Chapter 2

The effect of dewetting liquid composition on the dewetting of polystyrene thin film

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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.

2.1 Introduction

2.1.1 Basic theory and mechanism

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 such as in the areas of coatings, lubricants, adhesives, membranes and biological coatings this process is undesirable. 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, it is a useful phenomenon. [5–7]. Moreover, polymer blend film and bilayers can further assist in fabrication of embedded and encapsulated nanostructures [8–10]. Polymers are generally chosen for dewetting studies as most polymer have long chains due to which they high molecular weight and so viscosity is high and therefore dynamic is slow and so it allows to track evolution on a realistic time-scale. 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. Coating techniques like spin or dip coating are usually adopted for creating a thin polymer film on solid substrate and thus an intact flat film is obtained on a thermodynamically unstable, non-wettable substrate. On heating the polymer above glass transition temperature, the chain mobility increases that causes amplification of instability and hence decay or disintegration of the polymer thin film. The films that are relatively thicker are stabilized by the effect of gravity, but the films with thickness less than 100 nm spontaneously ruptures as at lesser film thickness the stability is strongly affected by the intermolecular forces across the film. The dewetting of thin polymer films by thermal or solvent vapour annealing has been explored extensively [1–5]. The most common form of thermally induced dewetting is the dewetting of the homopolymer film on an underlying substrate or the formation of holes on unsupported films.

The free energy of the droplet configuration is lower than that of the film, therefore, thin polymer films on substrates are essentially metastable or unstable. Instability or dewetting is trigerred by the intensification of intersurface attractive forces such as van der Waals, electrostatic etc., Thus, the prior existing undulations increase and causes dewetting. 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 ribbons that later decay into polymer droplets. The formation of droplets is caused by either Rayleigh instability that causes the polymer ribbons to decay into droplets or by the fingering instabilities of the moving rim of the edges of the holes. The growth velocity of hole is found to be dependent on the contact angle(Θ) and is also found to be constant with time. 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. The most commonly observed in unstable or metastable film is heterogeneous nucleation, in which nucleation initiates with arbitrary nucleation of holes at the sites of local heterogeneity in the polymer film, generally defect sites eg., dust particles or sites with high residual stresses. Dewetting process initiates with hole nucleation which eventually depends on the film thickness. Film having thickness<5nm dewet by spinodal dewetting whereas relatively thicker films (~50 nm) dewets by homogeneous nucleation. Film having thickness>50nm dewets by heterogeneous dewetting. Some researchers reported spinodal dewetting in 15 nm thick film, though it was found that the time dependence of instability wavelength does not fully support the classical theory of spinodal dewetting. [20] To prove such occurences various other reasons such as density variation along the film thickness, the effect of thermal noise, the selection of solvent for coating, cleaning procedures for substrate, the effect of molecular recoiling, the effect of thermal disturbances have been suggested. In high molecular weight polymers, the effect of residual stresses and drying of film played an important role in dewetting.

In most of the cases of dewetting, a thin polymer film is deposited on the substrate by spin coating. If a film is in metastable state i.e., the film is below the glass transition temperature of

polymer, it will not dewett even if S<0. On annealing or exposing it in solvent vapours or immersing it in water-solvent mixture, the glass transition temperature reduces and the mobility of polymer-chain molecules increases and dewetting of thin film takes place.

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 the dewetting-kinetics is governed by polymer viscosity. [23–33]. There are some excellent reviews, which have discussed important aspects of dewetting over the years [6,34–36] The effect of polymer slippage on the dynamics of the hole growth in the dewetting process of polymer solution films was investigated. Various factors such as film thickness, the molecular weight of the polystyrene, the solvent property and the substrate property were varied. In the case of low molecular weight PS film, there is no apparent slippage effect irrespective of the film thickness and the radius of the hole grows exponentially with time ($R \sim \exp(t/\tau)$. In the case of high molecular weight PS, the effect of slippage is always observed and all three stages of dewetting morphologies are observed depending on the film thickness. The dewetting dynamics of thin liquid films depends on system parameters e.g., wettability of substrate, viscosity, film thickness, surface tension of the liquid and the hydrodynamic slip boundary conditions. The dewetting velocity is dependent upon the substrate viscosity and on increasing the substrate viscosity, the dewetting velocity decreases. 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 Tg of the polymer below the room temperature, thus, the dewetting can occur at room temperature [29]. 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 [37–40]. 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 [37–40]. 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 [37,38]. The time evolution of dewetting was qualitatively similar in both the case [26–32,38]. 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 [38].

The dynamics and morphology of dewetting of metastable polystyrene films cast on silicon substrates was investigated by exposing it to the vapor sog good solvent, toluene and non-solvent, ethanol. Addition of more than 2 wt % of ethanol significantly increased the dewetting rate, increased the contact angle of polymer droplets and hole rims on the substrate, and caused extensive fingering that led to droplet shedding.[39]

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 [41].

Experimentally, the dewetting of thin polymer films has been investigated for a broad variety of materials, but due to easy availability of polystyrene, it is been widely used. Other polymers that are used are poly-dimethylsiloxane (PDMS), poly-methylmethacrylate (PMMA), per-fluoroalkylmethacrylate, perfluoropolyether (PFPE), polyethylenepropylene, etc.

True spinodal dewetting occurs in extremely thin films (h<5nm) and is therefore cannot be captured easily. Initially, there are undulations in the thin film. The average wavelength of undulations amplifies with time and later disintegrate into uniformly sized small droplets. Thicker films showed a combined effect of spinodal and nucleated dewetting.

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.

2.2 Materials and methods

2.2.1 Materials and chemicals

Polystyrene (PS) of average molecular weight 280 kg/mol procured from Sigma Aldrich, India was used in the experiments. HPLC grade chemicals used Methyl Ethyl Ketone, toluene, acetone, tetrachloroethylene (TCE), methanol, ammonium hydroxide, hydrogen peroxide, concentrated sulphuric acid were purchased from Merk, Mumbai, India. The materials like micropipette and micropipette tube, glass slide holder, vials, dropper were purchased from M.S. Scientific, India.

2.2.2 Equipments

The equipments used in the present work were spin coater, vortex mixer, hot plate, sonicator, laminar flow chamber, dessicator, hair dryer, etc.

2.2.3 Glassware

Beaker, measuring cylinders, pipette, volumetric flasks, petridishes etc. were used which were made of boro-silicate glass. Prior to use all the glass wares were sterilized with sulphuric acid and potassium dichromate and thereafter rinsed properly with distilled water.

2.2.4 Methods

2.2.4.1 Cleaning of Silicon wafers

The RCA-I cleaning protocol is a detailed multi-step cleaning procedure of silicon wafers developed by Werner Kern at Radio Corporation of America (RCA) laboratories in late 1960s. The silicon wafers were thoroughly cleaned before use in order to remove dust particles and organic contaminants from the substrate. The silicon wafers were cleaned by RCA1 protocol as shown in figure 5. In this firstly, the silicon wafers were soaked in 10% soap solution. Then the substrates were cleaned by brushing for 1min. for each substrate. Later it was rinsed without froth. Then it is boiled in Trichloroethylene (TCE) solution followed by boiling it into acetone and methanol. 511 solution is prepared by mixing 40 ml ammonium hydroxide, 40 ml of hydrogen peroxide and 200 ml of water in a beaker. The substrates are boiled in this solution at 100^{o}C for half an hour. Pirannah solution a highly oxidizing solution is prepared by mixing 3 parts of concentrated sulphuric acid to 1 part of hydrogen peroxide. The substrates were slowly dipped in this solution and kept for 15 min.

2.2.4.2 Spin coating

Thoroughly cleaned silicon wafers were coated by polymer films of desired thickness. Spin coating is the preferable method for application of thin, uniform films to flat substrates. Polymer is dissolved in a volatile solvent and the solution is spinned. The substrate is rotated at a high angular speed, ω and the liquid is spread over the substrate by centrifugal force and

thus the fluid thickness reduces. The solvent used is volatiles evaporates quickly leaving behind polymer thin film. Polystyrene solution of different concentration is dissolved in toluene. Before spin-coating, polymer solution was filtered through 0.2 μm PTFE filters. Thin films were spin coated at 3000 rpm for 1 min on (100) silicon substrates. The spin-coated PS thin films were then annealed in vacuum oven at 70°C for about 6 h for the removal of reminiscent solvent and to minimize the residual stresses. The film thickness is measured by ellipsometer (nanofilm EP3). In ellipsometer, the measured is the variation in polarization as the incident radiation interacts with the material in observation. The change in polarization is measured by the amplitude ratio and phase difference. As the signal depends on the thickness of the film hence it used for characterization of film thickness.

2.2.4.3 Dewetting procedure

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. Diffusion of MEK in PS reduces its glass transition temperature and allows PS film to dewet at room temperature. MEK also significantly reduces the interfacial tension. As MEK is a good solvent of PS water is added to limit the solubility of PS into the dewetting solution. Also, water and MEK are sparingly soluble therefore, acetone is added to form a homogeneous 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 65%. 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. The characterization of dewetted structures were done using optical microscope (Zeiss Axio observer Z1) and ImageJ software.

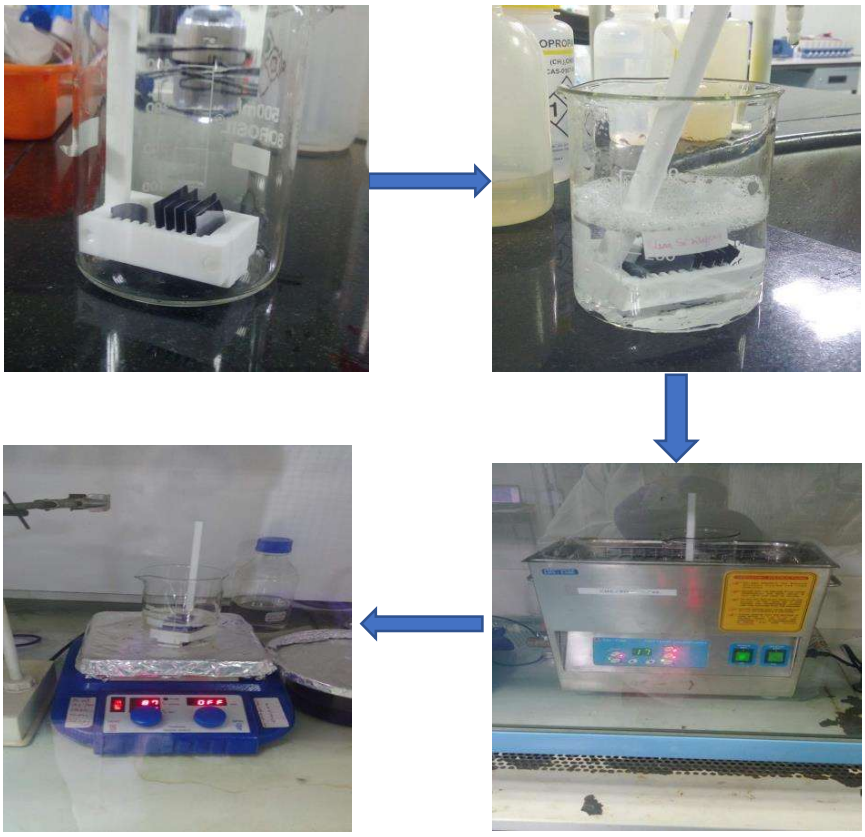

Figure 5: Schematic diagram of step-by-step cleaning procedure

2.3 Result and Discussion

2.3.1 Dewetting studies

The comparison of dewetting of polymer thin film has been done previously in air and in water–solvent mixture [38]. The sequence of changes in the morphology of the dewetting process was found to be qualitatively similar in both the cases [25–28,38]. It was found that for both the cases the dewetting initiated in even less than 5 s. However, it was found that the time scales for dewetting under the water–solvent mixture is much faster than that of in the air. For 50 nm thick film, the dewetting process completed in about 30 min. 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 [38].

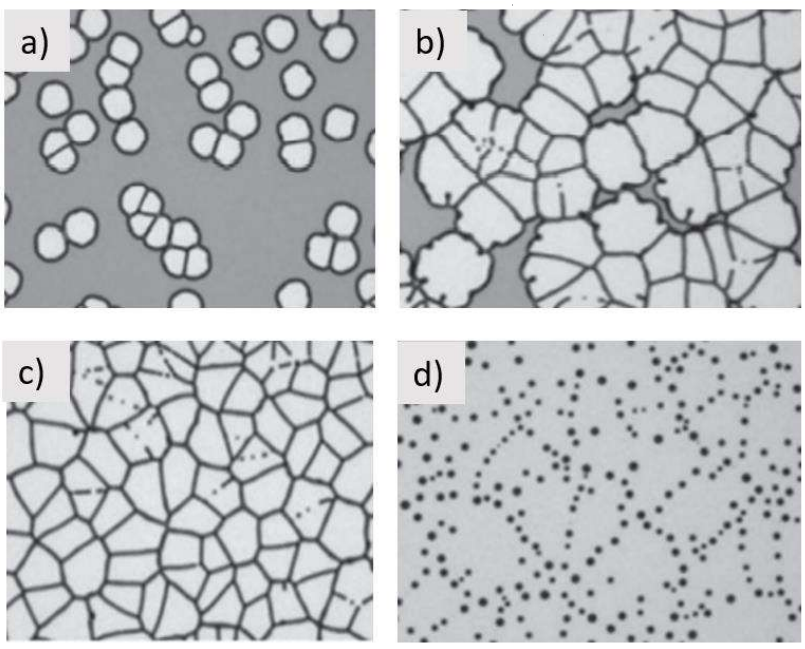

Figure 6: Optical micrographs of the three stages of dewetting in polystyrene thin films on silicon: (a) holes formation, (b) growth of holes, and (c) coalescence of holes to form polymer ribbons, and (d) formation of isolated droplets. Reproduced from ref.[39].

As shown in figure 6 dewetting, as mentioned earlier, starts with the nucleation of holes that initially grow in number and reach a maximum. The holes grow through the withdrawal of hole perimeter into the liquid film. A rim of liquid is formed ahead of the retracting front, which ultimately merges into other rims to form ribbons. The ribbons final decay into droplets outstretched in a cellular structure. After dewetting is completed, the contact line of droplets withdraws for about 1 hr.

The origin of the holes at the earliest stages of dewetting process has been accredited to two mechanisms: spinodal nucleation and nucleation due to defect sites. In spinodal dewetting, the characteristic length-scale(λ) variation is related to the film thickness by power law.

The characteristic feature size and the aspect ratio is greatly limited by weak van der Waals destabilizing force and high surface tension (γ). Both are related to the characteristic length scale of instability by:

$$\lambda = \sqrt{\frac{-8\pi^2\gamma}{\frac{\partial \Phi}{\partial h}}} \tag{2}$$

Here, h denotes film thickness, and ϕ denotes the excess inter molecular destabilizing potential (~h^{-3} for van der Waals forces of attraction).[40] Here, surface tension (γ) has dimensions of [MT^{-2}], whereas destabilizing potential is simply the excess Gibbs free energy per unit length and has dimensions of [$ML^{-1}T^{-2}$] which gives dimensions of λ as [L].

The characteristic instability wavelength (λ) is dependent upon interfacial tension(γ) and film thickness (h) in the case of air where the destabilizing van der Waals force is dominant in the given form:

$$\lambda = 4\pi\sqrt{\frac{\pi\gamma}{A_e}}h^2 \tag{3}$$

where A_e is effective Hamaker constant and has dimensions of [ML^2T^{-2}].[41]

In several reports, the exponent is found to be close to 2, in the case of dewetting in air. The long wave instability wavelength (λ) is dependent on the film thickness (h) as $\lambda \sim h^2$ [26,38] in case of thermal annealing. 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 weaker dependence on film thickness in the case of water-solvent mixture dewetting shows that not only surface tension is decreased but also there is a change in destabilizing potential. Also, in the case of water-solvent mixture, there is also a significant decrease in the Hamaker's constant (A_e) that causes increase in the feature size and also slower dewetting kinetics. But practically it is observed that there is an increase in instability. This change in dependence suggests that the dominant destabilizing force in case of under solvent-water dewetting may have electrostatic origins instead of van der Waals [38].

Equation 2 and 3 holds true for no-slip and weak slip condition (slip length<film thickness). The effect of strong slippage can result for increased instability and a decrease in exponent with respect to wavelength. [42] Kargupta et al. have discussed the effect of slippage on the initial instability growth and its wavelength. But it was found that for the effective Hamaker constant range, (1-5) X 10^{-21} J for the (SiOx/PS/water-MEK) system, both exponent and numerical values cannot be fitted with any positive value of the slip length. The slippage causes an increase in the wavelength of instability. But only slippage along with weak destabilizing van der Waals force and weakened surface tension cannot justify the decrease in wavelength when compared to air. Therefore, slippage cannot be considered as the mechanism in effect which is only responsible for decrease in instability wavelength.

It was observed earlier in the case of dewetting of PDMS thin films, that the destabilizing force increases. [43] The presence of electrostatic attraction($\phi=\varepsilon\varepsilon_o U^2/2h^2$) was accounted for the increase in the destabilizing force. This when put in equation (3) gives the scaling $\lambda \sim h^{-1.5}$.

Therefore, the possible increase in the destabilizing force in dewetting under water-solvent mixture can be accredited to the electrostatic force of attraction. In this particular case, the relation between instability wavelength(λ), film thickness(h) and interfacial tension(γ) is as follows:

$$\lambda_{el} = \frac{2\pi}{U}\sqrt{\frac{2\gamma}{\varepsilon\varepsilon_o}}h^{\frac{3}{2}} \quad (4)$$

Where U denotes the electrostatic potential difference across the film due to different work functions of the three different media.[41] Heier et al., also observed the role of destabilizing electrostatic potential in the liquid-liquid bilayer instabilities of supramolecular assemblies.[50]

The interfacial tension of PS and water–solvent mixture was reported to be 0.55 mN m^{-1}, which is nearly 50 fold reduction than the surface tension of PS in air (~30 mN m^{-1}) [38]. 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 [43].

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 [45]. 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 7 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.

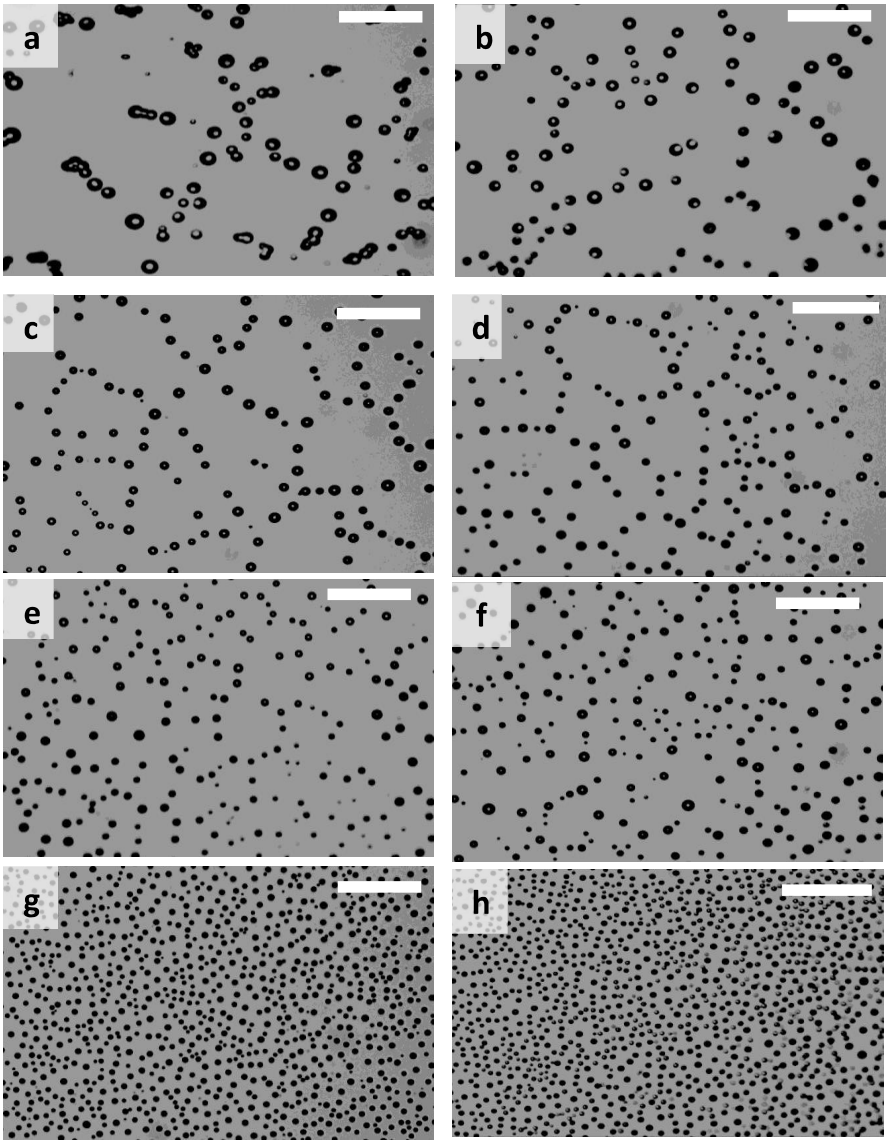

Figure 7: Length scale variation of dewetting of a 50 nm PS film on Si wafer. Optical micrographs for dewetting mixture compositions (water: solvent) of (a) 05:95, (b) 20:80, (c) 25:75, (d) 35:65, (e)40:60, (f) 50:50, (g) 55:45, (h) 65:35. (scale bar: 50 μm)

2.3.1.1 Effect on instability wavelength(λ)

Figures 8 show the variation of the instability wavelength (λ) with change in the water fraction of the dewetting mixture.

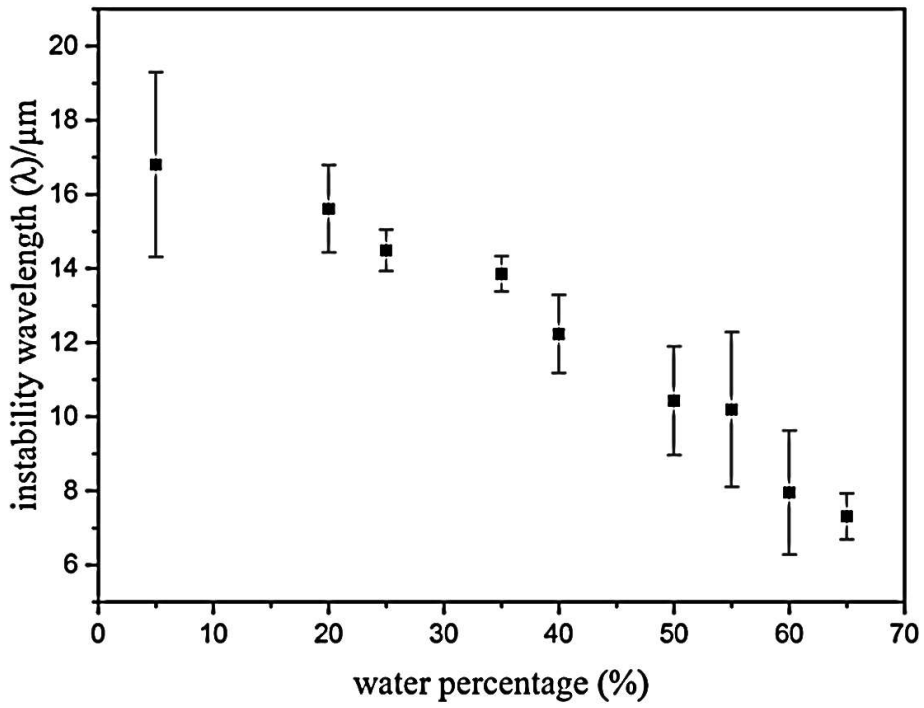

Figure 8: Effect of water fraction in the dewetting mixture on the wavelength of instability (λ).

The instability wavelength (λ) has been calculated based on the final dewetted structure, because the kinetics of dewetting was very fast and onset of instability was achieved very quickly and maximum number of holes cannot be determined accurately. Physically, λ denotes the average distance between two holes which at later stage of instability is approximately

equal to the average distance between two droplets. The λ has decreased from 16.8±2.5 to 7.3±0.6μm on increasing water percentage in the mixture from 5 to 65.

2.3.1.2 Effect on droplet diameter(d)

Figure 9 show the variation of the instability wavelength (λ) with change in the water fraction of the dewetting mixture. The droplet diameter for the same has decreased from 2.4 ± 0.3 to 1.31 μm.

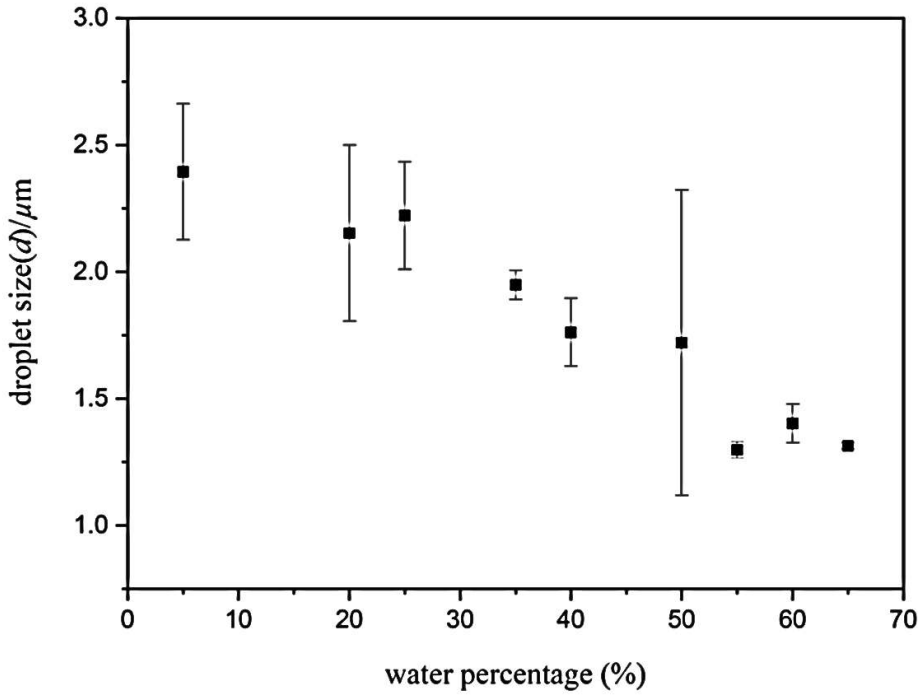

Figure 9: Effect of water fraction in the dewetting mixture on the droplet size (d).

2.3.1.3 Polymer is not soluble in dewetting mixture

The results commensurate with the observations from figure 8 where it can be observed clearly that when the water percentage is less, the droplet density is also lesser. But on increasing the percentage of water in the solution, the number of droplets per unit area also increases which yields a smaller value of λ. This suggests two possibilities for fewer droplets when water fraction is low in the dewetting mixture. MEK is a very good solvent for polystyrene. Therefore, first possibility is the limited dissolution of polymer in the dewetting mixture containing the good solvent MEK 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 [37,38]. Figure 10 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.

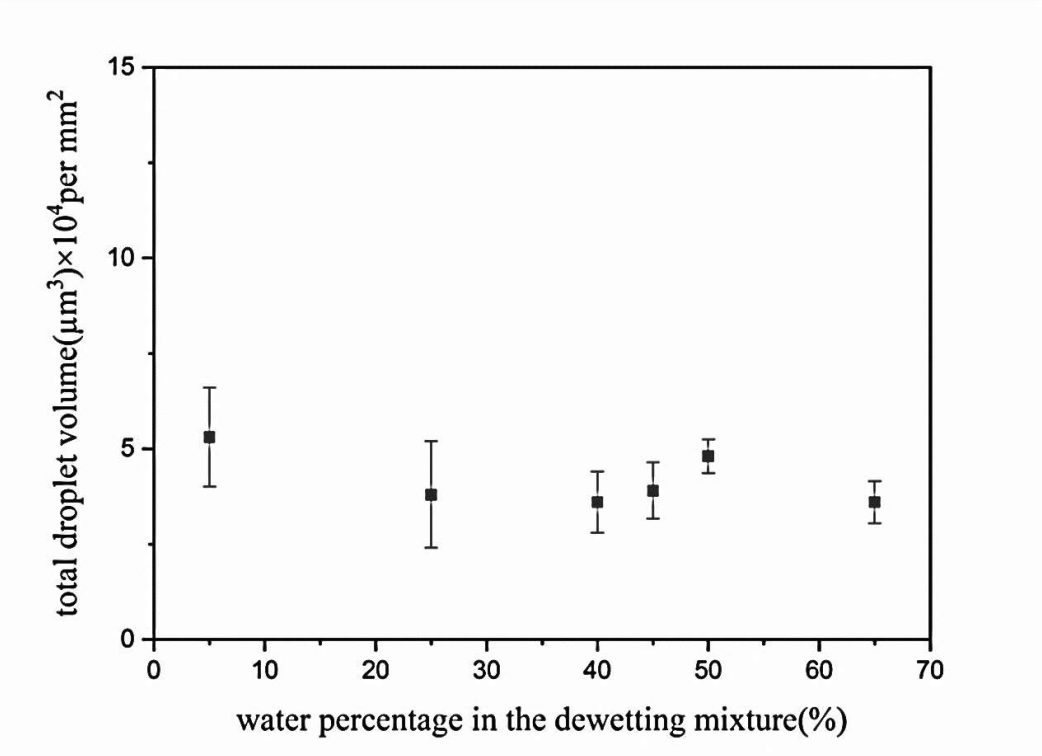

Figure 10: Total droplet volume (μm^3) per mm^2 as the fraction of water in the dewetting mixture is increased from 5 to 65%.

Table 1: Instability Wavelength (λ) and droplet diameter (d) for various composition of dewetting mixture.

Water Solvent ration	**Instability Wavelength(λ)/*μm***	**Droplet Diameter(d)/*μm***
0595	16.8±2.5	2.4 ± 0.1
2080	15.6±1.2	2.1
2575	14.5±0.6	2.2 ± 0.2
3565	13.8±0.5	2.0

4060	12.2±1	1.8±0.1
5050	10.4±1.5	1.8 ± 0.8
5545	10.2±2	1.3
6040	8.0±1.7	1.4 ± 0.5
6535	7.3 ± 0.6	1.3

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 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 a greater number of holes in the first phase of dewetting and thus, resulting in a greater number of droplets. This is also supported by figure 8, where droplet array formed after breaking of large polygons of polymer network is visible 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 [45]. 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 lift off and capture on a patterned substrate [29,38,46].

Also, observations were recorded at both extremes i.e., at more solvent size and at more water side. On increasing the solvent concentration beyond 90%, it was assumed that the droplets may disappear and the droplet density may decrease as MEK is a good solvent of PS it may be possible that dissolution of PS droplets may occur at very high concentration. But on keeping the dewetting time for more than an hour no change was observed.

Whereas on the other extreme i.e., on increasing the water content it was found that beyond 65%, initially nothing was observed but on further increasing the water concentration till 80% and beyond the presence of wrinkled structures were confirmed as observed in the figure 11.

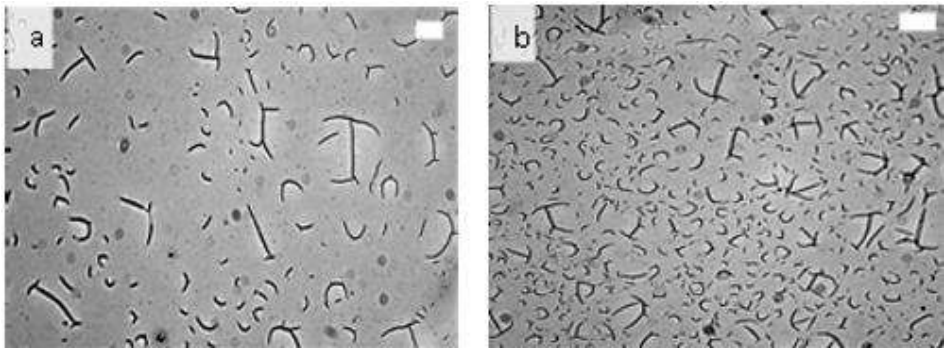

Figure 11: Wrinkle formation in 80:20 water: solvent ratio. a) Scale bar is 20 µm. b) Scale bar is 10 µm.

2.4 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 [37–40]. These features are of particular interest in fabricating polymeric nanolens arrays [37,43].Micro-patterned polymer surfaces have applications both for the selective attachment and and patterning for proteins and cells with varied applications as biomaterials and for the collection of water from the atmosphere.[48,49] 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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