Water-Solvent Mixture Induced Instabilities in 1D and 2D Polymer Structures

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By

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Chapter 5

Conclusion and Future Direction

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5.1 Conclusions

Patterning of thin polymer films have attracted intense attention for more than a decade, because of its interesting applications in the area of microfluidics, adhesives, bio-sensing, polymer solar cells, biomedical, micro and opto-electronic devices, micro reactors. Polymer thin film patterning by dewetting have gained more recognition due to their facile, easy and inexpensive approach and also it is a good alternative to other sophisticated micro-patterning techniques like photolithography, micro-nano printing and microfluidic techniques.

It has been observed that dewetting of unstable thin films (<100 nm) on non-wettable substrates proceeds by rupture of initially homogeneous film into holes which grows in size with time until they merge with the neighboring holes producing discrete droplets of polymer on the substrate. Formation of randomly placed holes or dry patches on film are generally elucidated by two mechanism i.e. spinodal dewetting in which holes formed due to surface disturbances caused by thermal or mechanical interfacial functions in the film thickness. On the other hand, heterogeneous nucleation of randomly distributed holes in the film is mainly caused by defected sites or presence of dust particles and impurities on the surface of thin film. Holes formed via this mechanism are randomly distributed. In polymer surface science, the glass transition temperature (T_g) is a critical parameter which is related to the thermal molecular motion. For ultrathin film depends on the film thickness, molecular weight of polymer and interactions between polymer chain and substrates.

Thermal dewetting initiates when polymer thin films on non-wettable solid substrates heated above the glass transition temperature while in solvent vapor induced dewetting, solvent vapor brought down the of the polymer below the room temperature. Hole formation starts when the inter-surface interaction between polymer and substrate such as Vander waals forces makes the film unstable. Over the time these holes grow in diameter by transfer of material to a rim around the hole and finally breaking into isolated droplets.

The main objective of the current thesis was to examine the dynamics and instability of spontaneous room-temperature dewetting of thin PS films in non-solvent-sovent media. The reduction in length-scale parameters of dewetting was achieved by varying the composition of dewetting mixture and also by modulating the surface properties of the substrate.

The main accomplishments and conclusions of the present research work may be summarized as follows:

- Traditional polymer patterning techniques typically employ top-down strategies like photolithography and imprint lithography.The bottom-up approach of self-organized dewetting can be used as one of the alternatives to these methods. There has been a great deal of theoretical and experimental research done on self-organized microstructures that result from the dewetting of ultrathin films (< 100 nm). Numerous studies have been done on the stability, mechanisms, and pathways of dewetting of liquid and polymeric films above the glass transition temperature. However, there are several main challenges, (i) restrictions on the pattern length scale and the feature size (ii) low aspect ratio because the contact angle of the droplet in the air is too small (iii) both the formation of closely packed structures and pattern alignment. The first two issues were significantly resolved by recent developments in the solvent/nonsolvent liquid mixture self-organized dewetting, which also overcame the surface tension restriction to lower the size restriction in the sub-100 nm zone.The study on the intensified dewetting of thin polymer films under a mixture of good solvent(methyl ethyl keone),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.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 fingering instability, whereas there is reduction in polymer viscosity. It is reported that in the presence of a good/non-solvent mixture, the polymer chain re-aligns to globular configuration that leads to larger interfacial slip and reduced polymer viscosity.

- We systematically analyse the role of dewetting mixture composition i.e., solvent to water ratio, 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. 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.
- It is concluded that the dissolution of the polymer in the 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.
- It is demonstrated that low-density, uniform OTS SAMs can be formed on glass substrates using vapor phase silane grafting. The time evolution of water contact-angles on these substrates showed quick formation of OTS SAMs (nearly 15 min) on glass which resulted in increasing the water contact angles on these substrates. The water contact angle increased with increase of exposure time to the OTS at faster rate initially, which then plateaued out to give nearly constant value of 70^{o}.
- Using these OTS grafted glass substrates for the self-organized dewetting of polystyrene thin

films under a dewetting solution of a good solvent (methyl ethyl ketone) and a non-solvent (water), provides a new method to control the length-scales of dewetting (λ and d).

- The wettability of the substrate plays an important role in determining the kinetics of dewetting and thus, controlling the length-scales of dewetting. A three-fold reduction in wavelength and two-fold reduction in droplet diameter was achieved by just varying the extent of OTS grafting on the substrate. This, combined with the film thickness variation and the dewetting liquid composition variation, provided greater flexibility in the fabrication process than the earlier reported methods to make high aspect ratio droplets for various applications such as microlenses.
- The dewetting of polymer nanofibers have been carried out to get aligned droplets and also to increase the number density of droplets. According to the Rayleigh-Plateau instability, the value of λ/d should be constant. However, in our case it is more complicated because the surface is also playing an important role in determining this and work should be done to determine the correct theory behind this.

5.2 Future Directions

- The effect on the length-scales of dewetting is investigated by using binary dewetting mixture. Comparison between dewetting in binary mixture environment and ternary mixture environment can be made.

- The role of non-solvent in regulating the behaviour of thin polymer films can be studied. The effect of non-solvent concentration in dewetting mixture on droplet diameter and instability wavelength of dewetted structures can be evaluated.

- The dewetting of thicker fiber diameter can be done. The limit of dewetting in terms of fiber diameter can be investigated. Its comparison with Rayleigh instability model needs to be further investigated.

- On increasing the water percentage in the dewetting mixture more than 70%, various wrinkling morphologies has been observed. Further studies in this regard related to their length-scale parameters can be made.