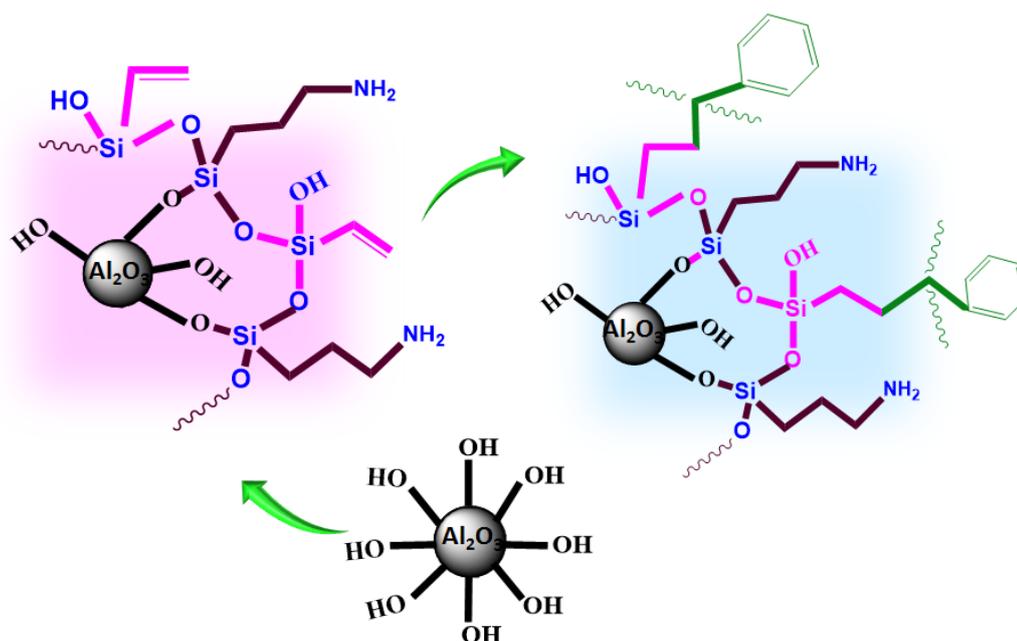

SYNTHESIS AND CHARACTERIZATION OF AMINO-FUNCTIONALIZED AMPHIPHILIC- ALUMINA NANOPARTICLES



2.1. ABSTRACT

Synthesis and characterization of amino-functionalized amphiphilic-modified alumina nanoparticles, which were used for producing breath-figure (BF) patterned polystyrene-alumina hybrid films with amino-functionalised cavities, are described in this chapter. The desired modification was accomplished by treating the particles with a mixture of aminopropyltriethoxysilane (AS) and vinyltriethoxysilane (VS) in ethanol followed by *in-situ* free-radical polymerization of styrene monomer through the vinyl group. Styrene/alumina (S/A) molar ratio was varied to produce particles having varying hydrophobic/hydrophilic (Hb/Hp) balance. The modified particles were characterised by FT-IR, dispersion characteristics in selected organic solvents

and polystyrene solutions by Dynamic light scattering (DLS) analysis. Dispersion-loading limit of the particles in polystyrene matrix was characterised by XRD and optical microscopic analysis of the hybrid films.

2.2. INTRODUCTION

The pre-requisite for producing particle-assisted breath figure (BF) patterned films with functionalized cavities is the introduction of proper functionality to the nanoparticles. Besides, the particles should be dispersible in polymer solutions and the suspensions should be stable for a reasonable period to avoid particle settling before drying off the solvent during the formation of films. The hydrophilic inorganic particles in general exhibit poor dispersion and suspension stability in organic solvents, demanding appropriate surface modification of the particles.

Inorganic nanoparticles have been widely used as a filler in polymers for several decades since the resulting polymer-inorganic hybrids often exhibited improved physical and mechanical properties (*Bruzaud et al, 2014*). Although many processing techniques are developed for the preparation of polymer inorganic hybrid nanocomposite, the challenge of the process lies in the dispersion of the inorganic nano fillers in the polymer frame work and to improve the compatibility between the filler and the matrix due to their high specific surface area. This problem is resolved to a great extent by the surface functionalization of particle. Trialkoxy silanes coupling agents having general formula $(RO)_3SiX$ were widely accepted for this purpose (*Arkles, 1977; Nishida et al., 2002*). Under suitable conditions, the active silanol group formed from the hydrolysis of alkoxy moiety (RO-) condenses with the hydroxyl group on the inorganic particle surface to form a stable oxane bond (*Truong et al., 2010*). The non-hydrolysable groups 'X' possess functionality and impart

desired characteristics to the inorganic particles. The functionalities present on the particle surface either improve compatibility or promote the chemical bonding between the inorganic fillers and the organic phase, thereby improving the stability of the nanocomposite (Li et al., 2007). Modification of the particles with an organic modifier which has a similar chemical structure of the matrix material is preferred for enhancing the compatibility with the organic phase (Tanev et al., 1994).

The main objective of the present investigation is to fabricate BF patterned polystyrene-alumina hybrid films with amino-functionalized cavities. Since the hydrophilic amino-functionalised alumina did not yield desired results, amphiphilic-modified particles were used. Amino-functionalised amphiphilic particles were produced by treating the particles with a mix of silanes bearing amino and vinyl groups, followed by polystyrene-modification through the vinyl group. The synthesis and characterization of amino-functionalised amphiphilic-alumina nanoparticles is presented in this chapter with an intention to use them as a breath figure stabilization constituent of polystyrene-alumina hybrid film

2.3. EXPERIMENTAL

2.3.1. Materials

The alumina particles (aps ~100nm) used in this work were purchased from Sumitomo cooperation, Japan. Commercially available polystyrene (Mol wt. ~ 3.2×10^5 , polydispersity of ~1.6) was used for making the hybrid films. 3-aminopropyltriethoxysilane (AS, 99%) and vinyltriethoxysilane (VS, 97%) were purchased from Aldrich Chemicals. Other materials used are benzoyl peroxide (SD Fine Chemicals Ltd, India), absolute ethanol (SD Fine Chemicals Ltd, India), toluene, tetrahydrofuran (THF), chloroform (CFM), and carbon disulphide (CS₂) (Synthetic

reagent, Merck Specialties Pvt. Ltd., India). Ninhydrin used for the qualitative analysis of amino group was purchased from S.D Fine chemicals.

2.3.2. Synthesis of Amino-functionalized Amphiphilic-Alumina Nanoparticles

2.3.2.1. Silane Treatment

Alumina powder (10g) was dispersed in 100 ml ethanol by sonication for 30 minutes. Simultaneously, a premix of AS and VS (0.3g) in 30 ml ethanol-water mixture (95:5 v/v) was magnetically stirred for 30 minutes. The hydrolysed silane mix thus obtained was added to the alumina suspension under magnetic stirring and stirring continued for 24 hrs. The silane-modified particles were separated by centrifugation, washed with ethanol and dried at 60 °C in a vacuum oven. AS:VS molar ratio was varied from 3:1 to 1:3. The silane-modified alumina particles are designated as A31, A11, and A13 based on AS/VS composition

2.3.2.2. Polystyrene Modification

Polystyrene-modification of silane-treated alumina powder was performed by the '*in-situ*' polymerization of styrene using benzoyl peroxide as the initiator. The styrene to alumina molar ratio was varied from 0.03 to 0.1. Typically, the silane-treated powder was dispersed in toluene and sonicated for 30 minutes (*Branson 3510 Sonicator, 100W-40Hz*). Desired amount of styrene and benzoyl peroxide (0.2 % of styrene) were then added to the dispersed particles. The mixture under nitrogen atmosphere and magnetic stirring was heated initially to 70 °C for 30-60 minutes and then at 90 °C for 12 hrs. The particles were coagulated by adding methanol and separated by filtration. The residue was washed with methanol-toluene mixture to remove free polymer and dried at 100 °C in an air oven.

2.4. RESULTS AND DISCUSSION

2.4.1. Nature of as-received and Surface Modified alumina particles

As-received alumina powder appeared as agglomerates (*SEM, JEOL JSM-5600LV*) of crystalline nanoparticles (figure.2.1 (A)), but dispersible in aqueous medium and protic solvents like alcohol under ultrasonication. The dispersed particles were nearly spherical in shape with size distribution in the range of 70-200 nm (figure 2.1(B)). On the other hand, the powder treated with AS/VS mix was dispersible in polar aprotic solvents like tetrahydrofuran and non-polar solvents like chloroform. However, its suspensions in solutions of polystyrene (PS) in such solvents (used for preparing hybrid films) were highly unstable such that the particles settled down as soon as the agitation was stopped. The XRD profile (figure 2.1 (C)) of the silane modified particles clearly showed the highly crystalline morphology. The TEM-EDAX analysis of the silane treated particles indicated the presence of Si atoms which confirmed the condensation of silanes on the alumina particle surface (Figure 2.1 (D)). Polystyrene-modified silane-treated (SA) particles exhibited suspension stability, depending on the styrene to alumina (S/A) molar ratio employed for the modification. SA particles yield as soft powder which were dispersible in common organic solvents. SA particles with styrene/alumina ratio > 0.07 were suitable for the preparation of nanocomposite with polystyrene as their suspensions in various organic solvents were stable for more than 30 min.

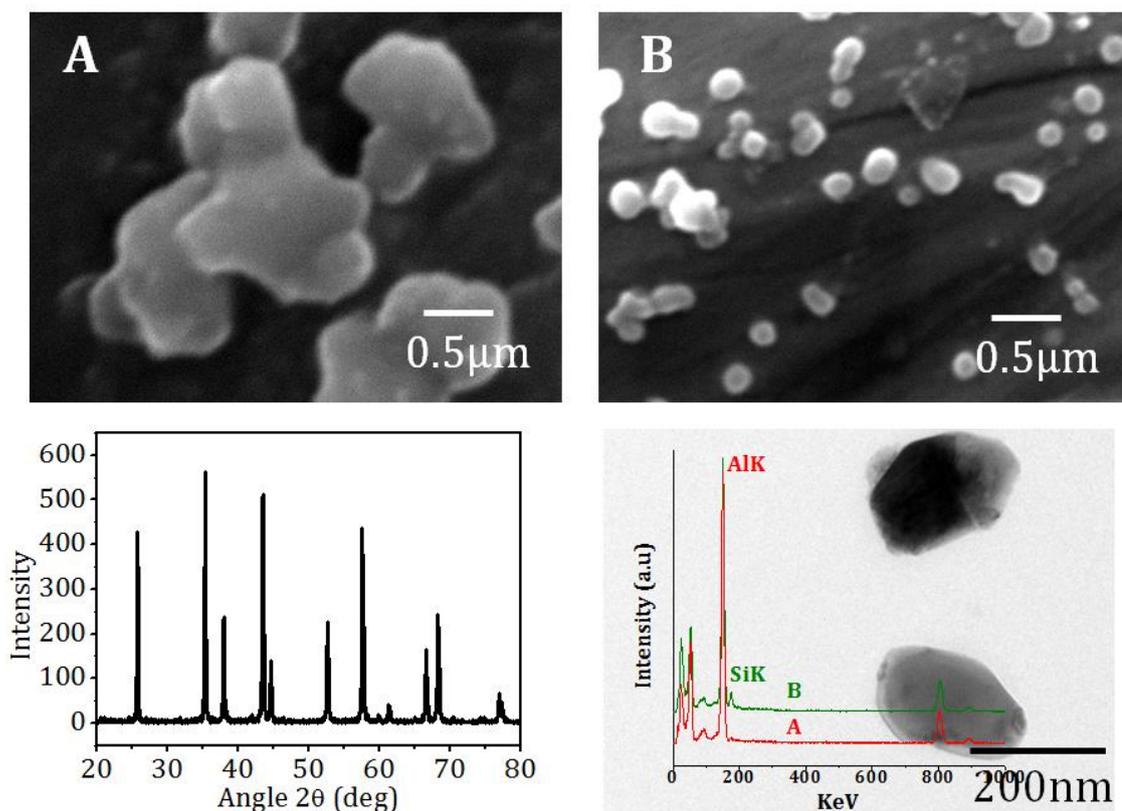


Figure 2.1. SEM images of (A) as-received alumina particles, (B) dispersed alumina particles (C) XRD spectrum of alumina (D) TEM image of silane treated particles along with the EDAX spectrum.

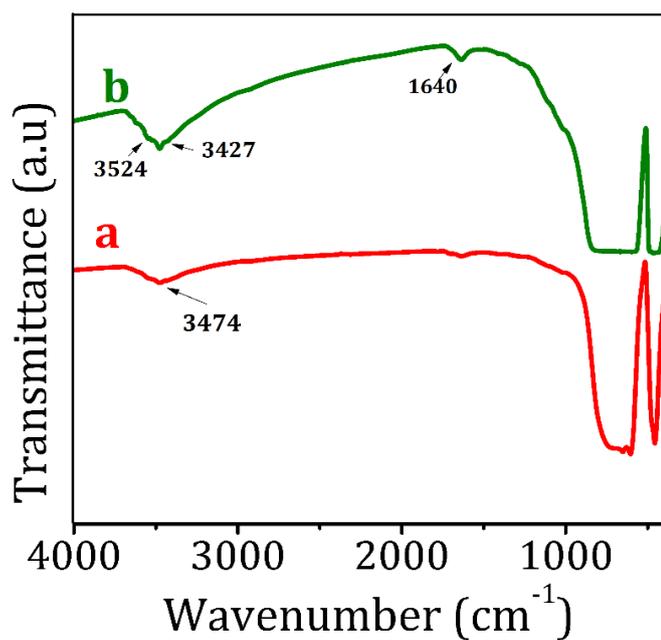
2.4.2. Characterization of Surface Modified Alumina Nanoparticles

2.4.2.1. Structure of Surface Modified Alumina Nanoparticles

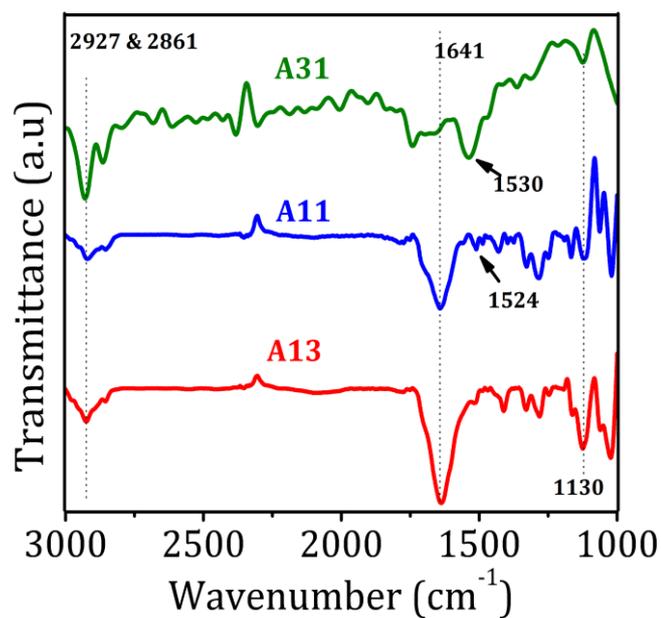
FT-IR (*Perkin Elmer Series FT-IR Spectrometer 2*) spectral data was used for arriving at the tentative structure of the modified alumina particles.

(i) Silane -treated Particles

Figure 2.2 shows the FT-IR spectrum of silane modified alumina particles which are designated as A31, A11, and A13, where the digits indicate the AS:VS ratio. The spectrum of the as-received alumina is also given for comparison (figure 2.2(a)).



(a)



(b)

Figure 2.2. FT-IR spectra of (a) as-received alumina and silane treated alumina (b) silane treated alumina particles A31, A11, and A13

The unmodified alumina showed mixture of OH bands from the surface hydroxyl groups, closely overlapping each other as a broad peak between 3700- 3400 cm^{-1} (Baraton 1996). For silane modified alumina particles additional peaks appeared at 3524 and 3427 cm^{-1} due to the symmetric stretching of amino group in AS and at 1640 cm^{-1} due to the -C=CH stretching frequency of VS.

Since the characteristic peaks of the functional groups of the modifiers were masked by the broad peaks of alumina, FT-IR analysis was carried out between 3000-1000 cm^{-1} for the comparative study of functional group vibrational frequencies of modifiers in A31, A11, and A13 (Figure 2.2 (b)). The formation of oligomeric siloxane on the particle upon silane modification was confirmed by the presence of peaks at $\sim 1130 \text{ cm}^{-1}$ due to the Si-O-Si stretching vibrations in the spectrum of all the three silane modified alumina particles. The presence of propyl group (-CH₂-) stretching vibrations at 2927 and 2861 cm^{-1} and -NH- in-plane bending vibrations at 1524-1530 cm^{-1} confirmed the presence of AS modifier on the particle. Similarly, presence of VS modifier was indicated by the peak observed at 1641 cm^{-1} due to the symmetric stretching of -C=CH group of vinyl silane modifier. IR spectra of silane treated particles also exhibited peak due C-N stretching vibrations of amino propyl group at $\sim 1024 \text{ cm}^{-1}$. From the intensities of the corresponding peaks, amino/vinyl ratio was found as 1:3.4, 1:1.9 and 1:0.25, respectively for A13, A11 and A31, which is approximately agreed with the experimental ratio of 1:3, 1:1 and 3:1. The observations clearly suggested that the oligomeric inter-condensation products of the silane are covalently linked to the particle surface.

The hydrolysis and condensation reactions of AS/VS mixture in water-ethanol medium take place under basic conditions due to the presence of basic amino

group on AS. The silane on hydrolysis converted to silanol group, and these active silanol group undergo condensation to form oligomers with the siloxane (Si-O-Si) bond (Arkles, 1977). This was followed by the condensation reaction with the surface hydroxyl group of metal oxide to form stable Si-O-Al linkage. The non-hydrolysable amino propyl group of AS modifier and vinyl group of VS modifier impart bi-functionality to the alumina particles (Figure 2.4). The hydrolysis and co-condensation of the mixture of AS and VS monomer mainly depends upon the molar ratio and reactivity of the initial monomer (Voronkov *et al.*, 1982). In dilute solutions, inter-condensation of AS and VS takes place in molar proportions in the mix (Nair, 2009). Although AS undergoes faster hydrolysis reactions, the self-condensation reactions of the hydrolysed VS take place rapidly due to the nucleophilic character associated with the vinyl group (Shi *et al.*, 2012). The effect will be more pronounced when AS/VS compositions contain relatively high concentration of VS. This may lead to a variation in the composition of vinyl and amino groups on A13 individual particle. On the other hand A31 exhibited relatively low dispersion in organic solvents due to the higher content of hydrophilic amino groups associated with the particles. Therefore, A11 (alumina particles treated with equimolar ratio of AS/VS silane) was selected for polystyrene modification.

(ii) Polystyrene-modified Amphiphilic Alumina (SA) Particles

Polystyrene-modification was performed by '*in-situ*' polymerization of styrene. Styrene/alumina (S/A) ratio was varied from 0.03 to 1. However, S/A value of 0.07 minimum was found necessary for the suspensions stability for 30 minutes. A11 particles modified with S/A ratios 0.07, 0.09 and 0.1 (designated as 0.07SA, 0.09SA and 0.1SA respectively) were used for further studies.

Figure 2.3 shows the FT-IR spectra (3000-1000 cm^{-1}) of polystyrene-modified alumina particles (xSA, where x corresponds to S/A mole ratio) along with that of A11. For xSA, the peak due to the $-\text{C}=\text{CH}$ vibrations (1641 cm^{-1}) was almost absent due to the involvement of vinyl group in the polymerization. On the other hand, the

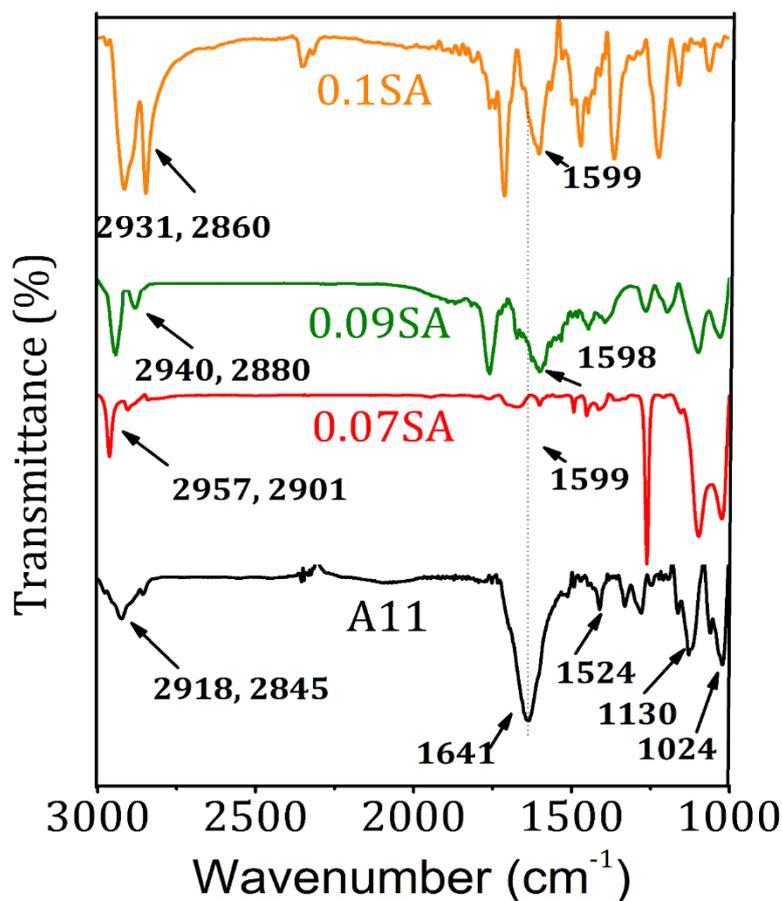


Figure 2.3. FT-IR spectra of SA particles in comparison with silane modified particles (A11)

intensity of the peaks due to alkyl chain (at ~ 2845 & $\sim 2918 \text{ cm}^{-1}$) and due to benzene ring (at $\sim 1599 \text{ cm}^{-1}$) increased with S/A ratio. Moreover, the peak for $-\text{C}-\text{N}$ -stretching at $1020-1060 \text{ cm}^{-1}$ in the A11 shifted to higher wave number for xSA with polystyrene content due to the strain experienced by the aminopropyl group in

presence of the polymeric chain. Polystyrene chain length increases with S/A ratio and the chains are covalently linked to the particle surfaces through vinyl groups.

The polymerization of styrene with the silane modified alumina particles created a polymer layer around the particle surface and grafted on to the particle through the vinyl moiety of the vinyl silane modifier. This was achieved by the participation of the vinyl double bond in the polymerization of the styrene due to its nucleophilic character. The schematic representation of the amphiphilic-modification on alumina particles were depicted in figure 2.4.

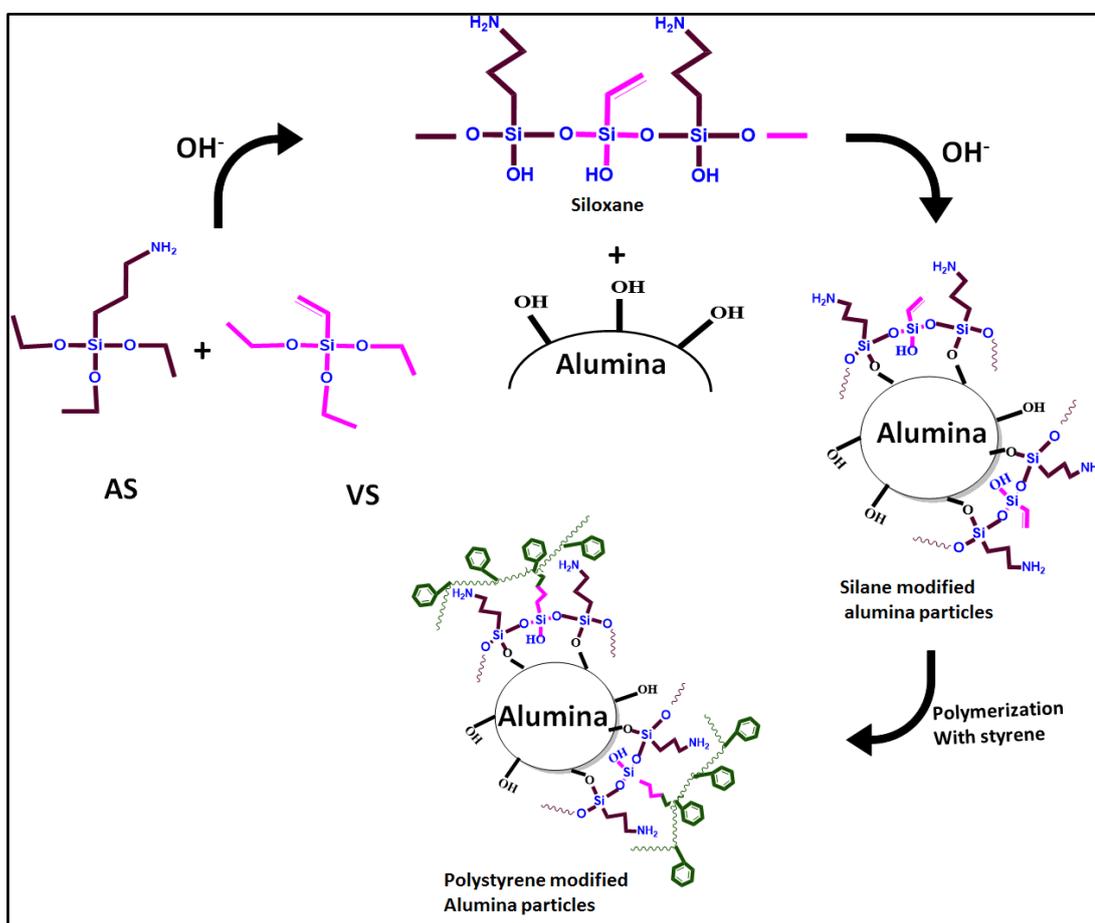


Figure 2.4. Mechanism of amphiphilic-modification on alumina particle surface

Based on the IR spectral studies, the assumed structure of silane treated alumina particles and SA particle were as shown in figure 2.5. These amphiphilic

alumina particles contain the free amino group which acted as a reactive site towards nucleophilic substitution reactions. On the other hand, the polymer chain present on the particles aided the dispersion of the SA particles in various organic solvent and in polystyrene solutions of various solvents.

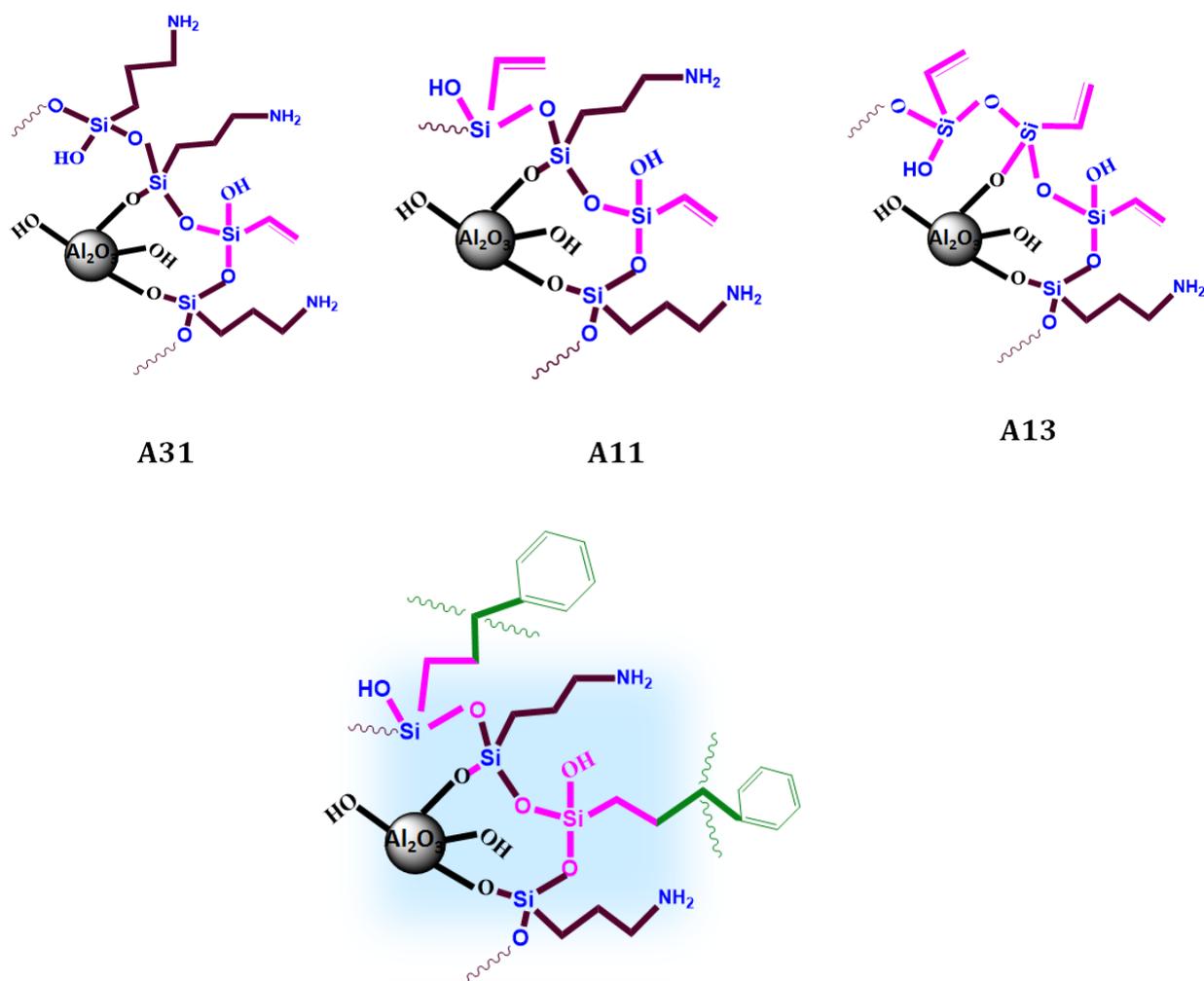


Figure 2.5. Assumed structures of silane treated particles (A31, A11 and A13) and SA particle

2.4.2.2. Hydrophobic/hydrophilic Balance

The hydrophilic amino group and hydrophobic polystyrene associated with the particles impart amphiphilic property to the modified particles. Hydrophilic /hydrophobic (Hp/Hb) ratio was calculated from the contents of aminopropyl silane

group and hydrophobic part (vinyl silane and polystyrene) by thermogravimetric analysis (TGA, Hitachi High-Tech STA 7200) of A11 and SA particles, assuming that A11 contain aminoprpyol and vinyl groups in equimolar proportions. TGA was carried out between a temperatures in the range of 30-700 °C under N₂ atmosphere.

Figure 2.6 depicts the thermogram and derivative thermogram of the SA particles along with the as-received alumina particles and A11. All the samples were thermally stable up to 250 °C. As-received alumina showed a weight loss of 1.1 % during the entire temperature program between 30-700 °C due to the dehydroxylation of surface hydroxyl groups present on the particles. The main weight loss of A11 occurred in a range of 300-700 °C caused by the pyrolysis and removal of aminopropyl and vinyl silanes adsorbed on the alumina surface. The corresponding percentage loss was about 1.75%. The small weight loss observed near 250-300 °C is due to the dehydroxylation of uncondensed hydroxyl groups associated with alumina and silanols (15-20% of alumina surface hydroxyls are available for condensation with silane molecules) and moisture absorbed by these sites.

The decomposition path of SA particles followed two-step weight loss, one at 300-500 °C and other at 500-650 °C. The former was caused by the pyrolysis of silane modifiers and the latter by the decomposition of polystyrene. It can be seen that the weight loss % due to polystyrene content on the particle increased with styrene/alumina (S/A) molar ratio. This was further confirmed by the DTG plots where the intensity of the peak corresponding to the decomposition of polystyrene which increased with increase in the S/A ratio. The percentage of residual water present on the alumina surface decreased with increasing amount of polystyrene on

the particle surface. Obviously, the hydrophobicity of the particles increased with the amount of polystyrene content on the alumina particles. Polystyrene prevents the free hydroxyls from adsorbing atmospheric moisture.

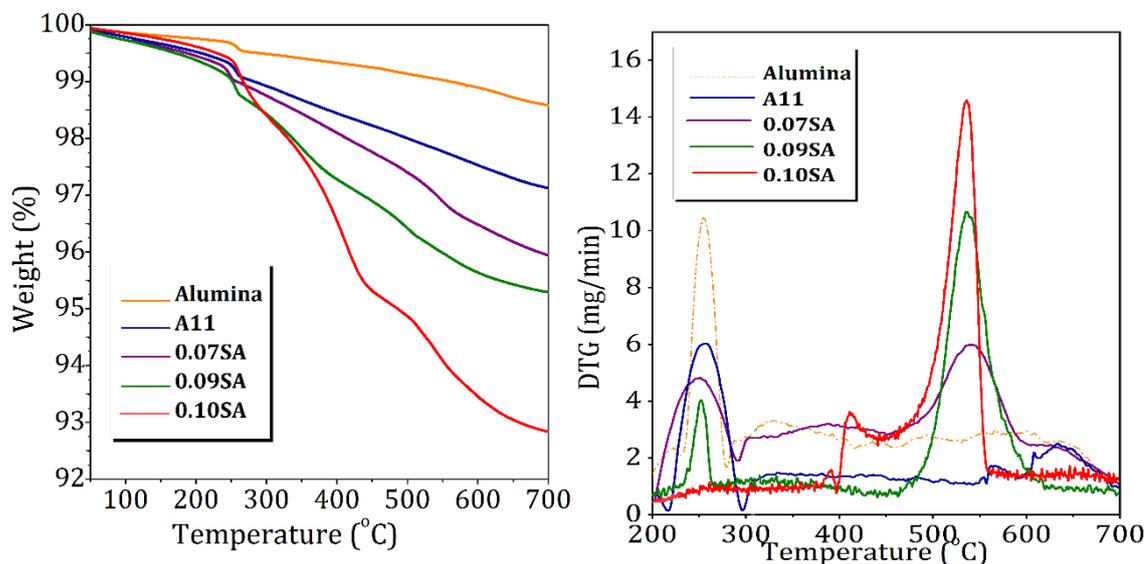


Figure 2.6. (A) TGA and (B) DTG plots of alumina particles, silane modified alumina particles (A11) and various SA particles with different styrene/alumina molar ratio

Table 2.1. Calculation of total polymeric content and the hydrophobic/hydrophilic ratio of the SA particles

Samples	Total Weight Loss (%)	Weight Loss due to silane(%)			Loss due to PS (%)	Hydrophilic (Hp) %	Hydrophobic (Hb) %	Hb/Hp Ratio
		Total	AS	VS				
A	1.1							
A11	2.9	1.8	0.94	0.81				
0.07SA	3.1	1.8	0.94	0.81	1.2	0.94	2.01	2
0.09SA	4.7	1.8	0.94	0.81	1.8	0.94	2.61	2.6
0.10SA	6.1	1.8	0.94	0.81	3.2	0.94	4.01	4

The hydrophobic/hydrophilic (Hb/Hp) ratio of the modifiers on the particle surface was calculated from the percentage of silanes and polystyrene content on alumina particles and was summarized in Table 2.1. The hydrophobic/hydrophilic (Hb/Hp) ratio calculated for 0.07SA, 0.09SA and 0.1SA particles were 2, 2.6 and 4 respectively. Hence, these particles are referred hereafter as 2SA, 2.6SA and 4SA respectively based on their hydrophobicity.

2.4.3. Dispersion Characteristics

The dynamic light scattering (DLS) (*Nano ZS Malvern Instrument*) analysis provides a method for analysing the dispersion behaviour of SA particles in different solvents. The experiments were performed for evaluating the effect of Hb/Hp ratio on the dispersion characteristics of SA particles

(i) Suspensions in Pure Solvents

Figures 2.7 (a-c). show DLS plots of SA (2SA, 2.6SA, and 4SA) particles suspensions in (15 mg/mL) in tetrahydrofuran (THF), chloroform (CFM) and carbon disulphide (CS₂) respectively. From the graph, it can be seen that the particles size distribution showed a wide variation with the Hb/Hp ratio and the type of the solvent. In all the three solvents, the average particle agglomerate size (higher size than the individual particles) decreased with the hydrophobicity of the particles. Table 2.2 summarised the average size of xSA particles in THF, CFM, and CS₂.

The variation in agglomerate size with hydrophobicity was more prominent in CFM and CS₂ than in THF. The average agglomerates size measured in THF was in the range of 390-458 nm. This can be explained as follows. Among the three solvents, THF is miscible with water while CFM and CS₂ are immiscible solvents. Hydration of amino group of the particles by moisture present in the system generates

electrostatic forces between the particles. It is well-known that electrostatic stabilization mechanism is more effective in dilute solutions. In addition, the polystyrene chain present on the SA particles promotes steric forces, the effect which

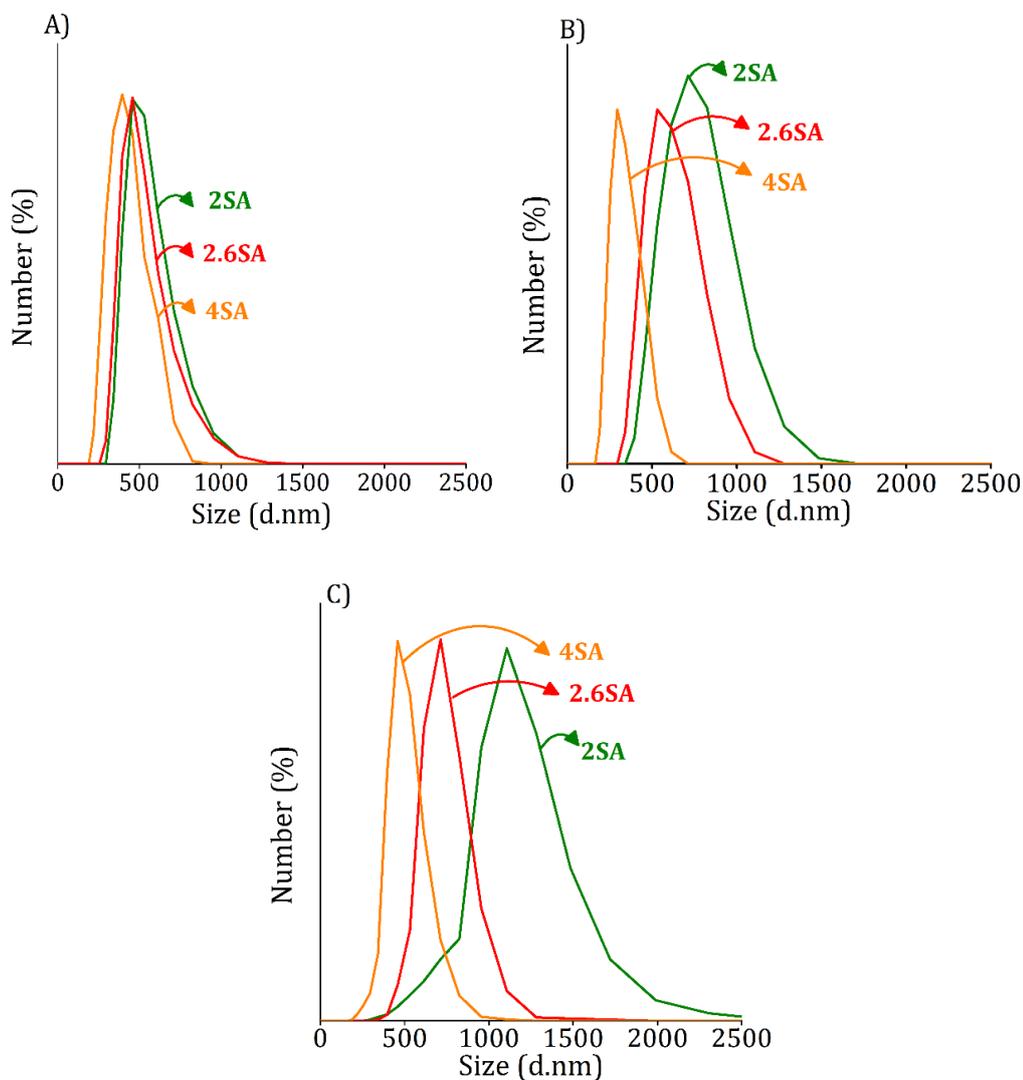


Figure 2.7. DLS plots for SA particles in (A) THF (B) CFM and (C) CS₂.

Table 2.2. Average size of SA particle agglomerates in THF, CFM, and CS₂ measured from DLS analysis

Sample	Average Particle Size (nm)		
	THF	CFM	CS ₂
2SA	458	712	1107
2.6SA	450	530	712
4SA	390	290	465

increased with the polymeric chain length. In short, electro-steric stabilization facilitated the dispersion of SA particles in THF. An effective dispersion was possible even with 2SA particles having an Hb/Hp ratio of 2. Furthermore, the increased polymeric content as in 2.6SA and 4SA particles improved the dispersion in THF indicated by the decrease in the average particles size from 458 nm to 390 nm.

In CFM and CS₂, the particles would experience only steric forces imparted by the polymeric chain present on the SA particles. Particle dispersion improved with increase in Hb/Hp value or polystyrene content in the particle. This could be explained by the interaction between the SA particles and the solvent which depends on the Hansen solubility parameter as well as the polarity of the solvent. According to Hansen solubility parameter, a polymer is soluble in a solvent if the interaction radius R_0 (calculated from the Hansen parameters δ_D , δ_P and δ_H) between the polymer and the solvent is <1 . The less is the value, the more will be the solubility (Hansen, 2007). Based on this calculation, solubility of PS is high in CFM and CS₂ than THF.

Similarly, improved dispersion can also occur with increase in the polymer content. Agglomerate size decreased in the order 4SA < 2.6SA < 2SA. But the particle agglomerate size in 4SA suspension in CS₂ showed a higher value compared to THF and CFM. SA particles are amphiphilic in nature, and a dipole-dipole interaction with the solvent cannot be ruled out. The polarity of THF, CFM and CS₂ are 1.63, 1.04, and 0 D respectively. CS₂ has a zero value of dipole moment and can disperse the amphiphilic-SA particles to a limited extent than THF and CFM. Therefore, a higher agglomerate size was obtained for 4SA particles in CS₂.

(ii) Suspension in Polystyrene Solutions

Particle suspensions in polymer solutions are used for producing micropatterned hybrid films. Good dispersion of the particles and suspension stability is desired for this purpose. Polystyrene (PS) was intended for hybrid films in our investigation. Therefore, it was customary to examine the dispersion characteristic of xSA particles in PS solutions. The suspensions were prepared by dispersing the particles (15 mg) in polystyrene solutions (15 mg/mL) using THF, CFM and CS₂ as the solvents. The suspensions are termed as 'PSA suspension' in the text.

PSA suspensions appeared cloudy indicating the existence of agglomerates which were larger than in pure solvent. Figure 2.8. (a-c) shows the DLS plots of various PSA suspensions in tetrahydrofuran (THF), chloroform (CFM) and carbon disulphide (CS₂) respectively.

From the graph, it is clear that the SA particle agglomerates in PS solution and the size of agglomerates depends on the Hb/Hp ratio of the SA particles as well as the dispersion behaviour in different solvents. From the plots, it is clear that the dispersion behaviour followed the same trend as that in pure solvents. The results are summarised in Table 2.3. It can be seen that the particle-agglomerates in PS suspensions exhibited appreciably higher size than in pure solvents. This may be attributed to stick-slip process that experience with the particles along with polymer chains within the suspension during dispersing. However, the suspensions were stable for more than 30 minutes well covering the working time required for the task.

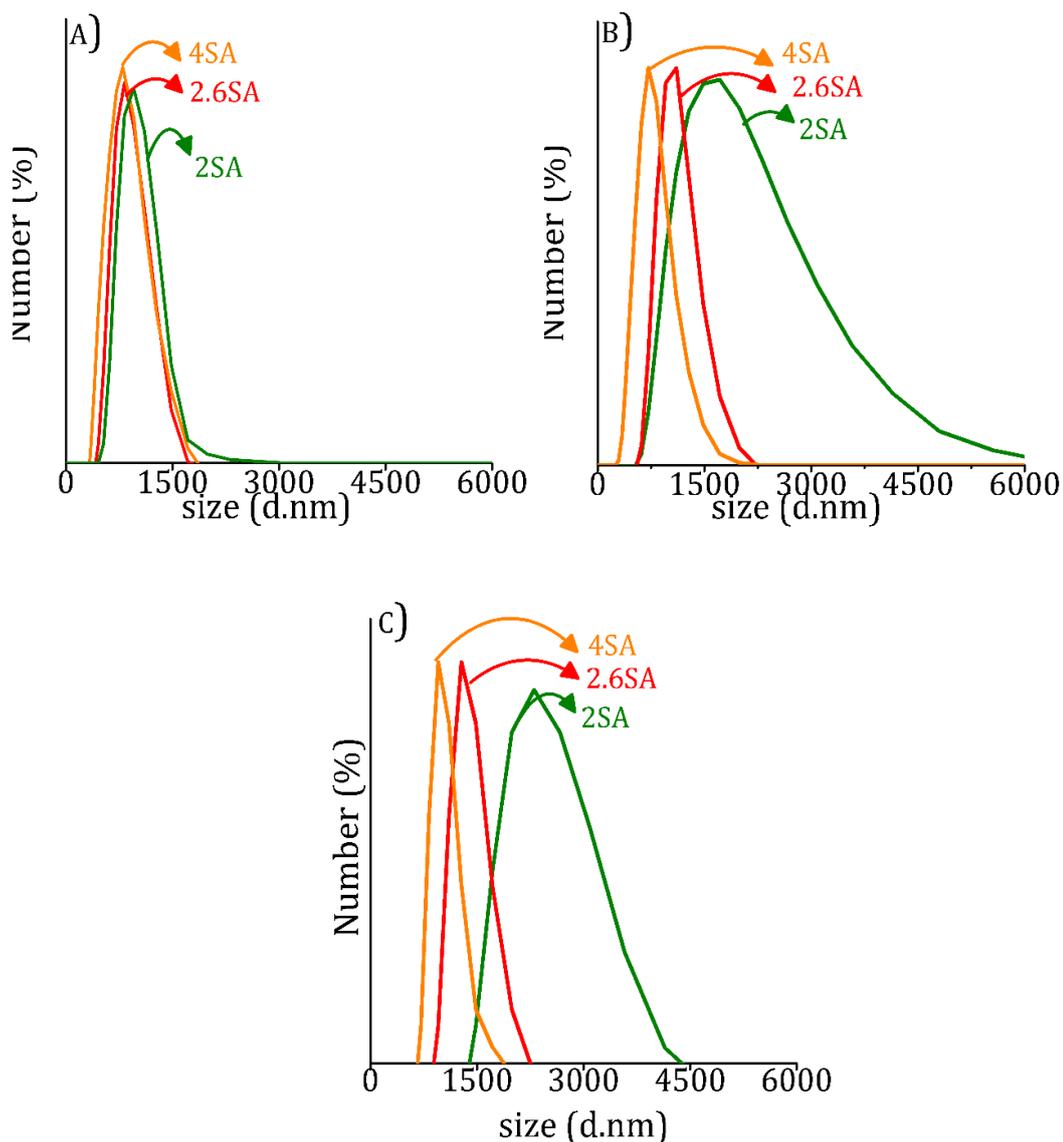


Figure 2.8. DLS plots for PSA suspensions in (A) THF (B) CFM and (C) CS2.

Table 2.3. The average size of SA particle agglomerates in polystyrene solutions of THF, CFM and CS2 measured from DLS analysis

Sample	Average Particle Size (nm)		
	THF	CFM	CS2
P2SA	955	1718	2310
P2.6SA	825	1095	1281
P4SA	800	712	978

2.4.4. Particle Dispersion loading Limit in Polystyrene Matrix

Loading of particles in a matrix meet a limiting point beyond which the dispersed particles begin to agglomerate. Particle-agglomeration in hybrids adversely affects their physical and mechanical properties (*Bruzaud et al, 2014*); microstructure also in the case micropatterned film. In order to study the change in dispersion state with particle loading, hybrid films containing different amounts of 2SA particles in polystyrene (PS) matrix were prepared by casting and drying their suspensions in THF. The experiment was conducted under non-humid conditions in a glove-box to obtain plain surfaces of the films. The hybrids are designated as P_x(ySA) where 'P' represents polystyrene (PS) matrix, 'SA' modified alumina, 'x' alumina content in wt % and 'y' represents H_b/H_p value.

The dispersion of the particles in hybrid films were analysed by X-ray diffractometric analysis (XRD-*Xeuss SAXS/WAXS system by Xenocs*). Figure 2.9 (A) shows the effect of particle concentration in P_x(2SA) system on the intensity of the peaks. Whereas alumina particles exhibited intense peaks at $2\theta=25.7^\circ$ and 35.3° (plot A) due to particle-particle interaction, PS was XRD silent at 2θ between 24° and 36° (Plot B). In the hybrid films, the peaks due to alumina were weak up to a particle concentration of 3 wt % (plot C &D) and then the intensity appreciably increased on increasing the particle concentration to 4 wt % and 5 wt % (plot E & F). Hybrids with well dispersed crystalline nanoparticles generally show shallow broad peaks for the particles and the peaks become dominant on particle agglomeration (*Tadayyon et al, 2011*). Present results indicated that the size of the particles and particle agglomerates increased due to further agglomeration when particle loading exceeded 3 wt % of polystyrene.

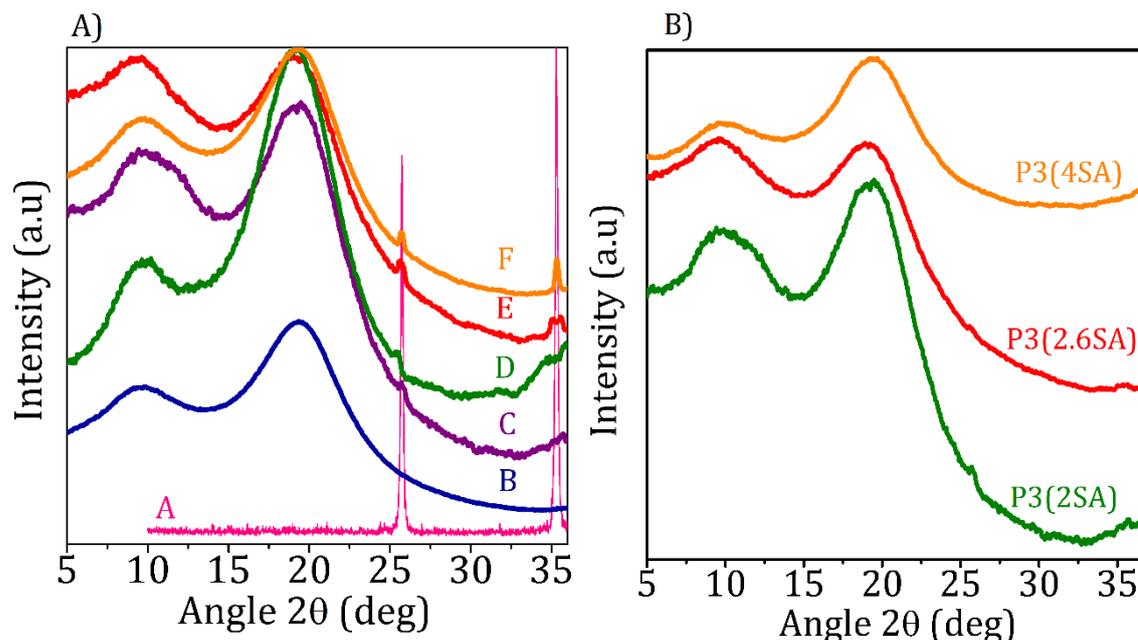


Figure 2.9. (A) XRD at 2θ between 5° and 36° of polystyrene/modified-alumina composite [Px(2SA)] films in comparison with that of the polystyrene matrix and alumina particles, showing the effect of particle concentration on its dispersion in the polymer matrix. (A) alumina, (B) polystyrene, (C) P2(2SA), (D) P3(2SA), (E) P4(2SA), and (F) P5(2SA). **Figure 2.9.** (B) XRD patterns of P3(ySA) films showing the effect of Hb/Hp balance on dispersion state.

It may be worthwhile to note that particle get dispersed better on increasing the Hb/Hp balance of the particles, as can be observed from Figure 2.9 (B). The improvement in particle dispersion is evident from the diminished intensity of the peaks in P3(2.6A) when compared to that in P3(2SA). The intensity further diminished in P3(4SA).

The particle dispersion-loading limit (3 wt %), as indicated by XRD was further confirmed by observing the hybrid films (with particle loading of 2, 3 & 5 wt %) using an optical microscope (*Leica optical Microscope*) under reflection mode. The films were treated with 'ninhydrin' reagent to produce dark shade to the particles exposed at the film surfaces. 10mM ninhydrin solution was prepared by dissolving

requisite amount of ninhydrin in methanol/water mixture (3v/1v). The hybrid films were immersed in the solution in a petri dish for 2hrs. The film was then taken out and dried to 50 °C in an air oven for 1h. Figure 2.10 shows the optical microscopic images of the films. While the spots were scattered in P2(2SA) and P4(2SA), they were more or less uniformly distributed in P3(2SA). This may be explained as following. It may be noted that the films were prepared using THF as the solvent. During formation of the film, the particles suspended in the medium experience a capillary flow induced by the fast evaporation of the solvent and move towards the film surfaces. Consequently, the particles get exposed at the dried film surface. The number of exposed particles depends on its concentration in the suspension. The number of particles increased with particle concentration in the film to a maximum at 3 wt % and then decreased. This shows that the particle dispersion-loading has reached the maximum in P3(2SA). Agglomeration caused reduction in the effective number of particles in P4(2SA). The agglomerated particles can be seen as domains having higher size than that observed in the other two hybrid films.

Kaiser Test (*Kaiser et al., 1970*) is a qualitative test used for the detection of primary and secondary amine using ninhydrin. Ninhydrin produces a deep blue colour known as Ruhemann's blue on reaction with free amines. The reaction mechanism is shown in chart 2.1.

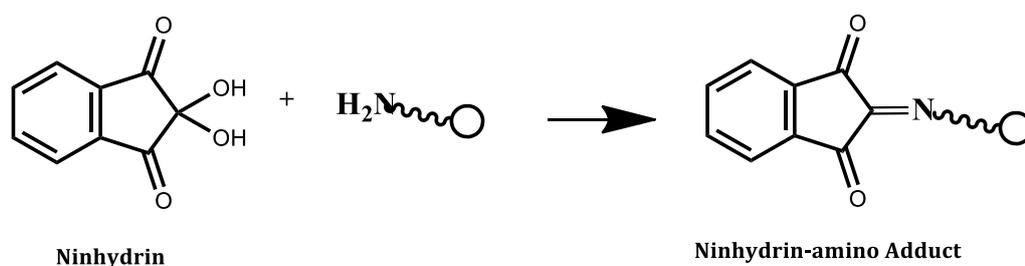


Chart .2.1. Reaction Mechanism of Kaiser Test.

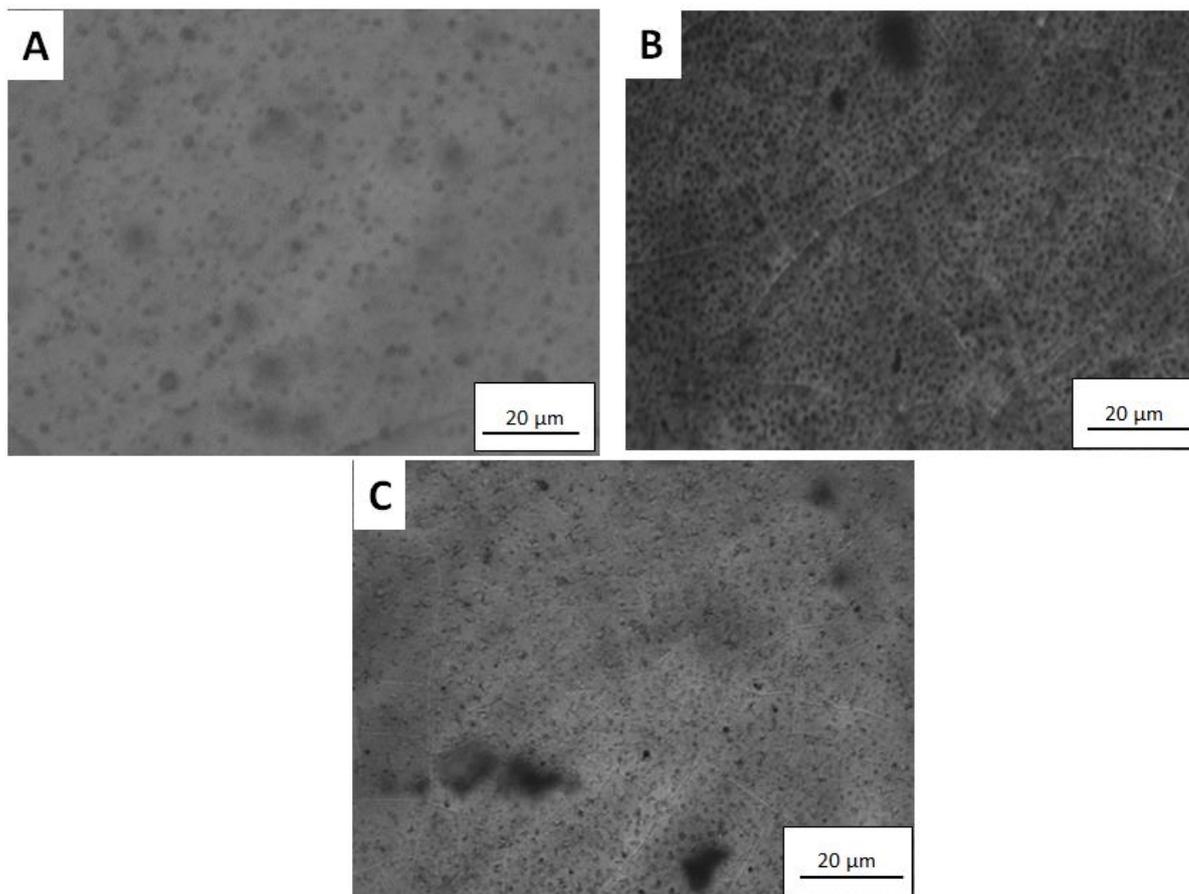


Figure 2.10. Optical microscopic images of ninhydrin treated PSA film (A) P2(2SA), (B) P3(2SA) and (C) P5(2SA).

Incorporation of the amphiphilic particles imparted hydrophilic property to the composites and the hydrophilicity increased as the particle concentration increased. Such a trend can be expected when the surface layer of the films carry increasing amount of particles, exposing the hydrophilic amino groups at the surfaces. The water contact angle measured on the film confirmed such as exposure of amino groups towards the film surface. Water contact angle measurements on the films surface showed that the angle gradually decreases from 101° for PS to 94° for P2(2SA), 87° for P3(2SA), 82° for P4(2SA) and to 76° for P5(2SA). The contact angle vales were summarised in Table 2.4.

Table 2.4. Contact angle of different PSA composite films

Hybrid Film	PS	P2(2SA)	P3(2SA)	P4(2SA)	P5(2SA)
Contact Angle (°)	101	94	87	82	76

2.5. CONCLUSION

Amino- functionalized amphiphilic alumina nanoparticles (SA particles) have been synthesised by a two steps modification process: (i) Silanization of alumina particles with the mixed silane solution of aminopropyltriethoxysilane (AS) and vinyltriethoxysilane (VS) and (ii) *in-situ* polymerization of styrene. The hydrophobic/hydrophilic (Hb/Hp) balance of the particles was tuned by varying the styrene/alumina molar ratio. The characteristics properties of the modified particles were probed by various analytical methods and concluded that the particles surface contain bi-functionality which is desired for our aim of fabricating amino functionalized breath figure cavities on polystyrene-alumina (PSA) hybrid film. The FT-IR analysis carried out on the SA particles confirmed the siloxane formation as well as the polymeric modification on the alumina particles surface. SA particles were dispersible in organic solvents and polystyrene solutions. The particles having Hb/Hp value greater than 2 showed dispersion stability for more than 30 min in dilute solutions of polystyrene, therefore, these particles were undergone different analytical procedure in an aim to fabricate breath figures on PSA hybrid films. Dispersion of the particles improved with increased Hb/Hp value. The particles exhibited a dispersion-loading limit of 3 wt % beyond which particle agglomeration occurred. We arrived at the conclusion that the modification of alumina particles with silane mixture (aminopropyltriethoxysilane and vinyl triethoxysilane) followed by

the polymerization with styrene monomer enhanced the dispersity and the compatibility of the particles in polystyrene matrix and facilitated the stability of the PSA composite films with evenly distributed particles. Since the goal of our investigation is the fabrication of amino functionalized breath figure cavities on the polystyrene alumina hybrid film, the amino functionalized amphiphilic-alumina nanoparticles can be successfully used for attaining the objective.