SUMMARY AND CONCLUSIONS

Micropatterned polymer/hybrid films have been of great interest to academia as well as industries for its potential for a wide range of advanced applications like dielectric components in sophisticated devices such as photovoltaic cells, surfaces for the growth of cells, pico-liter beakers for bio-analytical purposes etc. Appropriately functionalised patterns are often desired for finding applications. Among various templating methods, the "breath figure method" which uses water condensates as the dynamic templates, offers a versatile and inexpensive method for preparing the functionalized micropatterned films in a single step, avoiding the use of specially designed expensive templates, fabrication machineries and process such as calcination or dissolution to remove the templates and post-modification for functionalization. In addition, tuning of the morphological features is possible by varying the experimental conditions like humidity, temperature, solvent, polymer type, polymer architecture etc. Micropatterned polymeric films with functionalised pores/cavities can be produced in a single step using polymers with polar functional or mixing the polymers with oligomers containing the functional groups. However, the methods yield functionalized pores/cavities along with functionality present in other surfaces. This can be avoided by using functionalised nano-inorganic particle as additive in the polymer. Hence, the main objective of the present investigation is the preparation of drop-cast micropatterned polystyrene-alumina hybrid films with amino-functionalised cavities on a glass substrate and its characterisation. The other objectives include the study of various influencing factors such as the physical and chemical properties of the particles, solvent characteristics, substrate etc. on the breath figure morphology. Yet another objective was to explore the possibility of fabricating free-standing amino-functionalised free-standing micropatterned film (amino-FSM) by a simple casting process and tuning the morphology by varying thickness of the film.

The amino-functionalised amphiphilic alumina (SA) nanoparticles, for use as additives in polystyrene for preparation of functionalised hybrid films, was synthesised by treating the particles with a mixture of aminopropyl- triethoxysilane (AS) and vinyl-triethoxysilane (VS) followed by *in-situ* polymerization of styrene monomer through the vinyl group. Alumina particles having average size of 100nm was used for the modification. The AS/VS mole ratio was varied from 3:1 to 1:3 although the particles treated with AS/VS mix of equi-molar proportion was used for most of the studies. Particles having different hydrophobic/ hydrophilic (Hb/Hp) balance was obtained by varying styrene/alumina (S/A) molar ratio. Hb/Hp balance was calculated from TGA data for the un-modified, silane treated and polystyrene-modified alumina. Thus, amphiphilic alumina particles having Hb/Hp values of 2, 2.6 and 4 were prepared. These particles were characterised for their dispersion characteristics in selected organic solvents, which were used for preparing the solutions/suspensions for making the films, and employing Dynamic light scattering (DLS) analysis. The particles having Hb/Hp value ≥2 showed dispersion stability in dilute solutions of polystyrene for more than 30 minutes which was desired making the hybrid films. Dispersion-loading limit of the particles in polystyrene matrix was characterised by XRD and optical transmission microscopic analysis of the hybrid films. The particles exhibited a dispersion-loading limit of 3 wt %, beyond which particle agglomeration occurred.

Micropatterned polystyrene-alumina hybrid drop cast films with amino-functionalized breath figure (BF) cavities were initially prepared from suspensions of the SA particles in dilute polystyrene/tetrahydrofuran (PS/THF) solutions. Glass slide was used as the substrate material. Films with breath figures were produced by drying off the drop-cast of the suspension under ambient temperature of ~30 °C and relative humidity of ~80%. The optimized concentration of the suspensions (referred as PSA suspensions) for obtaining defined breath figures was 15 mg/mL. Moreover, the study on the influence of particle concentration on BF morphology revealed that uniform breath figure pattern was formed at particle dispersion-loading maximum of 3 wt % with respect to polystyrene, which was the particle dispersion-loading limit and deviation from this affected the regularity of the pattern. The study of the impact of Hb/Hp value of the SA particles on the BF morphology revealed that SA particles having Hb/Hp value of ~2.6 produced regular BF pattern. The variation in morphological features with respect to particle concentration, Hb/Hp value of the particles and its dispersion characteristics in THF were discussed. Formation of amino-functionalized cavities has been proven by the fluorescence microscopic images of fluorescamine-treated hybrid film. The study of the influence of the silane modifier ratio revealed that the particles which was treated with AS/VS mole ratio of 1:1 was more effective than the particles treated with AS/VS mole ratio of 3:1 and 1:3. The remarkable achievement of our investigation was the preparation amino- functionalised BF cavities which can be post-modified to contain desired functionalities by substitution reactions with ease owing to the reactive nature of the amino group. Another achievement was the preparation of BF patterned polystyrene from THF using the amino-functionalised particle as the additive, which otherwise was BF incompatible.

The influence of the solvents, particle size and substrate on BF morphology was also studied. The study ended up in a conclusion that different solvents behaved differently towards the BF formation in the hybrid films. The interaction between the amphiphilic-alumina particles and the solvent was a crucial factor which determined the BF morphology. Besides, the solvent characteristics such as water miscibility, evaporation rate and polarity were also vital factors. Similarly, the breath figure morphology was also influenced by the particle size. A camparison of the BF morphological features of hybrid films using alumina particles having average size of 100nm and 20nm revealed that both the particles were effective in producing uniform BF patterns, however the finer particles produced BF cavities relatively larger cavities with lower feature density (cavities/cm^2). Drop cast films were also produced on polypropylene (PP) sheet using particle suspensions in PS/chloroform solution with 3 wt % particles in order to the study the effect of substrate on BF formation and morphology. The results showed that BF pattern with higher cavity size and lower feature density, when compared to that was formed on glass substrate, was formed. However, particle accumulation in the BF cavity was observed. The variation in the morphological features was explained in terms the interaction between the substrate, polymer and the solvent.

Finally, possibility of fabricating free-standing micropatterned (Amino-FSM) polystyrene-alumina hybrid films amino-functionalized cavities using simple casting method was explored. Of different solvents, chloroform was found most suitable the purpose. Amino-FSM films were fabricated by casting the suspension of the particles (3 wt % w.r.t PS) in PS/chloroform (15 mg/mL) solution in a glass petri dish (3.5 cm dia.) and allowing the cast dry off under ambient conditions. The suspension volume and the particle loading were varied in order to study their effect on the BF morphological features. The study revealed that the pore size and pore density varied with the suspension volume/film thickness. The amino functionality present on the BF cavity in the FSM was estimated qualitatively by the spectrofluorometric studies after treating the FSM films with fluorescamine. While 0.91 μm thick FSM (0.2 ml suspension) exhibited through-pore structure with high pore density of $3.08\times10^8/cm^2$, 3 μm thick film (0.5ml suspension) produced the most uniform patter. The cavity size increased and the feature density decreased with increase of film thickness/suspension volume. When compared to drop cast films where the particle loading of 3 wt % was found optimum to produce regular pattern, FSM with regular pattern were possible using particle loading in the range of 3-5%. The probable reasons for the above observations were provided. FSM with 5 wt % particle loading (FSM-5%) showed an elevated percentage of amino groups as indicated by the fluorescence response with an intensity of 5.1×10^6 μA. An added advantage of the present system is the enhanced stiffness, mechanical property and thermal stability owing to the presence of the inorganic particles in the film. The amino functionality inside the cavity has many advantages in biological and biotechnical fields owing to the ease of post-modification of the reactice amino group. The amino functionality inside the BF cavity facilitates the selective immobilization of selected biomolecules like proteins, carbohydrates, DNA, etc. and also for the preparation of biofilms and cell adhesive materials.

Scope for future works include:

- Study of the substrate influence on BF morphology by considering other inorganic and organic substrates.
- *"In-situ"* synthesis of inorganic particles inside the BF cavities. The study of Ni and Fe deposition inside the BF cavity, owing to their catalytic properties, is in progress.
- Biomolecule immobilization on the amino-FSM and the preparation of biofilms.