CHAPTER 6

SYNTHESIS AND CHARACTERIZATION OF ALUMINUM PHOSPHATE AND SILICA COATED CNT AS FILLER MATERIAL IN POLYMER NANOCOMPOSITE

6.1 INTRODUCTION

A nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm, or structures having nano-scale repeat distances between the different phases that make up the material (Ajayan et al 2003). In general polymer nanocomposites perform the properties unique to nanoscale inclusions in bulk applications (Gupta et al 2010). Small volume of filler inclusion can result in significant property changes in the polymer nanocomposite. The transition from micro- to nano-particles changes its physical and chemical properties. The change in property occurs due to the increase in the ratio of the surface area to volume and the size of the particle. The higher surface area of the nano-particles enhances the interaction with the other particles within the mixture. Hence result in increases of strength, heat resistance, etc. Hence one can modify and improve the material performance by adding nanoscale inclusion without sacrificing the better polymer processability and light weight.

Polymer nanocomposites can be classified into layered silicate (clay) nanocomposites, carbon nanotube (CNT) composites and nanoparticulates (Ajayan et al 2003). Among these, CNT composite has attracted considerable attention due to their high mechanical properties that
occur due to the unique characteristics of CNTs (Atchudan & Pandurangan 2013). Usually straight chain aliphatic polymers are more suited as matrix materials for fabricating composites for structural application in space vehicles (Awaja et al 2010 and Ashton-Patton et al 2006). Although these polymers are light weight, but lacks thermal and structural stability. Epoxies type aromatic polymers, have higher strength and are thermally more stable than aliphatic polymers. It is possible to produce polymer nanocomposite with light weight, strength, stiffness, electrical conductivity, etc. by using aromatic polymers such as epoxies dispersed with carbon nanotubes.

Epoxy resins used for electronic packaging applications have low thermal conductivity as a major drawback. High thermal conductivity of CNTs due to the phonon-dominated ballistic heat transport is chosen as best reinforcing material. There are reports based on methods to reduce the thermal interfacial resistance by modifying the CNTs through covalent grafting (Yang et al 2010). Hence the dispersion of CNTs in the polymer matrix (Xie et al 2005) can be enhances along with the thermal conductivity (Wang et al 2009).

Aggregation of CNTs due to their high specific surface area, leads to poor dispersion of CNTs in the polymer matrix (Liu & Grunlan 2007). Thus modification of CNTs improves the dispersion and bonding strength at polymer–nanotubes interface (Spitalsky et al 2009). Thus, surface modification of CNTs is very necessary. Functionalization of CNTs can create useful functional groups onto the CNT surface by covalent method. These methods involve two major drawbacks: (1) during the functionalization reaction, defects are created on the CNT sidewalls and result in breakage of CNT into smaller pieces. Hence result in severe degradation in mechanical properties of CNTs and disruption of $\pi$-electron system in nanotubes. (2) During functionalization, the concentrated acids or strong oxidants often used
are considered harmful to environmental. Therefore, efforts to develop methods that are convenient to use, low cost and less damage to CNT structure are worth investigating.

In order to improve the flame retardancy of the materials, phosphorus-, nitrogen-, and silicon-based flame retardants are normally preferred. This is due to eco-friendly nature of these materials compared with the halogenated compounds (Shi et al 2009 and Hergenrother et al 2005). Epoxy resin nanocomposites reinforced with silica nanoparticles have attracted much attention due to the high stability of silica at high temperatures (Peng et al 2008) and the strong adhesion between silica and epoxy matrix (Ochi et al 2001). Liu et al (2003) have reported the synthesis of silica containing phosphorus epoxy resin nanocomposites from nanoscale colloidal silica. The thermal stability of composite was enhanced by adding silica nanoparticles. The glass transition temperature (Tg) has been observed to be depressed due to the plasticizing effect of the colloidal silica. Recently Suzuki et al (2011) have reported low thermal expansion property of the silica/epoxy resin nanocomposites consisting of mesoporous silica and fine silica nanoparticles. Also, Chen et al (2008) have observed different effects on the Tg, tensile modulus and fracture toughness by the addition of silica into the epoxy. There are reports on addition of silicon dioxide (SiO₂) particles to improve thermal stability in polymer composites (Yao et al 2006). SiO₂ are low cost, low density, low coefficient of thermal expansion and non-toxic. It is well suited for use as filler when exposed to extreme temperature conditions.

In the present work CNTs synthesized using stainless steel (chapter 4.2.3) was used for the preparation of composites. CNTs are modified with silica and aluminum phosphate using sol-gel method. CNT modified by aluminum phosphate was represented as AlPO₄@CNT, and CNT
modified by silica is denoted as SiO$_2$@CNT. The synthesized CNTs, AlPO$_4$@CNT and SiO$_2$@CNT were used as filler material in the epoxy matrix. The neat epoxy matrix and different wt. % of CNTs, AlPO$_4$@CNT and SiO$_2$@CNT filled nanocomposites were prepared by casting method. The thermo-mechanical properties such as flame retardancy, thermal stability, tensile strength, flexural strength and hardness were examined for neat epoxy matrix, CNT/Epoxy, AlPO$_4$@CNT /Epoxy and SiO$_2$@CNT /Epoxy nanocomposites.

6.2 EXPERIMENTAL

6.2.1 Materials

The chemicals used for the synthesis of AlPO$_4$ were ortho-phosphoric acid (Merck), aluminium nitrate (Merck) and ammonia solution (Thomas Baker). Ammonia solution was used to adjust the pH of the medium. The chemicals utilized for the synthesis of SiO$_2$ includes sodium metasilicate (Qualigens) as sources for silicon. The pH of the medium was adjusted using sulphuric acid (Merck). CNTs synthesized (chapter 4.2.3) by CVD, using stainless steel was used for the preparation of composites. Araldite LY 556 Resin was chosen as the polymer matrix. Aradur HY 951 was used as curing agent for the resin.

6.2.2 Synthesis of AlPO$_4$@CNT composite

For the preparation of AlPO$_4$@CNT composite, a solution of 0.05 mol of H$_3$PO$_4$ in 50 mL of deionised water was added drop wise to a solution containing 0.05 mol of Al(NO$_3$)$_3$ in 50 mL of deionised water with vigorous stirring. 10 mg of CNT was dispersed in the prepared solution and subjected to mechanical stirring for 30 min. Then, an aqueous ammonia solution (25%) was added drop wise until the pH of the supernatant was 4.5.
The white gel thus obtained was washed with deionised water, dried in air at 100 °C, and calcined in air at 400°C for 5 h.

6.2.3 Synthesis of SiO$_2$@CNT composite

SiO$_2$@CNT composite was prepared by dissolving 21.2 g of sodium metasilicate in distilled water, followed by addition of 10 mg of CNT in water. The mixture was added with 4N H$_2$SO$_4$ to bring the pH of the solution to 10.5 by mechanical stirring to form a gel. The white gel thus obtained was washed with deionised water, dried in air at 100 °C, and calcined in air at 400°C for 5 h.

6.2.4 Fabrication of neat epoxy, AlPO$_4$@CNT/epoxy and SiO$_2$@CNT/epoxy nanocomposite

Araldite LY 556 Resin was chosen as the polymer matrix. Aradur HY 951 was used as curing agent for the resin. AlPO$_4$@CNT and SiO$_2$@CNT particles were selected for filler materials. All samples were fabricated using the LY 556 along with the curing agent at a weight ratio of 130:13. The epoxy resin was first treated to an air release agent that was added at a weight fraction of 0.01% to assist in removing air bubbles from the epoxy. The epoxy resin was then degassed under vacuum to remove air entrapped in the epoxy. For fabrication of the hybrid composites, the fillers were then added at appropriate amounts to reach desired loading, and dispersed with a high speed mechanical mixer. It has been reported that shear mixing is one of the fabrication methods, which has been shown to provide good dispersion of fillers in the epoxy resin (Yasmain et al 2003). After incorporation of the filler the curing agent was added and dispersed with a high speed shear mixer again. Upon completion of the resin preparation the epoxy resin was poured into molds and cured at 60 °C for 2 h. Post curing was done in an oven at
150°C for 8 h. Hybrid composites were prepared using two different fillers, AlPO$_4$@CNT and SiO$_2$@CNT particles.

6.2.5 Specimen preparation for testing

Specimens were prepared from the neat epoxy, CNT/epoxy, AlPO$_4$@CNT/epoxy and SiO$_2$@CNT/epoxy composites as per the ASTM standards for thermo-mechanical investigations. The photographic images of the specimen are shown in Figure 6.1. For standard tensile Test, the specimens with a dimension of 165 mm X 19 mm X 3 mm were cut from the composite plate. The tensile test was conducted in Universal Testing Machine (UTM) as per ASTM D3039. Flexural test specimens with a dimension of 127 mm X 12.7 mm X 3 mm were cut from the composite plate and were tested in three point loading system applied by a simply supported beam as per ASTM D790. Standard hardness test specimens with a dimension of 173 mm X 56 mm X 42 mm were cut from the composite plate and a test was conducted in UTM as per ASTM D2240. Flammability of neat epoxy, CNT/epoxy, AlPO$_4$@CNT/epoxy and SiO$_2$@CNT/epoxy composites were studied by using flame retardant test. The method uses ASTM D635 standard (a modified version of ASTM D3801). Rectangular bars measuring 13 mm wide, 76 mm long and 3 mm thick were used as the test specimen.
6.2.6 Characterization Methods

TGA of the material was performed using a Mettler TA 3001 analyzer. Samples of approximately 10 mg were heated in air from 28 to 800°C at heating rate of 15 °C/min (The epoxy composite samples were cut into small pieces and were machined using the mechanical grinder). SEM was performed on a JEOL by placing the composites on nonconductive carbon tape. Flammability of neat epoxy, CNT/epoxy, AlPO₄@CNT/epoxy and SiO₂@CNT/epoxy are studied by using flame retardant test. The method used
a modified version of ASTM D3801. The mechanical properties were investigated for neat epoxy matrix, CNT/epoxy, AlPO$_4$@CNT/epoxy and SiO$_2$@CNT/epoxy composites by UTM as per ASTM standards. The tensile strength of the neat epoxy matrix and the composites were evaluated by using UTM (Model-H50. K-S Hounsfield test equipment Ltd, UK). Typically, the testing involves placing the sample over a fixed cross-section area and then drawn it with a controlled grip by gradual increasing force until the sample changes shape or breaks. Hardness of the composites was measured by UTM as per ASTM D2240.

The flexural test specimen having rectangular cross-section is bent until the fracture using a three point flexural test technique. Flexural strength is also known as modulus of rupture, bend strength, or fracture strength that represents a mechanical parameter for brittle material. It is defined as a material's ability to resist deformation under load. Figure 6.2 represent the set up of a transverse bending test. As per ASTM D790, a rod specimen having either a circular or rectangular cross-section is bent till fracture using a three point flexural test technique. The flexural strength indicates the highest stress experienced within the material at its time of rupture. It was measured in terms of stress ($\sigma$) according to equation (6.1).

$$\sigma = \frac{3FL}{2bd^2} \quad (6.1)$$

where,

- $F$ is the load (force) at the fracture point
- $L$ is the length of the support span
- $b$ is width
- $d$ is thickness
6.3 RESULTS AND DISCUSSIONS

6.3.1 SEM and TEM Images of AlPO$_4$@CNT and SiO$_2$@CNT Hybrid Materials

The morphology of aluminium phosphate coated CNT (AlPO$_4$@CNT) and silica coated CNT (SiO$_2$@CNT) hybrid materials were shown in Figure 6.3. The diameter of the tube before and after was noticed to be varying drastically. Figure 6.3 (a) and Figure (c), shows the morphology of AlPO$_4$@CNT. Figure 6.3 (b) and (d), demonstrate the morphology of SiO$_2$@CNT. The images depict the uniform coating of silica and aluminum phosphate over individual CNT. Thus homogeneous coating resulted in AlPO$_4$@CNT and SiO$_2$@CNT hybrid materials.
Further examination of the morphology of the composites was carried out with the aid of TEM analysis. Figure 6.4 (a) and 6.4 (c) shows the TEM images of SiO$_2$@CNT hybrid materials. Noteworthy the tubes possess hollow tubular morphology with uniform coating of silica over the tube surface. The diameter of the tubes with silica coating were in the range of 20-30 nm. The coating occurred individual for each tube. Figure 6.4 (b) and 6.4 (c), demonstrated the TEM images of AlPO$_4$@CNT hybrid materials. The diameters of the tubes were in the range of 50-60 nm. The surface of the tubes was very thick and rough. The hollow structure of the tubes was invisible. Presumably aluminum phosphate might have filled with
inner core of the tube. Presence of few aluminum phosphate nanoparticles filled CNT is clearly shown in Figure 6.4 (d). This may enhance the mechanical property of the nanocomposites. In addition, no agglomeration of AlPO$_4$@CNT was seen in the images.

![Figure 6.4 TEM images of (a) and (c) SiO$_2$@CNT hybrid materials; (b) and (d), AlPO$_4$@CNT hybrid materials](image)

6.3.2 Surface morphology studies of neat epoxy, CNT/epoxy, AlPO$_4$@CNT/epoxy and SiO$_2$@CNT/epoxy composite

The morphology of nanocomposite AC (AlPO$_4$@CNT/epoxy), SC (SiO$_2$@CNT/epoxy), C (CNT/epoxy) and NT (neat epoxy) are shown in
Figure 6.5. In order to investigate the failure mechanism, the SEM analysis was carried out on the fracture surface of the composite after the tensile test.

Figure 6.5 SEM images of (a) neat epoxy composite, (b) epoxy filled with CNT, (c) AlPO₄@CNT/epoxy and (d) SiO₂@CNT/epoxy

Figure 6.5 (a), represent the image of neat epoxy composite. Neat epoxy resin depicts a relatively smooth fracture surface, which confirms a brittle fracture behavior. This characteristic of neat epoxy is responsible for the low fracture toughness. Figure 6.5(b), shows the SEM image of epoxy filled with CNT. The CNTs were well dispersed in the epoxy matrix. The partially pulled out CNTs were clearly observed in the image. SEM images of modified CNTs filled nanocomposites, AC and SC are shown in Figure 6.5(c) and Figure 6.5 (d) respectively. The fracture surface of AC and SC shows rough surface. AlPO₄@CNT and SiO₂@CNT were observed pulled out
at fracture surface. The increased surface roughness denoted the crack tip path distortion due to the presence of surface modification of the CNT. This result in complexity of crack propagation in the composite. The modified CNT increased the dispersion of the filler and interfacial bonding between the CNT and matrix. This phenomenon makes the modified CNT filled composite to have superior tensile properties compared to others.

6.3.3 Thermogravimetric Analysis of Composites

The thermal stability of the composite was determined with the aid of thermogravimetric analysis. The thermograms of the fabricated AC (AlPO₄@CNT/epoxy), SC (SiO₂@CNT/epoxy), C (CNT/epoxy) and NT (neat epoxy) are shown in Figure 6.6. The weight loss with respect to temperature indicates the decomposition of the nanocomposites. In the case of neat epoxy, a small weight loss was observed at 150 °C due to the loss of moisture. In all composites, the degradation takes place in two main stages. The weight loss in the range of 250–320 °C attribute due to the homolytic scission of chemical bonds in the epoxy network (Macan et al 2006). The weight loss around 350–450 °C is due to the elimination of water molecules from oxypropylene groups (– CH₂– CH (OH) –) and the breakdown of the epoxy network (Grassie et al 1986). The weight loss around 450–600°C corresponds to the degradation of benzene rings of the cured epoxy nanocomposite due to the high C–C bonding energy (Zhu et al 2010). The epoxy modified with CNTs, AlPO₄@CNT and SiO₂@CNT shows the improved thermal stability and char yield of the epoxy resin. The weight loss observed for neat epoxy matrix was in the range of 320–350 °C where as for AC and SC, the weight loss observed in the range of 350–450 °C.
Figure 6.6 TGA curve for AC (AlPO$_4$@CNT/epoxy), SC (SiO$_2$@CNT/epoxy), C (CNT/epoxy) and NT (neat epoxy)

High thermal stability of AC and SC nanocomposites show that the decomposition temperatures of AC and SC are higher than that of neat epoxy resin. The order of thermal stability of the composites were AC>SC>C>NT. Hence it was confirmed that the thermal stability of the epoxy nanocomposite enhanced due to the presence of CNTs, AlPO$_4$@CNT and SiO$_2$@CNT.

6.3.4 Tensile Strength Test

The tensile strength of the composite SC, AC, C and NT were examined with the aid of stress-strain curve. The bar diagram illustrated in Figure 6.7, depicts tensile strength of SC, AC, C and NT were 43.68, 53.5,
43.89 and 42.13 MPa respectively. From the data it was proved that AC exhibited the maximum tensile strength.

![Tensile strength of epoxy nanocomposites](image)

**Figure 6.7 Tensile strength of epoxy nanocomposites**

The mechanism behind the increase in the strength is due to the particle-matrix interaction on molecular level. The strength of the polymer is mainly determined by the intermolecular force such as van der Waals and hydrogen bonding. These force strongly depend on the inter-molecular distance, is expected to influence mainly by the incorporation of nanoparticles. The decrease in tensile strength in particulate reinforced composite occurs mainly due to inhomogeneous distribution. This creates agglomeration, which acts as defects on which high local stress concentration may appear and hence leads to failure of the material.
The dispersion is expected to be more effective in the case of surface-modified particles, as the interparticle interaction become weaker. In addition, smaller the volume fraction of nanoparticle smaller will be the amount of agglomeration in the composite. Particle–matrix adhesion is another property. No reinforcing effect is achieved due to poor interfacial adhesion. The unmodified particle only interact with the matrix via hydrogen bond, whereas surface modified particle may be covalently bonded to the matrix which result in very strong interfacial adhesion.

6.3.5 Flexural Strength Test

Flexural test was performed on the various composite sample prepared based on the ASTM Standard D790. The Flexural test for the specimens was carried out with the aid of UTM. Upon experimental test, the maximum bending load for the composite plate was obtained. The specimens failed rapidly with “pinging” noises after reaching the maximum stress. The flexural strength of epoxy nanocomposites was in the order of AC > SC > C > NT which is clearly observed in Figure 6.8. The AlPO₄@CNT/Epoxy nanocomposites have high flexural strength of 135.1 MPa compared with other fillers due to strong interfacial bonding and bridging effect.
6.3.6 Hardness Test

Hardness is the property of a material that enables it to resist plastic deformation, usually by penetration. However, the term hardness may also refer to resistance to bending, scratching, abrasion or cutting. Hardness is not an intrinsic material property dictated by precise definitions in terms of fundamental units of mass, length and time. A hardness property value is the result of a defined measurement procedure. Hardness of the nanocomposites was measured by UTM as per ASTM D2240.

The hardness of neat epoxy, CNT/Epoxy, AlPO$_4$@CNT /Epoxy and SiO$_2$@CNT /Epoxy nanocomposites are shown in Figure 6.9. It was observed that AlPO$_4$@CNT /Epoxy possess the greater hardness compared to other
composites. AlPO$_4$@CNT/Epoxy exhibited a maximum hardness of 35 MPa. The order of hardness for each composites were AC>SC>C>NT. Presumably the uniform dispersion of fillers into the epoxy resin and the interfacial bonding between the fillers and resin is responsible for the enhancement of hardness.

![Figure 6.9 Hardness of epoxy nanocomposites](image)

6.3.7 Flame Retardant Test

Flame retardant test is used to find out the rate of burning and time of burning of composite material in horizontal or vertical position. The rate of burning for the neat epoxy, CNT/Epoxy, AlPO$_4$@CNT/Epoxy and SiO$_2$@CNT/Epoxy nanocomposites material were found by burning it in horizontal position as per ASTM D 635. ASTM D 635 is a standard method for finding out rate of burning and exact time of burning in horizontal position. The neat epoxy matrix burnt silently and quickly. But the CNT/Epoxy, AlPO$_4$@CNT/Epoxy and SiO$_2$@CNT/Epoxy nanocomposite material burnt with cracking nature and also time taken for burning increases.
The rate of burning (mm/min) for the neat epoxy, CNT/Epoxy, AlPO₄@CNT /Epoxy and SiO₂@CNT /Epoxy nanocomposites material are shown in Figure 6.10. This result shows that the addition of CNT, AlPO₄@CNT and SiO₂@CNT did not accelerate the ignition. Especially, the rate of burning of AlPO₄@CNT /Epoxy and SiO₂@CNT /Epoxy nanocomposite is very slower than others.

Figure 6.10  Flame retardancy of epoxy nanocomposites

The presence of silicon and phosphorus content in organic/inorganic flame retardants are considered efficient flame retardants. In addition, the graphene layers could prevent the gaseous diffusion and reinforce the carbon layers. Thus decorating CNT with AlPO₄ and SiO₂ can improve the flame-retardant efficiency of the composites. Moreover, several advantages are combined in this approach: (i) the silicon could strengthen the char layers in the condensed phase; (ii) the phosphorus could catalyze the char formation in the condensed phase and (iii) the CNT could prevent the gaseous
diffusion and reinforce the carbon layers in the condensed phase (Qian et al. 2013).

6.4 CONCLUSION

AlPO₄@CNT and SiO₂@CNT prepared by simple sol-gel method. The effect of these fillers in AlPO₄@CNT /Epoxy and SiO₂@CNT /Epoxy nanocomposites enhanced thermal stability of the nanocomposite. The modified CNT increased the dispersion and interfacial bonding between the CNT and matrix. Among various composites studied, AlPO₄@CNT /Epoxy exhibited an excellent tensile strength, flexural strength, hardness and flame retardant capacity. The value of tensile strength, flexural strength and hardness was observed to be 53.5 MPa, 135.1 MPa and 35 MPa respectively. Presence of phosphorous enhanced the flame retardant capacity of A.C. Hence, AlPO₄@CNT filled epoxy nanocomposite proved to best candidate for the fabrication of nanocomposite with better thermal stability, mechanical strength and flame retardancy.