterogeneous mixture. The plot presented in Figure 10 and Figure 11 shows the cross-sectional coating thickness for the compositions. With the increase in glue and powder concentration, the coating thickness also increases. However, in high binder and
powder concentration, the solvent concentration becomes lowest, and the shear stress of the mixture increases exponentially. This phenomenon can change the mixture into yield stress fluid, and it makes the dip-coating process very difficult. Moreover, the coating layer for this highly concentrated mixture becomes multi-layer thick and non-uniform throughout the layer.

Figure 11: Cross-sectional coating thickness at different location of substrates along the dipping length.
Figure 12: Coating thickness at the bottom and top of the rod for comparison.

For the same composition, evenly distributed coating layer is observed at the bottom section over the circumference. In contrast, a partial coat of particles is observed at the top, as plotted in Figure 12 and Figure 13. This can be attributed to spatial particle distribution in the stirred mixture. While moving inside the mixture, the magnetic stirrer makes a toroidal flow regime inside the mixture [55], and it results in non-Brownian motion acting over the micro-particles. The concentration gradient of powder forming a mismatched density with liquid adds a gravitational effect that results in a different upward flux of particles at different suspension locations. Different structural coating formation occurs on the substrate due to this difference in the upward flux of particles. For example, insufficient convective flux occurs at the top location, and abundant convective flux occurs at the bottom location. Figure 13 (a) & (b) presented the different coating formation at the top and bottom location resulted from the upward convective flux variation. Wang et al. described this convective flux variation at different suspension concentrations [46]. Due to this insufficient flux of particles at the top location, insufficient
coverage and arbitrary coating thickness can be observed. However, at the bottom location, the abundant flux of particles helps to form evenly distributed surface coverage and coating thickness over the circumference of the substrate as shown in Figure 13(a). To account for this variation, the weighted average of the coating thickness is measured over the cross-sectioned perimeter during thickness measurement. However, other than the topmost location (0.6 inches), the coating thickness variation along the dipping depth is somewhat steady as per Figure 11.

![Figure 13: Coating layer distribution in cross-section at the (a) bottom and (b) top location. The scale bar 100 µm.](image)

Figure 14 represents the cross-sectional picture of the substrate where the binder methyl methacrylate forms a polymeric bridge that helps the powder particles into the entrapment from the meniscus. This absorbed polymer coat around the particle helps them coagulate on the substrate and form a polymeric bridge. It works as a viscous film, which also helps in particle entrapment when the film thickness is larger than the particle diameter [56]. For example, with 20% particle volume fraction, the coating thickness remains around 10 µm, but the surface coverage increases from 18% to 72% by increasing the binder concentration from 5% to 11%. A similar scenario was observed for $\phi_p = 35\%$, where the surface coverage increases from 72% to 97% by increasing the binder volume fraction from 2.6% to 11.14%. We observed the maximum
average coating thickness of 36.57 µm at $\phi_p = 50\%$ and $\phi_p = 10.5\%$, which is a multilayer coating. Thus, the binder concentration ranging from 9-11 percent shows better particle transfer from the mixture over 90% surface coverage with a well-distributed coating layer.

Figure 14: Cross-section of the substrate. The red scale bar is for 100 µm.

Gradual increase of coverage with the increasing particle $\phi_p$ is observed and the maximum coverage is measured at $\phi_p = 50\%$. An increase in particle concentration accelerates the particle adhesion to the substrate. When the particle concentration is low, arbitrary scattered particle distribution is observed, referred to as the liquid regime. We observed full particle coverage on $\phi_p = 50\%$ with multilayer configuration on the coated substrate. These results are in good agreement with the maximum transfer of large particles from a heterogeneous mixture. However, with the high volume of powder concentration, the pseudo suspension delivers a disparate coating thickness pattern for its variable viscosity change. Furthermore, in maximum volume fraction, high upward convective flux was created by a high concentration of particles. So, the extensive gravitational effect that acts on the formation of the coating layer resulted in a non-uniform coating thickness at the bottom location, as shown in Figure 15. In contrast, with
moderate particle concentration ($\phi_p = 35\%$), this gravitational effect remains low, and the non-uniformity is not vivid. This helps to create a regular pattern of coating thickness over the substrate throughout the entire location. Thus, 35% volume fraction particles at medium binder level provide 97% surface coverage with uniformity.

Figure 15: (a) Non-uniform and (b) regular coating shape at the bottom and middle location of the same substrate with high particle and binder concentration. (100 µm scale bar).

**Conclusions:**

We have investigated the effect of particle and binder volume fraction simultaneously on solid transfer and coating characteristics from a density mismatching heterogeneous mixture. First, a workable range of volume fraction has been determined. The heterogeneous mixture is prepared, and thin metal rods are dipped under predefined conditions. An increase in binder and particle volume fraction increases the solid transfer. However, increasing the binder and powder concentration will decrease the solvent amount and may introduce complex rheological behavior, which will result in a non-uniform and thick disparate coating layer. The focus here is to investigate the process parameters that control the coating thickness over the substrate and optimize the material composition to achieve a well-distributed surface coverage. Analyzing the
cross-sectional and surface packing coverage, we have demonstrated the optimum composition of particles (35\%) and binder (9–11\%) for the effective solid transfer. In the future, the influence of binder chemistry on this solid transfer mechanism will be characterized to get the high potentiality of its application on cost-effective engineering applications.
CHAPTER 3

MICRO-PARTICLE ENTRAINMENT FROM DENSITY MISMATCHED LIQUID CARRIER SYSTEM

Abstract:

Micro-scale inorganic particles (d>1 µm) have reduced surface area and higher density, making them negatively buoyant in most dip-coating mixtures. Their controlled delivery in hard-to-reach places through entrainment is possible but challenging due to the density mismatch between them and the liquid matrix called liquid carrier system (LCS). In this work, the particle transfer mechanism from the complex density mismatching mixture was investigated. The LCS solution was prepared and optimized using a polymer binder and an evaporating solvent. The inorganic particles were dispersed in the LCS by stirring at the just suspending speed to maintain the pseudo suspension characteristics for the heterogeneous mixture. The effect of solid loading and the binder volume fraction on solid transfer has been reported at room temperature. Two coating regimes are observed (i) heterogeneous coating where particle clusters are formed at a low capillary number and (ii) effective viscous regime, where full coverage can be observed on the substrate. ‘Zero’ particle entrainment was not observed even at a low capillary number of the mixture, which can be attributed to the presence of the binder and hydrodynamic flow of the particles due to the stirring of the mixture. The critical film thickness for particle entrainment is \( h^* = 0.16a \) for 6.5% binder and \( h^* = 0.26a \) for 10.5% binder, which are smaller than previously reported in literature. Furthermore, the transferred particle matrices closely follow the analytical expression (modified LLD) of density matching suspension which demonstrate that the density mismatch effect can be neutralized with the stirring energy. The findings of this
research will help to understand this high-volume solid transfer technique and develop novel manufacturing processes.

**Introduction:**

Improved understanding of higher yield particle transfer processes during dip coating is critical to address current challenges facing the manufacture of next-generation materials and devices, including tubular structures, synthetic blood vessels [57], tissue scaffolds [25], flexible electronics [30], filtration systems [34], and meta-surfaces that regulate optical, acoustic, and magnetic waves [58]. Often, to achieve these functions, the solid substrate (i.e., flat plate, cylinder, convex surface [59]) is dipped into a liquid bath of colloids [60], sol-gels [38, 61], or suspensions [34, 35], which contains the positively or neutrally buoyant solid particles (usually sub-micron size) that will be delivered spatially. Particle transfer occurs at the three-phase boundary [62] during the withdrawal stage due to entrainment, when the viscous drag force becomes larger than the resistive capillary force. The simplicity, low cost, and reasonable control make this particle transfer process by dipping an extensively used method [54, 63].

Delivering or depositing nano-materials ($d<30$ nm) on a substrate by dipping into homogeneous density-matching solutions are commonly investigated for surface passivation [21], selective activation of surface energy [22], thermal barrier, antifouling, surface filtration [23] and meta-surface wave absorption or manipulation [24]. To facilitate the delivery of small particles, they are often entrained into a solution called a liquid carrier system (LCS). Both aqueous [64] and organic solvent carriers are commonly used as LCS, where a lower volume fraction of monodisperse particles ($<20\%$) forms a suspension. Leveraging the rheological properties of the mixture, particles are delivered on the substrate, including internal surfaces and porous architectures with possibly low volumetric flux. Dip coating can also deliver particles in complex
(e.g., bifurcated or branched) geometries such as refractory material coat for foundry cavity [65] and bio-compatible polymer coat to construct synthetic blood vessels [57]. Additionally, dip coating is often used for tissue scaffolds fabrication [25], porous structure joining [20, 48], oil/water separation [26], surface protection [28, 29, 66], soft robotics locomotion [67] and flexible electronics isolation [30].

A method to predict the dip coated film thickness on a plate geometry withdrawn from a non-evaporating, Newtonian fluid was first proposed in 1942 by Landau and Levich [31] and then Derjaguin, using the LLD equation, \( h = 0.94l_c Ca^{2/3} \). The liquid film thickness \( h \) depends on both fluid properties (i.e., surface tension \( \gamma \), density \( \rho \), viscosity \( \eta_0 \)) and dipping process parameters (i.e., withdrawal velocity \( U \)). These parameters are incorporated in the LLD equation with the dimensionless capillary number, \( Ca = \frac{\eta_0 U}{\gamma} \) and capillary length, \( l_c = \sqrt{\frac{\gamma}{\rho g}} \) for \( Ca < 10^{-2} \). It was later expanded for cylindrical geometries, since wires, ropes, fibers or tubes are extensively used in industrial, medical, and textile applications [32, 33, 68]. To define the cylindrical geometry, the Goucher Number, \( Go = \frac{r}{l_c} \), is often used which is the ratio between the vertical curvature expressed by capillary length, \( l_c \) and the azimuthal curvature expressed by fiber radius, \( r \). The modified LLD theory for cylindrical geometry is applicable for \( Go < 3 \) and is expressed as \( h = 1.34r Ca^{2/3} \) to predict the liquid film thickness on wires and fibers [68, 69].

When particles are added to the LCS, it starts to demonstrate complex behavior, which has received substantial attention in the literature. Solid particles in a liquid are considered obstacles to its rheological behavior and increase viscosity. At a relatively high particle volume fraction, the viscosity of the particle-laden mixture starts to follow a non-linear behavior. This non-Newtonian viscosity is commonly described by apparent viscosity \( (\eta_r = \frac{\tau}{\dot{\gamma}}) \) where \( \tau \) is the
shear stress and \( \dot{\gamma} \) is the shear rate. The apparent viscosity for a suspension can be normalized and reported as \( \eta_r = \frac{\eta(\phi)}{\eta_0} \). Einstein first described a formula for the viscosity of suspension with low particle concentration [32, 33]. This formula was then adjusted by Krieger & Dougherty [70] for high solid concentration, which provides effective viscosity for low to high shear rates [70-72]. Several other studies have described the suspension rheology [73], clogging in confined flows [74, 75] or the inertial suspension flow [76] for wet deposition of sub-micron particles.

Larger inorganic micro-scale particles \((d > 1\mu m)\) are commonly used in manufacturing industries (e.g., brazing powder, metal filler, and 3D printing powder). Understanding their transfer process from liquid carrier system can be beneficial for micro-nano manufacturing processes. For example, in transient liquid phase bonding, the interlayer (filler) metal particles need to be delivered on the faying surface for joining. By understanding their transfer physics from multi-phase fluid can open-up an economical manufacturing process for complex architecture including porous solid [20, 48]. Such understanding can be directly implemented to novel particle sorting technique of different size and density distribution [77, 78], inorganic material coating on 3D printed polymer surface [79], acoustic meta-surface for hypersonic boundary layer transition and stabilization [80], dust mitigation in both hydrophobic and hydrophilic surfaces [81] surface wettability and flowability improvement for medical devices [82] and thin-surface wicks for heat and mass transfer [83-85]. The micro-scale inorganic particles have reduced surface area and higher density, making them negatively buoyant in the LCS and challenging to yield high solid transfer due to the density mismatch causing them to settle in suspension. Additionally, due to the economical droplet-based fabrication techniques used (e.g., gas atomization, plasma atomization, and plasma rotating electrode process), the particle size distribution often follows a continuous, polydisperse exponential pattern, which is
commonly expressed with the Rosin-Rammler expression [86]. Their high yield delivery to hard-to-reach places (i.e., porous structure, inner surfaces) and large surface areas is often a functional requirement. The transfer mechanism of polydisperse particles is rarely investigated in this dip-coating process with a density mismatched heterogeneous mixture.

Earlier particle transfer by dip-coating research efforts can be classified broadly: (i) adhesion and peel test measurements of film strength, (ii) mono-layer formation of nano-particles, (iii) effect of process parameters (i.e., dipping angle, withdrawal speed, dwelling time, etc.) on the deposited layer, and (iv) characterizing the interfacial interactions at the molecular level [87]. The particle-surface adhesion force for entrainment can be categorized as: (i) electrostatic, (ii) van der Waals, (iii) covalent bond (iv) hydrogen bond and (iii) gravitational forces [51, 88, 89].

For submicron size particles, the electrostatic force and van der Waals are prominent for adhesion to the substrate due to their large specific surface area. However, for larger particles (> 1µm), the specific surface area is reduced, which makes them non-interacting and non-agglomerating particles in the liquid matrix or otherwise known as the non-Brownian regime [48, 90, 91]. The mechanism of non-Brownian microparticle (avg. Dia 40~550 µm) transfer has been studied by Palma et al. [35] and Gans et al. [34] using particles with a spherical morphology. The entrainment of the neutrally buoyant micro-particles in these studies was found to be directly related to the dimensionless capillary number. However, due to the higher particle to liquid density ratio, inorganic microparticles are prone to sedimentation in most liquid carrier systems and require additional considerations. As a result, additional kinetic energy is required to ensure the uniform dispersion of the particles in a ‘pseudo suspension’. Due to this additional complexity, particle transfer of large (>1 µm) inorganic, density mismatched, polydisperse
particles from a stirred mixture with high solid loading (> 20%) has not been fully investigated in the existing literature.

In this work, we investigate the transfer of micrometer-size inorganic powder particles from density mismatching mixture through the dip-coating process on a cylindrical substrate. A liquid carrier system (LCS) solution was prepared by combining a polymer binder and an evaporating solvent. Nickel-based brazing powder with a spherical shape and high density were used as the solid particles added to the LCS solution to prepare the density mismatching mixture. Particles were dispersed with the assistance of a magnetic stirrer to maintain the ‘pseudo suspension’ characteristics of the mixture. The particle transfer mechanism was characterized by surface coverage, film thickness, particle layer, solid loading, and the binder volume fraction. Based on the observations, the particle transfer process is differentiated into two regimes: (i) heterogeneous regime and (ii) effective viscous regime, which is parametrized with the dimensionless capillary number. The transferred particle matrices are compared with the analytical expression of a density matching suspension (modified LLD equation). We found that in the presence of binder, particles can be entrained on the substrate even below the critical film thickness \( h^* \geq 1.1a \), where \( a \) is the particle radius) reported earlier [49]. Furthermore, the transferred particle matrices of our ‘pseudo suspension’ is compared with the existing analytical expression of density matching neutrally buoyant suspension.

**Methodology:**

In this study, the density mismatching mixture was prepared with three components: binder, solvent, and solid particles. The binder and solvent acted as a liquid carrier solution (LCS) which helped transfer solid particles on the substrate. The polymethyl methacrylate (PMMA; \( M_w \sim 15000 \text{ g/mol} \); Sigma Aldrich) was the binder, which has low density (~1.19 g/cm\(^3\)), ~41 mN/m
surface tension, and is a benign, non-explosive and non-flammable material [40]. 1,3-Dioxolane (from Sigma Aldrich) was used as the solvent, which has 34.3 mN/m surface tension, ~1.06 g/cm³ density, and vapor pressure of 79 mmHg at 20 °C [92]. Brazing powder (Nicrobraz 51; Mesh 325; Wall Colomonoy Company, Ohio) was used as the solid inorganic particle (IP), which has a density of 7.89 g/cm³. Before mixing with LCS mixture, the particles were sieved with a Gilson Performer III shaker through a stainless steel 635 mesh to reduce its average particle size. After sieving, the average particle diameter was measured by analyzing the SEM image in ImageJ, which showed a 5.72 µm average diameter and a standard deviation of 3.09. The dipping mixture was prepared in 20 mL screw top, clear borosilicate glass, vial with the dimension of 75.5 × 22.5 mm provided by Fisher Scientific. The mixture preparation is shown in Figure 16 and discussed in detail elsewhere [91].

Figure 16: SEM micrographs of particles added to the homogeneous LCS to make the heterogeneous mixture. The mixture is stirred, and the rod is dipped for particle transfer.

The density mismatch between particles (7.89 gm/cm³) and the LCS solution will facilitate fast sedimentation of particles and drag them to the bottom. To resist the gravitational force, external kinetic energy in the form of agitation was applied to maintain a just suspending speed for the particles. A cylindrical magnetic stirrer was used that had a length and diameter of 14.9 mm and
5.95 mm, respectively. Stirring created a pressure difference (normal stresses so that the particles lifted off and stayed suspended, creating a dispersed mixture (‘pseudo suspension’). Cylindrical AISI 1006 mild steel rod with an average diameter of 1.06 mm (procured from ClampTite LLC) was used as the substrate for transferring particles. Rod samples were cleaned in an ultrasound bath with acetone for 10 minutes at 50 °C to remove any surface contaminant and passive film. The effective shear viscosity of the polymer solution (LCS) was determined by a rotating rheometer (Anton Paar Moduler Contact Rheometer; MCR302) using a flow curve test with shear rates ranging from 2 to 1000 s\(^{-1}\) and using a parallel plate geometry with 50 mm diameter and a gap of 0.2 mm. The surface tension and density of the LCS solution was calculated by the weighted average of binder and solvent [35, 93], which can be expressed as 
\[ \gamma = \gamma_{sv} + (1 - \phi_s)\gamma_b \]  
and \[ \rho_s = \rho_{sv} + (1 - \phi_s)\rho_b \]  
Where \( \gamma, \phi,\) and \( \rho_s \) denote for surface tension, volume fraction, and density of LCS solution, \( \phi_s \) for solvent volume fraction, and the subscript \( sv \) and \( b \) denotes solvent and binder, respectively.

Figure 17: Sample image of the 3D depth profile of liquid coating.

An in-house dipping station was used in our lab for this work. The construction of the dipping setup and the working process were discussed in our earlier work [86]. The dipping experiment was performed at 25 °C and atmospheric pressure with a low relative humidity of 20%, which allowed evaporation of solvent from the liquid-vapor interface (meniscus) during the dipping
process. The substrates were immersed into the density mismatching mixture at a constant speed (10 mm/s) and maintained for 10 seconds of immersion time, followed by the withdrawal at the same hoisting speed. The samples were kept at room temperature between 2-4 hours at a vertical position for drying before the polymer film thickness was measured using a VHX 7000 Digital 4K microscope (KEYENCE corp., IL). A narrow groove was created with a round edge cut on the substrate at three different locations and the 3D profile depth was measured and averaged as shown in Figure 17. High resolution 4K images of the dipped rod were taken with the same microscope and the images were analyzed with a script written in MATLAB. The image was transformed into gray scale and binary segmentation was performed using Otsu method [94]. Particles were separated by tracking the center using watershed algorithm and the particle boundary is identified with the closed contour. The length scale was measured for their average size. Additionally, the surface coverage was measured with the ratio of the area covered by the particle to the total area of the substrate surface at three locations (bottom, middle and top) using the same image analysis script.

Results:

**Solid loading of dipping mixture:** Adding binder and immiscible particles to a liquid transforms its rheological properties. The addition of particles will act as obstacles to the fluid flow which will induce a non-linear dependency under applied shear (non-Newtonian). At a higher volume fraction, the mixture may exhibit friction-induced continuous shear thickening (CST) or discontinuous shear thickening (DST) [95], causing a stress-induced solid-like shear jammed state. Similarly, adding binder will increase the viscosity, which may facilitate the particle adherence, but it may cause non-uniform coating due to the high viscosity nature of the mixture. The jamming volume fraction for random close packing (RCP) density is about 64%,
which may increase to \(~74\%\) for polydisperse particles [96]. In this paper, 5.69 \(\mu\)m average diameter particles with volume fraction \((\phi_p)\) 20\%, 35\%, and 50\% were investigated with 2.5\%, 6.5\% and 10.5\% binder volume fraction \((\phi_b)\). The remaining mixture contains solvent which can be defined as \(\phi_s = 1 - \phi_p - \phi_b\) as shown in Table 4.

Table 4: Composition of binder, powder, and solvent in the heterogeneous mixture

<table>
<thead>
<tr>
<th>Mixture Composition</th>
<th>% Volume Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binder ((\phi_b))</td>
</tr>
<tr>
<td>00</td>
<td>2.5</td>
</tr>
<tr>
<td>01</td>
<td>2.5</td>
</tr>
<tr>
<td>02</td>
<td>2.5</td>
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<tr>
<td>10</td>
<td>6.5</td>
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<tr>
<td>11</td>
<td>6.5</td>
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<td>12</td>
<td>6.5</td>
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<td>20</td>
<td>10.5</td>
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<tr>
<td>21</td>
<td>10.5</td>
</tr>
<tr>
<td>22</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Figure 18: Viscosity versus shear rate diagram for the liquid solution. The C00 to C22 corresponds to the compositions in Table 4, respectively.
Figure 19: Polymer film thickness as a function of capillary number. The grey line corresponds to the expected (theoretical) liquid thickness. The solid rectangular points represent the experimentally measured film thickness with standard error shown for each data point.

**Characterizing the liquid carrier system:** The viscosity versus shear rate data for the LCS was measured by the rheometer and is plotted in Figure 18. Little variation in viscosity ($\eta_0$) is observed at different shear rates, presenting the Newtonian behavior of the LCS solution. The viscosity of the 1,3-Dioxolane solvent was reported as 0.58 mPa.s at room temperature [97], which demonstrate that adding PMMA increases the viscosity of the LCS solution. It should be noted that the viscosity of the most dilute LCS (C00) solution was found slightly lower than the solvent viscosity at higher share rate using 50 mm parallel-plate geometry. This can be attributed to the very low viscosity and resulting torque which are close to the limits of the instrument. Concentric cylinders or a cup attachment geometry may provide more accurate viscosity for very
dilute solution, however the parallel plate geometry was used because of the range of viscosities tested. Expected film thickness after dipping is determined by Equation (1) which combines the capillary number and Goucher number [49] expressed as

\[ h = \frac{1.34rCa^{2/3}}{1 + 2.53G_o^{1.85}/[1 + 1.79G_o^{0.85}]} \]  

(1)

Both the experimental and expected film thickness are shown in Figure 19. The capillary number relied upon the viscosity variation due to binder volume fraction while keeping the withdrawal speed at 10 mm/s (medium speed). However, the experimental measurement always lags the semi-empirical equation (Eq 1) by Dincau et al. [49], which is derived for a non-evaporating liquid and thus, considered a wet film thickness. In evaporating solvent case, the resultant film thickness is governed by the evaporation rate, which is impacted by the diffusivity of the polymer-solvent system. As the solvent evaporates, a dense polymer rich skin layer forms at the liquid vapor interface decreasing the diffusivity and increasing the resistance to solvent evaporation [98].

To understand the evaporation rate and the polymer film compactness of our LCS system, a droplet test was performed. Three LCS compositions (00, 11 and 22) with 3.5, 11.1 and 23 wt. % binder were investigated for solvent evaporation. A 23 µL droplet of LCS solution was placed on a glass slide at the same conditions as the dipping experiment (20 °C) and the mass was measured every 30 minutes for a total of 300 minutes. The difference between the mass is due to the evaporation of the solvent which is plotted in Figure 20. The evaporation rate is high during the initial 30 minutes, and it evaporates little afterwards. Additionally, more solvent evaporates at the lower binder concentration than the higher binder concentration. For example, 67.1%, 96.7% and 99% of total solvent weight evaporated from composition 22, 11 and 00 after 30
minutes, respectively. This phenomenon contributes to the difference between expected and measured film thickness and describes the lower thickness in the measured film shown in Figure 19. As the evaporation continues at a different rate for different compositions after dipping, the generated film will have a hard surface and viscous core, potentially generating a porous film. As a result, the coated film is relatively easy to remove which has been also observed in our experiment.

Figure 20: Solvent evaporation from the LCS in terms of remaining solvent amount (%) vs time (min)

Characterizing the dipping mixture: The addition of particles into a LCS can form an emulsion [99] or a suspension [100, 101], or a solidus mixture [96], which often demonstrate non-linear rheological behavior (i.e., shear-thinning or thickening) under an applied force. Particle laden suspensions have been divided into three different regimes: dilute ($\phi_p \leq 0.1$),
semi-dilute ($0.1 < \phi_p \leq 0.25$), and concentrated ($\phi_p > 0.25$) [102-104]. In dilute or semi-dilute regimes, the viscosity mostly maintains linear rheological behavior (like Newtonian), which can be often measured experimentally with a rheometer [96]. However, in the presence of a high-volume fraction, inorganic micro-particle, measuring the viscosity with a rheometer is challenging as it gives inconsistent results due to the plate-particle contact. The Krieger & Dougherty model [70] has been used in the literature [105, 106] to predict the mixture viscosity, which correlates the LCS viscosity with the volume fraction of particles (Equation 2).

$$\eta(\phi_p) = \eta_0 \left(1 - \frac{\phi_p}{\phi_{p,max}}\right)^{-B\phi_{p,max}} \tag{2}$$

In Equation 2, $\eta_0$ is the liquid viscosity, $\phi_p$ is the particle volume fraction, $\phi_{p,max}$ is the maximum packing of the powder and $B$ is the Einstein coefficient, which is dependent on the particle shape. For random close packing of spherical particles, $\phi_{p,max} = 0.64$ [107] and $B = 2.5$. The dimensionless capillary number ($Ca$) of the mixture is the determined by using the mixture viscosity as: $Ca(\phi_p) = \frac{\nu}{\gamma} \eta(\phi_p)$.

To disperse the high-density particles in the LCS, the mixture was stirred to maintain the just suspended speed while minimizing the vortex. Measuring the impact of the Brownian motion and inertia effects is necessary because they induce additional bulk stress in a suspension [108]. Both the Peclet number [103, 104], $Pe = \frac{6\pi \mu_0 a^3 \dot{\gamma}}{kT}$ and the Reynolds number [105], $Re = \frac{\rho_0 a^2 \dot{\gamma}}{\mu_0}$ were determined for the mixture at shear rate 2 and 1000 s$^{-1}$. Here $k = 1.38 \times 10^{-23}$ JK$^{-1}$ is the Boltzmann constant, $T$ is the absolute temperature ($25^\circ$C), $\eta_0$ is the solution viscosity and $a$ is the average particle radius. The Peclet number ranges between $10^3$ to $10^6$ and Reynolds number ranges between $10^{-9}$ to $10^{-12}$ for our mixture, which falls within the Non-Brownian regime.
Figure 21: Schematic of fluid streamlines and dip coating mechanism. $S^*$ denotes for the stagnation point, $h$ for expected liquid thickness, $h^*$ for the critical film thickness, $r$ for fiber radius, and $U$ for withdrawal velocity.

**Characterizing the particle transfer and coating:** During the retraction of the substrate rod, the mixture velocity is directed downward, and the intermolecular forces between mixture and substrate surface help the particles adhere to the substrate. The solvent evaporation continues after extraction of the substrate and a dense polymer rich skin layer forms as shown in Figure 21. The adhesive force exhibits enough attracting force to the solid particles to avoid the gravitational effects and helps the particles adhere to the substrate. Microscopic images of the coated rod at three different locations were used for each specimen to average the coating thickness and particle coverage as shown in Figure 22. By changing the volume fraction of the mixture, two coating regimes are observed: i) heterogeneous regime and ii) effective viscosity regime. With a low particle volume fraction ($\phi_p = 20\%$), a coating film was created with fewer inorganic particles clustered into an irregular pattern as shown in Figure 22. This coating regime
is referred to as the heterogeneous regime because of the irregular formation. When the volume fraction of particles increased to 35% and 50% in the mixture, the liquid film entraps abundant particles to the substrate from the meniscus. Moreover, the high binder concentration ($\phi_b = 10.5\%$) increases the viscosity and decreases the evaporation rate, which also influences the adhesion of particles. Thus, a more uniform arrangement of the particles can be observed on the substrate, which is expressed as the effective viscosity regime shown in Figure 22. These regimes are coherent with the regimes reported by recent literature with neutrally buoyant particles [34, 35]. However, no ‘zero-particle’ regime can be observed here even at a lower capillary number. By using the theoretical suspension viscosity and the capillary number obtained by equation (2), the theoretical coating thickness was calculated and compared with our experimental data. Surface coverage is also measured and plotted against the capillary number in Figure 23.
Figure 22: Surface morphology of the coated substrate at different volume fractions of binder ($\phi_b = 2.5\%, 6.5\%$ and $10.5\%$) and particles ($\phi_p = 20\%, 35\%$ and $50\%$). The pictures were taken $1000\times$ zoom. The dashed green line bounded figures correspond to the heterogeneous regime and the red solid line bounded figures show the effective viscosity regime. 50 $\mu$m scale bar.
49

Figure 23: Surface coverage (%) and particle laden film thickness as a function of capillary number. The circular hollow dotted point represents the film thickness, and the rectangular solid dotted point represents the surface coverage by particles. 50 µm scale bar.

Discussion

Formation of the heterogeneous film: The entrainment of particles on the liquid film begins when the viscous drag force becomes larger than the resistive capillary force. The liquid film thickness, particle size, and volume fraction influence the entrainment of particles. At a lower volume fraction of binder and particles, the capillary effect remains high. As a result, fewer small particles are entrained in the relatively thin liquid film. Colosqui et al. [56] provided a threshold capillary number, \( Ca^* \), for 2D plate geometry with respect to the Bond number, \( B_0 = \left( \frac{a}{l_c} \right)^2 \).

Particles will assemble or entrain inside the meniscus at \( Ca^* > 0.6B_0^{0.75} \). The above condition is further modified as \( Ca^* > 0.24B_0^{0.75} \) by Sauret et al. [78], reducing the threshold capillary number and hence the critical film thickness for entrainment. However, for cylindrical
geometries like fiber and wires, Dincau et al. [49] derived the expression considering the particle and cylinder radius as:

\[ Ca^* \cong 0.645 \left( \frac{\alpha a}{3r} \left( 1 + \frac{2.53Go^{1.85}}{1 + 1.79Go^{0.85}} \right) \right)^{1.5} \]  

(3)

Here, \( \alpha \) represents the complex shape of the meniscus around the particle and has been considered as \( \alpha = 1.1 \) to determine the threshold capillary number [49]. The threshold \( Ca^* \) is calculated from the above equation as \( 7.95 \times 10^{-5} \), which is smaller than the \( Ca \) for the LCS used in this work, and therefore, indicating particle entrainment from the meniscus. However, fewer particles are observed in this regime and they are often clustered as shown in Figure 22. The effects of convective flux acting on the particle-laden mixture varies due to particle polydispersity, which creates a variation in the viscous drag force for entrainment. We observed that the particle coated thickness is higher than the expected (theoretical) values, which is derived for homogeneous precursor with monodisperse particles. This increase in thickness of the particle laden film can be attributed to the entrainment of large particles (> 10 \( \mu m \)) on the substrate increasing the average thickness above the expected value. Moreover, the continuous evaporation of solvent increases the capillary forces on the surface to cause the particles to cluster. Lower polymer content will enable quicker evaporation and a thinner film. As the polymer film dries, its capillary forces between the particles will pull the particles together to form the clusters, creating a heterogeneous regime which can be observed in Figure 22.

**From heterogeneous to the effective viscous regime:** In the effective viscous regime, particle entrainment is significantly higher, which can be seen in the coverage. Multi-layer particle entrainment is also observed in this regime. As the particle volume fraction and binder concentration increase, the rheology of suspension will demonstrate non-linear behavior (non-
Newtonian), and the effective viscosity will change with the applied shear rate. Both surface tension and viscosity of the particle-laden mixture will increase, which will cause the capillary number to increase. Due to the complex viscous behavior, the LLD equation can’t accurately predict the coating layer thickness, which can be seen in Figure 23. Different researchers have previously studied dense suspension. Bonnoit et al. [109] studied 20 to 140 µm dia. neutrally buoyant particles at 15 to 55% volume fraction and they showed deviation from Newtonian viscosity at 40% volume fraction. Similar non-Newtonian behavior is also reported for spherical particles over 40% volume fraction which often demonstrate shear thinning behavior [105]. The particle morphology (size and shape) in the suspension defines its rheological behavior and at a higher volume fraction (>50%), the particle-laden suspension may exhibit solid-like shear jammed state [110-112]. Dip coating has been performed with dense suspensions (ϕp =40%) and neutrally buoyant micro-particles [34] and a thick coating regime was observed, which was attributed to non-Newtonian behavior of the mixture. In our work, three different particle volume fractions (20, 35 and 50%) were considered and we assumed no yield stress behavior in the pseudo suspension. The effective viscous regime is observed at the combination of high particle and binder volume fractions (compositions 02, 12, 22 and 21). At a higher solid loading, more particles will be near the boundary layer during extraction and entrained particles will create a rough surface topology. This newly generated transient roughness will help entrain more particles that are draining due to the capillary force, resulting in the multi-layer particle entrainment observed in the effective viscous regime.

**Influence of particle volume fraction:** At low capillary number (≤ 3 × 10⁻³), relatively smaller particles adhere in a heterogeneous pattern on the substrate, which can be attributed to the low polymer layer thickness demonstrated in Figure 19. The experimental thickness at lower
capillary number is higher than the theoretical thickness ($h_{LP}$) due to the presence of large particles (avg. dia. 5.69 µm) and their polydisperse size distribution (Figure 23). At 20% particle volume fraction (compositions 00, 10, and 20), the dipping mixture behaves similar to semi-dilute suspension, and lower particle coverage and coating thickness are observed compared to other compositions. In this regime, the particles mostly adhered as a single layer and assembled in a disordered cluster pattern. This behavior is likely caused by the drying polymer film that may pull the particles together to form the clusters. A transition zone can be observed as the particle volume increases to 35%, which also increases the capillary number. At capillary number $>3 \times 10^{-3}$, the upward convective flux increases, and the viscous drag force starts to dominate the particle adhesion. As a result, more particles adhere to the substrate, and multilayer particle coating starts to form. At this range, the coverage transitioned to the effective viscosity regime for almost full coverage (>90%) and after few layers of particle adhesion, the entrainment reaches to steady-state due the surface asperities created by the entrained polydisperse particles. Thus, with the combined effect of roughness due to asperities and the hydrodynamics created by the stirring motion, the thickness became steady as the capillary number increases, which is shown in Figure 23.

**Influence of density mismatching:** Due to the density mismatch between the particles and the liquid carrier system, external stirring energy is provided to counter the effect of gravity. Because of the larger particle size (>5 µm), the van der Waals forces between IPs are not enough for particles to adhere to each other [96], and thus, they do not coagulate. With the just suspending stirring speed, the heterogeneous mixture turns into a pseudo suspension, making it dippable. No study exists to predict the thickness or the particle coverage for a density mismatched heterogeneous mixture (negatively buoyant and polydisperse micro particles). In our
study, we accounted for the density difference in both \( h \) and \( Ca \) by considering weighted volume fractions. While comparing the particle transfer matrices of the ‘pseudo suspension’ with the existing analytical expression of density matching suspension, the trends are similar. Thus, providing the stirring energy in the form of ‘just suspending speed’ into the heterogeneous mixture helped it to behave more like a ‘pseudo suspension’ and the density difference had little effect on the particle transfer as shown in Figure 22. However, the effect of stirring energy or speed on such heterogeneous mixture has yet to be investigated fully.

**Influence of binder concentration:** When the dipped substrate is withdrawn from the heterogeneous mixture, the solvent tends to evaporate from the substrate. During solvent evaporation, the concentration of polymer increases and the layer transitions from a viscous liquid to a gel-like solid which helps the particles to adhere to the coated substrate. The polymer coat around the particles acts as a deformable softshell on the hard solid particles, which increases the contact surface between particle and rod at the meniscus. Simultaneously, the increase in viscosity due to solvent evaporation and contact area increases the adhesion force acting on the particles. With an increase in binder volume fraction, the evaporated dense boundary layer will contain more binder molecules which increases the viscosity and decreases the drying rate. This will facilitate the entrainment of larger particles, increasing the particle coverage on the substrate and preventing draining of them from the substrate. The minimum film thickness required for neutrally buoyant particle entrainment \( (h^*) \) on a plate geometry has been reported as \( h^* \geq 2a \) [105]. Recent experimental studies suggested \( h^* \geq 0.33a \) for plate geometry [78] and \( h^* \geq 1.1a \) for fiber geometry [49]. However, we found entrained particles at lower \( h^* \) which is further investigated in the next section. The transition between heterogeneous and effective viscous regime is observed in compositions 01, 11, and 21 where binder
concentration varies with a fixed particle volume fraction (35%). Over 90% coverage is observed at 35% particle volume and 10.5% binder volume in the effective viscous regime. Thus, higher surface coverage can be achieved with high binder concentration at a fixed particle volume fraction.

**Influence of the withdrawal velocity:** The transition between the heterogeneous regime and the effective viscous regime is attributed to the capillary number, which is controlled with particle and binder volume fractions. However, withdrawal velocity, \( U \) effectively changes the capillary number and the entrainment of particles. The convective flux on particles occurs due to the influence of solvent evaporation and capillary rise during the withdrawal process [46, 51, 52]. At a draining regime with a withdrawal speed (1~10 mm/s), the substrate moves faster than solvent evaporation [38]. However, at a lower withdrawal speed (<1 mm/s), the convective flux is stopped by solvent evaporation since the influx of particles is limited here. Furthermore, with higher withdrawal velocity (>10 mm/s), the spatial discrepancy in particle influx occurs due to the low solvent evaporation and gravitational effects, which resulted in a disordered cluster pattern, as shown in Figure 24.
Figure 24: Surface morphology of the coated substrate at different withdrawal velocities at compositions 11 and 21. The picture was taken 1000X zoom. The scale bar is 50 µm. The green outlined images present the particle entrainment on optimized velocity.

To investigate the critical film thickness, $h^*$, for density mismatching system with stirring motion, the entrainment behavior was studied for two compositions (composition 11 and 21) with lower withdrawal velocity, as shown in Figures 24 and 25. Below 5 mm/s, low particle coverage is observed and only small size particles are entrained which suggests a lower $h$. The film thickness $h$ is predicted with the modified power-law given by Equation (1). For both compositions, particles can be seen entrained following the two-regimes discussed earlier. We did not observe a liquid regime or ‘zero-particle’ regime. There are two possible reasons for this observation: (i) particles are entrained at a lower $h^*$, i.e., $\alpha < 1.1$ or (ii) smaller particles ($2\alpha < 5.6\mu\text{m}$) from the poly-disperse distribution are entrained on the substrate, which will reduce the threshold capillary number ($Ca^*$).

The average particle diameter for 0.01 mm/s was measured as 4.3 µm and 4.2 µm, which is smaller than the bulk particle average. For these particles, the threshold capillary number $Ca^*$ for particle entrainment was calculated using Equation (3) to be $5.81 \times 10^{-5}$ and $6.07 \times 10^{-5}$, respectively. For $Ca^*$ below these values, no particles should entrain on the substrate. However,
the capillary number for compositions 11 and 21 are as $3.1 \times 10^{-6}$ and $6.8 \times 10^{-6}$ at 0.01 mm/s speed, which are below $Ca^\ast$. Additionally, in both circumstances, particles entrained for $\alpha = 0.16$ and $\alpha = 0.26$, respectively, which suggests that the critical film thickness, $h^\ast$, is significantly smaller than previously reported for particle entrainment. Since we have used polymer binder in our mixture, it facilitates the particle entrainment with lower liquid film thickness. A polymer rich boundary layer with higher viscosity is the possible reason for the particle to be entrained with lower $\alpha$ and hence $h^\ast$.

Figure 25: Thickness as a function of capillary number for different withdrawal velocities (0.5 to 20 mm/s). The grey line corresponds to the LLD law thickness. The hollow circle is for composition 11 (6.5% binder and 35% powder) and the solid square is for composition 21 (10.5% binder and 35% powder). The scale bar is 50 µm.

Conclusions: In this paper, the entrainment of solid micro-particles was investigated on a cylindrical substrate withdrawn from a bath of pseudo suspension of non-Brownian particles dispersed in a Newtonian fluid with an evaporating solvent at 20% to 50% solid concentration.
For the LCS, we found lower experimental thickness from the expected film thickness equation (Eqn 1) due to solvent evaporation. However, the addition of inorganic micro-particles modified the film thickness significantly.

After changing the volume fraction of the mixture (i.e., binder, particle) we observed two coating regimes. In semi-dilute suspension of 20% particle concentration, we observed the liquid film with a few clustered particles in an irregular pattern. This regime was observed in a low capillary number below $3 \times 10^{-3}$. At a capillary number over $4 \times 10^{-3}$ more particles were entrained on the substrate at a uniform arrangement with 35% and 50% particle concentration. High binder volume fraction also facilitates particle adhesion in this regime. To explore a possible zero-particle regime, we changed the withdrawal velocity and observed particle entrainment below the threshold capillary number. Particle entrainment was observed with low liquid film thickness due to the evaporation of the solvent and generating a polymer rich dense layer at the interface to create a boundary layer that acts like a softshell for particle adhesion. The results also showed that smaller particles adhered on the substrate from the polydisperse distribution. From our analysis, we rationalized our experimental results with the theoretical predictions. Our results also provide a better understanding of the film thickness behavior from heterogeneous mixture preparation. Additionally, we found that with just suspending speed stirring energy, the density mismatched mixture behaves like pseudo suspension. The transferred particle matrices closely follow the analytical expression of a density matching suspension which demonstrate that the density mismatch effect can be neutralized with the stirring energy. This micro-particle transfer mechanism from density mismatched multi-phase mixture can be leveraged in coating processes for surface protection, surface modification, surface cavity filling, particle sorting and dust mitigation applications.
CHAPTER 4

EFFECT OF MW OF PMMA ON PARTICLE TRANSFER BY DIP COATING PROCESS FROM LIQUID PARTICLE CARRIER SYSTEM

Abstract

When substrate is inserted in the suspension, solid particles entrained into the substrate during the withdrawal of the substrate. The participation of binder in the suspension greatly influences the entrainment of the particles. In this work, the binder content on different molecular weight (MW) was investigated to study the viscous behavior of liquid carrier system (LCS) and its influence on particle entrainment. 120K and 350K PMMA showed dilute conditions even with high LCS viscosity (6 mPa.s) due to their low polymer content. However, 15K PMMA showed highly viscous gel-like behavior on 4 and 6 mPa.s viscosity for its high polymer loading. Smaller particles entrainment was observed in dilute conditions of mixture which reduces the polydispersity of solid particles used in the suspension. However, the gel-like solution suspension provided similar particle size distribution like bulk solid particles. These results can be used to reduce the polydispersity of solid particles in suspension by changing the binder condition. Also, it can be applied to high-yield solid transfer and particle sorting process.

Introduction

Liquid thin film technology has undergone continuous development in the last decade and is widely used in many industrial applications [113, 114]. This film formation process can be carried out either directly using physical processes or indirectly using chemical and electrochemical reactions [115]. Thin films are applied for the production of different sensors [116-119], nano coating for hydrophobic surfaces [120], and optical displays [121-123]. Many
researchers worked on the development of the interesting field of thin liquid films. Light-emitting polymers (LEP) are deposited on indium tin oxide (ITO) substrate by using sputtering [124-126]. The thickness of the polymer film formed in this process is 50 nm. In another work, Carter et al. [127] used Poly(3,4-ethylenedioxythiophene), PEDT, doped with Polystyrene Sulphonic acid (PSS) for the formation of a thin film of the order of 70-100 nm by the spin coating process. Danglad-Flores et al. [128] found the thickness of the dry polymer film is 150 nm in the spin coating process while using the solution of Polystyrene (PS)-b-Poly(methyl methacrylate) (PMMA) and toluene.

Recently thin film technologies are used to carry the nano/micron-sized particles to the desired location by controlling the polymer film thickness. Several nanomaterials-based bottom-up coating techniques such as chemical vapor deposition (CVD) [129, 130], magnetron sputtering [131, 132], and physical vapor deposition (PVD) [133, 134] can be used for the development of products based on 1 to 10 µm thick films. Dip-coating is another method of creating constant film thickness over the substrate, from several to hundreds of micrometers depending upon the coating process parameters [135]. In one of the dip-coating works Gans et al. [34] measured the average liquid film thickness while coating with silicone oil. They showed the liquid film thickness remains constant over a range of withdrawal speeds depending upon the diameter of the particle used in the suspension. They found the average liquid film thickness is 20-30 µm between 0.02 and 0.1 mm/s for the 20 µm particles and the film thickness is 100–150 µm between 0.05 and 1 mm/s for the 140 µm particles. In another work on dip-coating, Dincau et al. [136] showed the variation of non-dimensional liquid film thickness capillary number at different fiber radius and viscosity of the silicone oil.
Dip-coating is a simple and facile for the film formation over a plate, fiber, and irregular shaped object. Materials are transferred at the solid-liquid interface during the withdrawal of the substrate from the suspension [137]. The thickness of the polymer film for a non-evaporating solution formed over the substrate is first predicted by Landau and Levich and then Derjaguin which is known as the famous LLD equation [31, 138]. The thickness of the polymer film, in their work, is dependent on the withdrawal speed \((U)\) of the substrate from the suspension, the viscosity of the suspension \((\eta)\), and the capillary length \(l_c = \sqrt{\gamma/\rho g}\), where \(\gamma\) and \(\rho\) are the surface tension and density of the fluid respectively and \(g\) is the acceleration with respect to gravity. The entrainment regime is dependent on the capillary number \(Ca = \eta U/\gamma\) which is denoted as the ratio of the viscous force and surface tension force. In small capillary number \((Ca < 10^{-2})\), the thickness of the polymer film is determined by the competition between viscous force and surface tension force only, and the LLD equation of thickness is \(h = 0.94l_cCa^{2/3}\). On the other hand, at larger capillary number, the gravity is dominant over the surface tension force which leads the equation of thickness is \(h = l_cCa^{1/2}\) and due to the gravitational drainage, non-uniform layer thickness is observed over the substrate [34]. The relevant parameter to find the film thickness over the cylindrical substrate is \(Go = R/l_c\) [139]; where \(R\) is the radius of the cylindrical substrate and \(l_c\) is the capillary length. The modified LLD equation to calculate the film thickness over fiber for \(Go < 3\) is \(h = 1.34RCa^{2/3}\) [68, 140].

Film formation over the substrate is straight-forward process in dissolved state of the polymer. When the solvent evaporates the polymer chain interpenetrate and goes through a gel state which form a film while further drying [141]. Faustini et al. [142] discussed the formation of polymer layer over the substrate considering the evaporation of the solvent. Solvent evaporation-based technique is widely applied in thin layer wick production [83] and polymer nanocomposites.
Yimsiri and Mackley [145] showed that the viscosity of the suspension substantially rises when the solvent (Xylene) evaporation proceeds during the film formation process. In one of our previous articles [146] discussed the effect of binder percentage on the evaporation rate.

The molecular weight of polymers is one of their most important properties, as it determines the solution properties of polymer chains as well as their capability to sterically stabilize them [147, 148]. Molecular weight controls the length of the polymer chain and entanglements which controls the viscosity of the suspension. Yimsiri and Mackley [145] showed the relationship between the polymer layer thickness and molecular weight of the polymer in dip and spin coating process. They used the blend of two different polymers namely poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene-co-TFB) (Host 1), with a weight ratio of approximately 5:95. The molecular weight of host 1 is 95000 and three different molecular weights of F8BT (151000, 61400, and 504000) are used as polymer and Xylene as solvent. The relationship between the viscosity of the suspension and the molecular weight of the polymer is determined by the Mark-Houwink equation [149]. Choi et al. [150] investigated the effect of molecular weight on the nanocomminution of itraconazole particles during drug deliveries. The size of the particle used in the transfer process is 100-120 nm and seven different molecular weights (7200 g/mol, 10400 g/mol, 12700 g/mol, 17000 g/mol, 18800 g/mol, 21900 g/mol, and 28800 g/mol) of the polymer are used in their work. They also observed a decrease in the diffusion rate of chains and an increase in the physical adsorption of a polymer with the increase in molecular weight. Moreover, Tanaka et al. [151] reported the effect of the molecular weights on the morphology of the polystyrene (PS)/poly (methylmethacrylate) (PMMA) composite particles by the solvent evaporation method. The diffusion rate of the polymers generated in the second polymerization process at a given weight fraction of polymer is determined by the
molecular weight of the polymer, and this influences the final particle shape during the particle production process [152-154]. In another work, for two different molecular weights (200 and 400 g/mol) of polyethylene glycol (PEG), the effects of particle-particle interaction and carrier fluid viscosity on the rheological features of calcium carbonate (CaCO$_3$) and silica (SiO$_2$) nanoparticle suspensions are studied [155]. The effects of two different molecular weights (400 g/mol, and 2000 g/mol) of the carrier liquid (polypropylene glycol) and spherical fumed silica particles (average size 12 nm) on shear thickening behavior [156] and rheological characteristics are discussed [157]. All the articles discussed here show the effects of change in the molecular weights during the transfer of nanoparticles.

To our best knowledge, the effect of the molecular weight on the transfer of micro-particles is yet not disclosed. In this work, the effect of the molecular weight of the polymer on the evaporation rate of the solvent is discussed. We investigated the effect of the molecular weight of the polymer binder at same viscosity of the suspension on micron-sized particles transfer. Polymer with three different molecular weights (15k, 120k, and 350k) are used in the experiments to observe the effects of the molecular weight. The particle transfer at same polymer content in the suspension (variable viscosity and molecular weight) is also disclosed here.

**Materials and Methodology**

The suspension used in the experiment is consist of liquid solvent, granular binder, and solid metal particles. 1, 3 Dioxolane and Poly-methyl methacrylate (PMMA) are used as solvent and binder respectively for all the experiments. The density of the solvent and the binder are 1.06 g/cm$^3$ and 1.06 g/cm$^3$ respectively at room temperature (RT = 25°C). According to the popular aphorism "like-dissolve-like," the solubility of the organic compound is determined. Due to the similarity in the chemical structure between binder and solvent, 1, 3 Dioxolane is used as the
solvent for the binder PMMA. PMMA is an extremely stable material, or inert, with strong chemical bonds that prevent the chain from being modified [158]. According to Shi et al. [159], PMMA can construct a porous matrix over the substrate while film formation and this structure remain unchanged due to strong mechanical properties. This porosity of the film can hold the particles depending upon the thickness of the film. Due to this property, PMMA is widely used in nano-material transfer [160, 161]. One of the drawbacks of using PMMA is thermal degradation. Moreover, the solution prepared using PMMA is transparent which provides better control over the suspension by visualization. As we did all the experiments at room temperature, and due to the above-mentioned advantageous properties, we have chosen PMMA as the binder in our experiments. All the binder and solvent are procured from Sigma Aldrich, USA. In order to observe the effect of the molecular weight of the binder in the film formation, we used three different molecular weights (15000, 120000, and 350000). With the increase in molecular weight of the polymer, the size of the polymer chain and the entanglements in the chains increase. In the ambient temperature, these entanglements result in higher mechanical properties and viscosities due to more energy required to break or loosen the chain entanglements [162]. At higher temperatures (above the glass transition temperature of the polymer) the long chain backbone of PMMA splits and reacts with itself at high temperatures, changing the chain length of the polymer [163] so as to change the viscosity of the suspension. The solution of the binder and the solvent is the liquid carrier system (LCS) for the particles. A magnetic stirrer is used to dissolve the binder in the solvent and the dissolution (no gel is found) of the binder is confirmed by Dynamic Light Scattering (DLS) experiment which is done by Zetasizer. The viscosity of the suspension is measured by Anton Paar MCR 302 Rheometer applying a flow curve test using a 50 mm diameter parallel plate with a 0.2 mm gap filled with sample.
Brazing powder (Nicrobraz LM; Wall Colmonoy company, Ohio; Spherical dia range ~0-100 µm) is used as solid inorganic particles which have the density of 7.97 g/cm³. Gilson Performer III shaker through Stainless Steel 635 Mesh (20 µm) in our lab to reduce polydispersity. After sieving, the reduced particles are captured in images using SEM and analyzed the particle size in ImageJ. The average particle size of the distribution is found 7.56 µm with a standard deviation is 3.98. AISI 1006 mild steel rod with an average diameter of 1.06 mm (procured from ClampTite LLC). After cleaning the rods, acetone is used in the ultrasound bath for 10 minutes at 50 ºC to remove the passive film over the substrate.

Solid particles in the LCS mixture create density imbalance which facilitates the sedimentation and phase separation on the mixture. External kinetic energy in the form of agitation is provided to withstand with the gravitational force of the particles by using a magnetic stirrer at 750 rpm and it created a uniform distribution of particles on the LCS, acting as pseudo suspension. An in-house custom made dip coating setup is used for all the experiments which is described in one of our previous articles [77]. When the substrate is inserted into the suspension, porous thin film of PMMA is created over the substrate. Due to the rotational motion of the particles, particle is attached into the thin polymer film. During the experiments, the immersion time is 10 seconds and the withdrawal speed is 20 mms⁻¹. The solid substrates were analyzed using VHX 7000 Digital 4K microscope (KEYENCE corp.).

YOLO V5 was used as a computer algorithm to analyze the 300×200 µm² microscopic images. The images were cropped into 416×416-pixel size and then trained on the annotation software, Roboflow, before measuring the test images. For training the images, four different category images including monodisperse layer cluster, monodisperse non-cluster, polydisperse layer cluster, polydisperse layer non-cluster, was considered to identify all kinds of test images. By
using this automated computational tool, the particle size was identified with an accuracy of 97.3% to 99.6%. During the analysis, three different images were taken for the datasets of particle size distribution and surface coverage in each composition. The particle distribution and surface coverage in each mm² is shown in figure 29, 30 and 31.
Table 5: Composition of suspension mixture, viscosity, and particle size

<table>
<thead>
<tr>
<th>Solution Viscosity (mPa.s)</th>
<th>PMMA weight (g)</th>
<th>Particle vol %</th>
<th>Solvent vol %</th>
<th>PMMA vol %</th>
<th>PMMA wt %</th>
<th>Average Particle size ± Standard deviation (µm)</th>
<th>Capillary Number, Ca</th>
<th>Total particle count per unit mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>15K PMMA</td>
<td>1.91</td>
<td>0.58</td>
<td>10</td>
<td>83.07</td>
<td>6.93</td>
<td>4.45</td>
<td>6.68±2.76</td>
<td>1942</td>
</tr>
<tr>
<td></td>
<td>3.99</td>
<td>1.12</td>
<td>10</td>
<td>76.55</td>
<td>13.45</td>
<td>8.60</td>
<td>7.31±3.06</td>
<td>3353</td>
</tr>
<tr>
<td></td>
<td>6.05</td>
<td>1.33</td>
<td>10</td>
<td>74.03</td>
<td>15.97</td>
<td>10.19</td>
<td>7.77±3.68</td>
<td>3276</td>
</tr>
<tr>
<td></td>
<td>0.72</td>
<td>0.06</td>
<td>10</td>
<td>89.28</td>
<td>0.72</td>
<td>0.46</td>
<td>4.61±2.33</td>
<td>443</td>
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<tr>
<td></td>
<td>0.75</td>
<td>0.15</td>
<td>10</td>
<td>88.21</td>
<td>1.79</td>
<td>1.15</td>
<td>3.75±1.56</td>
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<tr>
<td></td>
<td>0.81</td>
<td>0.22</td>
<td>10</td>
<td>87.31</td>
<td>2.69</td>
<td>1.74</td>
<td>3.62±1.35</td>
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</tr>
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<td>120K PMMA</td>
<td>1.91</td>
<td>0.19</td>
<td>10</td>
<td>87.71</td>
<td>2.29</td>
<td>1.47</td>
<td>5.04±1.71</td>
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<td>3.99</td>
<td>0.42</td>
<td>10</td>
<td>84.94</td>
<td>5.06</td>
<td>3.26</td>
<td>5.81±2.19</td>
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<td>10</td>
<td>83.03</td>
<td>6.97</td>
<td>4.48</td>
<td>6.82±3.18</td>
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<td>89.28</td>
<td>0.72</td>
<td>0.46</td>
<td>3.46±1.17</td>
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<tr>
<td></td>
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<td>10</td>
<td>88.21</td>
<td>1.79</td>
<td>1.15</td>
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<td>2.04</td>
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<td>10</td>
<td>87.31</td>
<td>2.69</td>
<td>1.74</td>
<td>4.11±1.99</td>
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<tr>
<td>350K PMMA</td>
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<td>10</td>
<td>89.28</td>
<td>0.72</td>
<td>0.46</td>
<td>4.70±1.11</td>
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<tr>
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<td>0.15</td>
<td>10</td>
<td>88.21</td>
<td>1.79</td>
<td>1.15</td>
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<td>0.22</td>
<td>10</td>
<td>87.31</td>
<td>2.69</td>
<td>1.74</td>
<td>5.70±2.80</td>
<td>4020</td>
</tr>
</tbody>
</table>
Results

Characterizing the liquid viscosity and evaporation: The liquid carrier solution is prepared by mixing the solvent with polymeric binder on different concentrations. The molecular weight (MW) of polymers and the polymer concentration both works as a resistant to the solvent flow. High MW polymers exhibit long molecular chain that enhances the intermolecular interactions which provides resistant to the solvent flow and increase the viscosity. Moreover, high concentration of polymer also provides resistance to the solvent flow since the polymer chains overlaps and entangles at insufficient space having more polymer molecules in the solution and reduce the mobility of solvent flow which increases the viscosity [164]. In this work, the influence of both the MW and concentration variation have been discussed on the particle transfer mechanism. Three different MW of PMMA (15K, 120K and 350K) was used in the polymer solution in different concentrations. From the viscosity experiment and the fitting polynomial curves for different MW, the estimated volume fraction was found with different viscosities with negligible error (high R² values) similar to Rahimi et al. [165].
Solvent evaporation is crucial during the dip coating process. It is very important to identify the polymer resistance on the rate of solvent evaporation. In our previous article, we described the influence of binder concentration and its corresponding viscosity on the solvent evaporation and found that solvent evaporation becomes slower with the increase of binder concentration and viscosity for a single MW of polymer because it forms a hard surface of viscous core generating a porous film [146]. In this work, the influence of MW of polymer at same viscosity have been analyzed on solvent evaporation. Similar experimental protocols have been followed here as our previous article where a 23 μL droplet of LCS solution was placed on a glass slide of same viscosity (4 mPa.s) at different MW (15K, 120K and 350K) of PMMA. The droplet mass was measured in every 30 minutes in total of 180 minutes. The remaining solvent after evaporation is
plotted against time in Figure 27. For same viscosity it was observed that 15K PMMA has slightly lower evaporation rate compared to 120K and 350K PMMA due to the high concentration of polymer at 15K which also follows the evaporation theory of polymer solution discussed by Geng et al. [166]. This high concentration of polymer provides more resistance on the solvent evaporation and results in relatively higher liquid layer thickness that accumulates more particles on the surface of the substrate.

![Graph showing solvent evaporation as a function of time in different MW polymer solution](image)

Figure 27: Solvent evaporation as a function of time in different MW polymer solution

**Study on pseudo suspension:** The addition of hard powder particles on the LCS solution modifies it to a phase separated mixture due to their high-density difference (~8 times). The external kinetic energy provided by a magnetic stirrer helps the particles rotate continuously
throughout the LCS solution which transforms it to a pseudo suspension. Suspension with different volume fraction of particles has been studied before in literatures and it is divided into three regimes considering the volume fraction of particles: dilute ($\phi_p \leq 0.01 \sim 0.02$), semi-dilute ($\phi_p \leq 0.25$), and concentrated ($\phi_p > 0.25$) where $\phi_p$ is the particle volume fraction [96]. Suspension in dilute regime is considered as a Newtonian fluid and concentrated regime as a non-Newtonian fluid. In semi-dilute regime, suspension behaves like approximately Newtonian fluid. Gilbert et al. identified Newtonian behavior on glass bead suspension of 80 μm to 100 μm particle diameter when $\phi_p = 34.3\%$ [167]. Also, Pasquino et al.[168] observed Newtonian behavior PMMA spheres (~ 14 μm dia.) based polyisobutylene and polydimethylsiloxanes carrier suspension on a volume fraction ranging from 2% to 10%. In this work, particle volume fraction, $\phi_p = 10\%$ is applied on the pseudo suspension which can be considered as a Newtonian fluid. Also, particles in concentrated regime on the pseudo suspension in our previous article showed non-Brownian behavior which can also be predicted with $\phi_p = 10\%$ volume fraction in this work.

**Discussion**

**Expected viscosity behavior:** When different MW of polymer is considered on LCS solution, the rheology of LCS varies depending on the MW or concentration variation of polymer. Einstein provided a linear relationship between solid loading of hard spheres and viscosity for dilute suspension. This relationship can be extended to polymer solutions considering the polymer coil as an impenetrable sphere through which the solvent is unable to flow [169]. So, the viscosity ($\eta$) of dilute polymer solution will be expressed as a function of concentration of polymer.
\[ \eta = \eta_s(1 + c[\eta]) \] (4)

Where \( \eta_s \) is the viscosity of the solvent, \( c \) is the polymer concentration, and \([\eta]\) is the intrinsic viscosity. The expected viscosity (\( \eta \)) of polymer solution is plotted as a function of polymer concentration, \( c \), in figure 28 considering the linear relationship of equation 4. The higher concentrations for the 15K PMMA deviate from linearity, suggesting non-dilute solutions at higher concentrations.

Figure 28: Viscosity as a function of concentration for 350K (diamond), 120K (circle), and 15K (square) PMMA in solution over the entire sample range. 15K has two fitting curves considering low \( R^2 \) value (green) and high \( R^2 \) value (orange).
After considering the dilute conditions below 0.05 g/mL of PMMA, a more linear trend with higher \( R^2 \) valued is plotted on figure 28. This reveals that several concentrations for 15K PMMA cannot be considered in dilute conditions and should follow the expression as:

\[
\eta = \eta_s (1 + c[\eta] + k_H c^2[\eta]^2)
\]  

(5)

Where \( k_H \) is the Huggins coefficient, which is a measure of excluded volume effects due to polymer solvent interactions [170]. These interactions become more significant at higher concentrations and the solution could behave differently from dilute conditions at higher concentrations.

The intrinsic viscosity \([\eta]\) can be calculated using the slopes in figure 28 for each molecular weight shown in table 6 where the solvent viscosity \( \eta_s \) is considered as 0.59 mPa.s. The intrinsic viscosity is a function of molecular weight following the Mark-Houwink equation [149], expressed as:

\[
[\eta] = kM^a
\]

(6)

Where \( k \) and \( a \) are constants. From the data in Table 5, the parameters are calculated to be \( a = 0.83 \) and \( k = 0.014 \frac{mL}{g} \left( \frac{mol}{g} \right)^{0.83} \). The deviation in particle size and surface coverage can be described using the variation of intrinsic viscosity and the deviation of 15K PMMA from the dilute conditions.
Table 6: Intrinsic viscosity of different molecular weight PMMA in dioxolane

<table>
<thead>
<tr>
<th>Molecular weight (kg/mol)</th>
<th>Intrinsic Viscosity (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>42.0</td>
</tr>
<tr>
<td>120</td>
<td>227</td>
</tr>
<tr>
<td>350</td>
<td>588</td>
</tr>
</tbody>
</table>

**Formation of low viscous region:** While the substrate is pulled out from the suspension, a thin liquid film is formed on the substrate. The liquid film is the key factor which provides the viscous drag force and particles entrain on the substrate when the viscous drag force becomes larger than the resistive capillary force. This liquid film contains mainly the polymer binder and a portion of the solvent entrapped on the polymer core shell. The liquid film is mainly influenced by the viscosity of LCS solution and the concentration of binder on the LCS solution. When the viscosity of LCS remains low (less than ~ 1.3 mPa.s), the solvent evaporation becomes faster due to the thin polymer shell. The particles are in range from 1 to 20 μm and large particles need enough contact area which lacks on this thin shell. Also, low viscosity and low content of binder have high evaporation rate and results in thin liquid film and it can’t provide enough binding strength. Therefore, large particles dragged down easily for the lack of binder content and high evaporation rate. Only particles less than ~10 μm was observed in this low viscosity region. For example, 120K PMMA LCS solution with 0.92 mPa.s viscosity exhibits very small size of particle entrainment ranging from 2 μm and 10 μm with an average of 3.46 μm diameter. Also, in 0.81 mPa.s viscosity of 15K PMMA LCS solution provides particle entrainment from 2 μm to 9 μm with an average of 3.62 μm diameter. In this way only small size of particle ≤ 10 μm is captured on this low viscous region as shown in figure 32.
Transformation to high viscous region: When the viscosity of LCS solution increases, large particles tend to adhere on the liquid film. When the viscosity of LCS becomes larger (≥ 1.3 mPa.s) particles accumulation started shifting towards all ranges. However, in between 1.3 mPa.s to 2 mPa.s both small range and all range of particles were captured using different MW of polymer binder. When 350K PMMA was used in LCS solution having 2 mPa.s viscosity, small particles ranging from 3 μm to 11 μm was entrained on the substrate. But 15K PMMA LCS solution captured almost all range of particles (3 μm to 18 μm) at 2 mPa.s. Therefore, LCS
viscosity from 1.3 mPa.s to 2 mPa.s works as a transition viscosity where both small and all range of particles were transferred to the substrate. When the viscosity becomes larger than 2 mPa.s, all of LCS solution with different MW of PMMA exhibits all range of particles. The polymer shell gets thicker in high viscosity which restrain the solvent from evaporation and increase the liquid film thickness. The thicker the liquid film thickness, the more binding strength and more contact area forms for the particle entrainment. The liquid film thickness has a threshold value of thickness below which the large particles do not get enough strength for the entrainment and with high viscosity (≥ 2 mPa.s) this liquid film thickness gets thicker and provides the required strength for large particle entrainment. For example, considering the 2 mPa.s LCS viscosity, 15K PMMA provides all size of particle distribution entraining large particles since it has high concentration of polymer which exceeds the threshold liquid film thickness for large particle entrainment. However, at 2 mPa.s LCS viscosity, 350K PMMA provides a narrow smaller particle distribution since it has low concentration of polymer which increases the solvent evaporation and makes a thinner liquid film thickness than 15K PMMA of same viscosity. This thin liquid film remains below the threshold value for large particles entrainment and cannot provide enough strength to adhere large particles.
Effect of LCS viscosity: The LCS solution viscosity is mainly driven by the variation of MW of PMMA and its volume fraction. When the viscosity remains similar for different MW, more polymer content is required for low MW polymer at the same volume of LCS mixture (7 ml). High polymer content tends to reduce the mobility of solvent flow and the number of polymer molecules becomes higher with the content. In similar viscosity of LCS solution, 15K has the maximum polymer content and it resists the solvent evaporation more forming thicker liquid film thickness on the substrate. Therefore, more particles get adhered between liquid film covering more surface area than the low polymer content mixture of high MW polymer at similar
viscosity of LCS solution. Also, in high viscosity and polymer content, the liquid film is thicker which helps large particles to adhere on the liquid film limiting the gravitational effect. Therefore, in high viscous region, larger particle was entrained on the substrate covering more surface area. In 120K and 350K samples in similar viscosity, according to figure 3, all these viscosities are dilute conditions. However, for 15K samples, 4 and 6 mPa.s are not in dilute conditions as indicated in figure 3. The concentrated regime will create different flow behaviors, independent of viscosity. The increased polymer-polymer interactions at these viscosities for 15K could lead to more gel-like behavior, slowing particle movement relative to a dilute system. For example, in similar viscosity experiment at 6 mPa.s viscosity, 350K PMMA suspension provides smaller particles entrainment (avg. dia. 5.7 μm) and low surface coverage (12.7%) since larger particles are significantly low here for thin liquid film with low concentration of polymer at same viscosity. However, with 15K PMMA suspension at 6 mPa.s, large particles were captured (avg. dia. 7.77 μm) and more surface coverage was achieved on the substrate (19%) shown in figure 7 due to its high concentration of polymer and thicker liquid film.

![Graph](image)

**Figure 31:** Surface coverage in similar weight and similar viscosity.
In similar weight experiment, the polymer content remained fixed at the LCS solution, but viscosity varies with the change of MW of polymer. At same polymer content, high MW polymer derived LCS solution provides higher viscosity due to its longer chain length and entanglements. As the viscosity increases with the MW of polymer, the polymer layer resists the evaporation of solvent and gets more thicker entrapping more solvent on its shell or core which increase the liquid layer thickness. This liquid layer facilitates all size of particles entrainment limiting its gravitational effects. Thus, the surface coverage as well as the particle size increase with the increase of the viscosity. For example, in 0.22g weight of different MW polymer derived suspension, 15K PMMA has low viscosity (0.81 mPa.s) and it entrains very less coverage of particles (0.46%) with an average particle diameter of 3.62 μm. However, with similar weight 0.22g, 350K PMMA one has high viscosity, and it provides high surface coverage (12.7%) than similar weight of 15K PMMA suspension. In figure 31 surface coverage at similar weight, the significant jump to molecular weight increases at the same mass loading which can be described by the Mark-Houwink relationship.

\[
\frac{[\eta]_{350}}{[\eta]_{120}} = \left(\frac{350}{120}\right)^{.83} = 2.3
\]

\[
\frac{[\eta]_{350}}{[\eta]_{15}} = \left(\frac{350}{15}\right)^{.83} = 8.9
\]

The 350K PMMA has 2.3 times higher viscosity than 120K and 8.9 times higher viscosity than 15K PMMA which will lead to the additional surface coverage which is visible all same mass loading shown in figure 31. Moreover, the similar weight samples are all in the dilute polymer
regime, so their particle size is dictated by viscosity of the polymer solutions and the amount of polymer in the solution. Low levels of polymer lead to smaller particles because they are small enough to adhere to the surface with little ‘glue’ while the larger particles cannot adhere.

Figure 32: Comparison of bulk particle size with low and high viscous region. Scale bar is 25 µm.
Figure 33: Cumulative size distribution comparison with bulk particles at similar weight and similar viscosity.

When the cumulative size distribution of similar weight and similar viscosity samples is compared to the bulk nicrobraz LM powder, in figure 33, a significant difference on the particle size of samples is observed compared to bulk particles. In similar viscosity, samples in dilute condition showed 80% small size of particles less than 10 µm. However, the concentrated gel-like samples of 15K at 4 and 6 mPa.s viscosity showed almost similar distribution like bulk particles. In similar weight samples, the cumulative particle size distribution is shifted towards left side compared to bulk distribution reducing the average particle size since all these samples are in very dilute conditions.
The variation of MW of polymer and its mass loading changes the viscosity as well as capillary number, \((Ca)\) of LCS and it’s corresponding pseudo suspension. As the particle concentration is constant \((\phi_p = 10\%)\) and the concentration of polymer changes with their MW, the capillary number varies with the viscosity changes which can be presented with Krieger & Dougherty equation, described in our previous article [146]. In similar viscosity of LCS, the capillary number remains closely similar to each other for different MW of polymer although the polymer mass loading varies. This variation of polymer mass loading results in different size of particles entrainment which is independent of capillary number shown in figure 34. For example, in \(Ca\) of
3 \times 10^{-3} \text{ the 350K PMMA has the lower avg. particle size of 4.94 \, \mu m whereas the 15K PMMA has higher avg. particle size of 7.31 \, \mu m closer to the bulk particle size (7.56 \, \mu m).}

**Conclusions:**

In this paper, the entrainment of solid particles using three different MW of polymer at LCS mixture was investigated to understand the influence of polymer binder on solid transfer process. In LCS solution, the effect of polymer mass loading and polymer MW was certainly visible on the particle size and its coverage distribution. In experiments, the 120K, 350K and 15K (2 mPa.s) samples showed dilute solution behavior which has less viscosity and it resulted smaller particle size distribution compared to the bulk Nicrobraz LM particles. However, in 4 mPa.s and 6 mPa.s viscosity of 15K samples, it follows concentrated gel-like behavior and showed similar particle size distribution as bulk particles which is independent of the viscosity of pseudo suspension. Also, the results showed that, with low viscosity, evaporation effect becomes influential, and it solely depends on the polymer content. However, with high viscosity, evaporation effect can be minimized with the polymer shell and high solution layer thickness. These results can provide a clean picture of the binder behavior and its influence on the particle transfer process which opens-up the possibility of particle sorting process from a polydisperse suspension mixture and high-yield material transfer for porous structure joining process.
CHAPTER 5

CONCLUSIONS

The above research works exhibits an optimized and efficient solid transfer process through dip coating from a density mismatch mixture which can be applied on particle sorting and material joining process. After investigating the cross-sectional area and surface packing coverage it was observed that 35% particles and 9-11 % binder (15K PMMA) can be a effective and optimum solid transfer composition in concentrated suspension. In LCS mixture dipping, measured liquid polymer layer thickness was found lower than the expected film thickness due to the solvent evaporation. Particle entrainment was observed at very low liquid film thickness. At very small capillary number ($Ca \sim 3.1 \times 10^{-6}$), particles were entrained due to rich polymer boundary layer with high viscosity at 35% particles and 6.5% binder (15K PMMA). It was also observed that the critical film thickness for particle entrainment was reduced to $h^* = 0.16a$ for 6.5% binder and $h^* = 0.26a$ for 10.5% binder, which are lower than the prior literatures. While changing the MW of the binder polymer, the viscosity of LCS was increased with high MW at the same concentration of binder due to longer polymer chain and entanglement which facilitates the intermolecular interactions and provides resistant to the solvent flow. In similar weight and similar viscosity experiment it was observed that with high MW (120K and 350K), high viscosity can be achieved with low concentration of polymer and the viscosity increases linearly with concentration like dilute solutions. However, to get high viscosity (4 and 6 mPa.s) at LCS solution with low MW polymer (15K), high concentration of polymer loading is required, and the viscosity does not follow the linear increase with concentration creating a gel-like behavior. In dilute conditions, smaller particle entrainment was observed and in gel-like conditions the particle size distribution was showing similar to bulk particles (Nicrobraz LM) distribution.
REFERENCES


BIBLIOGRAPHY OF THE AUTHOR

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