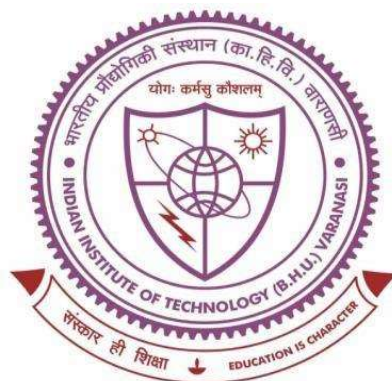


Water-Solvent Mixture Induced Instabilities in 1D and 2D Polymer Structures



Thesis submitted in partial fulfilment

for the award of degree

Doctor of Philosophy

By

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2022

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It is certified that the work contained in the thesis titled "**Water-Solvent Mixture Induced Instabilities in 1D and 2D Polymer Structures**" by **Priti Yadav** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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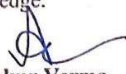
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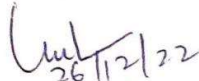

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TABLE OF CONTENTS

Table of Contents	vi
List of Figures	ix
List of Tables	xi
List of abbreviations	xii
Abstract	xiii
1. Introduction	2
1.1 Historical background	2
1.2 Surface instabilities	5
1.3 Surface instability utilized to pattern surfaces	5
1.3.1 Dewetting	5
1.3.2 Phase separation of block copolymers and polymer blends	6
1.3.3 Template guided structuration	6
1.3.4 Electrohydrodynamic patterning	6
1.3.5 Surface patterning due to Thermal-gradient	7
1.3.6 Breadth figures	7
1.3.7 Water-ions induced nanostructuration	7
1.3.8 Nanobubble assisted nanopatterning	8
1.3.9 Reaction-diffusion surface patterns	8
1.3.10 Growth processes: crystal growth and aggregation	8
1.3.11 Surface wrinkling	9
1.4 Patterning of surfaces with polymer	9
1.4.1 Top-down polymer patterning techniques	9
1.4.1.1 Mask based patterning technique	10
1.4.1.2 Printing and writing techniques	10
1.4.1.3 Molding Techniques	11
1.4.2 Bottom-up patterning techniques	11
1.4.2.1 Macromolecular Assembly	11
1.4.2.2 Polymeric nano/microparticle assembly	12
1.4.2.3 Layer by layer assembly	12
1.5 Dewetting	13
1.5.1 Reason for polymer to be chosen for film formation	16
1.5.2 Necessary condition for film to become unstable	17
1.6 Motivation	18
1.7 Research objectives	19
1.8 Structure of the thesis	19
References	20

2. The effect of dewetting liquid composition on the dewetting of polystyrene thin film.	30
Abstract	31
2.1 Introduction	31
2.2 Materials and methods	36
2.2.1 Materials and chemicals	36
2.2.2 Equipments	36
2.2.3 Glasswares	37
2.2.4 Methods	37
2.2.4.1 Cleaning of silicon wafers	37
2.2.4.2 Spin coating	38
2.2.4.3 Dewetting procedure	41
2.3 Result and Discussion	41
2.3.1 Dewetting studies	46
2.3.1.1 Effect on instability wavelength(λ)	47
2.3.1.2 Effect on droplet diameter(d)	48
2.3.1.3 Polymer is not soluble in dewetting mixture	51
2.4 Conclusion	52
References	
3. The effect of surface properties on the length-scales of dewetting.	58
Abstract	58
3.1 Introduction	58
3.1.1 The lotus effect	62
3.1.2 Surface Models and Characterization	64
3.1.2.1 Surface models	64
3.1.2.2 Wetting behaviour	65
3.1.3 Conventional fabrication of hydrophobic surface	66
3.1.3.1 Creating a surface rough on hydrophobic material	67
3.1.3.2 Modifying a rough surface with hydrophobic coating	67
3.1.4 Chemical modification with silane	68
3.1.4.1 Formation of silane monolayer	68
3.1.4.2 Silane coupling agents	69
3.2 Materials and methods	70
3.2.1 Materials and chemicals	70
3.2.2 Equipments	70
3.2.3 Glasswares	70
3.2.4 Methods	71
3.2.4.1 Cleaning of Silicon wafers	71
3.2.4.2 Silanization	71
3.2.4.3 Dewetting procedure	72
3.3 Result and Discussion	72

3.4 Conclusion	79
References	79
4. The formation of aligned droplets by dewetting of electrospun Polystyrene nanofibers and its comparison with Rayleigh Plateau Instability	86
Abstract	87
4.1 Introduction	87
4.1.1 Basic theory and mechanism	87
4.2 Material and method	89
4.2.1 Materials and Chemicals	89
4.2.2 Equipments	90
4.2.3 Glasswares	90
4.2.4 Methods	90
4.2.4.1 Cleaning of glass slides	90
4.2.4.2 Deposition of electrospun Polystyrene fiber	91
4.2.4.3 Dewetting procedure	92
4.3 Results and Discussion	93
4.3.1 Deposition of fibers on unsilanized substrates and annealed at lower temperature(60°C)	96
4.3.2 Deposition of fibers on silanized substrate and annealed at lower temperature (60°C).	98
4.3.3 Deposition of fibers on unsilanized substrate and annealing at a higher temperature (120°C).	100
4.3.4 Deposition of fibers on silanized substrate and annealing at a higher temperature (120°C)	102
4.3.5 Comparison with Rayleigh-Plateau instability model	104
4.3.6 Multiple times dewetting	105
4.4 Conclusion	105
References	106
5. Conclusions and Future directions	109
5.1 Conclusion	109
5.2 Future directions	112
List of Publications	114

LIST OF FIGURES

Figure No.	Figure Caption	Page no.
Figure 1	Schematic diagram of a thin film instability	4
Figure 2	Polygons are arranged in a Voronoi tessellation pattern through the coalescence of dewetting holes.	14
Figure 3	In the case of a thicker (200 nm) polystyrene coating, there would be rim instability.	14
Figure 4	Surface tension diagram of a liquid droplet on a solid substrate	16
Figure 5	Schematic diagram of step-by-step cleaning procedure	39
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	40
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.	44
Figure 8	Effect of water fraction in the dewetting mixture on the wavelength of instability (λ).	45
Figure 9	Effect of water fraction in the dewetting mixture on the droplet size(d)	46
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%.	48
Figure 11	Wrinkle formation in 80:20 water: solvent ratio. a) Scale bar is 20 μm . b) Scale bar is 10 μm .	50
Figure 12	Diagram demonstrating the cleaning mechanism on smooth (a) and rough (b) super-hydrophobic surfaces.	62
Figure 13	SEM images of <i>Nelumbo nucifera</i> (lotus) showing a highly rough surface microstructure.	63
Figure 14	SEM images of a water strider leg.	64
Figure 15	The water contact angle (θ) shown as the angle between the plane of a surface and the tangent at which the liquid droplet makes contact with the surface.	61
Figure 16	Figure explaining Young's equation.	65
Figure 17	(a) Wenzel model and (b) Cassie Baxter model	66
Figure 18	Reaction of silanes with hydroxilated surfaces	68
Figure 19	Silane coupling agent	69
Figure 20	Reactions where silane is acting as a coupling agent.	70

Figure 21	Schematic diagram of preparation of SAM on glass substrate in a desiccator by vapor phase silanization and subsequent coating of PS thin film and its dewetting under mixture of water and solvent.	72
Figure 22	The mechanism of covalent linking of OTS molecules on glass surface.	73
Figure 23	Effect of change in the surface density of grafted OTS molecules (which is a function of OTS vapor exposure time for glass) on water contact angle (θ) on glass substrate.	74
Figure 24	Optical micrographs for dewetted PS films on glass substrates with varying extent of OTS vapor exposure. Length scale variation of a 50 nm PS film on glass substrate for (a) bare glass and glass substrates exposed to OTS vapor for (b) 17 min, (c) 4 hrs and (d) 12 hrs.	77
Figure 25	Variation in instability wavelength (λ) and diameter (d) with the level of silanization in terms of reaction time (h).	78
Figure 26	Schematic of electrospinning process.	89
Figure 27	Schematic diagram of experimental setup	93
Figure 28	In-situ dewetting of nanofibers on unsilanized substrates and annealed at lower temperature (60°C)	96
Figure 29	In-situ dewetting of nanofibers on silanized substrate and annealed at lower temperature (60°C).	98
Figure 30	In-situ dewetting of nanofibers on unsilanized substrate and annealing at a higher temperature (120°C).	100
Figure 31	In-situ dewetting of nanofibers on silanized substrate and annealing at a higher temperature (120°C)	102
Figure 32	Dewetting of nanofibers on previously dewetted substrates	105

LIST OF TABLES

Table No.	Table Caption	Page No.
Table 1.	Instability wavelength (λ) and droplet diameter (d) for various composition of dewetting mixture	48
Table 2	Operating parameters	94
Table 3	Solution Parameters	94
Table 4	Processing Parameters	95
Table 5	Length-scale parameters for dewetting of nanofibers on unsilanized substrates and annealed at lower temperature(60°C)	97
Table 6	Length-scale parameters dewetting of nanofibers on silanized substrate and annealed at lower temperature (60°C).	99
Table 7	Length-scale parameters for dewetting of nanofibers on unsilanized substrate and annealing at a higher temperature (120°C).	101
Table 8	Length-scale parameters for dewetting of nanofibers on silanized substrate and annealing at a higher temperature (120°C).	103

LIST OF ABBREVIATIONS

Abbreviation	Nomenclature
PS	Polystyrene
PMMA	Polymethylmetacrylate
WCA	Water contact angle
DMF	Dimethylformamide
MEK	Methyl ethyl ketone
RCA	Radio Corporation of America
T_g	Glass transition temperature
PDMS	Polydimethylsiloxane
MEMS	Microelectromechanical
S	Spreading coefficient
λ	instability wavelength
d	droplet diameter
SAM	Self-Assembled Monolayer
LB	Langmuir-Blodgett film
HPLC	High-performance liquid chromatography
EBL	Electron beam lithography
OTS	Octadecyltrichlorosilane

ABSTRACT

Surface patterning is important in many areas of research and technology. In the recent two decades, a number of lithographic techniques have been developed, enabling the creation of surface micropatterns with sub micrometer-level resolution. It is possible to create well-controlled topographical or chemical micropatterns using conventional lithographic techniques for microfabrication. There are an increasing number of applications that require for simultaneous control of surface features at the nano- and microscales, driving the creation of innovative, economically viable microfabrication techniques that can incorporate topographical and chemical micropatterning. Due to their tremendous diversity in terms of chemical composition, characteristics, and processing methods, patterned polymer films are becoming ever more significant in relation to an increasing variety of applications. Microelectronics, optics, and biomedicine are just a few of the industries where polymer coatings are used.

Dewetting can be also used as one of the patterning techniques. Dewetting is a common occurrence, such as when a water coating breaks down into individual droplets on a Teflon-coated pan or a filthy window pane. Thin liquid film dewetting results from the instability of the liquid film on the solid surface and is dependent on the interaction of attractive intermolecular forces with unfavourable surface interactions. Droplets form as a result of self-organization and pattern formation during dewetting. Due to the growing usage of thin polymer films as coatings, lubricants, adhesives, membranes, and biological coatings, etc., there have been extensive investigations on the dynamics of instabilities and structure formation in these films. Dewetting and instability are undesirable in the majority of these applications. However, in some other cases it can lead to the formation of various useful and interesting features. It can also be used to create patterns on a meso and nano-scale over a wide area. On a flat,

homogeneous surface, dewetting begins with the nucleation of randomly located holes at a specific mean spacing. These holes expand and consolidate over time, resulting in randomly distributed polymer droplets. The initial thickness and the interfacial tension of the polymer film determine average diameter and mean separation of dewetted structures.

In the present work, patterns are produced by dewetting various 1D and 2D polymer structures such as thin films and electrospun nanofibers and these dewetted structures can be utilized in various applications such as organic field transistors, electronic devices and biological application such as cellular patterning. Further, the characteristic length-scale parameters such as droplet size and mean spacing is tuned by various techniques such as varying the dewetting mixture composition and by modifying the wettability properties of the substrates. Also, more ordered and aligned structures are produced by dewetting of nanofibers.

In the first chapter of the thesis, we systematically examine how the water to solvent ratio in a dewetting mixture affects the length scales of instability. Previously, only one composition of water-solvent dewetting mixture was tried but here we had varied the dewetting mixture composition. Here, the 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%. It is determined how the amount of water in the dewetting mixture affects the instability wavelength (λ) and droplet diameter (d). As the water concentration is increased from 5% to 65% in the dewetting mixture, it is observed that the instability wavelength (λ) for 50 nm thick PS film is decreasing from approximately 17 to 7 μm . Similarly, the droplet diameter has decreased from 2.4 to 1.3 μm on increasing the water percentage. This is considerably smaller than the instability wavelength in air, which for the identical PS film is close to 50 μm . The mechanism of the observed change in the length scale is presented, and the solubility of PS in the dewetting mixture is also explored.

In the second chapter of the thesis, we present a straightforward technique for modifying the lengthscales of self-organized dewetting of polystyrene thin films by varying the extent of silane grafting on the substrate. By exposing glass substrates to varying concentrations of OTS vapour in a controlled, low-pressure environment, self-assembled monolayers (SAM) of octadecyltrichlorosilane (OTS) were deposited onto the substrates. When the duration of time exposed to the OTS vapours was increased from a few minutes to several hours, measurements of the water contact angles on the treated glass surfaces showed that the contact angles could be constantly increased from 40° to 70° . On the modified glass substrates, polystyrene (PS) thin films were spin coated, and water-solvent mixture induced dewetting of the PS thin films was done; the dewetting kinetics depended on the spreadability of water on the surface. By increasing the amount of OTS exposure, we noticed a decrease in the length scales of dewetting, notably the droplet size (d) and instability wavelength (λ). While the droplet diameter (d) reduced from 2.5 to 1.6 μm , the wavelength (λ) for a 50 nm thick PS film decreased from 12 to 4 μm .

In the last chapter, we had discussed the dewetting of electrospun nanofibers. The dewetting of thin films lead to random structures. The randomness of the dewetted structures restricts this method's potential as a soft patterning technique in several applications. To impose a long-range order in the dewetted structures, a number of ways have been investigated. Various works had been done on physico-chemically structured surfaces and it was found that more ordered assemblies can be formed over such surfaces. Here we use one easy way to align droplets where instead of 2D structures we do dewetting on 1 D structures i.e., nanofibers. To get more number density of droplets and more aligned droplets we had switched from film configuration to fibre configuration. We have also done its comparison with Rayleigh-Plateau's instability model.

It has been found that the length scale of dewetting decreased with an increase in the water fraction in the dewetting mixture due to the faster kinetics of the hole-growth. Also, by just

varying the amount of OTS grafting on the substrate, a three-fold reduction in wavelength and a two-fold reduction in droplet diameter were obtained. These techniques can be used as an additional way to control the droplet size that was obtained after dewetting. Finally, summary and overall conclusions based on the achievements are presented in the thesis.