Communications to the Editor

The Critical Role of Solvent Evaporation on the Roughness of Spin-Cast Polymer Films

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Solvent casting of polymers is routinely used to prepare coatings in a wide range of industrial and biological applications.[1−13] The roughness of these films is often critical to their applications, and in particular, roughness strongly impacts their optical, barrier and frictional properties. Despite its technological importance, little systematic understanding exists of the factors which control surface roughness.[3−5] Here we show that solvent-rich films have insufficient time to level and heal surface roughness created by Marangoni instabilities when the solvent is rapidly evaporating. In contrast, no Marangoni flow is seen for slowly evaporating solvents, and hence, the surfaces of the resulting films are always smooth. Films of controlled roughness can thus be obtained simply by varying the solvent evaporation rate. The critical role of solution leveling is also emphasized by dynamic contact angle measurements. Even though complete wetting is expected, the spreading time for solutions in volatile solvents is larger than the solvent evaporation time. Thus, these solutions do not spread completely and thus yield large advancing contact angles. These results point to the important effect of fluid leveling when polymers are cast from volatile solvents, and suggest strategies (e.g., control of evaporation rates) for controlling the roughness of the resulting films.

Two hydrophobic polymers which are glassy under ambient conditions, polystyrene [PS] and poly(ethyl methacrylate) [PEMA], were spin cast from solution on to smooth silicon wafers. 2.54 cm diameter Si wafers [Semiconductor Processing] were cleaned by piranha etching [30/70 mass % H_2O_2/H_2SO_4], followed by a 30 s etch in a 1 mass % HF etch, to create a passivated SiH surface. Preliminary measurements were also performed on the rubbery poly(vinylmethyl ether) on the hydrophilic, native oxide layer of silicon. Since similar results are obtained for all polymers studied, we believe that our conclusions are quite general. In all cases the polymers wet their respective substrates. Two PS samples obtained from Polymer Source had number-average molecular weights [M_n] of 196 700 and 965 000

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Table 1. Physical Properties of Solvents Employed[a]

solvent	γ (dyn/cm)	P_{vp} (bar)	R_a (nm)
dichloromethane	27.84	0.4570	144
acetone	23.70	0.2374	
chloroform	27.14	0.2350	79
tetrahydrofuran	27.31	0.2150	65
propyl bromide		0.2156	54
carbon tetrachloride	26.95	0.1240	66
ethyl acetate	23.97	0.1210	49
methyl propionate	25.06	0.0889	28
benzene	28.88	0.1130	23
methyl ethyl ketone	23.96	0.1040	
methyl *n*-butyrate	25.19	0.0429	20
toluene	28.52	0.0342	19
1,1,2-trichloroethane	34.70	0.0228	28
methyl isobutyl ketone	23.90	0.0187	14
tetrachloroethylene	31.74	0.0199	23
m-xylene	29.02	0.0107	17
styrene	32.00	0.0086	15
dichlorobenzene		0.0007	35

[a] γ is the surface tension. P_v the vapor pressure and R_a the roughness of the resulting polymer films.

with polydispersities of 1.07 and 1.15, respectively. A PEMA [Scientific Polymer Products] of M_n = 90 000 with a polydispersity of 1.58 was also utilized. Solutions of 1.5 and 1.3 mass % for the low and high molecular weight PS, respectively, and 2.1 mass % PEMA were prepared in a variety of common good solvents [see Table 1]. We only employed good solvents to avoid complications associated with the phase separation in the drying film. For the selected concentrations, ≈300 nm thick films are produced when spin cast from toluene at 200 rpm. The wafers were flooded with polymer solutions and dried under quiescent conditions [listed as 0 rpm] or spin coated at speeds ranging from 200 to 7500 rpm, either in air or in an atmosphere saturated in solvent vapor. The film thickness, roughness and the lateral sizes of surface features were characterized using single wavelength ellipsometry [Rudolph], profilometry [Tencor], by tapping mode AFM [Topometrix Instruments], or by reflection optical microscopy. The roughness is reported as the average absolute deviation about the mean film height [R_a], which is proportional to the RMS value for a Gaussian distribution of roughness. Dynamic advancing contact angles were measured using a goniometer with a crosshair eyepiece. Solvent or solution drops were placed on a silicon wafer, and the advancing contact angle was measured as soon as the contact line became "fixed". The uncertainty in contact angles is larger for faster evaporating solvents since the contact angle obtained after the "pinning" of the contact line changes continuously due to evaporation.
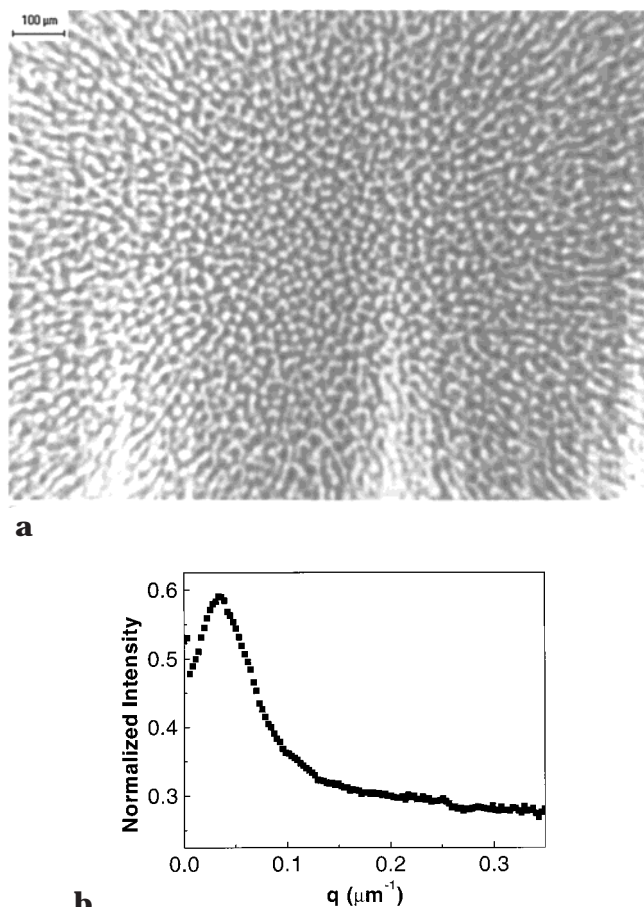
Figure 1a shows the average roughness of all of the PS and the PEMA films cast at 200 rpm in air plotted as a function of solvent vapor pressure, P_{vp}. Each data point represents the average over three different samples, with measurements performed on three different re-
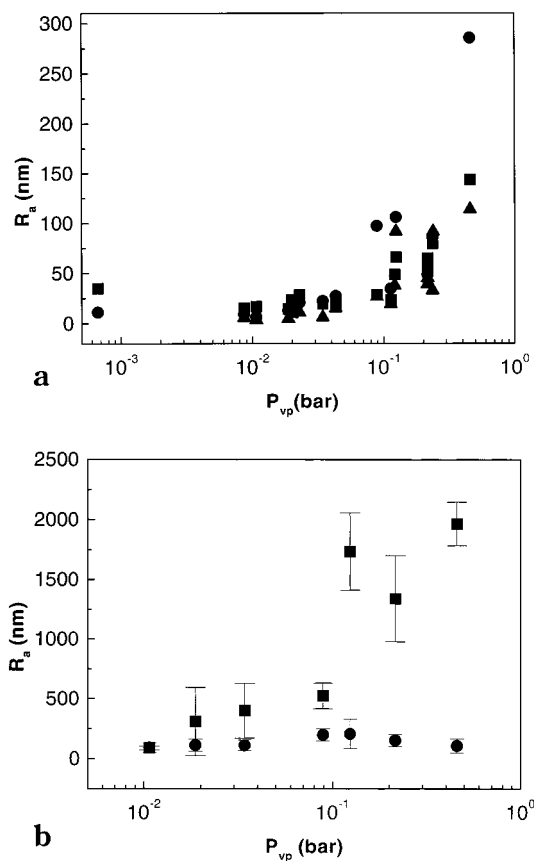
Figure 1. (a) Average film roughness, R_a, as a function of solvent vapor pressure, P_{vp} for films spin cast at 200 rpm: triangles, PEMA; squares, PS-200; circles, PS-1000. (b) Average absolute roughness (R_a) as a function of P_{vp} of dip coated (0 rpm) films (thickness of order 1 μm), cast in open air (squares) and in the presence of nearly saturated vapor (circles).

Figure 2. (a) Optical micrograph of PS-200 spin cast at 7500 rpm using THF ($P_{vp} = 0.215$ bar). (b) One-dimensional Fourier transform of central (isotropic) region of optical micrograph.

gions of each sample. The roughness, and its standard deviation, increase monotonically with solvent P_{vp}, especially when $P_{vp} > 0.1$ bar [10^4 N/m^2]. These trends persisted for all casting conditions, including quiescent conditions, where the thicknesses of the fully dried films are comparable for all solvents [Figure 1b]. Thus, variations in film thickness with casting solvent do not explain these trends. In contrast, for each given solvent, the roughness decreased with increasing spin speed, and we found that R_a scaled linearly with film thickness. We also examined the influence of solvent surface tension on the surface roughness but find no apparent correlation [Table 1]. We therefore conclude that the roughness of the coating films is primarily dictated by the solvent evaporation rate.

We eliminate the possibility of skin formation due to increased polymer concentration near the air surface as a primary cause of this effect, since it is accompanied by "bursting" of trapping solvent. This results in the creation of holes in the film with a size distribution in the range 0.1−10 μm. Such effects are predominantly observed in films thicker than $\approx$300 nm, and do not provide a clear peak in the Fourier transform of a reflection optical micrograph of the film surface. Lateral images of a representative rough thin film always yield a single peak in the Fourier transform, as discussed below [Figure 2], suggesting that some other mechanism plays a dominant role in this context. To understand the origin of this roughness in films cast from volatile solvents we examine a reflection optical micrograph of

the surface of the low molecular weight PS spin cast from tetrahydrofuran [$P_{vp} = 0.215$ bar] at 7500 rpm [Figure 2]. We attribute the cells in this figure, following past work,[12,13] to Maragoni instabilities induced by the rapid evaporation of the solvent.[14] The scale of the patterns is $\approx$30 μm [Figure 2b]. This interpretation of surface roughening was confirmed by adding fine aluminum powder to visualize the flow instabilities in situ. For these experiments, we closely followed a procedure recommended by Sakurai et al.[13] For slow evaporating solvents [with $P_{vp} <$0.1 bar], no evidence of a Marangoni instability was found.

The ratio of the lateral pattern size to the average film height of the fully dried polystyrene films is $\approx$400, independent of film thickness. Since the aspect ratio of Marangoni cells has previously been determined to be of order 1,[14] we speculate that the following physical picture might be operative. For dilute solutions of polymers in rapidly evaporating solvents, the fast solvent evaporation results in the creation of Marangoni instabilities, which roughen the air surface of the film. As solvent evaporates, the viscosity of the film increases to a point where the instabilities are no longer created. At this point, the lateral sizes of the surface roughness are fixed, and since the aspect ratios of the dried films are much greater than that predicted for standard Marangoni patterns, we conclude that the arrest of Marangoni flow occurs early in the drying process.[15]

The major focus is now on why the rough surface of a film, which has a viscosity similar to that of the pure solvent, does not level so as to reduce its surface energy.
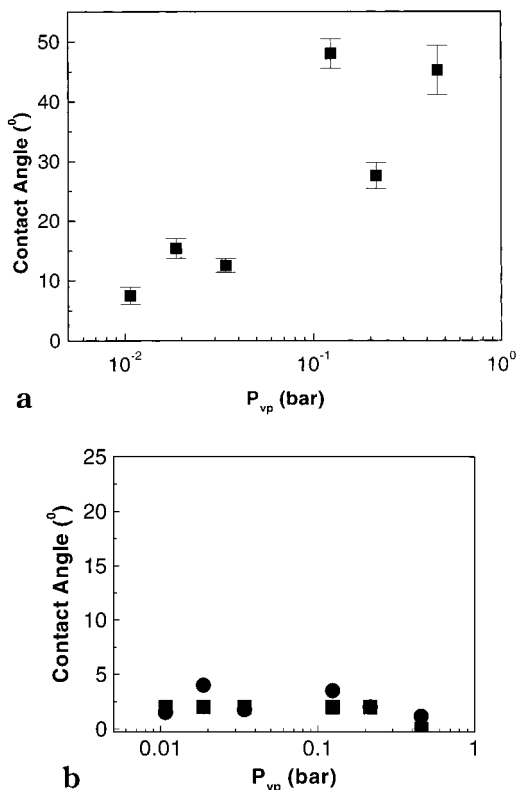
Figure 3. (a) Dynamic contact angle as a function of solvent vapor pressure for 6% PS-200 solutions, cast in open air. (b) contact angle as a function of solvent vapor pressure for films cast in the presence of nearly saturated solvent vapor. Key: 6% PS-200 solutions (circles) and neat solvents (squares).

Since the primary factor inhibiting film leveling is the rapid evaporation of solvent, we define the ratio λ of the fluid "leveling" time, τ_{level}, to the solvent evaporation time, τ_{evap}, as a measure of the competition between these processes. The evaporation time, $\tau_{\text{evap}} \equiv \rho h/E$, has been estimated in previous work,[16,17] where E is the solvent evaporation rate per unit area and unit time, ρ is the density, and h is the film height. The leveling time is not easily determined. We note, however, the analogy of this situation to two related problems, the spreading of solutions on solid surfaces,[18] and the spreading of solutions on liquids.[19] In both cases, the spreading time is estimated as $\tau_{\text{spread}} \approx \eta L^*/\gamma\theta^m$, where L^* is the characteristic length scale for the spreading drop, θ is its contact angle, and m is a positive exponent which assumes different values in these two cases. In the absence of additional information, we postulate that the same expression also describes the leveling time for surface imperfections in drying films. Combining these two equations, and utilizing the fact that, $h/L^* \approx \theta$, we obtain $\lambda = (\tau_{\text{level}}/\tau_{\text{evap}}) \propto (\eta L^*/\theta^m \gamma/\rho h/E) = (\eta E/\gamma \rho \theta^{m+1})$. Since E at any spin speed tracks P_{vp}, it is clear that the film leveling tendency, as embodied in λ, decreases with increasing P_{vp}. Consequently, films created with more volatile solvents will be rougher due to flow instabilities, coupled to the inability of the resulting film surface to level fast enough before it becomes "frozen" into a dried state having a very long viscoelastic relaxation time. These findings are consistent with the experimental results shown in Figure 1.

To provide more evidence for the critical role of surface leveling, we have measured advancing contact angles of the same polymer solutions on passivated Si wafers in air. Since the solvents and polymers indepen-

dently wet the substrate, zero contact angles are expected in the absence of solvent evaporation. However, the competition between drying and spreading is expected to inhibit spreading for large E. We draw analogy to the recent work by Witten,[1] where it was shown that solvent evaporation rates were highest at the edge of an evaporating drop. For rapidly evaporating solvents, since the polymer concentration is highest at the rim, the viscosity there can get large enough that the contact line can get pinned.[20] The resulting advancing dynamic contact angle then provides a measure of the flow leveling effect. Figure 3a shows that the low molecular weight PS, has large, well-defined contact angles ($>15°$), especially when solvents with $P_{\text{vp}} > 0.1$ bar are employed. We have investigated the reasons for the apparent minimum at $P_{\text{vp}} = 0.2$ bar, which corresponds to THF. We speculate that THF, which is a polar solvent with strong affinity for the surface, is an anomaly. However, a measured contact angle of 25° for the THF solutions strongly points to the importance of solvent evaporation. We therefore stress that the leveling phenomena, which are critical for determining film surface roughness, also dictate the contact angles of the polymer solution droplets. In fact, use of an $m = 3$ value in the expression for λ, which is appropriate to describe the spreading on solid substrates,[18] suggests that λ goes from a value below 1 to a value above 1 when a $P_{\text{vp}} = 0.1$ bar is crossed, supporting our hypothesis that λ is the control parameter governing the dynamic contact angle of spreading drops. In this calculation, we assumed a typical γ value from Table 1, a density of 1 g/cm^3 and a viscosity of 0.01 dyne·cm/s^2. Given the variations in parameters for the different solvents, our estimates of a crossover at $\lambda = 1$ are accurate to within an order of magnitude.

To provide conclusive evidence of the role of leveling in both contexts we have conducted experiments in the presence of a vapor saturated in the solvent of interest. In all cases we find that films created by this process are smooth, with a roughness that is independent of P_{vp} [Figure 1b]. Moreover, these solutions spread completely (i.e., yield contact angles $< 15°$) [Figure 3b]. Since only E has changed in these experiments, we conclude that the value of λ can be readily manipulated by tuning this variable. This result is exploited in commercially available, but empirically designed spin coaters where smooth films are prepared by saturating the atmosphere with the solvent vapor of interest.

Our measurements show that surface roughness of dip coated or spin cast films from good solvents can be controlled by varying the evaporation rate of the solvent, E. For large E values, the film surface is roughened by flow instabilities, and the film remains rough because the leveling time is too large compared to the solvent evaporation time. In contrast, no Marangoni instabilities are seen for the slow evaporators, i.e., $P_{\text{vp}} < 0.1$ bar. We also observe that the rapid solvent evaporation causes solutions that are normally expected to wet a substrate to yield large, advancing contact angles. Our measurements stress the importance of evaporation rate and leveling in controlling film roughness, and show that contact angle experiments are a valuable tool to determine the conditions to obtain films of desired "gloss".

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(20) Note that we do not require the evaporation at the edges to be more rapid to see this effect. Rather, what is required is that the evaporation rate be large enough to prevent the drop from spreading completely.

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