Nanoparticle-Textured Surfaces from Spin Coating

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Rough surfaces composed of discrete but relatively uniform nanoparticles were prepared from a lightly sulfonated polystyrene ionomer by spin coating from tetrahydrofuran (THF) or a THF/methanol mixture onto a silica surface. The particle morphology is consistent with the spinodal decomposition of the film surface occurring during spin coating. The particles are well wetted to the silica, and if heated for a long time above the ionomer’s glass-transition temperature, the particles flow and coalesce into a smooth, homogeneous film.

Introduction

The wettability of surfaces plays an important role in many biological and industrial applications. Thin coatings are usually prepared by evaporating the solvent from a polymer solution that has been placed on a solid substrate. Typical coating processes include painting, dip coating, solution casting, and spin coating. The roughness of the surface of the coating can be detrimental to applications such as optics and tribology but advantageous in the design of surfaces that mimic nature (e.g., superhydrophobic surfaces where the roughness usually consists of regular microscopic or nanoscopic features or micro- and nanohierarchical structures).1,2 In the latter applications, various complicated top-down or bottom-up approaches are necessary to control the surface roughness and geometry.1 This letter describes a facile method for obtaining a nanometer-scale textured surface that may be due to spinodal decomposition at the liquid/vapor interface of a spin-coated polymer film.

Experimental Details

The surfaces were prepared by spin coating sulfonated polystyrene ionomers onto silica surfaces. Polystyrene ($M_w = 4000$ g/mol, $M_w/M_n = 1.06$) was sulfonated to 2.5 mol % (an average of one sulfonate per chain) with acetyl sulfate,3 and the sulfonic acid derivative product was converted to an alkali metal salt (M-SPS, where M = Li, Na, K, Rb, or Cs) by titration with the corresponding alkali metal hydroxide. The glass-transition temperature ($T_g$) of all of the M-SPS ionomers was 88 °C. The ionomers were deposited onto silicon with a native oxide layer from a 1% solution by spin coating (SCS Corp., model P6700) at room temperature with a rotor speed of 3000 rpm.

The surface morphology of the films was imaged with an atomic force microscope, AFM, (MFP-3D, Asylum Research, Inc.) using tapping mode and silicon tips (radii of curvature $\approx 5–10$ nm) with a spring constant of about 2.5 N/m. Scanning electron micrographs were obtained with a JEOL-6335F (Japan Electronic Optics Ltd., Tokyo, Japan) field-emission scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV. The ionomer specimens were sputter coated with gold to prevent arcing.

Results and Discussion

For spin coating from solutions made with toluene and toluene/methanol mixtures, the ionomer formed a coherent, smooth thin film, $\sim 30$ nm thick, with excellent wetting properties on the silica.4 However, when either THF or a (9/1 v/v) THF/methanol mixture was used, the surface was rough and composed of discrete
but relatively uniform nanometer-sized particles wetted to the silica surface, as shown by the SEM image of Rb-SPS in Figure 1. The distribution of particle sizes is shown in Figure 2. Surfaces of the other alkali metal salts spin coated from THF or the THF/methanol mixture were similar, though the choice of the ionomer cation affected the size of the particles. The choice of solvent used and the polymer molecular weight also affected the particle size, but qualitatively, all of the prepared surfaces had similar morphology. When heated above the \( T_\text{g} \) of the ionomer, the particles coalesced into a coherent, wetted film (Figure 3), which rules out dewetting as the origin of the peculiar morphology shown in Figure 1. The homogeneous, smooth film shown in Figure 3c resists dewetting even at temperatures \( > T_\text{g} + 50 \, ^\circ\text{C} \).

One possible explanation for the origin of this particle morphology is spinodal decomposition of the film surface during spin coating. The stability of a submicrometer polymeric film is determined by the interplay between the film surface energy, long-range van der Waals interactions between the liquid and substrate, and the polymer confinement within a film thickness \( h \).

If the film thickness \( h \) experiences undulations \( u(x, y) \), then the change in the film free energy per unit area due to such undulations is given by the following equation,\(^4\)

\[
\Delta F(h) = \frac{1}{2}\gamma (\nabla u)^2 + \frac{A_{\text{eff}} u^2}{2\pi h^4}
\]

(1)

where \( \gamma \) is the surface energy of the polymer/air interface, \( A_{\text{eff}} = A + 0.9k_B T \) is the effective Hamaker constant that has contributions from the long-range van der Waals attraction\(^5\) and polymer confinement,\(^6\) \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The film is unstable if the \( A_{\text{eff}} \) coefficient is negative (i.e., \( A < -0.9k_B T \)). In that case, the free energy of the film decreases when the film thickness is modulated with spatial periodicity, \( \lambda \), larger than the so-called healing length, \( \xi \).

\[
\xi = h^2 \left( \frac{2\pi\gamma}{A_{\text{eff}}} \right)^{1/2}
\]

(2)

Thus, the thickness fluctuations at long wavelengths \( \lambda > \xi \) are amplified, and the film becomes wrinkled. The thinnest region of the film nucleates holes, which expand by creating a ridge. The ridge is unstable because of Rayleigh instability and spontaneously fragments into droplets of size

\[
R \propto \sqrt{h \xi} \propto h^{1/2}
\]

(3)

The size of the droplets can be controlled by changing the original film thickness, the cation used for the ionomer, and the solvent used for spin coating, which changes the value of the Hamaker constant, \( A \). The surface shown in Figures 1 and 2 has an average droplet radius of \( R \approx 150 \, \text{nm} \) (Figure 3), and a typical droplet thickness of \( h \approx 300 \, \text{nm} \). Using these film parameters, one can estimate that the healing length, \( \xi \), is on the order of 75 nm, and eq 3 predicts that a characteristic ratio, \( A_{\text{eff}}/\gamma \approx 29\pi \times 10^5 \, \text{nm}^2 \), is necessary for the formation of the nanoscale-size droplets. One might reasonably expect that for other polymer/solvent systems with similar characteristic ratios one should expect the formation of similar nanoscale droplets.

An alternative explanation for the phenomenon observed in this work is Marangoni instabilities as discussed by Strawhecker et al.\(^7\) That paper described the effect of the solvent evaporation rate on the roughness of a spin-cast polymer film. Although those authors observed roughness values comparable to the size scale of the particles seen in the present study, their spin-cast materials were films and not discrete particles. And the size scale of the heterogeneities (in their case, film undulations) were much larger (\( \sim 30 \, \mu\text{m} \)) than the particle sizes and separation of the particles in this letter (\( \sim 300 \, \text{nm} \)). Still, there are sufficient similarities between the two phenomena to warrant additional investigation of the origin of the ionomeric particles discussed in this letter.

The size and shape of the particle-patterned surfaces were consistent with the requirements for superhydrophobic surface geometry,\(^\text{17}^\text{17} \) and the contact angle of water on various particle-textured surfaces made with different salts of the ionomer were measured with a custom-built goniometer. In general, the surfaces were not superhydrophobic (contact angles were \( < 100^\circ \)). However, that may be a consequence of the polar nature of the polymer. In an aqueous environment, one would expect the metal
sulfonate groups to reside at the surface of the particles, which would provide a favorable environment for wetting by water. Zhai et al.8 prepared surfaces with nanoscale roughness by layer-by-layer deposition of polyelectrolytes followed by acid treatment to produce a honeycomb structure that was then coated with silica nanoparticles. Their surfaces also did not exhibit superhydrophobicity because of the hydrophilic nature of the polyelectrolytes and the silica, but when the surface was coated with a semifluorinated silane by chemical vapor deposition, the surface did exhibit superhydrophobicity. One might reasonably expect that a similar silanation of the M-SPS nanoparticle surfaces will also produce increased hydrophobicity of the ionomer particle surfaces.

Conclusions

A facile method for producing a surface with nanoscale roughness, which is believed to involve the spinodal decomposition of a film surface, was developed and consisted of spin coating a lightly sulfonated polystyrene (SPS) ionomer from a THF or THF/methanol solution. The nanoparticles produced by this method were well bound to the silica surface used in the spin-coating operation. The surface morphology was metastable but quite robust if the temperature ($T_g$) was maintained below the polymer glass-transition temperature. When heated above $T_g$, the nanoparticles flowed and coalesced into a homogeneous and well-wetted film on silica.

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