

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.

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ACKNOWLEDGEMENTS

It is my great pleasure to express my deep sense of gratitude to Dr. C. Pavithran and Dr. T.P.D. Rajan, my thesis supervisors, for suggesting the research problem and for their guidance, support and encouragement that led to the successful completion of this work.

I would like to express my sincere thanks to Dr. B.C. Pai for being a source of motivation and encouragement during my research work at CSIR-NIIST.

I thank Dr. A. Ajayagosh, Director and Dr. Suresh Das, former director of the CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST), Trivandrum, for providing the necessary facilities for carrying out this work.

I would like to thank Dr. Prabhakar Rao, Dr. Boje Gowd, Dr. J.D. Sudha, Dr. V.S. Prasad, Dr. Saiju Pillai, Dr. A.R.R. Menon, present and former Scientists of the Materials Sciences and Technology Division and chemical science and technology Division, for the help and support.

I sincerely thank Dr. Ramesh Narayanan, Mr. Srinath Jonnalagadda, VSSC, Trivandrum, Mr. M. Saravanakumar and Mr. Vineeth, Rajiv Gandhi Centre for Biotechnology (RGCB), Trivandrum for the help in Nanoidentation, MALDI and Contact angle Measurement Studies.

I extend my thanks to Akhil S. Karun, Praseeda S. Nair, Resmi V.G., Dr. Deepa J.P., Dr. Adarsh N., Ramya S., Annu Raju, Jerin K. Pancrecious, Sarah Ulato, Shaiju S., NagendraBaku, Rohini K.P., Neethu S., Ramakrishnan S., Renjith S., Ashish A., Molji V., Reshma, Sreemanu K.M., Asha Susan Chacko for their valuable help.

I thank all the members of the Photosciences and Photonics and other Divisions of CSIR-NIIST for their help and cooperation. I would like to thank Mr. Chandran and Soumya for SEM analysis Mr. Robert Philip and Mr. Kiran for TEM, Mr. Peer Muhammed for TG analysis and I also thank Mr. Shaiju S for XRD analysis, Mr. George and Mr. Bejoy Muhammed K.S. for IR spectral and spectrofluometric studies.

Words are inadequate to express my gratitude to my family members who constantly stood as a source of encouragement and confidence. I take this opportunity to pay respect to all my teachers who guided and blessed me.

I thank Council of Scientific and Industrial Research (CSIR), Government of India for financial assistance.

Lakshmi V.

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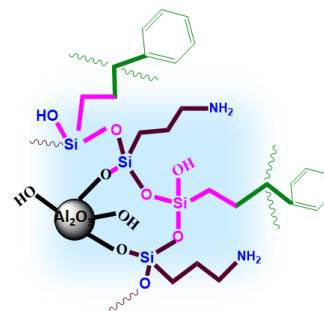
PREFACE

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

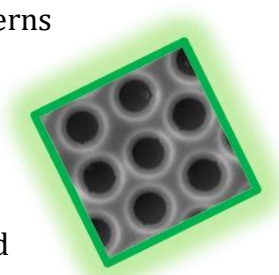
The synthesis of amphiphilic modified alumina nano particles and the importance of amino functionality on the particle surface forms the subject matter of second chapter. Here, the modification of nano alumina particles (SA) was carried out by a silane modification followed by grafting with



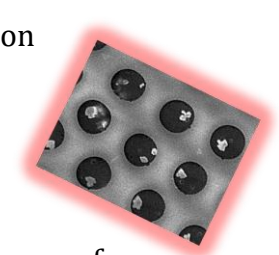
polystyrene chain by free-radical polymerization with styrene in presence of benzoyl peroxide (BPO). The styrene/ alumina molar ratios were varied to prepare modified particles having different hydrophobic/hydrophilic (Hb/Hp) ratio. These modified particles were characterized and the dispersion behavior 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 spectrofluorimetric studies. Moreover, the enhanced mechanical strength of the FSM due to the presence of alumina particle were probed by nanoindentation 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.



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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 - atactic Polystyrene
14. \bar{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. CHCl₃ – 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 alii/alia*
34. Feature/cm² – 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. H_p – 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 – Polymethylmethacrylate
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. SiO₂ – Silica
- 85. SPS – Star Polystyrene
- 86. T₁₀₀ – Decomposition temperature at 100% weight loss
- 87. T₅₀ – 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