

## Suppression of Dewetting in Nanoparticle-Filled Polymer Films

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**ABSTRACT:** The perturbing influence of nanosize filler particles on the dewetting of spun-cast polymer films is investigated. Previous studies have shown that spun-cast films of unentangled polystyrene (PS) and polybutadiene (PB) dewet acid-cleaned silicon wafers when the films are annealed above their bulk glass transition temperature  $T_g$ . It is also known that “impurity” particles tend to promote dewetting in thin polymer films. Here we demonstrate that the addition of a small amount of  $C_{60}$  fullerene nanoparticles to the spin-casting polymer solution leads to an inhibition of dewetting in thin ( $L < 100$  nm) PS and PB films cast on both acid-cleaned and carbon-coated silicon wafer substrates. Neutron reflection measurements indicate that this effect is associated with the formation of a diffuse fullerene layer near the solid substrate. Evidently, the immobilized fullerene particles form an enrichment layer at the solid boundary and “pin” the contact line of the growing dewetted (“dry”) regions so that hole growth in the filled films becomes arrested at a scale which diminishes with increasing filler concentration. Above a relative filler–polymer mass fraction of 1%, we no longer observe hole formation by atomic force microscopy on the time scales of our measurements (typically on the order of hours), suggesting the existence of a critical filler surface coverage for the *suppression* of dewetting. The roughness of the fullerene layer probably also contributes to the modification of the surface wetting properties through a change in the surface energy of the substrate, as suggested by recent measurements on substrates “roughened” by other means such as irradiation of polymer film substrates, grafting of polymer chains, etc.

## Introduction

The saying that “like dissolves like” is a useful rule of thumb for understanding the solubilities of fluid mixtures and we can similarly understand the general tendency for fluids to wet materials having a similar chemical composition. These simple compatibility rules also explain the difficulty in producing stable organic polymer films on inorganic substrates. Such films are increasingly being used in technological applications involving dielectric coatings, resist layers for lithography, electronic packaging, optical coatings, nonlinear optical devices, lubricating surfaces, etc.<sup>1–3</sup> Producing stable and defect-free films is particularly problematic in very thin films (thickness,  $L < 10$  nm) where thermally induced fluctuations of the polymer–air film boundary (“capillary waves”) tend to cause film rupture.<sup>4–8</sup> Stabilization of these films against dewetting is a problem of fundamental technological importance.

Various strategies have been utilized to “stabilize” thin polymer films. Dewetting can be greatly suppressed in high molecular weight (entangled) or glassy polymer films ( $T < T_g$ ) spun-cast from solution. It is difficult for these films to equilibrate so that surface energetics is less of a factor governing surface wetting. A shortcoming of this approach is that dewetting still tends to occur, albeit on long time scales. The “aging” of the film structure and associated formation of film defects over time can be detrimental to the applications for which the films were intended. Recent work has also shown that the tendency toward polymer film dewetting on inorganic substrates can be inhibited through grafting polymer layers onto the solid substrate with and without the addition of high molecular weight polymer,<sup>9</sup> sul-

fonation and metal complexation of the polymer,<sup>10</sup> and the introduction of specialized end groups onto the polymer with a high affinity for the inorganic substrate.<sup>11</sup> At present, these film stabilization effects are not well understood theoretically, but it seems clear that a combination of equilibrium (modification of polymer–surface interactions) and kinetic stabilization effects (entanglement and changes in  $T_g$ ) are generally involved.<sup>12,13</sup>

In the present paper, we adopt a novel strategy to *inhibit* the dewetting of thin polymer films based on the introduction of  $C_{60}$  fullerene nanoparticles into the spin-casting polymer solution. This stabilization is contrary to the usual experience where film inhomogeneities often lead to “cratering” (hole formation).<sup>14,15</sup> Stange et al.<sup>16</sup> and Jacobs et al.<sup>17</sup> have recently emphasized the importance of small particulates and air bubbles in nucleating the formation of holes in polymer films so there is evidence that film heterogeneities can have a detrimental effect on film stability. The nanoparticle fillers correspond to a very different size scale, however, and it is not immediately clear what influence such heterogeneities would have on the stability of polymer films. We show that the addition of even a very small amount (relative filler–polymer mass fraction,  $\phi_{\text{filler}} = 0.01\%$ ) of fullerene particles to the spin-casting solution leads to a strong *inhibition* of film dewetting for polystyrene and polybutadiene films in a thickness range between 20 and 50 nm. The films were cast on acid-cleaned silicon wafers and carbon-coated silicon wafers. Control measurements on unfilled films having nearly the same thickness indicated a conventional pattern of dewetting for this thickness regime.

There are a number of possible explanations for the filler-induced film stabilization. Since we normally observe the enrichment of the polymer components of

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polymer mixtures to the boundaries of thin polymer films, it seemed likely to us that this phenomenon had its origin in an enrichment of the filler particles to one or both of the film interfaces. Such an enrichment might change the polymer–substrate interaction, surface viscosity and could influence hydrodynamic fluid displacement processes (e.g., capillary waves) associated with film rupture and hole growth that are crucial for the initiation and propagation of the dewetting process. We then pursued measurements focusing on the surface properties of the filled films. Measurements included water contact angle to monitor changes in the surface energy of the polymer–air boundary, atomic force and optical microscopy to examine the morphology of the dewetting films, and neutron reflection (NR) to examine the height distribution of the fullerene within the film. NR measurements on the as-cast films indicated fullerene enrichment to the solid substrate so that much of the surface segregation is complete in the as-cast films. This led us to consider the dewetting of polymer films on model smooth carbon-coated silicon wafers whose surface chemistry was expected to be similar to the fullerene enrichment layer. Preliminary calorimetry and viscometry measurements were also performed on the filled polymers to check for conspicuous evidence of particle–particle and particle–polymer association transitions that might explain the observed film stabilization effect.

## Experimental Section

Low molecular weight polystyrene (PS) and polybutadiene (PB) samples were purchased from Goodyear Tire and Rubber Co.<sup>18</sup> with reported average molecular masses<sup>19</sup> and polydispersity values of  $M_n = 1800$ ,  $M_w/M_n = 1.19$  and  $M_n = 2760$ ,  $M_w/M_n = 1.08$ , respectively. The glass transition temperature ( $T_g$ ) of pure PS was determined by differential scanning calorimetry (DSC) to be  $55 \pm 2$  °C while the  $T_g$  of PB is estimated to be  $< -50$  °C. PS was purified upon receipt by filtration, followed by freeze-drying. C<sub>60</sub> fullerenes (“buckyballs”)<sup>18</sup> were purchased from Aldrich Chemical Co. and dissolved in toluene before addition to the polymer solutions. The fullerene particles readily dissolved into the spin-casting polymer solutions where the relative fullerene mass fractions to polymer were in the range 0.01–5% for PS and 1% for PB. We were also able to make stable mixtures of fullerene and polymer, indicating the fullerene is miscible with PS and PB at room temperature. The polymer–fullerene mixtures and the spin-casting solutions containing fullerene were optically transparent and had a light violet color, as often found for fullerene solutions in organic solvents. Spin-casting solutions were all prepared in toluene and were spun-cast at various speeds ranging from 2000 to 6000 rotations per minute (rpm) to obtain films ranging from 20 to 50 nm in thickness.<sup>20</sup> Polyme/toluene solutions were filtered through 0.2  $\mu$ m PTFE filters before spin-coating. (It is difficult to determine the exact fullerene concentration of the spun-cast films since the concentration ratio of polymer to filler may not be maintained during spin-casting because of filler adsorption and other nonequilibrium effects associated with the spin-coating process.) The silicon wafer substrates were acid cleaned with a 70/30 volume ratio solution of 96% H<sub>2</sub>SO<sub>4</sub> (Mallinckrodt<sup>18</sup>)/30% H<sub>2</sub>O<sub>2</sub> (J.T. Baker<sup>18</sup>) for 1 h at 80 °C and rinsed in deionized water before spin-coating. Films were also spun onto Si wafers uniformly coated with freshly evaporated carbon ( $\approx 100$  nm thick) under high vacuum.

Small-angle neutron scattering (SANS) measurements on filled bulk PS samples containing up to 1% fullerene mass fraction do not show evidence for a  $q^{-4}$  power law scaling (scattering intensity versus wavevector) or other power law scaling which would be symptomatic of the aggregation of fullerene particles into compact or fractal clusters, respectively.

Clustering would be apparent even at low fullerene concentrations because of the high contrast between the fullerene and the polymer solution. Given this lack of aggregation, at least for these low concentrations of filler, we expect the relative filler concentration in the dried film to be proportional to the filler concentration in the spin-casting solution. Fullerene particle aggregation cannot be excluded in the dried film (see Discussion section).

Optical microscopy (OM) indicated that the PS films were smooth and uniform when inspected immediately after spin-coating. The films were annealed under vacuum at 45 and 85 °C above the glass transition of the PS ( $T = 100$  and 140 °C, respectively) to observe the dewetting process. Since the glass transition of PB is well below room temperature, annealing at higher temperatures was not necessary to induce dewetting. Reflective optical images were obtained using a Nikon optical microscope with a digital Kodak MegaPlus CCD camera attachment. Atomic force microscopy (AFM) images of the surface patterns were taken using an Explorer TopoMetrix instrument. Contact angle measurements were estimated by dropping 5  $\mu$ L of deionized water on the film surface with values averaged from four droplet readings using a Rame-Hart contact angle goniometer. Glass transition temperatures of filled and unfilled PS films were measured using a Perkin-Elmer differential scanning calorimeter (DSC).

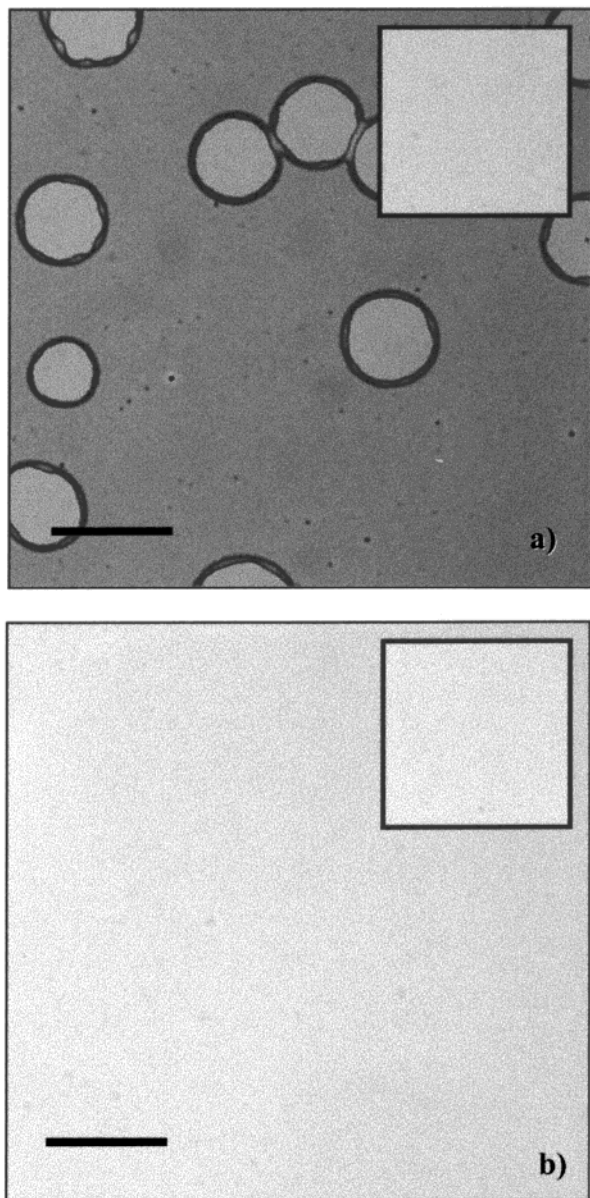
Neutron reflection<sup>21</sup> (NR) measurements were performed on a thin PS film containing a relative fullerene–polymer mass fraction of 5%, prepared on polished acid-cleaned Si wafers (diameter = 100 mm, thickness = 5 mm) using the cleaning procedure described above. The film was prepared by spin-casting a solution from toluene containing a total solid (PS and fullerene) mass fraction of 2% at 2000 rpm to prepare a film approximately 100 nm thick. NR measurements were conducted on the NG7 reflectometer at the NIST Center for Neutron Research (NCNR). At NG7, neutrons of wavelength  $\lambda \approx 4.8$  Å are collimated and reflected from the horizontally placed sample, and the reflected beam monitored by a shielded He<sup>3</sup> pencil detector. The desired neutron momentum ( $q$ ) range is attained by changing the angle of incidence ( $\theta$ ) while keeping the detector at  $2\theta$  position with respect to the incident beam.

## Results

Parts a and b of Figure 1 show optical micrograph images from 50 nm thick films of pure PS and PS with fullerene–polymer relative mass fraction of 1%, respectively. Both films were annealed identically at 140 °C for 20 min. This comparison indicates that the filled polymer film is “stabilized” against dewetting on this time scale by the presence of the fullerene particles. The insets of Figure 1a,b show that the polymer films are uniform and homogeneous immediately after spin-coating. Once annealed above the bulk glass transition of PS ( $T_g \approx 55$  °C), the pure PS polymer exhibits a normal pattern of dewetting (nucleation of holes at early stage as in Figure 1a, followed by hole growth and coalescence).<sup>4,10</sup> In contrast, the 1% filled PS film remained smooth on the spatial scales probed by the optical measurements. Since it is unclear whether the inhibition of film dewetting is a kinetic or equilibrium effect, we annealed a representative 1% fullerene film over a 48 h period. Optical measurements indicated that the film remained smooth over this time period. This preliminary measurement indicates that either the fullerene brings about an equilibrium stabilization or a long-term kinetic inhibition of film dewetting. In any event, the film dewetting process is inhibited over appreciable time scales, and we next focus on the generality of the effect and try to understand its cause.

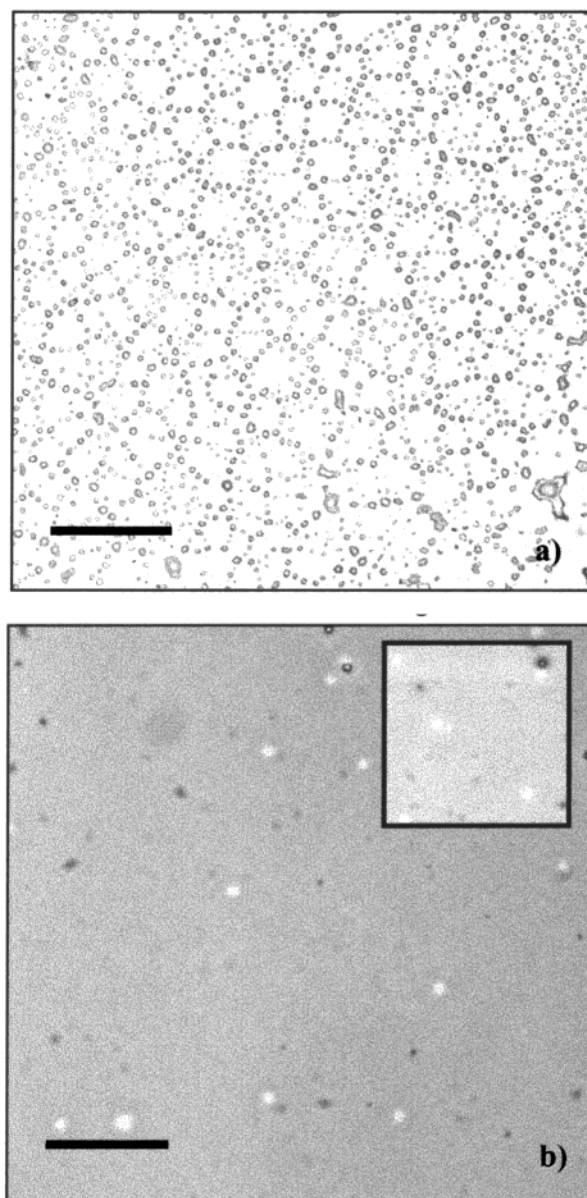
We can gain some insight into the generality of the film stabilization effect by considering the influence of the fullerene filler on the dewetting of another model





**Figure 1.** Optical micrographs showing dewetting of 50 nm polystyrene films prepared by spin-casting polymer solutions onto acid-cleaned silicon wafers after annealing at 140 °C for 20 min: (a) PS, (b) PS with fullerenes ( $\phi_{\text{filler}} = 0.01$  in toluene). Insets show films prior to annealing (scale bar = 300  $\mu\text{m}$ , same for insets).

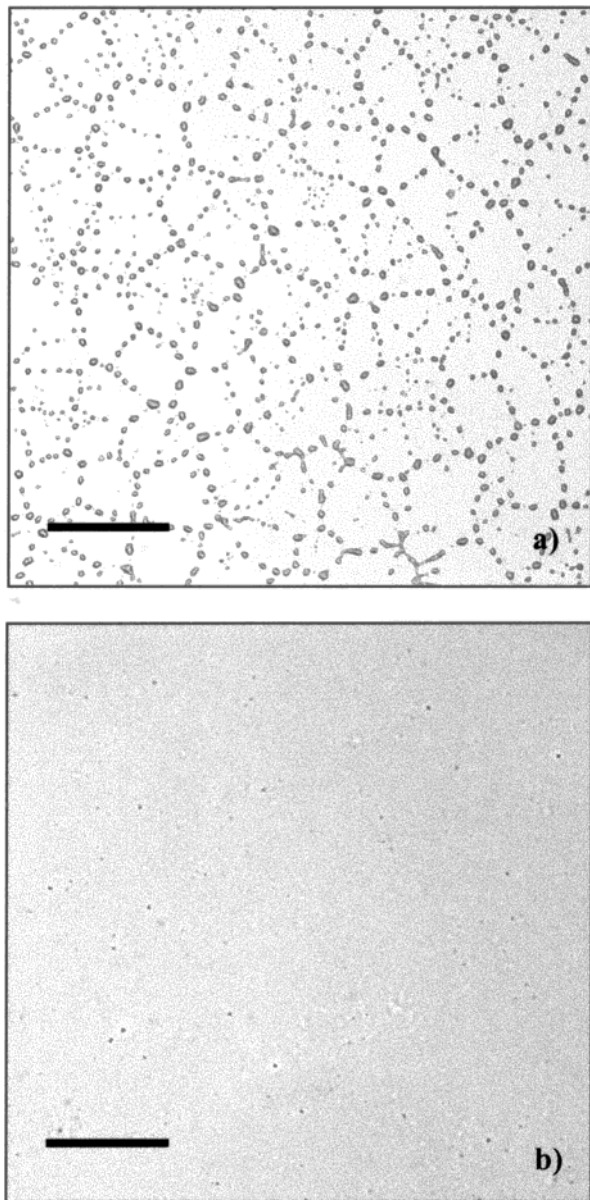
polymer. An elastomeric polymer, polybutadiene (PB), provides a good contrast to the glassy PS polymer, both in its mechanical properties and in differences of surface energy.<sup>3</sup> Figure 2a shows an optical micrograph of a PB film dewetting from the silicon substrate measured 5 min after spin-coating. The film is approximately the same thickness ( $\approx 50$  nm) as the PS films shown in Figure 1. Since room temperature is well above the  $T_g$  of PB, dewetting occurs rapidly, giving rise to classic late-stage droplet pattern shown in Figure 2a. The dewetting of the filled PB film ( $\phi_{\text{filler}} = 0.01$ ) in Figure 2b is contrasted with the unfilled PB film of Figure 2a of similar thickness ( $\approx 50$  nm). By comparison, the filled film was stable against large-scale dewetting for a period greater than 8 h. Film stabilization by the nanofiller then occurs for both PS and PB filled films ( $\phi_{\text{filler}} = 0.01$ ;  $L \approx 50$  nm).



**Figure 2.** Optical micrographs showing dewetting of 50 nm polybutadiene films 5 min after spin-casting polymer solution onto acid-cleaned silicon wafers: (a) PB, (b) PB with fullerenes ( $\phi_{\text{filler}} = 0.01$  in toluene). Inset of (b) shows the same film after 8 h (scale bar = 300  $\mu\text{m}$ , same for insets).

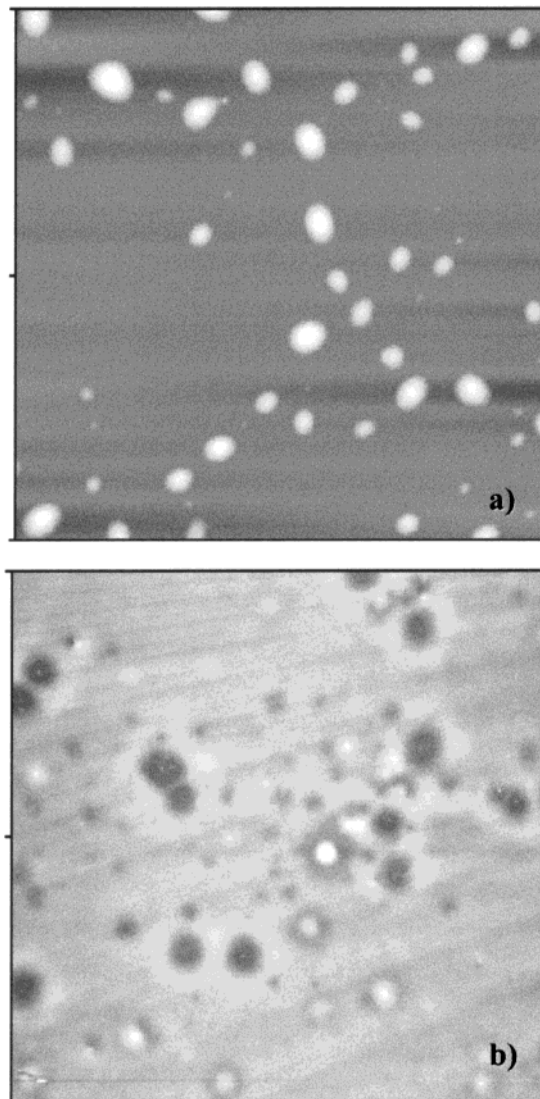
We next consider the influence of film thickness and fullerene concentration on the suppression of film dewetting by the filler. Figure 3a shows a thinner PS film ( $L \approx 20$  nm) that was annealed at 100 °C for 30 min. The rate of film dewetting is faster in the thinner film as expected,<sup>4</sup> but the dewetting process is otherwise normal for a film of this thickness.<sup>6</sup> In contrast, a 20 nm filled PS film with a small concentration of fullerene ( $\phi_{\text{filler}} = 0.005$ ) showed no appreciable dewetting after 30 min of annealing at 100 °C. Optical microscopy measurements performed after further annealing at elevated temperatures (140 °C for approximately 3 h) did not provide any indications of dewetting (Figure 3b), which was surprising given the very low concentration of filler employed in these measurements.

We then examined the films at a much higher magnification using AFM to determine if there was any important fine structure in the filled polymer films that might give us a clue into the origin of the film stabiliza-



**Figure 3.** Optical micrographs showing dewetting of 20 nm polystyrene films: (a) PS annealed at 100 °C for 30 min, (b) PS with fullerene mass fraction,  $\phi_{\text{filler}} = 0.005$  in toluene, annealed at 100 °C for 30 min, and then further annealed at 140 °C for 2.5 h (scale bar = 300  $\mu\text{m}$ ).

tion effect. Figure 4a shows AFM of the same 20 nm unfilled film imaged in Figure 3a (annealed for 30 min at 100 °C). The droplets in this figure have a height on the order of 100 nm, and the dark background indicates the bare dewetted silicon substrate. Figure 4a provides a reference point for comparison to the fullerene-filled polymer film, prepared to have a similar film thickness and annealing history. Next, we contrast the relatively smooth looking optical image of the filled PS film shown in Figure 3b ( $L \approx 20$  nm; annealed for 30 min at 100 °C and 3 h at 140 °C) with its AFM image shown in Figure 4b. Interestingly, the dewetting of this filled polymer film with a very low filler concentration occurs only at a scale resolvable by our AFM. This image suggests that the growth of dewetting regions is arrested by the pinning of the contact lines of the growing holes. Such a pinning mechanism could arise from an inhomogeneous distribution of nanofiller bound to the substrate. This would also lead to a broad distribution of hole sizes

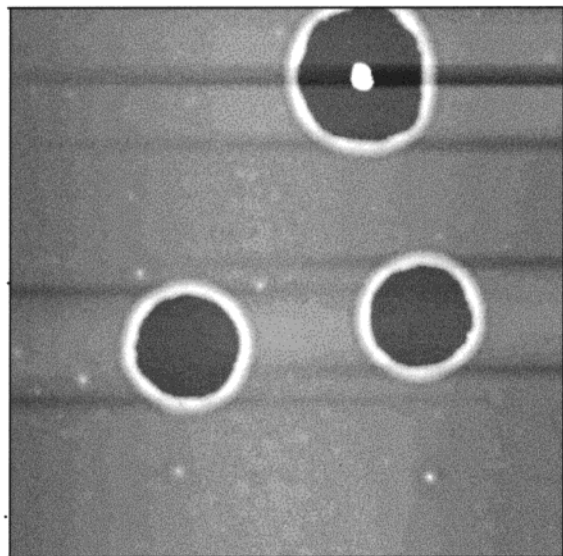


**Figure 4.** AFM images of PS films with and without nanofiller (fullerene) particles. Images correspond to the same films whose optical micrographs are shown in Figure 3, but at a higher spatial resolution (image width = 100  $\mu\text{m}$ ). Film thicknesses are estimated to be 20 nm. (a) PS annealed at 100 °C for 30 min, (b) PS with fullerene mass fraction,  $\phi_{\text{filler}} = 0.005$  in toluene, annealed at 100 °C for 30 min (almost no dewetting observed), and then further annealed at 140 °C for 2.5 h. Note the height scale bar in (b) is 1/16 that in (a), so the absolute heights in the filled film are significantly smaller compared to those in the unfilled dewetted film.

as observed in Figure 4b. It is notable that both the AFM (not shown) and optical images (see Figure 1b) of PS films having a higher filler concentration (e.g.,  $\phi_{\text{filler}} = 0.01$ ) show no evidence of hole formation so that the observation of holes is limited to low filler concentrations. Although the films having a low filler concentration have a more limited effect on achieving film stabilization against dewetting, they are helpful for understanding the origin of the film stabilization effect.

We can obtain further insight into the “pinning” of the hole growth by examining more closely the early stages of dewetting in unfilled films where hole formation dominates the film dewetting process. The contrast between the filled and unfilled films is particularly apparent in these earlier stages of film dewetting. Figure 5 shows a representative AFM image of hole formation in an unfilled PS film ( $\approx 35$  nm) that was

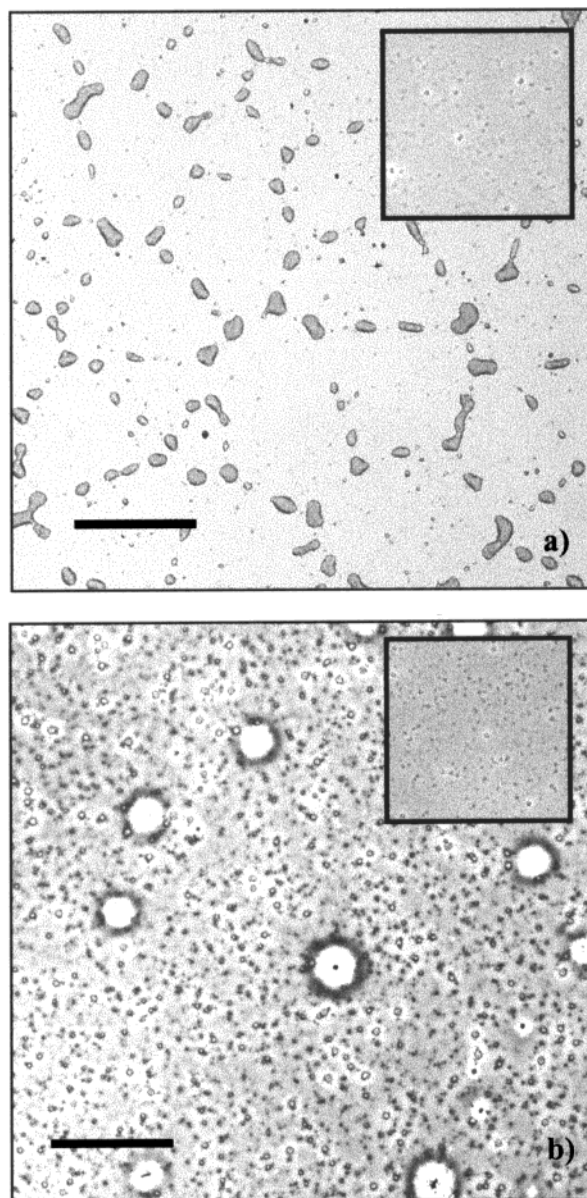




**Figure 5.** AFM image of an unfilled 35 nm thick PS film ( $M_w = 4000$ )<sup>6</sup> dewetting from an acid-cleaned silicon wafer after annealed for 25 h at 115 °C (image width = 100  $\mu\text{m}$ ). The top hole may be induced by a nucleating site such as dust. The holes are comparatively more uniform than that found in filled films.

obtained in a previous study of thin polymer film dewetting.<sup>6</sup> The polymer molecular weight in this former study was higher so the kinetics is slower, even at a higher temperature. This image is representative of hole formation in the early stage of dewetting in unfilled films (see also ref 4 for further examples). The hole size and shape are more uniform in comparison to filled polymer films (Figure 4b), characteristic of film dewetting without filler (Figure 5). The kinetics of hole growth is even more distinctive between the filled and unfilled films. Holes that form in the unfilled film grow steadily in time and undergo a complex coalescence kinetics at a late stage of dewetting,<sup>4,6</sup> while the holes of the unfilled film become pinned at a scale corresponding to the early stage of dewetting without filler. After pinning, the film structure shows no detectable evolution on the time scales of our measurements (8 h). The time scale of this pinning process is discussed below in connection with the influence of filler concentration on the size of the pinned holes.

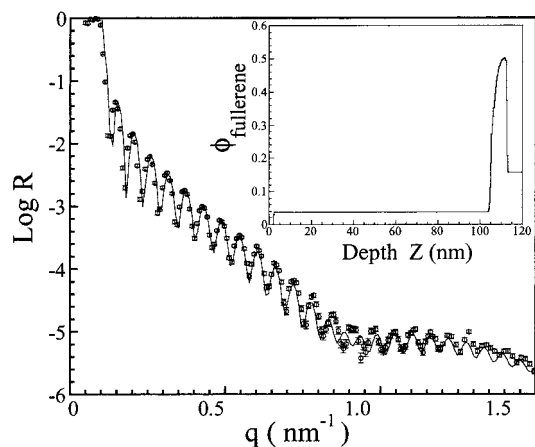
It would evidently be interesting to consider polymer films cast directly on fullerene-coated substrates to determine whether the suppressed dewetting had its origin in a change in the polymer–substrate interaction through filler adsorption. Unfortunately, fullerene films cannot be utilized directly because of their high solubility in the solvents used in spin-coating the polymer films. We then considered the dewetting of PS and PB films on evaporated carbon films that we expected to have similar surface energies as a  $\text{C}_{60}$  fullerene layer. Figure 6a shows a pure 50 nm PS film on an evaporated 50 nm thick carbon layer after annealing at 140 °C for 20 min. This film exhibits ordinary late stage dewetting, but the rate of dewetting is *greater* than for the silicon wafer. The change in kinetics can be appreciated by comparing Figure 6a with Figure 1a which show the dewetting of PS films on acid-cleaned silicon and carbon-coated silica wafers, respectively. The films have the same thickness and annealing history (see figure captions for specification) and are compared at the same observational scale. Clearly, the dewetting pattern scale



**Figure 6.** Optical micrographs showing dewetting of 50 nm PS films prepared by spin-casting solutions having polymer mass fraction 1% onto carbon-coated silicon wafers, annealed at 140 °C for 20 min: (a) PS, (b) PS with fullerenes,  $\phi_{\text{filler}} = 0.01$ . Insets show films prior to annealing (scale bar = 300  $\mu\text{m}$ , same for insets).

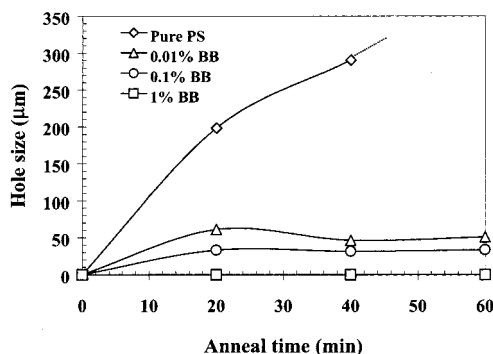
for the PS film on the carbon-coated silicon wafers is much larger than the acid-cleaned wafer, consistent with a more rapid dewetting from the carbon-coated substrate. It is apparent that the carbon-coated surfaces do not lead to inhibited dewetting as observed for the fullerene-filled films. Dewetting on the evaporated carbon film occurs similarly to the acid-cleaned silicon substrate, apart from a change in the rate of dewetting. Figure 6b shows a fullerene-filled PS film ( $\phi_{\text{filler}} = 0.01$ ) on a carbon-coated substrate under identical annealing conditions, and we again find inhibited dewetting in the filled film.

We note that the carbon-coated film surface is relatively smooth (except for occasional bumps, rms roughness is  $\approx 0.5$  nm by AFM). Assuming the fullerenes segregate to the substrate surface, our contact line pinning model of dewetting suppression suggests that an essential difference between the carbon-coated film



**Figure 7.** Neutron reflectivity from a 100 nm thick PS film containing fullerenes,  $\phi_{\text{filler}} = 0.05$ . Inset shows the volume fraction profile for the fullerene concentration in the film. Observe the fullerene segregated layer ( $\approx 5$  nm) at the silicon boundary with no detectable segregation at the air-polymer surface. The interface between the fullerene segregated layer and the PS film is diffuse. Error bars on data represent one standard deviation.

and the fullerene enrichment layer of the spun-cast film is the relative sharpness of the polymer-substrate interface and the in-plane uniformity of the carbon surface. (It is well-known that the evaporation of solvent-cast films of fullerenes in nonpolar solvents such as toluene gives rise to fractal dendritic structures, and this clustering of the fullerene was also anticipated in polymer-fullerene films cast from nonpolar solvents.<sup>23</sup>) We checked for the presence of a layer of enriched filler concentration at the solid substrate through neutron reflection (NR) measurements. These measurements had a depth resolution of about 1 nm for a PS film of moderate thickness,  $L \approx 100$  nm, and a relatively high filler concentration ( $\phi_{\text{filler}} = 0.05$ ) was employed to enhance sensitivity of our NR measurements. The solid line fit to the as-cast film reflectivity data in Figure 7 and the inset shows the relative fullerene concentration or "composition profile". The fullerene particles indeed form an approximately  $5 \pm 0.5$  nm thick layer of enriched concentration near the silicon substrate. This enrichment apparently forms because the fullerene-silicon substrate interaction is *less unfavorable* than the PS-silicon substrate interaction. (PB enriches to the silicon substrate in PS/PB blends for a similar reason.) The extent of this layer, however, is influenced by the nonequilibrium conditions of the film-casting process. The interface of the fullerene enrichment layer is diffuse, as expected on the basis of previous observations showing the tendency of fullerene particles to form fractal dendritic structures on the solid substrate of evaporating films.<sup>25</sup> We anticipate that the roughness of the polymer-fullerene interface is greater in the cast films containing lower concentrations of fullerene because the substrate should only become completely covered at higher filler concentrations. It is difficult to characterize the in-plane structure of the polymer-fullerene interface using NR, but it may be possible to use grazing incidence X-ray scattering or other methods (e.g., secondary ion mass spectroscopy) to obtain information about the in-plane heterogeneity of the surface layer of fullerene enrichment. NR data also indicate that there is no detectable enrichment of the fullerene particles at the polymer-air interface so that mechanisms of suppressed dewetting relying on the segrega-



**Figure 8.** Dewetting hole size in PS films ( $L = 50$  nm) as a function of fullerene filler mass fraction and annealing time at  $140^\circ\text{C}$ . The pure PS film shows approximately  $200\ \mu\text{m}$  hole growth by 20 min that start to impinge upon one another at longer times. The holes in the fullerene filled films do not grow ("pinned") beyond the first 20 min of annealing.

tion of the fullerene to the polymer-air interface can be excluded.

Indirect information about the heterogeneity of the fullerene layer can be determined by varying the fullerene concentration and thus the fractional coverage of the solid substrate by the fullerene particles. According to our view of the suppressed dewetting due to contact line pinning, dewetting should occur within surface regions free of fullerene and become arrested when the contact line of the growing holes impinge on rough fullerene-rich regions of the substrate. This conceptual model should lead to an inverse dependence of the average hole size on the filler concentration, hole sizes that are polydisperse because of the fluctuations in the surface coverage by the fullerene, and most importantly the hole growth is predicted to "pin" at long times in this model. The average scale of the dewetting holes diminishes with an increasing filler concentration where the precise decrease depends on the particular geometrical form of the fullerene particle clustering on the substrate. To test the *prediction* of a decrease of hole size with increasing concentration in nanoparticle filled films, we made a series of filled PS films ( $L \approx 50$  nm) having a concentration range with mass fraction  $0.0001 < \phi_{\text{filler}} < 0.05$  in the spin-casting solution. As shown in Figure 8, the optical microscopy images indicate that the hole growth became pinned after 20 min of annealing at  $140^\circ\text{C}$  in all cases. Calculation<sup>23</sup> of the average hole size was determined by measuring the diameter of holes, giving average hole diameters at 20 min of  $50.8 \pm 1.1$  and  $32.7 \pm 0.8\ \mu\text{m}$  for the  $\phi_{\text{filler}} = 0.0001$  and  $\phi_{\text{filler}} = 0.001$  films, respectively. The hole size did not evolve in time, confirming also that the holes are "pinned". Both optical and atomic force microscopy indicated the absence of detectable holes for the films having  $\phi_{\text{filler}} = 0.01$  and  $\phi_{\text{filler}} = 0.05$  so that there appears to be a critical filler coverage beyond which hole formation becomes suppressed even in AFM measurements. Figure 1b shows an optical image of the  $\phi_{\text{filler}} = 0.01$  concentration film after annealing at  $140^\circ\text{C}$  for 20 min. It is noted that the average hole size of the unfilled PS film under the same annealing conditions and film thickness ( $L \approx 50$  nm) equals  $200 \pm 12\ \mu\text{m}$  after 20 min, and that the holes are still growing. These observations confirm that the scale at which the dewetting holes pin diminishes with filler concentration and support our interpretation of the suppressed dewetting in terms of contact line pinning induced by a rough layer of filler particles at the solid substrate.



**Table 1. Average Contact Angles Obtained by Measuring the Contact Angle of 5  $\mu\text{L}$  of Deionized Water Droplets on the Various Film Surfaces<sup>a</sup>**

film description	contact angle (deg)
PS film	$87.3 \pm 1.3$
fullerene filled PS film ( $\phi_{\text{filler}} = 0.01$ )	$88.1 \pm 1.1$
spin-coated fullerene layer	$69.5 \pm 4.5$
evaporated carbon layer	$65.5 \pm 1.0$

<sup>a</sup> Error bars are limiting values estimated from five measurements.

To further confirm the lack of significant segregation of the fullerene to the air–polymer interface indicated by NR, we characterized the polymer–air surface energy through contact angle measurements. Table 1 shows results of water contact angle measurements on the filled and unfilled polymer films. Contact angle measurements between all PS/fullerene surfaces and deionized water yielded angles of  $\approx 90^\circ$ , so that the surface energy seems to be relatively unchanged from that of pure PS films. A contact angle of about  $70^\circ$  was observed for deionized water droplets on the evaporated carbon films, and the same value was found for spun-cast fullerene layers. These observations are consistent with our hypothesis that the fullerene and carbon layers should have similar surface energies. The measurements do not exclude the possibility that the rough nature of the fullerene layer in the filled films changes the effective surface interaction substantially from the case of a smooth surface, leading perhaps to an equilibrium film stabilization effect. Large changes in the surface energy of films due to surface roughness have been observed<sup>24</sup> so that the inhibition of film dewetting due to fullerene and other nanoparticles is likely due to a combination of kinetic and equilibrium effects.

## Discussion

Our measurements on the dewetting of thin polymer films in the absence of filler follow a conventionally observed pattern, and there seems to be a good theoretical working model to understand these observations.<sup>4–8</sup> We first summarize conventional film dewetting without filler for comparison with our new measurements on fullerene-filled films. At an early stage of film dewetting undulations form at random positions on the film surface, some of which nucleate to form holes exposing the substrate (Figures 1a and 5). Some of these undulations are induced by thermal fluctuations and some derive from large-scale heterogeneities within the film (dust, air bubbles, etc.). The holes formed at an early stage of dewetting are circular and have an elevated polymer rim at the edge of holes associated with the film rupture process. At a later stage of dewetting, the holes coalesce, leaving a frothlike pattern having long threadlike rims about the dewetted regions. Finally, the threadlike structures break up by a capillary instability and form patterns of droplets resembling a Voronoi tessellation pattern (Figures 3a and 4a) similar to those observed commonly in soap froths.

Fullerene-filled polymer films having the same quench history and film thickness are found to have a qualitatively different morphology. In films having a very dilute concentration of filler ( $\phi_{\text{filler}} = 0.005$ ), we initially observe hole growth as in unfilled films of similar thickness, but the holes stop growing (“pin”) and the usual hole coalescence process characteristic of film dewetting is greatly inhibited. The hole configurations of the films

with low filler concentrations are also unusual because of their size polydispersity. Apparently, the growth becomes “pinned” by the fullerene filler so that the dewetting is restricted to a mesoscopic scale. In accordance with this interpretation of suppressed dewetting, the average size of the “pinned” holes scale could be tuned by increasing the filler concentration. Hole formation apparently ceased to occur for a sufficiently high filler concentration on the time scales of our measurements. The long-term stability of these filler modified films needs further investigation, but the present investigation shows that the effect persists over many hours and that the filled films are dramatically different than films without filler.

The unusual hole polydispersity in the films having very low fullerene concentrations was the key observation that suggested to us the prevalence of contact line pinning in filler-induced suppression of film dewetting. In hindsight the effect is rather obvious since it is well-known that contact line pinning is a controlling factor in fluid spreading on rough surfaces.<sup>26–28</sup> The growth of a hole in a dewetting film and the evolution of the dewetting process requires that the contact line of the dewetting holes can move. The existence of hole pinning and hole size polydispersity imply that the filler particles are firmly fixed to the solid substrate and thus a strong interaction between the nanoparticle and the substrate. It is also likely that the interparticle interaction must be reasonably attractive in order to form fractal aggregate structures at the solid substrate<sup>22</sup> [Fullerenes can form fractal (dynamic) clusters in solution even under equilibrium conditions in nonpolar solvents such as benzene.<sup>25</sup>] Neutron reflection measurements confirmed that the fullerene particles segregate to the solid substrate in the PS films. The in-plane heterogeneity of filler is expected to diminish with increasing filler concentration if contact line pinning is the source of the suppression of film dewetting. At present, it is difficult to map out the in-plane distribution of fullerene particles within the film, but it is possible to indirectly probe this variable by changing the filler concentration over an appreciable range. For low filler concentrations, there should be substantial fluctuations in the in-plane filler concentration leading to dewetting locally in regions relatively free of filler particles. This hypothesis would suggest that the average size at which the dewetting holes “pin” should vary inversely with filler concentration. The size of the holes decreases with an increase of the fullerene concentration in the filled PS films, and no holes are observed even at the scale of AFM measurements in fullerene filled ( $\approx 50$  nm thick) films cast from solutions having a filler mass fraction as large as  $\phi_{\text{filler}} = 0.01$ . This suggests that a critical size of the surface irregularity might exist in the filled polymer films, and reentrant dewetting might be expected at high filler concentrations if the filler enrichment layer becomes dense and uniform. Our measurements point broadly to the importance of in-plane surface irregularity on the dewetting of polymer films.

Other possible interpretations of our observations of inhibited dewetting in fullerene-filled polymer films were also considered. Neutron reflection measurements showed that little or no segregation of the fullerene to the polymer–air boundary occurred so that it is unlikely that the effect is caused by a change in the film surface tension by the fullerene. Observation of PS and PB

dewetting from relatively smooth model carbon substrates, meant to mimic the surface energy of fullerene-coated substrates, showed a similar tendency toward dewetting so that a simple change in the surface chemistry does not explain the inhibited dewetting by the nanofiller. The interface width of the fullerenes enrichment layer found by NR is broader than that between PS and an evaporated carbon film (measurements not shown) so the diffuseness of the segregated fullerene layer on the silica substrate thus seems relevant to understanding the filler-induced film stabilization. Finally, we have performed some measurements to check whether the particle–particle or particle–polymer association process (i.e., some kind of “gelation” process) is responsible for the film stabilization. We might expect this to lead to a substantial change in the viscosity and/or the glass transition temperature. Our preliminary measurements show no appreciable change in the glass transition temperature or the viscosity of the casting solution for fullerene concentrations up to a mass fraction of  $\phi_{\text{filler}} = 0.01$ . (Measurements are not shown given the negative nature of the results.) The tendency of fullerene to aggregate in nonpolar solvents at equilibrium<sup>25</sup> and to form complex crystalline structures in evaporating films<sup>22</sup> does suggest that further measurements are needed to exclude the possibility that the fullerene particles form some kind of network structure in the dried films, however. Future measurements will have to measure the viscoelastic properties of the dried films directly rather than the casting solution since the clustering of filler particles is characteristically sensitive to particle concentration. We tentatively conclude that interparticle association effects are not important in our observations of filler-induced stabilization, but further measurements are required to fully establish this conclusion.

All our results seem to imply that fullerene nanoparticles influence film dewetting by altering the geometrical structure of the solid substrate on which they enrich, leading to a profound change in the apparent film wettability. It seems likely that this effect has both kinetic (contact line pinning) and equilibrium (change of surface energy arising from surface roughness) contributions. The phenomenon is dramatic and potentially useful in producing stable films, but quantification of the effect requires better means to determine the in-plane distribution of the filler near the solid substrate and the properties (viscosity, surface energies) of the spun-cast films.

There have been other recent studies of dewetting in nanoparticle filled films that give additional insights into the dewetting of filled films. Cole et al.<sup>29</sup> find that the addition of alkanethiol-coated evaporated gold particles in poly(*tert*-butyl acrylate) leads to a pattern of dewetting essentially *unchanged* from the unfilled polymer film, apart from a slowing down of the kinetics attributed to an increased film viscosity. Cole et al.<sup>29</sup> also noted that depth profiling measurements of their filled films using Rutherford backscattering spectrometry indicate that the gold particles did not segregate to the film boundaries. This suggests that the association of the filler to the boundary might be essential to our observation of suppressed dewetting by filler additives. Ohara and Gelbart,<sup>30</sup> however, have noted that nanoparticle filled films can exhibit pinning with mobile alkanethiol-coated gold nanoparticles where the pinning arises from the increased filler concentration near the

contact line of the growing dewetted regions. However, filler-induced contact line pinning leads to rather uniform holes with rings of enriched nanoparticle concentration at their periphery.<sup>30</sup> In our measurements the filler particles are apparently fixed by adsorption to the substrate so that the holes become pinned over a wide range of scales.

Although we are not aware of any former measurements indicating the suppression of dewetting through the addition of nanoparticles to spun-cast polymer solutions, there has been other work suggesting that surface roughness can inhibit the dewetting of polymer films. Kerle et al.<sup>31</sup> showed that the roughness of spun-cast films can be modified by irradiation (irradiation characteristically roughens the surface of the polymer substrate, but the surface chemistry also becomes modified so the interpretation of these irradiation measurements is not simple) and that a dewetting polymer substrate can be converted to a wetting substrate when the substrate was irradiated at high levels. This effect was attributed by Kerle et al.<sup>31</sup> to surface roughening, and this mechanism of suppressed dewetting is consistent with our interpretation of inhibited dewetting in nanoparticle-filled films. In both of these investigations of dewetting inhibition, the substrate roughness and chemistry are both modified. “Rough” films can also be obtained in the growth of grafted chain layers, especially at low grafting densities,<sup>32</sup> and surface roughness is probably a contributing factor in the inhibited dewetting found in films containing surface grafted chains.<sup>9</sup> Previous works provide no quantification of the suppressed dewetting and its relation to surface irregularity. This task is difficult because both kinetic and equilibrium factors probably contribute to the observed film stabilization, making it difficult to identify the precise mechanism by which film “roughening” leads to an increased stabilization against dewetting. Former measurements have also indicated that surface roughness can enhance the tendency toward dewetting in small molecule liquids<sup>24</sup> so there is much to understand about the influence of substrate roughness and modulations of the surface interaction on film stability.

Our measurements and those of Kerle et al.<sup>31</sup> both suggest the need for systematic studies of dewetting from substrates having well-characterized roughness and surface chemistry. In particular, the impact of different types of surface roughness (corrugation patterns, fractal surfaces) on the dewetting of polymer films should be systematically investigated to understand how boundary geometry influences the polymer–surface interaction and the pinning process.<sup>33,34</sup> Dewetting on chemically modulated substrates should also be investigated where the pattern sizes of the dewetting regions are varied to determine whether the hole sizes and shapes can be tuned through surface patterning. In the case of nanoparticle-induced stabilization it is important to establish whether a sharply defined critical filler concentration exists at which suppression of dewetting occurs. (Preliminary studies indicate that transmembrane proteins have a stabilizing effect on lipid layers exposed to air,<sup>35</sup> and there are potential health care related ramifications of filler-induced film stabilization in biologically relevant films.) We plan to examine whether the nanoscale of the filler particles is essential to the film stabilization process by a comparative study of the influence of relatively large carbon black and



fullerene fillers on film dewetting. Our most recent measurements show that small silica particles (12 nm average radius) suppress the dewetting of PS films on silicon substrates,<sup>36</sup> providing further evidence of the robustness of the nanoparticle suppression of dewetting effect.

### Conclusion

The addition of "impurities" to polymer films is generally considered to have a detrimental effect on the film wetting properties. Indeed, small particles and air bubbles in polymer films have been found to cause film dewetting.<sup>16,17</sup> Heterogeneities on the film substrate have also been implicated in causing film dewetting. The present paper shows that the addition of nanofiller particles to a spun-cast polymer film can actually stabilize the film against dewetting. The evidence available suggests that the fullerene particles segregate to the solid substrate and modify the polymer-surface interaction and geometry. The diffuseness of the adsorbed filler layer and the heterogeneity of the filler concentration within the plane of the layer are apparently important for understanding the observed film stabilization. Similar film stabilization effects have been seen in films cast on substrates roughened through irradiation<sup>30</sup> so that filled films appear to provide a different strategy for modifying the substrate geometry and chemistry. Regardless of the specific process or processes responsible for the stabilization observed in our measurements, the effect promises to be an important means of controlling thin polymer film dewetting for applications such as optical and electronic coatings, adhesion, sensors, etc. The evidence available suggests that the stabilization process may be an equilibrium phenomenon, making the method useful for achieving the long-term stabilization of polymer films and coatings.

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### References and Notes

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- (18) Certain commercial materials and instruments are identified in this article to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the NIST nor does it imply that materials or equipment identified are necessarily the best available for the purpose.
- (19) According to ISO 31-8, the term "molecular weight ( $M_n$ )" has been replaced with "relative molecular mass", symbol  $M_{r,w}$ . The conventional notation, rather than the ISO notation, has been employed for this article.
- (20) It is difficult to determine whether the concentration of filler in the spun-cast film layer is the same as the casting solution since an undetermined amount of filler may wash off during spin-casting. The neutron reflectivity fits were not sensitive to fullerene concentration in the film for a mass fraction of 5%. Filler concentration in the paper therefore refers to that in the casting solution; e.g.,  $\phi_{\text{filler}} = 0.01$  refers to the filler mass fraction relative to the polymer mass in solution.
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