



## Original Article

## Fundamental understanding of centrifugal micromolding for high fidelity patterns



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## ABSTRACT

Centrifugal casting is a convenient and effective approach for producing micro-patterns from ceramic suspensions. However, the fundamental mechanisms for this approach are elusive and require an in-depth investigation. In this work, basic theories related to centrifugal casting and particle interaction energy of the dispersed suspension are analyzed with the consideration of the micro patterning process, the repulsive steric/electrostatic/depletion energy, and the attractive van der Waals energy. A well dispersed suspension with weak flocculation improves the flowability of the suspension and enables high fidelity pattern formation. From the centrifugal casting point of view, a higher solids loading suspension under an intermediate centrifugal speed is beneficial for high fidelity micro pattern formation. This study provides important guidance for centrifugal micromolding of high fidelity patterns.

## 1. Introduction

Micro-patterning [1–4] has attracted great attention in the sub-micron and micron regimes. Among different techniques, photolithography and soft lithography are the widely adopted strategies for micron patterning [5]. However, photolithography requires proper photosensitive materials, well-designed masks, and special light sources, which has limited its use. Soft lithography relies on an elastomer as a mold, and can make micro-patterning repeatedly by stamping. Replica molding [6–8], microtransfer molding [9,10], microcontact printing [11,12], solvent-assisted micromolding [13,14], and micromolding in capillaries [15,16] are the specific types of soft lithography. Due to its simple process, low cost, flexibility, and easy operation, soft lithography has been used to produce versatile patterns from liquids on planar and non-planar surfaces. Polydimethylsiloxane (PDMS) has been used extensively as a mold/stamp material [17] due to its elastomeric, UV transparent, low temperature curable, and low Young's modulus characteristics [18]. Therefore, micro patterning with PDMS molds has been expanded to generate micron/sub-micron ridges and rod features based on ceramic suspensions [19–21].

However, making high fidelity micro patterns for ceramic suspensions presents great challenges. Different from pure liquids, ceramic suspensions are a mixture of liquid and solid particles with much higher viscosities. When the feature sizes are reduced to the micron scale, it becomes extremely difficult to create high fidelity patterns with soft

lithography due to agglomeration of particles and poor flowability of the suspensions. It was found that soft lithography based on the PDMS molds tends to produce good patterns for high solids loading suspensions, such as ~30 vol% ZnO and TiO<sub>2</sub> [20,21]. Lower solids loading suspensions of 20 vol% can cause pattern fidelity loss [20]. However, with centrifugal assistance, micro-patterns are produced [22]. It is believed that at least two aspects, suspension quality and centrifugal induced acceleration, alter the micro-pattern formation process. The particles should be well dispersed and agglomeration should be reduced so that the suspension can easily flow into small feature cavities in the mold. Nonetheless, the fundamental understanding of centrifugal casting on patterning micron-sized features remains elusive. Due to the soft nature of the PDMS molds, the high centrifugal force may also lead to the deformation of the PDMS molds, hindering high fidelity pattern formation.

In this study, we focused on a TiO<sub>2</sub> nanoparticle suspension and explored the possible impact from the centrifugal patterning process. Solids loadings of 10 vol%, 15 vol%, and 20 vol% were studied. Particle interaction energies were calculated. The surface morphologies of the dried micron ridge patterns (3 μm width) with different centrifugal speeds were evaluated and the fidelities of the micro-patterns were characterized with respect to line edge roughness (LER). Sediment volume fraction and pattern pressure during the centrifugal casting were explored based on centrifugal theories. An in-depth understanding of micro-pattern formation from nanoparticle suspensions with centrifugal

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assistance was finally obtained.

## 2. Theoretical analysis

### 2.1. Particle interaction energy

Theoretically, the interaction energy between two particles can be calculated by the following equation:

$$V_{\text{Total}}(h) = V_A(h) + V_S(h) + V_E(h) + V_D(h) \quad (1)$$

where  $V_A(h)$  is the attractive van der Waals energy,  $V_S(h)$  is the repulsive steric energy,  $V_E(h)$  is the repulsive electrostatic energy, and  $V_D(h)$  is the depletion interaction energy. The van der Waals energy  $V_A(h)$  can be expressed as [23]:

$$V_A(h) = -\frac{A}{6} \left[ \frac{2a_p^2}{4a_p h + h^2} + \frac{2a_p^2}{(2a_p + h)^2} + \text{Ln} \left( \frac{4a_p h + h^2}{(2a_p + h)^2} \right) \right] \quad (2)$$

where  $h$  is the distance between particle surfaces,  $a_p$  is the radius of a particle, and  $A$  is the Hamaker constant,  $5.35 \times 10^{-20}$  J for  $\text{TiO}_2$  in an aqueous solution [24].

The steric interaction energy  $V_S(h)$  arises when the particles have a distance smaller than twice of the adlayer thickness ( $2L$ ). When the particle surface distance  $h$  locates between  $L$  and  $2L$ ,  $V_S(h)$  can be expressed by [23]:

$$V_S(h) = \frac{32\pi a_p K_B T}{5\nu L^4} \phi_p^2 \left( \frac{1}{2} - \chi \right) \left( L - \frac{h}{2} \right)^6 \quad (3)$$

where  $K_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\phi_p$  is the average volume fraction of polymeric segments within the adlayer (0.37),  $\chi$  is the Flory-Huggins solvency parameter (a measure of solvent quality, 0.47 for water [25]), and  $\nu$  is the molar volume of the solvent.

When the particle surface distance  $h$  is between 0 and  $L$ , the adlayers mix with each other, and the elastic contributions dictate the interaction potential energy. The steric energy  $V_S(h)$  can be expressed by the sum of the mixing term  $V_{S, \text{mix}}(h)$  and  $V_{S, \text{elastic}}(h)$  [23]:

$$V_{S, \text{mix}}(h) = \frac{4\pi a_p L^2 K_B T}{\nu} \phi_p^2 \left( \frac{1}{2} - \chi \right) \left( \frac{h}{2L} - \frac{1}{4} - \text{Ln} \frac{h}{L} \right) \quad (4)$$

$$V_{S, \text{elastic}}(h) = \frac{2\pi a_p K_B T L^2 \rho_{\text{ad}}}{M_w} \phi_p^2 \left\{ \frac{h}{L} \text{Ln} \left[ \frac{h}{L} \left( \frac{3-h}{2} \right)^2 \right] - 6 \text{Ln} \left( \frac{3-h}{2} \right) + 3 \left( 1 - \frac{h}{L} \right) \right\} \quad (5)$$

where  $\rho_{\text{ad}}$  is the density of the adlayer species,  $M_w$  is the molecular weight of the adlayer species (polyethylene glycol, PEG).

The adlayer thickness on the particle surface  $L$  (with nm unit) can be estimated by [26]:

$$L = 0.06(M_w)^{0.5} \quad (6)$$

where  $M_w$  is the average molecular weight of the adlayer species (PEG2000).

The electrostatic energy  $V_E(h)$  of the spherical particles can be expressed as [23]:

$$V_E(h) = 2\pi a_p \epsilon_0 \epsilon_r \zeta^2 e^{-\kappa h} \quad (\text{when } \kappa a_p < 5) \quad (7)$$

$$V_E(h) = 2\pi a_p \epsilon_0 \epsilon_r \zeta^2 \text{Ln}(1 + e^{-\kappa h}) \quad (\text{when } \kappa a_p > 10) \quad (8)$$

where  $\epsilon_0$  is the permittivity of vacuum ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $\epsilon_r$  is the dielectric constant of the solvent ( $\sim 78.40$  for an aqueous system at room temperature [27]),  $\zeta$  is the surface potential estimated from the zeta potential,  $\kappa^{-1}$  is the Deby-Hückel screening length, which can be expressed by [23,27]:

$$\kappa^{-1} = \left[ \frac{\epsilon_0 \epsilon_r K_B T}{2e^2 N_A (1/2 \sum c_i Z_i^2)} \right]^{\frac{1}{2}} \quad (9)$$

where  $e$  is electron charge,  $N_A$  is Avogadro's number,  $c_i$  is the molar density of the ions of type  $i$ ,  $Z_i$  is the valence of the ions of type  $i$ . Since  $\text{HNO}_3$  is used to tailor the pH value in this work, only  $\text{H}^+$  ions contribute to the Deby-Hückel screening length. At room temperature, a simplified expression of Eq. (9) can be written as [27]:

$$\kappa^{-1} = 0.1515(C_{\text{H}^+})^{-\frac{1}{2}} \quad (10)$$

where  $C_{\text{H}^+}$  has the unit of mol L<sup>-1</sup>, and  $\kappa^{-1}$  has the unit of nm.

Due to the presence of free polymer in the suspension, the depletion forces can promote flocculation or destabilization of primary colloidal particles. Although the concentration of the depletion species in the suspension is low, the effect on the suspension stability can be drastic. The depletion interaction energy  $V_D(h)$  can be expressed by [23,28]:

$$V_D(h) = 0 \quad (\text{when } h > 2\Delta_{\text{dep}}) \quad (11)$$

$$V_D(h) = \frac{a_p \phi_{\text{dep}}^2 K_B T}{5\Delta_{\text{dep}}} (12 - 45\lambda + 60\lambda^2 - 30\lambda^3 + 3\lambda^5) \quad (\text{when } 2\Delta_{\text{dep}} \geq h > \Delta_{\text{dep}}) \quad (12)$$

$$V_D(h) = -\frac{3a_p \phi_{\text{dep}} K_B T \lambda^2}{\Delta_{\text{dep}}} + \frac{a_p \phi_{\text{dep}}^2 K_B T}{5\Delta_{\text{dep}}} (12 - 45\lambda - 60\lambda^2) \quad (\text{when } h \leq \Delta_{\text{dep}}) \quad (13)$$

where  $\phi_{\text{dep}}$  is the volume fraction of the free polymer in the suspension,  $\Delta_{\text{dep}}$  is the depletion layer thickness,  $\lambda$  has the expression of:

$$\lambda = \frac{(h - \Delta_{\text{dep}})}{\Delta_{\text{dep}}} \quad (14)$$

### 2.2. Centrifugal consolidation

In a dispersed suspension without any external force, a particle experiences three forces during the sedimentation process under the gravitational field [29]: gravitational force  $\vec{F}_g$ , hydrodynamic drag force  $\vec{F}_d$ , and random Brownian force  $\vec{F}_b$ . The gravitational force can be expressed as:

$$\vec{F}_g = -\Delta\rho g V_p \vec{z} \quad (15)$$

$\Delta\rho$  is the density difference between the particle and liquid,  $g$  is the acceleration due to gravity,  $V_p$  is particle volume,  $z$  is the distance in the vertical direction from the bottom of the sediment.

The hydrodynamic drag force is:

$$\vec{F}_d = -\lambda_{\text{St}} a_p \eta_s \vec{v}_d \quad (16)$$

$\lambda_{\text{St}}$  is Stokes drag coefficient,  $a_p$  is particle radius,  $\eta_s$  is liquid viscosity, and  $v_d$  is particle drift velocity.

When an equilibrium state is achieved for a particle at balanced forces, the resulting particle drift velocity  $\vec{u}$  can be expressed as:

$$\vec{u} = -u_0 \vec{z} \quad (17)$$

$$u_0 = \frac{\Delta\rho g V_p}{\lambda_{\text{St}} a_p \eta_s} \quad (18)$$

$u_0$  is Stokes settling velocity. For spherical particles:

$$u_0 = \frac{2a_p^2 \Delta\rho g}{9\eta_s} \quad (19)$$

For a flocculated suspension, the movement of particles during the sedimentation is affected by both direct and indirect interactions. The indirect force is mainly from the hydrodynamics of the fluid. Thus, the Stokes settling velocity can be modified by multiplying a coefficient

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