

Chapter 3

Concentration dependent Self-Assembling Studies of Polystyrene-Clay Nanocomposites using Adduct Modified Clays

3.1. ABSTRACT

The morphology and self-assembling properties of a series of Polystyrene (PS)-clay nanocomposites are investigated via *in situ* free radical polymerization using Adduct modified clay (AMC). Adducts are synthesised by reacting quaternary ammonium salt with unsaturated organic acid like Acrylic acid, Cinnamic acid and Oleic acid. The resulting reactive cation is used to organo-modify the Na⁺-MMT. Polystyrene clay nanocomposites (PSC) prepared by effectively dispersing styrene monomers into the interlayer regions of organophilic clay hosts are used for studying solvent assisted Self-assembling property in THF. Among the three polystyrene clay nanocomposites, PSC-AC was found to exhibit better self-assembling properties than PSC-CC and PSC-OC. Microvesicles of uniform size were produced from solution concentration of 2.5 mg/mL. Micropatterned PSC film with concavity size of 1 to 1.5 μm was obtained by drop-casting PSC solution (20 mg/mL) under relative humidity of 70-80% and a uniform film of PSC was obtained at a solution concentration of 50 mg/mL and above. Solvent-assisted self-assembling studies are characterized using Optical microscope (OM) and Scanning electron microscope (SEM). The Guest-encapsulation of PSC vesicles are gained by encapsulating with fluorescent dyes and oil by Fluorescent microscope.

3.2. INTRODUCTION

Polymer-clay nanocomposites have attracted the attention of several researchers, primarily because significant improvements in physical properties can be achieved at low clay concentrations (Chen., 2004; Fischer., 2003; Pavlidou and Papaspyrides., 2008). The dispersion of nanolayers of clay mineral in the polymer matrices, providing a large surface area due to high aspect ratio of the clay platelets is considered to be responsible for such an improvement in properties (Weon and Sue., 2005). Polymer-clay nanocomposites can be prepared by three different methods: (a) in situ polymerization (Sain and Khatua., 2011; Zeng and Lee .,2001) (b) melt processing (Guduri and Luyt., 2008) and (c) solution casting (Nevalainen et al., 2009). Depending on the interaction between clay layers and polymer chains intercalated and exfoliated type of nanocomposites are formed. The exfoliated clay morphology is considered to be most desirable because of significant improvement in properties of the nanocomposites arising out from high level of dispersion of the clay platelets in the matrix polymer (Fu and Qutubuddin., 2001).

In recent years, solvent assisted self-assembly of polymer clay nanocomposites have attracted the attention of several researchers, both in the academic and the industrial communities. Self-assembly of silicate layers to form microvesicles, micropatterned polymer film and uniform film surfaces was obtained by changing PSC loading with THF as solvent. The PSC materials have become an important part of research due to enormous advantage of using nanoclay in polymer matrix, as compared to the conventional fillers. Vesicles have been receiving intense research interest due to their potential applications in drug encapsulation/delivery

system (Nair et al., 2010; Tanner et al., 2011; Bellomo et al., 2004), dyes and ink, catalysis, as microcontainers, or reactors and sensors. Various methods approved for the synthesis of polymer, inorganic and organic-inorganic hybrid vesicles which include solvent-assisted self-assembly of amphiphilic polymers, rod-coil diblock polymers, dendrimers, and foldamers and sacrificial template method. As compared to polymer vesicles, an inorganic and organic-inorganic hybrid vesicle shows superior strength and resistance. But they often require tedious synthetic strategy involving sacrificial template and layer-by-layer self-assembly. Various attempts have been reported in literature for the preparation of hybrid vesicles by solvent-assisted self-assembly.

Nowadays two- or three- dimensional micropatterned polymer surfaces have gained increasing interest because of its potential applications in modern science and technology (Cole., 2008; Cui et al., 2008; Jeong et al., 2010; (Zhang et al., 2007; (Hiller et al., 2002;). Various techniques, such as soft lithography (Tung et al., 2007), self-assembly of block copolymers (Liu et al., 2007; Wang et al., 2006), solvent-nonsolvent-polymer solution phase separation (Widawski et al., 1994), breath-figure method (Escal et al., 2012; Stenzel et al., 2006; Bunz., 2006; Zhang et al., 2014), and replication method using different templates (Ke et al., 2010; Galeotti et al., 2011; Li and Zhang., 2007) . However, in most of the cases fabrication of micropatterned polymer surfaces needs expensive and delicate equipment and also specially designed and synthesized starting polymer materials. Recently Nair et al., 2010 reported microvesicles through self assembly of polystyrene clay nanocomposite particle and also micropatterned PCN films by breath-figure method.

In this paper, an attempt is made to prepare microvesicles of uniform size and also two-dimensional micropatterned polymer surfaces by using adduct modified clay by varying the polystyrene-clay nanocomposite loading (1 mg/mL – 20 mg/mL) in tetrahydrofuran (THF) solvent. Another application of PSC is that uniform polymer films can be prepared using THF solvent at a higher concentration above 50 mg/mL.

3.3. EXPERIMENTAL

3.3.1. Materials.

Styrene monomer (99%), Oleic acid (OA), Acrylic acid (AA), Cinnamic acid (CC) and Cetyl Trimethyl Ammonium Bromide (CTAB) was purchased from Sigma-Aldrich Chemicals, USA. Sodium montmorillonite (Na^+ -Mt) was obtained from Southern Clay Products, USA with a cation exchange capacity (CEC) of 92.6 meq/100g. The initiator Benzoyl peroxide (BPO) from SD Fine Chemical Ltd., India was recrystallized from ethanol. Ethanol, Methanol, Toluene and Tetrahydrofuran (THF) of HPLC grade were obtained were obtained from Merck Specialties Pvt. Ltd., India.

3.3.2. Methods

3.3.2.1. Modification of Clay

Modification of Na^+ -MMT using adduct was adopted for the first time. Adducts have a cationic centre along with a reactive functional group which take part in the intercalation reaction with styrene monomer. The modification of the Na^+ -MMT (0.5 wt.%) is done by ion exchange reaction using adduct in deionised water. Adducts are synthesised by reacting quaternary ammonium salt (CTAB)

with unsaturated acrylic acid (AA). The resulting reactive cation is used to organo-modify the Na⁺-MMT. The 1:1 equimolar concentration of the AA-CTAB mixture (equivalent to 2 CEC of the clay) was slowly added to the clay suspension at ambient condition and was magnetic stirred uninterrupted for 48 hrs. The adduct modified clay suspension is recovered by ultra-centrifuging at 5000 rpm for 30 min. Product purification is done through washing and ultra-centrifuging the sample repeatedly with ethanol to remove any excess of intercalating agent. Finally the organo-modified clay is dried overnight in vacuum oven at 80°C to obtain Acrylic acid - CTAB adduct modified clay (AC-AMC).

The same procedure was used to prepare Cinnamic acid-CTAB and Oleic acid-CTAB adducts modified clay. The resultant modified clays were identified as (CC-AMC) and (OC-AMC), respectively.

3.3.2.2. Synthesis of Polystyrene Clay Nanocomposite.

The Polystyrene-clay nanocomposite (PSC) was synthesized by in situ intercalative polymerization of styrene with the AC-AMC. The PSC loaded with 10 wt.% adduct modified clay (AMC) were used for further studies, since the maximum yield and better self-assembling property was obtained at these loadings. Preferred amount of the modified clay was dispersed in 1g of styrene by ultra-sonication and benzoyl peroxide (2 wt.% of the monomer), was added under nitrogen atmosphere and magnetic stirred (~1000 rpm) for 12 h. Polymerization was carried out by keeping in a temperature controlled oil bath at 70°C for 3 h during which gelation of the mix occurred and then at 90°C for 10 h to obtain the nanocomposite. The residue was dispersed in toluene and reprecipitated by

adding methanol. The product obtained was filtered, and dried at 60°C in vacuum under reduced pressure. The yield was noted and was used for self-assembling studies of the PSC. Vesicles were prepared from solution of PSC particles in THF at concentration of 2.5 mg/mL by drop-casting the solution on a glass plate followed by evaporation of the solvent at ambient temperature. Guest-encapsulated vesicles were prepared by adding fluorescent dyes such as Rhodamine-6G (R-6G), 8-Anilinonaphthalene-1-sulfonic acid (ANS), and R-6G dye with triglyceride oil as guest molecules following the above procedure. Unencapsulated guest molecules were removed by repeated washing using methanol. Micropatterned PSC surfaces were obtained by drop-casting 20 mg/mL of PSC particle in THF on a glass slide under ambient conditions. Uniform film of PSC particles were obtained at a higher concentration above 50 mg/mL THF solvent.

3.3.3. Characterization Techniques

Self-assembly and morphological changes of PSCs were characterized using Scanning Electron Microscopy (SEM) Samples for SEM were prepared by drop-casting dilute solutions of PSC in THF on glass slides, followed by evaporation of the solvent at ambient temperature All the samples were dried at ambient conditions overnight. SEM images were taken in JEOL JSM-5600 LV scanning electron microscope using samples provided with a thin gold coating using JEOL JFC-1200 fine coater. Dye-encapsulated vesicles were characterized using Leica DMLB2 fluorescence microscope. Release characteristics of the encapsulated dye molecules were studied using SPEX-FluorologF112X spectrofluorimeter.

3.4. RESULTS AND DISCUSSION

Solvent assisted self-assembling study and formation of Polystyrene-clay nanocomposite particle by in situ polymerization of styrene with 10 wt % POSS-modified clay having reactive vinyl groups was reported earlier (Nair et al., 2010). Therefore, PSC with 10 wt % clay loading was used for further studies.

3.4.1. Self-assembled uniform microvesicles

In the present study various morphologies were observed by concentration dependent self assembly of PSC particles in THF solvent. The self assembled structures were characterized by SEM, Optical microscopy and Fluorescence microscopy. Formation and mechanism of polymer nanocomposite particle, vesicle and micropatterned film using POSS-modified clay nanocomposite was reported earlier in our work (Nair et al., 2010). As the POSS preparation was tedious and requires several days for its formation, here we adopted a much simpler step for clay modification using adducts. These adduct modified clay nanocomposite exhibited better self-assembling properties in solvent like THF and also resulted in significant improvement in physical and barrier properties. It was observed that nanocomposite prepared using AC-AMC at 10 wt % clay loading produces more uniform vesicles and micropatterned film than other to modified composite. Self-assembling studies were carried out by drop-casting solutions of PSC in THF at different concentrations (i.e., 1, 2.5, 20, 60 mg/mL) showed different dimensions and morphological features. Upon drying the solvent different self assemblies like particles, vesicles (hollow microspheres), microporous films and uniform non-patterned films were obtained as observed

under SEM, optical and fluorescence microscopy. Therefore, concentration dependent aggregation and morphological transitions were studied in detail by observing the change in the microscopic features of drop-cast residues with increasing concentrations of PSC solutions in THF.

The changes in self assembling features were initially examined by Optical Microscopy (OM). Figure 3.1, 3.2, and 3.3 shows the optical micrographs of drop-cast residues of PSC-OC, PSC-CC and PSC-AC, respectively at different concentrations. At 2.5 mg/mL PSC/THF concentration, almost uniform microspheres were observed. More or less uniform microporous structure was observed at 20mg/mL concentration and finally a featureless film at a higher concentration of 50 mg/mL was observed for all the PSC in THF solvent.

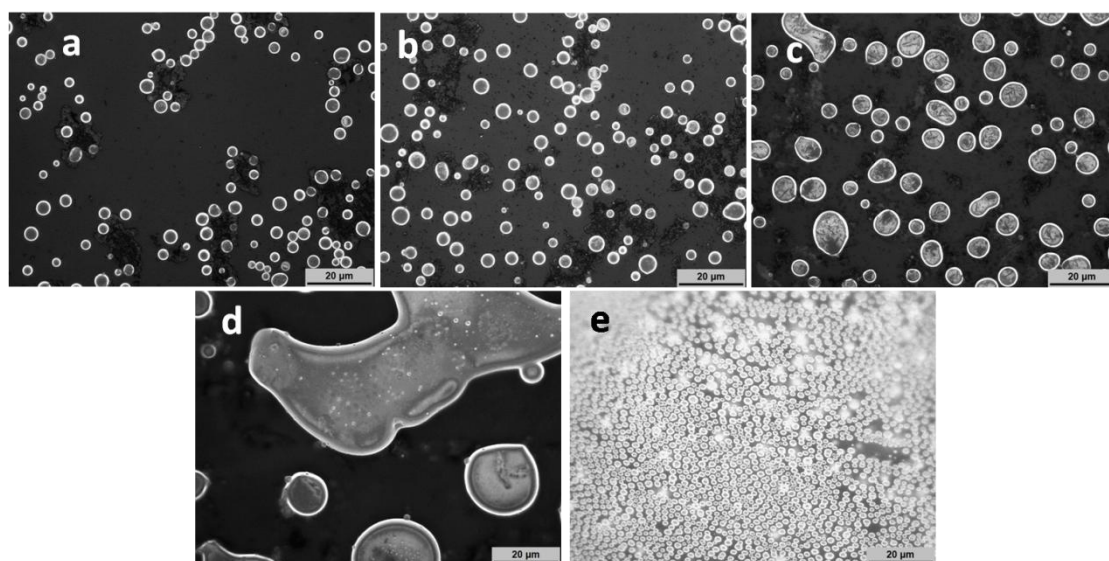


Figure 3.1. Optical micrographs of PSC-OC at (a) 1 mg/mL (b) 2.5 mg/mL (c) 5 mg/mL (d) 15 mg/mL and (e) 20 mg/mL concentration in THF solvent

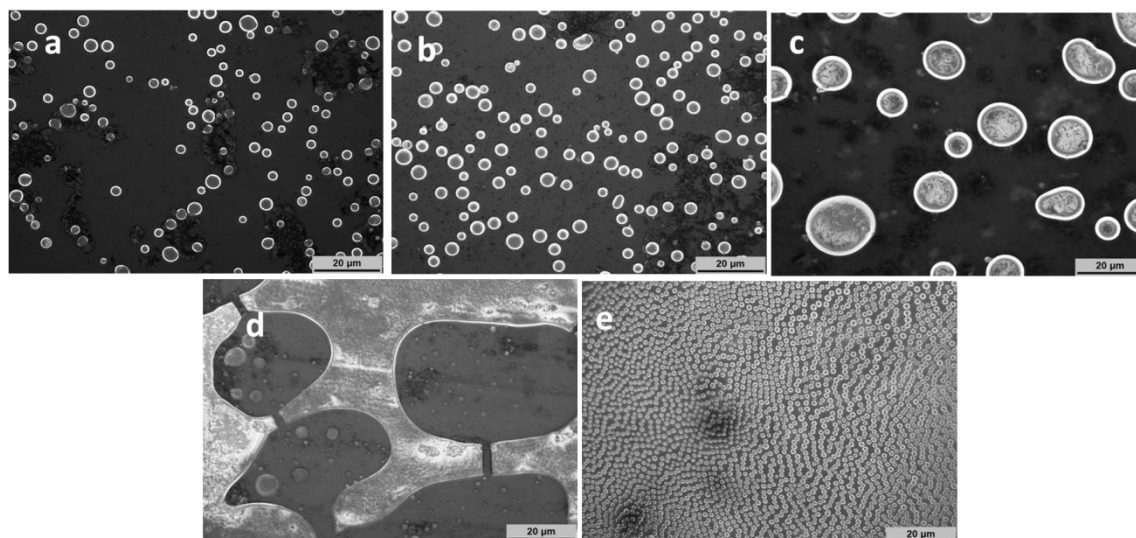


Figure 3.2. Optical micrographs of PSC-CC at (a) 1 mg/mL (b) 2.5 mg/mL (c) 5 mg/mL (d) 15 mg/mL and (e) 20 mg/mL concentration in THF solvent

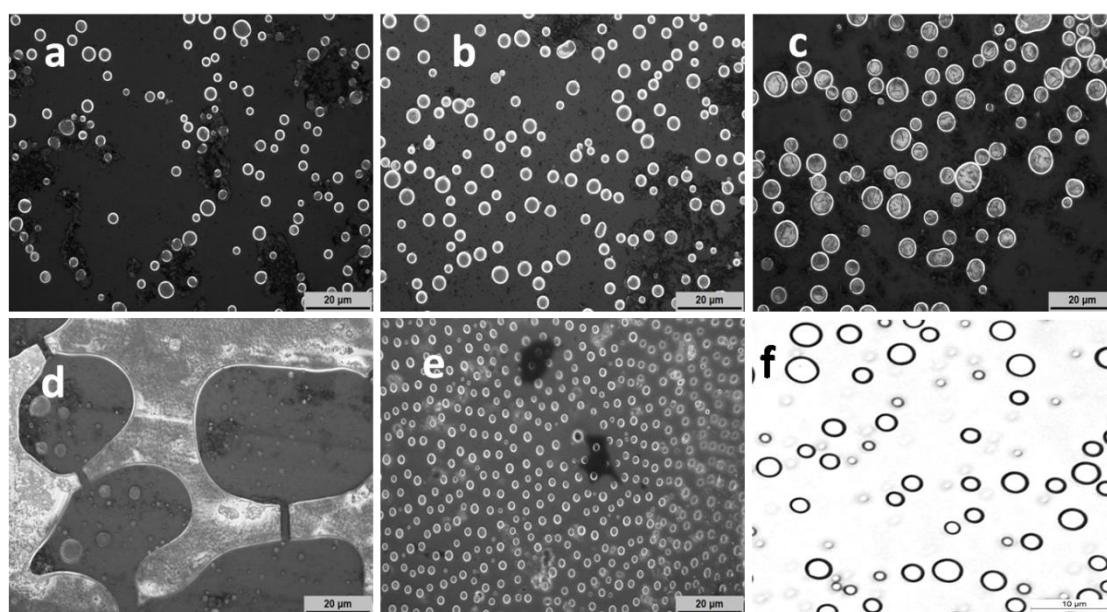


Figure 3.3. Optical micrographs of PSC-AC at (a) 1 mg/mL, (b) 2.5 mg/mL, (reflection mode) (c) 5 mg/mL, (d) 15 mg/mL, (e) 20 mg/mL and (f) 2.5 mg/mL (transmittance mode) concentration in THF solvent

Since uniform microsphere and uniform micropatterned film was obtained using PSC-AC than other two PSCs, further self-assembling studies were carried out using PSC-AC. A clear picture of the aggregation patterns and morphological transition of PSC-AC was obtained by SEM. Figures 3.4 and 3.5 shows the SEM images of drop-cast residues from solutions of different concentrations. As reported earlier, the residue from concentration of 0.001 mg/mL showed particles of nanometre size (Nair et al., 2010). The particle size significantly increased with increase in concentration and larger particles and microspheres were found at 1 mg/mL concentration as shown in Figure 3.4a. Whereas, at 2.5 mg/mL concentration in THF the residue was mainly microspheres (vesicles) of size in the range of 2 - 3 μm by consuming all the primary particles (Figure 3.4b & 3.4c).

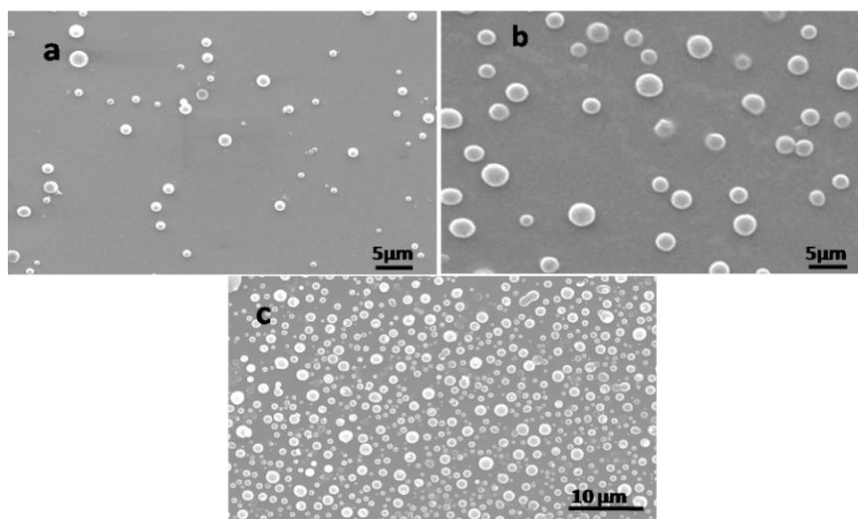


Figure 3.4. SEM micrographs of (a) 1 mg/mL PSC-AC/THF, (b) and (c) 2.5 mg/mL PSC-AC/THF showing concentration dependent formation of vesicle

The hollow and vesicular nature of the spheres was confirmed further by Fluorescence microscopy.

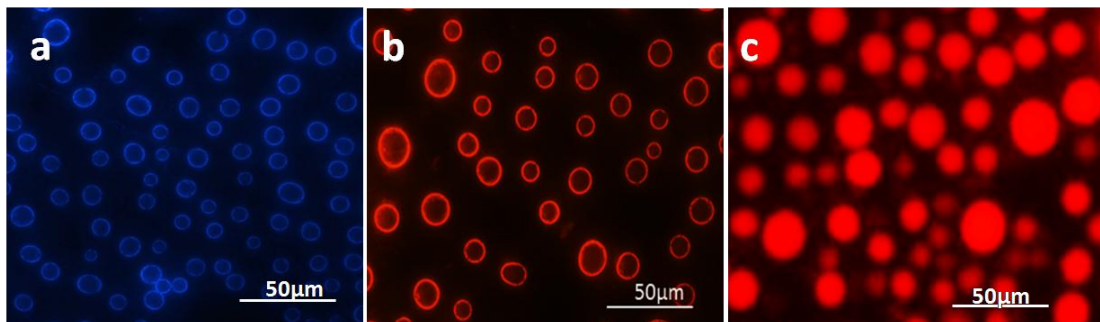


Figure 3.5. (a) Fluorescent micrographs of vesicles containing 8-anilinonaphthalene sulfonic acid (ANS), (b) Rhodamine 6G (R6G) and (c) triglyceride oil containing R6G at 2.5mg/mL PSC-AC/THF

Figure 3.5a, 3.5b, and 3.5c respectively, shows the fluorescent micrographs of the guest encapsulated vesicles containing dyes like 8-anilinonaphthalene sulfonic acid (ANS), Rhodamine 6G (R6G) and triglyceride oil in which R6G was dispersed. The sample was prepared by drop-casting and drying of PSC-AC solution containing different fluorescent dyes. Fluorescence was due to dye adhering to the inner walls of the dried vesicles. Oil-encapsulated vesicle appeared fully fluorescent due to uniformly dispersed dye in the oil phase filling the inner volume of the vesicles.

The mechanism suggested for the formation of vesicle is similar to that reported in our earlier. Here, PSC particle act as bilayers with stacked silicate layers bearing free edge-hydroxyls sandwiched between hydrophobic PS layers. Similar to block copolymers when dissolved in suitable solvents they spontaneously self assemble into bilayer through H-bond, di-polar interaction and columbic interactions. As the bilayer grows in size, they close to form vesicle due to high surface tension. THF acts as a good solvent for the PS surface layers but a

poor solvent for the cross-linked silicate layers. Interparticle interaction through the solvated PS layer is prevented due to steric repulsion. Instead, H-bonding interactions between the particles through hydroxylated edges of the silicate layers favour formation of extended bilayer, which closes to form a microvesicle.

3.4.2. Micropatterned polystyrene-clay nanocomposite film

From SEM images mixed morphologies were observed at concentrations between <5 mg/mL and >20 mg/mL (Figures 3.6). Figure 3.6a shows solution concentration at 5 mg/mL in which non-uniform vesicles were observed. At 10 mg/mL (Figure 3.6b) PSC-AC/THF giant vesicles of size $> 5\mu\text{m}$ was observed. And as concentration was increased to 15 mg/mL (Figure 3.6c) broken vesicles was observed.

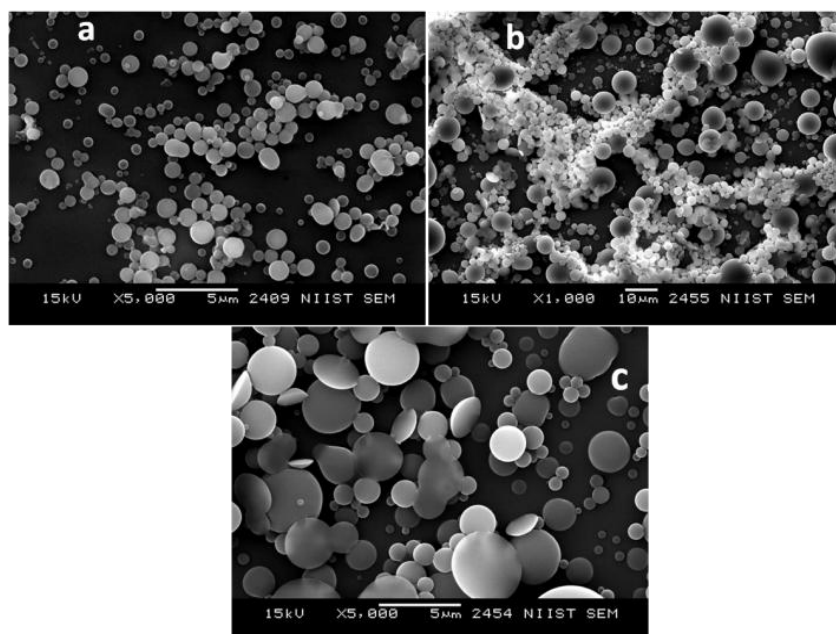


Figure 3.6. SEM micrographs of of PSC-AC/THF at (a) 5 mg/mL, (b) 10mg/mL, and (c) 15 mg/mL solution concentration

This can be explained as, when the concentration increases beyond a critical volume closure of extended bilayer become difficult due to volume constraint. Therefore instead of bending of individual lamella, coalescence of the layers during drying of the solvent leads to the formation of microporous or neat film. This mechanism was followed for the formation micropatterned film by vesicle fusion and generally produces 3D porous structure. However evolution of more or less uniform microporous structure was observed at solution concentration 20 mg/mL PSC-AC/THF (Figure3.7) in which open pores formed a two-dimensional array over a solid film and the mechanism proposed was breath figure. The surface of the micropatterned film with concavity diameter ranging from 1 μm - 1.5 μm and thickness of the strut from 300-800 nm was obtained at 20 mg/mL of THF.

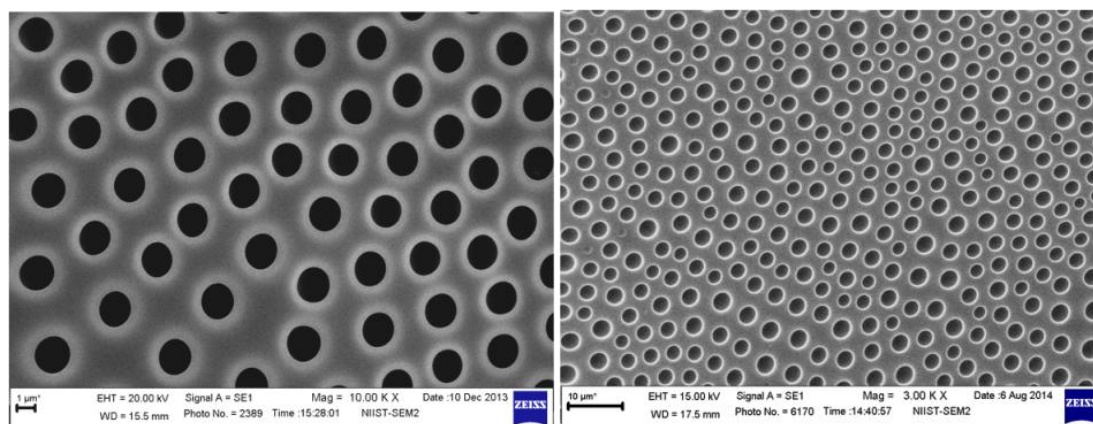


Figure 3.7. SEM micrographs of PSC-AC micropatterned film from 20 mg/mL PSC-AC/THF at high and low magnification

The mechanism suggested for the formation of 2D microporous film is breath figure or moisture induced phase separation. Pore size mainly depends on relative humidity, solution concentration and solvent evaporation rate. However

breath figure does not form in an atmosphere that has less than 50 % relative humidity. In the present study a high ambient humidity of 70-80% relative humidity is maintained during drop casting of polymer solution. And this results in the nucleation of the water droplets on the surface of the solution due to evaporative cooling. Subsequently, these water droplets start growing and rafts of non-coalescing droplets were formed. These droplets organise on the surface in to highly mobile hexagonally close packed array and starts sinking into the solution. Array of pores are formed on drying of the remaining solvent and leaves the imprint of the water droplets in the film. And these water droplets were channelled through the hydrophilic inter-phase between PSC particles as shown in Figure 3.8.

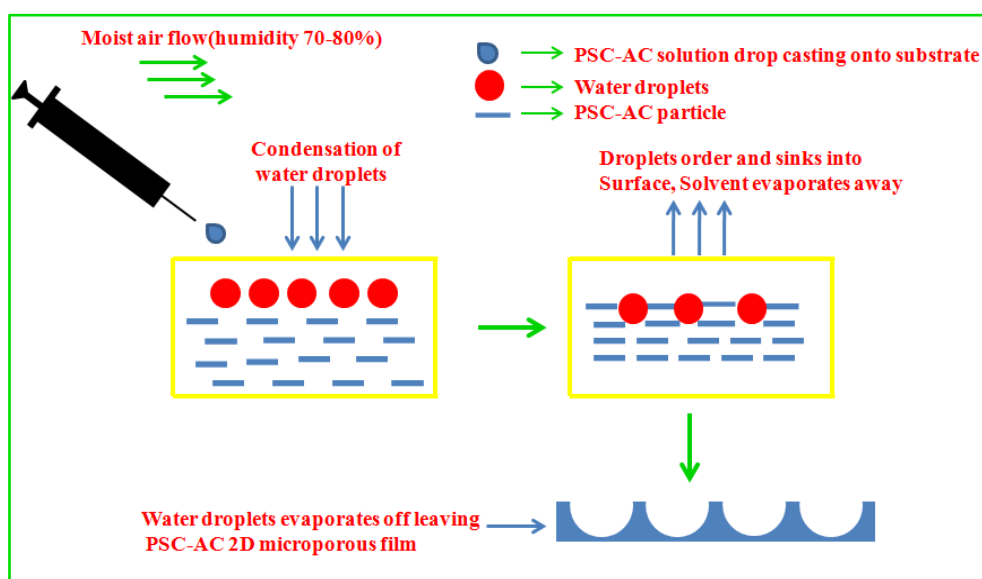


Figure 3.8. Formation of micropatterned film of PSC-AC by Breath figure mechanism

Further, at 30 mg/mL solution concentration sinking and deformation of uniform microporous film was observed (Figure. 3.9a) and at 40 mg/mL a clear view of

intermediate state of both porous film and non-patterned film was observed in Figure. 3.9b. At very high concentration above 50 mg/mL formation of a solid film or a non patterned PSC film was only observed in THF solvent. Figure 3.9c shows the broken edge of solid film at 60 mg/mL PSC-AC/THF. This was due to high viscosity of solution which prevents the sinking of water droplets on to the polymer surface and restricts the formation of concavities.

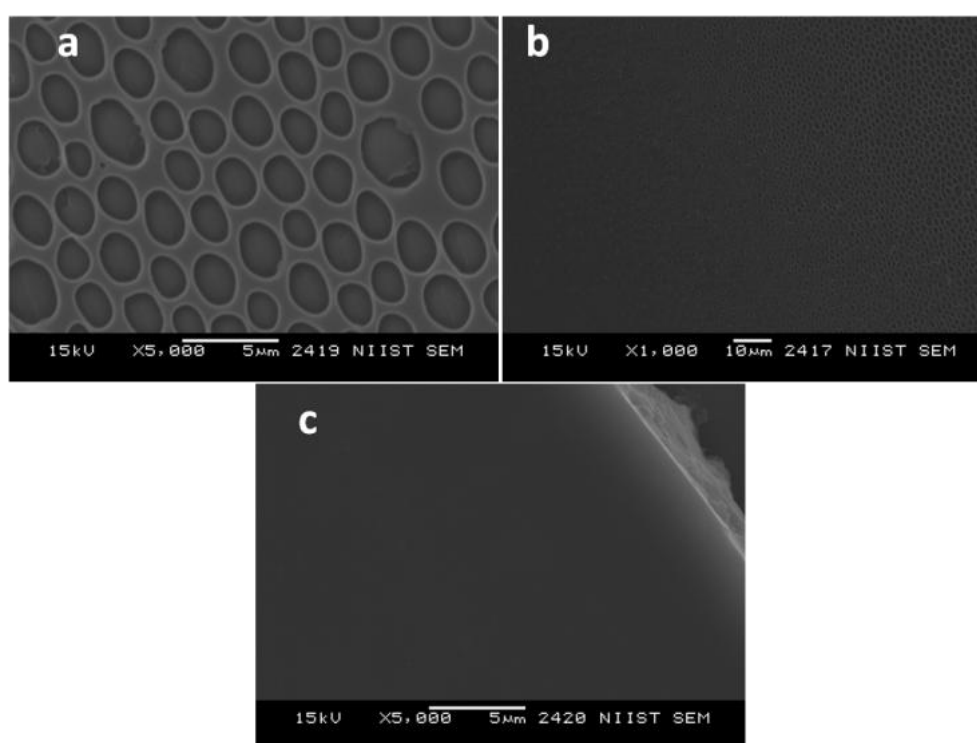


Figure 3.9. SEM micrographs of of PSC-AC/THF at (a) 30 mg/mL, (b) 40 mg/mL, and (c) 60 mg/mL solution concentration

3.5. CONCLUSIONS

In-situ polymerisation of styrene with three different adducts modified clay having reactive functional groups were used for nanocomposite preparation. Among the three composite, PSC-AC was found to exhibit better self-assembling properties rather than PSC-OC, PSC-CC. PSC-AC particle exhibited solvent

assisted self assembly in highly volatile THF solvent by varying the solution concentration from range (1-50 mg/mL). Uniform vesicles of 2-3 μm are produced by lateral association of PSC-AC particle through H-bonding interactions between edge hydroxyls of the silicate layers on drop casting and drying of the PSC-AC solution on glass slide. The potential use of these vesicles was they can be used as microstorage system and drug delivery vehicles. And relatively uniform two dimensional microporous film with concavity diameter 900nm -1.2 μm of long range order were produced at solution concentration of 20-40 mg/mL. The mechanism for the formation of two dimensional microporous film was breath figure mechanism in which the extended bilayers formed closely packed lamellar arrangement. These micropatterned films can find application in several fields such as scaffolds. Above 50 mg/mL concentration formation of a solid film or a non patterned PSC-AC film was obtained due to high viscosity of PSC-AC solution which prevents the sinking of water droplets on to the polymer surface and restricts the formation of concavities. These neat films at 50 mg/mL concentration can be used for anti-corrosion application as protective coatings for metals and alloys due to its non-patterned film formation in which the exfoliated clay platelets act as effective barrier against attacking species by increasing the diffusion pathway.