DECLARATION

I hereby declare that the Ph. D. thesis entitled: "**PARTICLE ASSISTED MICROPATTERNING ON POLYMER-ALUMINA NANOCOMPOSITE FILMS**" is an independent work carried out by me and it has not been submitted anywhere else for any other degree, diploma or title.

(LAKSHMI V.)

JUNE 12, 2015

CERTIFICATE

This is to certify that the work embodied in the thesis entitled: **"PARTICLE ASSISTED MICROPATTERNING OF POLYMER-ALUMINA NANOCOMPOSITE FILMS"** has been carried out by Ms. Lakshmi V. under my supervision and guidance at the Minerals and Metallic Materials, Materials Sciences and Technology Division of the CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Trivandrum and the same has not been submitted elsewhere for a degree.

(T.P.D. Rajan) (C. Pavithran)

Thesis Supervisors

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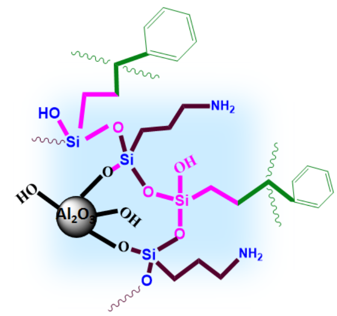
CONTENTS

PREFACE

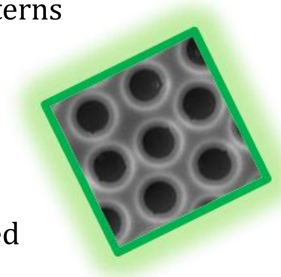
The amino functionalized micropatterned polymer and hybrid composite films have attracted much attention due to their inherent ability to be used for various biological and energy storage applications. The amino functionality inside the concavities of the pattern endowed the patterned film with favorable properties for further modification of the film for various biological applications like immobilization of biomolecules by simple chemical reactions. Furthermore, these hybrid films possessed enhanced mechanical strength due to the accumulation of alumina particles at the cavity wall. Micropatterned inorganic hybrid films have been well explored in the literature, however, the amino functionalized micropatterned hybrid films attracted much less attention. The breath figure method which utilized the mobile array of water droplet condensed on the polymer solution surface as a template has been employed for the fabrication of micropatterned polystyrene alumina nanocomposite films. The amino-functionalized amphiphilic alumina particles used for the hybrid film preparation migrate towards the water/solvent interfaces of breath figures and stabilize the water droplets that condensed on the polymer solution surface.

The present thesis is based on the patterning on polystyrene-alumina nanocomposite film has been divided into five chapters. The first chapter presents the overview of the micropatterned polymer films, with particular emphasis on breath figure techniques and its mechanism which is a versatile method for the fabrication of micropatterned polymer films. The different factors affecting the breath figure mechanism and review of various synthetic strategies in this methods are some of other the aspects included. In addition, the specific objectives of the present thesis were briefly described at the end of this chapter

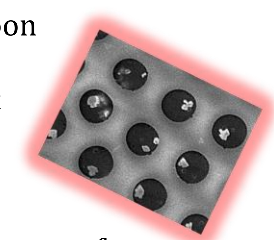
The synthesis of amphiphilic modified alumina nano particles and the importance of amino functionality on the particle surface forms the subject matter of second chapter. Here, the modification of nano alumina particles (SA) was carried out by a silane modification followed by grafting with polystyrene chain by free-radical polymerization with styrene in presence of benzoyl peroxide (BPO). The styrene/ alumina molar ratios were varied to prepare modified particles having different hydrophobic/hydrophilic (Hb/Hp) ratio. These modified particles were characterized and the dispersion behavior was studied in various organic solvents and in polystyrene matrix. We observed different dispersion characteristics for amphiphilic-particles in solvents like tetrahydrofuran, chloroform and carbon disulphide. The solvent characteristics and the interaction between the SA particles with the solvents were responsible for the different dispersion behavior of these particles.



The third chapter deals with the fabrication of amino functionalized micropatterned polystyrene-alumina hybrid films by incorporating the amphiphilic-modified alumina particles in polystyrene/THF solution. Breath figure technique has been used to produce concavities on the surface of the film by simple casting of the polystyrene-modified alumina suspension (PSA) in tetrahydrofuran on a glass substrate. The concentration dependent morphological variation was probed by analyzing film prepared from different concentrations (2.5 to 50 mg/mL) of PSA/THF solutions under optical microscopy, SEM and AFM. Uniform patterns were observed at a concentration of 15 mg/mL. We were successful in creating relatively uniform BF patterns with a BF incompatible polystyrene with the aid of amphiphilic-modified alumina particles. Such a particle-assisted mechanism suggests that the physical and chemical properties of the particles decides final morphology of the BF pattern. The particle loading of the amphiphilic-particles were varied from 1 to 5 wt %, and the corresponding change in the morphology of the pores had been studied. The results indicated that uniform BF cavities were formed at the dispersion loading maximum of 3 wt %. The influence of Hb/Hp balance of the amphiphilic-modified alumina particles on the BF morphology had been studied using THF as a solvent. The effect of AS:VS modifier ratio on the BF morphology was also studied and a particle-assisted breath figure mechanism has been proposed based on the observations.



The fourth chapter of the thesis emphasis the various parameters that influence the BF patterns on the PSA hybrid film such as solvent, particle size and substrate. The solvent effect has been studied with SA particles having different Hb/Hp ratio by dispersing the particles in PS solutions of chloroform (CFM), carbon disulphide (CS2), dichloromethane (DCM) and compared with that of tetrahydrofuran (THF). We end up in different conclusions for different category of solvents. The results further confirm the influence of particle property like the dispersion characteristics and the interfacial behavior at the water /solvent interface on the breath figure morphology formed on the PSA hybrid film. Breath figure patterns were created using amphiphilic-modified alumina particles



having average particle size of 20nm. The BF cavity size increased with the particle size and the phenomenon was explained based on the difference in adsorption energy of particles having different size. The polypropylene films were used as the substrate to generate BF patterns using PSA suspensions under the same experimental condition as that of glass substrate. The observations clearly indicated the substrate influence and explained based on the interaction between substrate, the polymer matrix and the solvent.

The fifth chapter deals with the fabrication of amino functionalized free-standing amino functionalized micropatterned (amino-FSM) polystyrene-alumina nanocomposite films by a simple casting method on a glass petri dish. The PSA suspension in chloroform which create uniform BF cavities in the drop cast film was selected for the FSM preparation. The morphological tuning was carried out by varying the thickness of the film and the particle loading. The amino functionality on each film was estimated by spectrofluorimeteric studies. Moreover, the enhanced mechanical strength of the FSM due to the presence of alumina particle were probed by nanoindentaion studies. So, the enrichment of amino functionalities inside the cavity of FSM via one step breath figure approach has many advantages in biological and biotechnical fields owing to the ease of modification of the reactive amino ligand and facilitates the selective immobilization of biomolecules to even other inorganic nanoparticles. Finally, a summary and conclusion of the whole investigation was described briefly.

Sl. No	List of Figures	Page

List of Tables

List of Charts

List of Abbreviations

1. $(RO)_3SiX$ - Trialkoxy silanes
2. μm – Micrometer
3. 2.6SA - Polystyrene modified amphiphilic alumina particles with Hb/Hp =2.6
4. 2SA – Polystyrene modified amphiphilic alumina particles with Hb/Hp =2
5. 4SA - Polystyrene modified amphiphilic alumina particles with Hb/Hp =4
6. A – Projected contact Area
7. A11 – Silane treated alumina particles having AS:VS =1:1
8. A13 - Silane treated alumina particles having AS:VS =1:3
9. A31 - Silane treated alumina particles having AS:VS =3:1
10. AFM – Atomic Force Microscopy
11. $AgNO_3$ – Silver Nitrate
12. Amino-FSM – Amino Functionalized Free Standing Micropatterned Film
13. aPS – actactic Polystyrene
14. aps – average particle size
15. APTES – Amino propyl triethoxy Silane
16. AS – Aminopropyl triethoxy Silane
17. AS/VS – Amino silane to vinyl silane ratio
18. AuNP – Gold Nanoparticles
19. BCP - Block copolymer

20. BF – Breath Figure

21. CA – Contact Angle

22. CdS – Cadmium Sulphide

23. CdSe – Cadmium Selenide

24. CFM – Chloroform

25. $CHCl_3$ – Chloroform

26. CS2 – Carbon disulphide

27. DCM – Dichloromethane

28. DLS - Dynamic light scattering

29. DTG – Digital thermogravimetry

30. E – Adsorption Energy

31. $E_{(eff\ )}$ – Young's Moduli

32. EDAX - Energy Dispersive Spectroscopy

33. *et al.* – *Et allii/alia*

34. Feature/cm^2 – feature per unit area

35. FSM – Free Standing Micropatterned Film

36. FT-IR – Fourier transform infrared

37. g – Gram

38. GPa – Giga Pascal

39. h – Hour

40. H- Harness

41. Hb – Hydrophobic

42. Hb/Hp – Hydrophobic/Hydrophilic balance

43. HC – Honeycomb

44. h_f – Final Displacement

45. h_{max} – Maximum depth of indentaion

46. Hp – hydrophilic

47. HRP - Horseradish peroxide

48. mg – Milligram

49. Mg/mL – milligram per milliliter

50. Mol. Wt. – Molecular Weight

51. mp – Melting point

52. MPa – Mega Pascal

53. $NaBH_4$ – Sodium Borohydride

54. nm – Nanometer

55. NP – Nanoparticles

56. OM – Optical Microscopy

57. P- Load

58. PDMS – Poly dimethylsiloxane

59. PET – Polyethylene

60. PLLA – Poly(Lactic acid)

61. PMMA – Polymethylmethaacrylate

62. PP – Polypropylene

63. PS – Polystyrene

64. PS/CFM - Polystyrene solution in chloroform

65. PS/CS2 - Polystyrene solution in carbon disulphide

66. PS/DCM - Polystyrene solution in dichloromethane

67. PS/THF – Polystyrene solution in tetrahydrofuran

68. PSA – Polystyrene-Alumina Nanocomposite

69. PSA/CFM – Polystyrene-alumina suspension in CFM

70. PSA/CS2 – Polystyrene-alumina suspension in CS2

71. PSA/DCM – Polystyrene-alumina suspension in DCM

72. PSA/THF – Polystyrene-alumina suspension in THF

73. PU – Polyurethane

74. QD – Quantum dots

75. R – Particle Radius

76. RO- alkoxy

77. S – Conformational Entropy

78. S/A – Styrene to Alumina molar ratio

79. SA – Polystyrene modified Alumina Nanoparticles

80. SA11 - Polystyrene modified amphiphilic alumina particles with AS/VS = 1:1

81. SA13 - Polystyrene modified amphiphilic alumina particles with AS/VS = 1:3

82. SA31 - Polystyrene modified amphiphilic alumina particles with AS/VS = 3:1

83. SEM – Scanning electron microscopy

84. SiO_2 – Silica

85. SPS – Star Polystyrene

86. T_{100} – Decomposition temperature at 100% weight loss

87. T_{50} – Decomposition temperature at 50% weight loss

88. TEM - Transmission electron microscopy

89. TGA – Thermogravimetric Analysis

90. THF – Tetrahydrofuran

91. $TiCl_4$ – Titanium tetrachloride

92. TiO_2 – Titanium dioxide

93. UP – un-patterned

94. v/v – volume per volume

95. VS – Vinyltriethoxy Silane

96. XRD – X-ray Diffractometer

97. z_0 – Interfacial energy

98. γ_s – Surface tension of solvent

99. γ_w – Surface tension of water

100. $\gamma_{w/s}$ – Water solvent interfacial energy

101. δP – Dipolar intermolecular force