



Intensified dewetting of polystyrene thin film under water-solvent mixture: role of solvent composition

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Abstract. Intensified dewetting of ultrathin polystyrene (PS) films induced by immersing in a homogeneous mixture of good solvent and water was previously reported to push the limits of dewetting to the sub-100 nm scale. Here, we systematically analyse the role of dewetting mixture composition, i.e. solvent to water ratio, on the length scales of instability. The effect of the solvent concentration in the dewetting mixture on the instability wavelength (λ) and droplet diameter (d) are determined. The instability wavelength (λ) for 50 nm thick PS film was found to be decreasing from nearly 17 to 7 μm as the solvent concentration is decreased from 95 to 35% in the dewetting mixture. This is significantly smaller than the instability wavelength in air, which is nearly 50 μm for the same PS film. The solubility of PS in the dewetting mixture is also examined and the mechanism of observed variation in the length scale is proposed.

Keywords. Dewetting; polystyrene; thin films; instability wavelength; length scale.

1. Introduction

The instability in thin polymer films coated on a rigid substrate has been extensively studied over last decade. Dewetting is a spontaneous process by which a thin film ruptures and arrange itself into randomly placed droplets [1–4]. In many of the applications, this process is undesirable, such as in paints and coatings. But in other applications, where instability in polymer thin films results in many important structures used in areas like biotechnology, sensors, actuators, nanolithography and biomolecules patterning [5–7]. Moreover, polymer blend film and bilayers can further assist in fabrication of embedded and encapsulated nanostructures [8–10].

Due to the low vapour pressure and tunable viscosity polymers being commercially available, thin polymer films with high molecular weight is considered to be ideal for these kinds of studies. The dewetting of thin polymer films by thermal or solvent vapour annealing has been explored extensively [1–5]. Dewetting of thin film initiates with nucleation that causes the formation of dry patch or a hole. The hole grows by transfer of material away from the nucleation enclosing the hole. As the hole continues to grow in size, it coalesces with adjacent holes resulting into ribbons of polymer along their contact lines. The dewetting process completes when all the holes merge forming polygons consisting of polymer droplets. Nucleation occurs by spinodal dewetting or by airborne particles falling on the surface of the thin film. The spinodal dewetting is caused by the increase in the surface disturbances caused

by the thermal or mechanical fluctuations [1–5, 11–19]. The tendency of the surface tension to form a smooth film is diminished by the destabilizing forces and the surface disturbances eventually grow and hit the surface to form a hole. Length-scale of dewetting is dependent upon various factors, such as thickness of the film, interfacial interactions between polymer and substrate and surface tension, whereas polymer viscosity governs the dewetting-kinetics [20–30]. There are some excellent reviews, which have discussed important aspects of dewetting over the years [6, 31–33].

Solvent vapour-induced dewetting of the thin films is similar to the thermal dewetting process. In solvent-induced dewetting process, the solvent vapours reduce the T_g of the polymer below the room temperature, thus, the dewetting can occur at room temperature [26]. However, the greater stabilizing surface tension does not allow formation of features smaller than few micrometres.

However, in recent years, some studies have been carried out on dewetting under water–solvent media [34–37]. When the polymer film gets in contact with the good solvent molecules, the polymer chain mobility increases and the glass transition temperature (T_g) reduces below the room temperature and the film dewets [34–37]. It has been established that the dewetting performed in the water–solvent mixture shows significantly faster kinetics and smaller length-scales as compared to corresponding dewetting of identical thin films carried out by either heating above T_g or in air saturated with vapours of the solvent [34, 35]. The time evolution of dewetting was qualitatively similar in both the cases

[23–29,35]. The study on the intensified dewetting of thin polymer films under a mixture of good solvent (methyl ethyl ketone), non-solvent (water) along with a homogenizing third solvent (acetone) has been conducted to overcome surface tension limitation and thus, achieving nearly an order of magnitude reduction in the dewetting wavelength (λ), droplet size (d) and the dewetting time [35].

It is also reported that a good solvent and a non-solvent dewetting mixture induced an increase in the rate of dewetting and polymer-substrate contact angle. Higher rims formed around the holes of the substrate and an increase in the fingering instability, whereas there is reduction in the polymer viscosity. It is reported that in the presence of a good/non-solvent mixture, the polymer chains re-align to globular conformation that leads to a larger interfacial slip and reduced polymer viscosity [38].

In the present study, we systematically analyse the role of dewetting mixture composition, i.e. solvent to water ratio, on the instability wavelength (λ) and droplet diameter (d). We have also addressed the possibility of limited solubility of polymer in the dewetting mixture, especially where the mixture has majority phase as solvent.

2. Materials and methods

Polystyrene (PS) of average molecular weight 280 kg mol^{-1} from Sigma, Aldrich, was used to make polymer solutions in HPLC grade toluene. Thoroughly cleaned silicon wafers were coated by polymer films of desired thickness. Thin films were spin coated at 3000 rpm for 1 min on (100) silicon substrates. The spin-coated PS thin films were annealed in vacuum oven at 70°C for about 6 h for the removal of remnant solvent and to minimize the residual stresses. The film thickness is measured by ellipsometer (nanofilm EP3). Annealed thin films of PS were placed in dewetting chamber containing liquid mixture of water and solvent, where the solvent used is methyl ethyl ketone (MEK) and acetone in a fixed ratio of 7:3. MEK is a good solvent for PS, but has only limited solubility with water, therefore, acetone is added to facilitate mixing of MEK into water and hence, forming a homogeneous dewetting mixture. Dewetting mixture was prepared by adding water to the solvent mixture (MEK and acetone) in different proportions, where water fraction is varied between 5 and 75%. Composition of this mixture is an important factor to tune the interfacial tension of the polymer film. The dewetting was carried out at the room temperature. MEK being the good solvent of PS, reduces its glass-transition temperature and allows dewetting to happen at the room temperature, whereas water prevents the dissolution of PS in the solvent [35].

3. Results and discussion

The comparison of dewetting of polymer thin film has been done previously in air and in water–solvent mixture [35].

The sequence of changes in the morphology of the dewetting process was found to be qualitatively similar in both the cases [22–25,35]. However, it was found that the time scales for dewetting under the water–solvent mixture is much faster than that of in the air. A much faster dynamics of the dewetting observed in the water–solvent mixture signifies an increase in the instability of the thin film either by intensification of destabilizing force or reduced stabilizing force or both [35].

Dewetting, as mentioned earlier, starts with the nucleation of holes that initially grow in number and reach a maximum. The long wave instability wavelength (λ) is dependent on the film thickness (h) as $\lambda \sim h^2$ [23,35]. However, it was found that the dewetting in water–solvent mixture shows comparatively weaker dependence on the film thickness, where $\lambda \sim h^{1.5}$. This change in dependence suggests that the dominant destabilizing force in case of under-water dewetting may have electrostatic origins instead of van der Waals [35].

The interfacial tension of PS and water–solvent mixture was reported to be 0.55 mN m^{-1} , which is nearly two orders of magnitude smaller than the surface tension of PS in air ($\sim 30 \text{ mN m}^{-1}$) [35]. The value of interfacial tension for water–solvent mixture is vanishingly small and hence, should not be a determining factor for instability wavelength (λ) for a particular film thickness under varying compositions of water and solvent in the mixture. However, it has been reported that the length scale can vary with variation in the proportion of water–solvent mixture for photoresist thin films [39].

To study the effect of the composition of dewetting mixture on the length-scales of dewetting PS thin film of uniform thickness (50 nm) was dewetted under mixture of water and solvent, where the fraction of water was continuously increased from 5 to 65%. When the water fraction was $<5\%$, we have seen some inconsistency in the dewetted pattern, where number of droplets seen varied from no droplets to very few droplets accumulated in smaller areas suggesting some dissolution and slipping or rolling of droplets on the substrate as predicted in a recent study [38]. Similarly, dewetting has started, but not completed even after 3 h when water fraction was $>70\%$. We did not observe any change in the morphology of the film when the water fraction was $>80\%$. Figure 1 shows optical micrographs of 50 nm PS films, which are completely dewetted under water–solvent dewetting mixtures of different compositions. It is evident from these images that there are significantly fewer droplets in case of 5% water in the dewetting mixture and as the water percentage is increased in the dewetting mixture, the number of droplets per unit area increases and the size of droplets decreases.

Figures 2 and 3 show the variation of the instability wavelength (λ) and droplet diameter (d) with change in the water fraction of the dewetting mixture. The instability wavelength (λ) has been calculated based on the final dewetted structure, because the kinetics of dewetting was very fast and

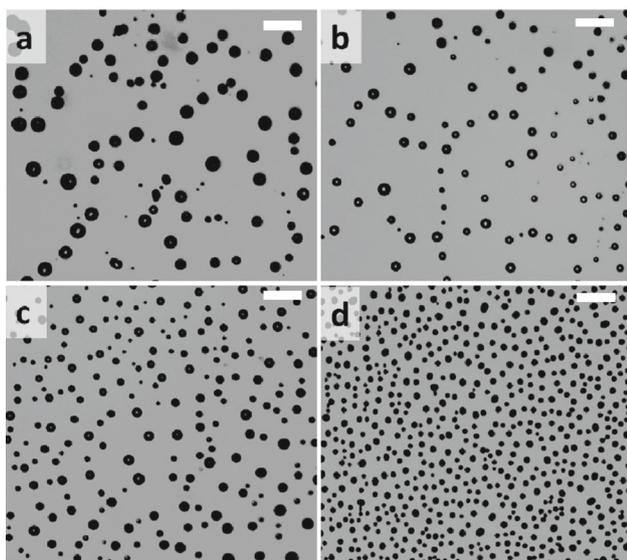


Figure 1. Length scale variation of dewetting of a 50 nm PS film on Si wafer. Optical micrographs for dewetting mixture compositions (water:solvent) of (a) 05:95, (b) 35:65, (c) 50:50, (d) 65:35 (scale bar: 20 μm).

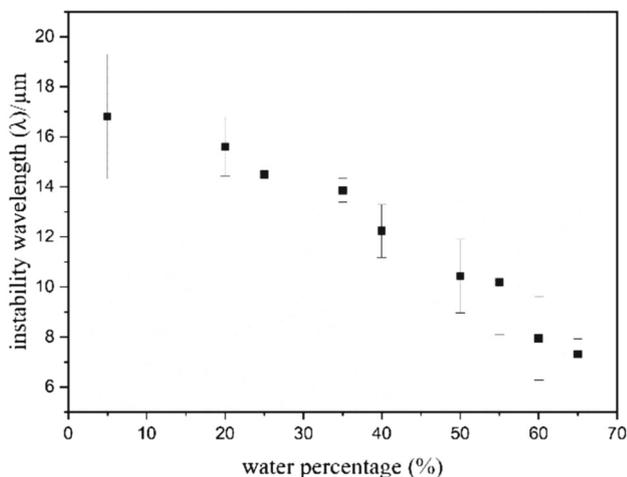


Figure 2. Effect of water fraction in the dewetting mixture on the wavelength of instability (λ). λ decreases from nearly 17 μm at 5% water to 7 μm at 65% water. Initial thickness of the PS film is 50 nm.

onset of instability was achieved very quickly and maximum number of holes cannot be determined accurately. The λ has decreased from 16.8 ± 2.5 to 7.3 ± 0.6 μm on increasing water percentage in the mixture from 5 to 65. Similarly, the droplet diameter for the same has decreased from 2.39 ± 0.27 to 1.31 ± 0.013 μm .

This result commensurate with the observations from figure 1 and suggests two possibilities for fewer droplets when water fraction is low in the dewetting mixture. First possibility is the limited dissolution of polymer in the dewetting

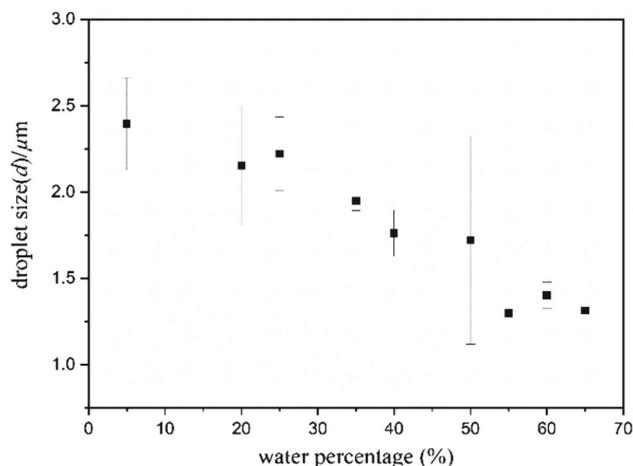


Figure 3. Effect of water fraction in the dewetting mixture on the droplet size (d). d decreases from nearly 2.39 ± 0.27 μm at 5% water to 1.31 ± 0.013 μm at 65% water. Initial thickness of PS film coated on silicon substrate is 50 nm.

mixture when the solvent fraction is more. This can explain disappearance of smaller droplets by dissolution in the dewetting liquid and leave only bigger droplets in fewer numbers. To test this hypothesis, we have taken 1 g of PS in the granular form and placed it in 50 ml vial with 50 ml dewetting mixture of maximum solvent fraction (i.e. 95% solvent and 5% water). The vial was vigorously shaken for 5 min and then, polymer granules were allowed to settle down at the bottom for 30 min. Afterwards, supernatant clear liquid was removed and swollen polymer at the bottom of the vial was dried first in ambient conditions for 24 h and then, under vacuum at 110°C overnight. Remaining polymer in the vial was weighed and it was found that there was no change in the weight of polymer in the detection limit of 1 mg. However, there is still a possibility of polymer getting dissolved in the dewetting media in minuscule amounts considering the high surface area in thin film configuration. To test this further, we have calculated the total volume of polymer droplets per unit area from the optical microscope images considering all droplets to be of hemispherical shape, which is a reasonable assumption based on the previously published data [34,35]. Figure 4 shows there is no considerable change in the total volume of the polymer droplets per unit area as the water fraction is increased from 5 to 65%. This concludes that possibility of substantial dissolution of polymer in the dewetting mixture can safely be discarded and this cannot be a reason for the dependence of droplet size and wavelength on the composition of dewetting mixture.

With the possibility of polymer getting dissolved in the dewetting media being discarded, there must be some change in the mechanism or kinetics of dewetting that is responsible for the change in length scale of dewetting. It has been observed that the kinetics of dewetting slows down as we increase water fraction in the dewetting mixture. Complete

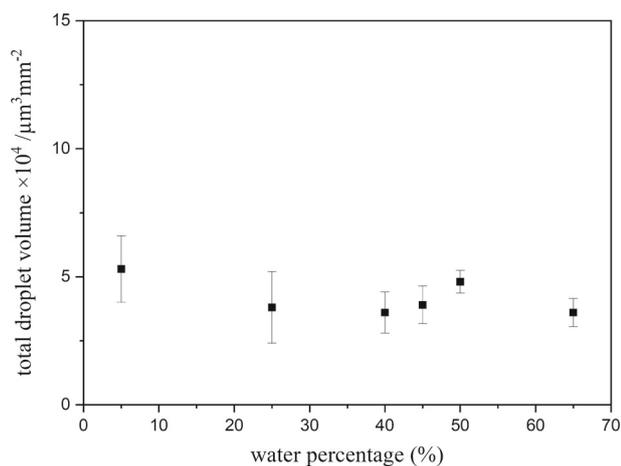


Figure 4. Total droplet volume (μm^3) per mm^2 as the fraction of water in the dewetting mixture is increased from 5 to 65%.

dewetting of 50 nm PS film has taken about 30 min in 65% water mixture, whereas dewetting was almost instantaneous for water fraction $<20\%$ in dewetting media. This suggests that in lower water fraction dewetting mixture, dewetting can be completed with fewer holes forming at the onset, which grow quickly in size and not allowing nucleation of more holes in the initial phase of dewetting. Whereas, for higher water fractions, the kinetics is slow which allows for the nucleation of more number of holes in the first phase of dewetting and thus, resulting in more number of droplets. This is also supported by figure 1, where droplet array formed after breaking of large polygons of polymer network is visible in figure 1a, b and to some extent figure 1c and the average size of the polygon can also be seen decreasing with increasing water fraction (slower kinetics of dewetting). Similar observations were made earlier in the case of dewetting of photoresist film [39]. This phenomenon is of special interest in case of fabrication of polymeric nanolens arrays, where one can tune the lens size without changing the initial film thickness. Particularly, in situations where coating films of smaller or larger thicknesses may require change in the protocol, such as film liftoff and capture on a patterned substrate [26,35,40].

4. Conclusion

Dewetting of polymer thin film under a mixture of solvent and non-solvent (water) has proved to be an important technique due to its ability to produce significantly smaller (sub-100 nm), large aspect ratio droplets, at a much faster speed [34–37]. These features are of particular interest in fabricating polymeric nanolens arrays [34,40]. In this work, we have studied the effect of varying the compositions of dewetting mixture (solvent–water) on the length scale of dewetting (droplet size and spacing). It has been found that

due to increase in the solvent fraction in the dewetting mixture, the length scale of dewetting increased, because of the faster kinetics of the hole-growth, which limits the number of nucleated holes in the first phase of dewetting. This has provided one additional parameter, other than the initial film thickness, to tune the size of the droplets formed after dewetting. We have also concluded that the dissolution of the polymer in dewetting mixture was found insignificantly small and hence, played no role in the increase in the length scales of the dewetted structures at higher solvent fractions and the faster dewetting kinetics can solely explain the phenomenon.

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