Development and characterization of silicon carbide incorporated graphene amine-based polymer nanocomposites for structural applications

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Abstract. In this research work, 0.3 mass% of graphene amine (GA) reinforcement was used in epoxy resins for development of graphene amine-based polymer composites using casting technique and subjected to annealing at 60 °C for 3 hour using heat controlled oven. Silicon carbide (SiC) was incorporated into GA based-polymer composite with different mass percentages (0.25-1.0 mass% with respect to epoxy resins) to enhance properties for structural applications and developed specimens were designated as S, S-1, S-2, S-3 and S-4. The physico-chemical changes in the resulting nanocomposites were investigated using Fourier transform infrared (FTIR) spectroscopy, thermo gravimetric analysis (TGA) and Mechanical testing including tensile test were done. Among the developed specimens, 0.75 mass% of SiC incorporated GA based-polymer composite exhibited superior properties for structural applications.

1. Introduction

Engineering materials are classified as metals, polymers, ceramics and composites. Metals are mostly of higher weights and they lose their strength at higher temperatures. High density polymers exhibit good thermal properties as well as good strength to weight ratios hence they can be employed in aerospace industries [1]. Ceramics are the best in thermal properties and hardness but because of their higher brittleness they have limited applications in industries. Composites are the materials, which are formed by combining two or more different kind of materials. Desired properties of materials can be achieved by composite materials for desired applications. This is why many researches and innovations are going on in field of composite materials for optimization in several engineering applications. Polymer composites due to their easy processing, low cost and outstanding toughness...
and strength properties [2], find vast range of engineering applications nowadays. For this reason polymer composites are evolving and becoming more and more popular.

Epoxy was found by Dr. Castan of Switzerland and Dr. Greenlee of USA in 1936 [3]. Epoxy is a thermoset plastic having many useful engineering properties, such as ease of processing, good thermal and chemical stability, low cost, good dimensional stability (lesser shrinkage during moulding) and good tensile strength [4, 5]. For these reasons it is important to study the properties of nano composites with epoxy as base matrix. Some of the major applications of epoxy and epoxy based nano composites encompass automotive, aerospace, sports material, marine, biomedical devices and as adhesives etc [6]. To cure epoxy resin there involves a chemical reaction in which epoxy groups in resins react with a hardener (for ex: K-6 hardener) to construct a three dimensional, highly crosslinked polymer. Depending on the chemical composition of hardener used to cure epoxy resin, the curing temperature differs from 5 to 150°C [7]. But because of brittleness property of epoxy resins, they are limited to certain engineering applications therefore there is a scope to decrease its brittleness and hence improve its properties.

In recent years polymer nano composites with amplified mechanical, electrical, thermal and fire resistive properties have been developed and studied [8-12]. It is important to renovate the existing materials and advance the new materials with enhanced properties for future engineering applications. Nano materials are the materials of grain sizes in nm scale (i.e.10⁻⁹m). Nano graphene amine (GA) is one such nano material which is having high aspect ratio and larger surface area per unit weight (210-300 m²/g). amine functionalized graphene is produced by combined effort of CVD (chemical vapor deposition) and chemical graphite exfoliation method on which further treatment is done to introduce sulfonated group at the edges and surfaces. It is found that graphene amine exhibited optimal mechanical, chemical and thermal properties at its 0.3wt% composition with base matrix [13]. It was reported that graphene could improve the friction, wear properties and the thermal conductivity of the materials, such as epoxy [14, 9].

Meanwhile, nano silicon carbide (SiC) is having a good hardness (9.5 mohs), also it has good thermal stability properties, low thermal expansion and it is resistant to chemical reactions [15]. It can be incorporated into the polymer matrix to enhance the thermal properties as well as mechanical properties into the resulting composite material. Even though, among the various polymer composites, silicon carbide/polymer nanocomposites are the frequently investigated in the literatures. And they also utilized in various type of applications, such as automotive, electronics and aerospace applications furthermore they also employed in many industrial products because of their good thermal and mechanical properties [16].

The objective of this work was to study the effects of addition of nano SiC into the GA/epoxy composite material. In this work, the optimized wt% of GA kept constant in SiC/GA/epoxy composite and wt% of nano SiC was varied in steps of 0.25wt% from 0 wt% to 1.0 wt%, in order to prepare different samples namely S-0,S-1,S-2,S-3 and S-4. The mechanical and chemical properties of developed samples were analyzed to study the effect of addition of nano SiC into the GA/epoxy polymer matrix.

2. Experimental section

2.1. Materials

Epoxy resin Lapox L-12 with K6 hardener was purchased from Atul Ltd. Lapox L-12 is a unmodified epoxy resin of medium viscosity and Hardener K6 is low viscosity room temperature curing liquid hardener were used as polymer matrix. Nano graphene amine, length avg X&Y dimensions=1-10 microns, thickness average Z dimensions=2-3 nm, surface area = 210-300 m²/g with purity > 97% was
purchased from United nanotech innovations pvt.ltd and used as reinforcement. Nano SiC powder with hardness = 9.5(Mohs), density at 288 K = 3.216 (g/cm³) and purity = 99%, beta was purchased from Reinste Nano Ventures Pvt. Ltd and used as reinforcement for optimization.

2.2. Preparation of plane epoxy with 0.3wt% of nano GA.

The quantity of nano GA was taken 0.3wt% of total mould volume dimensions. Quantity of epoxy resin and K6 hardener are taken in the ratio of 9:1 of remaining 99.7% of total mould volume dimensions. The base sample was prepared by mixing nano GA with prepared epoxy(matrix) using ultrasonic sonicator in order to ensure the dispersion of nano particles in the matrix. Hence prepared mixture was poured in the mould and kept for 24 hrs to cure. After 24 hrs the cured sample was taken out of the mould and cut into different shapes for different characterizations.

2.3. Preparation of nano SiC incorporated nano GA – polymer composites.

Different samples of nano SiC composites were prepared according to the wt% of SiC. 4 samples were prepared by varying the nano SiC wt% ranging from 0.25wt% to 1.0wt% in steps of 0.25wt%. The prepared samples were sonicated using ultrasonic sonicator to ensure the dispersion of nano particles in the matrix. After sonication all the samples were poured into the mould to prepare different shapes for mechanical and chemical characterizations.

2.4. Calculation of quantity of material for moulding.

Example: for sample-2 (i.e. nano Graphene amine=0.3%, nano SiC=0.5%)  
Density of Epoxy = 1162 kg/m³  
Total volume of specimen,  
Volume = l × b × t  
Where, l = length of the mould cavity in mm.  
b = breadth of the mould cavity in mm.  
t = thickness of the mould cavity in mm.  
Volume = 230×160×3  
= 1.104×10⁻⁴ m³.  

Total weight of sample materials  
Weight = Volume × Density of epoxy  
= 1.104×10⁻⁴×1162  
= 0.12828kg.  
Weight = 128.28gm ≈ 130gm.  

Weight percentage of Epoxy and K-6 hardener in plane sample,  
Weight of epoxy = 90% of epoxy × Total volume (because epoxy and hardener should be kept in the ratio of 9:1)  
Weight of epoxy = 0.9 × 130  
Weight of epoxy = 117gm.  
Weight of hardener = 10% × Total volume  
Weight of hardener = 0.1×130  
Weight of hardener = 13gm.  
0.5% of nano SiC(x) = (0.5/100)×117 = 0.585gm.  
0.3% of nano Graphene amine(y) = (0.3/100)×117 = 0.351gm.  
Remaining epoxy weight(z) = 117-(x + y)  
= 117-(0.585+0.351)  
Remaining epoxy weight(z) = 116.064 ≈ 116gm.  
x + y + z = 0.581+0.351+116 = 117gm.
Weight of hardener can be calculated using ratio and proportions,
117:13 = 116: Weight of hardener
117 × Weight of hardener = 116 × 13
Weight of hardener = (116 × 13)/117 = 12.88gm.

2.5. Thermogravimetric analysis (TGA)

The thermal stability of the composites was determined by thermogravimetric analysis (Mettler Toledo TGA 2). The samples were heated from 30 to 800°C at a heating rate of 10°C/min. Experiments were carried out with an average mass of 10.0 mg.

2.6. Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption of a solid, liquid or gas. Samples were made into powders and embedded in potassium bromide (KBr) pellets at a ratio of 1:100 in weight. The FTIR spectra of nano Graphene amine (GA), nano SiC, S-0, S-3 and S-4 samples were recorded on a Nicolet 6700 spectrometer (Nicolet Instrument Corporation, USA) over the range of 400 to 4000 cm⁻¹ with a 4 cm⁻¹ resolution and 32 scans. The FTIR of the samples were carried out with a Nicolet 6700 FTIR spectrometer.

2.7. Tensile tests

Tensile testing, also known as tension testing, is a fundamental materials science test in which a sample is subjected to a controlled tension until failure. The results from the test are commonly used to select a material for an application, for quality control, and to predict how a material will react under normal forces. Properties that are directly measured via a tensile test are ultimate tensile strength, maximum elongation and reduction in area. From these measurements the following properties can also be determined: Young’s modulus, Poisson’s ratio, yield strength, and strain-hardening characteristics. Uniaxial tensile testing is the most commonly used for obtaining the mechanical characteristics of isotropic materials. For anisotropic materials, such as composite materials and textiles, biaxial tensile testing is required.

3. Results and discussion

3.1. TGA results:

![Figure 1. TGA thermogram of epoxy, nano GA, nano SiC composites with different contents of nano SiC](image)
TGA is a valuable and simple method in evaluating thermal stability of materials [15]. In Fig.1, we considered the temperature at 88.85% weight loss as a measuring point. GA incorporated sample, degraded 88.85% of its initial quantity around 445°C whereas SiC incorporated GA epoxy composite degraded the same quantity around 625°C. From this it is evident that SiC incorporated GA epoxy composite material demonstrated higher thermal decomposition temperature compared to GA epoxy composite material. Therefore from these details it can be inferred that by increasing the wt% of SiC in the GA epoxy composite material, the thermal stability of the material is increased.

| Samples                                      | T$_i$(°C) | MRDT(°C) | D half(°C) | FR(%) |
|----------------------------------------------|-----------|----------|------------|-------|
| Epoxy + nano GA(0.3%)                        | 319.99    | 791.81   | 377.66     | 4.54  |
| Epoxy + nano GA(0.3%) + nano SiC(0.25%)      | 325.17    | 792.01   | 374.27     | 5.34  |
| Epoxy + nano GA(0.3%) + nano SiC(0.5%)       | 326.72    | 791.36   | 377.39     | 5.63  |
| Epoxy + nano GA(0.3%) + nano SiC(0.75%)      | 314.82    | 792.68   | 376.22     | 8.86  |
| Epoxy + nano GA(0.3%) + nano SiC(1.00%)      | 329.34    | 791.85   | 379.59     | 10.03 |

T$_i$(°C) = initial decomposition temperature
MRDT(°C) = maximum rate of decomposition temperature
D half(°C) = it is the temperature when 50wt% of material has decomposed.
FR(%) = final residue (the amount left after the end of heating).

3.2. FTIR results:

![Figure 2. FTIR of nano GA, nano SiC and S-0, S-4 composites with different contents of nano SiC.](image-url)
The reaction between Graphene amine, silicon carbide with epoxy polymer is confirmed with the help of FTIR spectra illustrated in fig.2. The broad peak around 3400 cm$^{-1}$ is due to N-H stretching [15] and a medium peak around 1100 cm$^{-1}$ is due to C-N stretching, it confirms the material is GA. The broad peak around 3450 cm$^{-1}$ is due to the presence of moisture content and the absorption peak around 800 cm$^{-1}$ is assigned to stretching vibrations of Si-C bonds, it confirms the material is SiC[16]. In S-0 and S-4, a characteristic peak around 3450 cm$^{-1}$ is due to O-H bond stretching. The peak of aliphatic and aromatic C-H stretching is present around 3000 cm$^{-1}$, C=C stretch of aromatic rings and C-C stretching of aromatic rings are present around 1600 cm$^{-1}$ and 1500 cm$^{-1}$ respectively. The C-O-C stretching of ethers and oxiranes are found around 1030 cm$^{-1}$ and 830 cm$^{-1}$ respectively. This provides the evidence for the epoxy polymer [17,18].

3.3. Tensile test results:

![Figure 3. Load vs Displacement diagram of samples S-0 to S-4](image)

Tensile test is simple technique to determine tensile strength of developed materials. In Fig.3. Load vs Displacement characteristics of samples S-0 to S-4 are depicted. load vs displacement graph shows about elasticity property of a material. According the graph, S-3 i.e. 0.75wt% SiC shown maximum elongation and maximum load as compared to other samples. Also an increase in elongation of S-3 about 15.9% greater than S-0 is been reported. This indicates that at 0.75wt% of SiC in epoxy matrix increases its tensile strength to a maximum peak, further increase in SiC wt% will diminish the elasticity of the resulting composite material, as it is confirmed by the peak of S-4 (1.0wt% of SiC). Fig-4 shows the stress vs strain characteristics of samples S-0 to S-4 which is helpful in determining the maximum ultimate tensile stress, fracture stress and young’s modulus of the developed samples. According to Fig-4 graph, the tensile strength of composites is decreasing with increasing wt% of SiC. It is because of the brittle nature of the SiC nano particles.
4. Conclusion

In this study, we reported the effect of addition of nano SiC into the GA/epoxy polymer matrix. We found a method to prepare the nano SiC/nano GA/epoxy composites. We prepared 5 samples by varying nano SiC wt% at a rate of 0.25wt% in the range of 0wt% to 1.0wt% while preparing samples we also calculated the volume of material required to fill the mould cavity for casting. Later we studied their chemical and mechanical properties by performing TGA, FTIR and tensile tests. The TGA test results revealed that with increase in wt% of nano SiC addition into the GA/epoxy composites shown an increase in the thermal stability of the resulting composites. GA/epoxy composite degraded 88.85% of its initial quantity around 445°C whereas SiC incorporated GA/epoxy composite degraded the same quantity around 625°C. The FTIR spectra results demonstrated the reactions between SiC, GA and epoxy went well. The tensile test also shown good results, the tensile strength of composites till 0.75wt% addition of nano SiC was increased but further increase in SiC wt% resulted a decrease in elasticity of the developed composites. From this it is evident that the optimum quantity to enhance tensile properties for addition of nano SiC into GA/epoxy composite is found to be 0.75wt%. From this research work it is expected to be beneficial for various engineering applications such as developing fire resistant casings for electrical devices, aerospace applications and automotive applications.

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