Effect of particle morphology on flexural properties of functionally graded epoxy-alumina polymer nanocomposite

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Abstract
Functionally graded polymer nanocomposites (FGPNC) were synthesized by dispersing alumina nanoparticles (spherical and rod shape) in epoxy by sonication technique. Gradation in the thickness direction was achieved by varying the wt% of nanoparticles. Samples of layered FGPNC were prepared by casting layers of neat epoxy and nanocomposites having 0.25, 0.5, 0.75 and 1 wt% of nanoparticles one by one in a vertical acrylic mould. Flexural properties of FGPNC samples were evaluated by three point bending method. FGPNC samples were loaded from neat epoxy side and nanocomposite side. Increments of 18% and 16% in flexural strength and 19% and 20% in flexural modulus were recorded for FGPNC with spherical and rod shape nanoparticles respectively compared to that of layered neat epoxy for loading from neat epoxy side. Whereas when load was applied from nanocomposite side, an improvement of 13% in flexural modulus of FGPNC was seen while flexural strength of FGPNC increased by 8%–9% over that of layered neat epoxy for both the types of nanoparticle.

1. Introduction

High strength to weight ratio of polymers and great protection against environmental degradation makes it advantageous for structural applications. Industries such as aerospace, automobile and defence are using polymer materials because of its unique properties. Thermoset polymers such as epoxy possess highly cross linked structure which imparts better mechanical properties to them in comparison to thermoplastics. Uncured resin of thermosets remains in the liquid state at room temperature due to which it is easier to process. Mechanical properties of epoxies can be improved by reinforcing micro or nano size inorganic particles in it [1–6].

Product manufacturing and development units are looking for the materials that can perform multifunctions. Functionally graded materials (FGMs), a new class of material system developed by researchers to meet these requirements, have varied microstructures that can be formed by non-uniform or uniform dispersion of the reinforced phase in the matrix of dissimilar properties, sizes and shapes. Variation of material properties or structure in any geometrical direction for the FGMs is their key difference in comparison to that of homogeneous materials or laminated composites. FGMs possess improved performance for various applications such as heating barrier coatings, bone and dental implants, thermoelectric devices, defense equipment such as bullet proof jackets and helmets, and space flight structures [7]. Nowadays, functionally graded composites coating are widely used in mechanical and tribological applications [8–10]. Composite coatings of a second phase material generally hard oxides (Al₂O₃, TiO₂ and SiO₂) and carbides (SiC and WC) in metals or polymers are deposited on substrates. Composite coating of SiC micro/nano particles and Ni was applied on pure nickel substrate to have excellent mechanical and tribological properties [8]. An improvement of 62% in hardness was reported for samples coated with composites having SiC nanoparticles of size 10 nm compared to pure nickel electrodeposits [8]. In a similar work SiC having an average size of 5 μm and 0.3 μm along with Ni was coated on mild steel substrate [9]. It was reported that Composite coatings of 5 to 8 vol% of 0.3 μm SiC with Ni leads to better corrosion resistance and a lower residual stress in comparison to pure nickel coating and Ni–SiC composite coatings containing even 23 vol% 5 μm particles. High speed insect impact was...
 prevented by developing thermal alternating polymer nanocomposite (TAPNC) coating by Bayer et al [10]. Coating was developed by infusing the hydrophobic perfluerinated acrylic copolymer and hydrophobic surface functional silicon dioxide nanoparticles by successive thermal treatments. The surface coating was tested using dry pencil hardness test. Test conducted by producing scratch from 2B pencil held at 45° angle produces scratch on the surface which damaged super-hydrophobic nature of the surface. This nature of surface, prevent the accumulation of insect residues. Polymer based FGM is a recent development in this field. These FGMs are formed by the combination of two or more than two dissimilar polymeric materials or by the dispersion of nano and micro phase materials in the polymer [11–14].

Flexural properties of continuously graded functionally graded polymer nanocomposite (FGPNC) of epoxy reinforced with short, medium and large carbon fiber was studied experimentally [15, 16]. In these studies, higher flexural modulus for FGPNC was reported compared to that of neat epoxy irrespective of loading direction. Whereas increased flexural strength was reported when load was applied on the particle rich side. Recently mechanical properties of the layered FGPNC were studied [17–19]. Misra et al [17] fabricated quartz fabric reinforced functionally graded composite using silica powder. When thickness of pure silica layer was increased in FGM, drop in flexural strength and flexural modulus was reported. Doddamani et al [18] studied compressive and flexural properties of functionally graded synthetic foam (FGSFs) of the epoxy and censosphere. A brittle failure of FGSFs under flexural loading was reported and the movement of crack from tensile side to compressive side of the specimen was seen. An improved specific flexural modulus of 5%–34% for FGSFs over that of plain synthetic foam was reported. Fracture toughness of layered FGPNC of epoxy and carbon nanotubes was investigated experimentally by Kurd et al [19]. Results showed that stepped gradation did not help in improvement of fracture toughness of FGPNC compared to that of non-graded samples.

Alumina, Al₂O₃, is a ceramic metal oxide of great importance as building material, refractory material, electrical and heat insulator, due to its high strength, corrosion resistance, chemical stability, low thermal conductivity, and good electrical insulation. These characteristics make this oxide an excellent material for structural, microelectronic and technological applications [20]. Reinforcement of alumina nanoparticles into epoxy resin is widely done by the researchers to improve important mechanical properties such as tensile modulus [3, 21, 22], fracture toughness [5, 21, 23, 24], flexural properties [3, 6, 23], resistance to fatigue crack propagation [3, 25, 26], and impact properties [27], even at low filler contents. Further alumina nanoparticle is easily available and is less expensive than other nanoparticles such as carbon nanotube, TiO₂ etc So, alumina nanoparticle is selected to study the effect of gradation of alumina nanoparticles on the flexural properties of polymer nanocomposites.

A lot of research work have been reported on simulation of various properties of FGPNC [28–32]. Whereas experimental investigation of FGPNC is meagre. In the present work an innovative process to fabricate layered FGPNC of epoxy and alumina nanoparticles has been established. Effect of gradation and shape of alumina particles on flexural properties of FGPNC is investigated. Monolithic samples of nanocomposites of epoxy and alumina nanoparticles that were used as layers of FGPNC were also fabricated. Tensile properties of monolithic samples of nanocomposites were determined to analyze the results obtained for FGPNC.

2. Experimental details

2.1. Material system

In the present work, epoxy and alumina nanoparticles (rod shape and spherical) were used to fabricate FGPNC. Epoxy resin LY556®, (an unmodified Bisphenol—A) was cured with an aliphatic primary amine, hardener HY951®. Both epoxy resin and hardener were procured from Huntsman Advanced Materials, India. Spherical alumina nanoparticles (density: 3.5–3.9 g cm⁻³ and specific surface area: 35 m² g⁻¹) and alumina nanorods (density: 4.0 g cm⁻³ and specific surface area: 40 m² g⁻¹) were procured from NanoAmor, USA and Sigma–Aldrich, India respectively. Diameter of spherical alumina nanoparticles and alumina nanorods was in the range of 27–43 nm and 10 nm respectively, while the length of nanorods was less than 50 nm.

2.2. Preparation of nanocomposites

Sheets of 5 mm thickness of monolithic nanocomposites were fabricated by casting in vertical acrylic moulds. Nanocomposites were synthesized by in situ polymerization technique [6]. Alumina nanoparticles were first dispersed in acetone using ultrasonication. Epoxy was added in this mixture by stirring and the mixture was again sonicated. A mix of epoxy and nanoparticles was obtained by partial distillation of acetone followed by degassing. Hardener, HY951 in the ratio of 1:10 was added and mixed gently to avoid entrapment of air bubbles. This mixture was poured into vertical acrylic mould and was cured at 25 °C for a day.
2.3. Preparation of FGPNC

FGPNC samples had one layer of neat epoxy and four layers of nanocomposites having 0.25, 0.5, 0.75 and 1 wt% of alumina nanoparticles. These layers of 1 mm thickness were casted in vertical acrylic moulds. First required amount of mix for neat epoxy (a mix of epoxy resin and hardener in the ratio of 10:1 by weight) was poured gently in a mould with a cavity of 1 mm thickness. It was cured at 25 °C for 12 h. Then the mould was opened and thickness of the mould was increased by 1 mm. Subsequently one layer of nanocomposites having 0.25 wt% of nanoparticles was casted on the previously casted semi cured layer. Then it was allowed to cure at 25 °C for 12 h. The detailed procedure for the preparation of mix for nanocomposite is given in section 2.2. Similarly three more layers of nanocomposites of 0.5, 0.75 and 1 wt% of nanoparticles were casted one by one to fabricate the FGPNC sheet of 5 mm thickness. After casting the last layer of nanocomposites (1 wt% of alumina nanoparticles), it was cured at 25 °C for 24 h. Then the mould was opened and FGPNC sheet was taken out.

Sheets of FGPNC having a size of 130 mm × 130 mm × 5 mm were fabricated using spherical alumina nanoparticles and nanorods. Samples of different sizes were machined from these sheets following ASTM standards for different types of tests.

3. Characterization

Dispersion of alumina nanoparticles in epoxy matrix was analyzed through transmission electron micrographs (TEM) of nanocomposites. Slices of 80–90 nm were cut using a diamond knife on ultra-cut Ultramicrotome (Leica EM UC6, India) at room temperature to prepare samples for transmission electron microscopy. These slices were kept on carbon coated copper grids and were seen in TEM (JEM-1400 TEM JEOL, Japan) at an accelerating voltage of 120 kV.

Further to cross verify the dispersion of alumina nanoparticles, Energy Dispersive x-ray spectroscopy (EDX) spectra and elemental maps were analyzed for the individual layers of FGPNC in field emission scanning electron microscopy (FESEM) (Nova NanoSEM 450, US). Samples of the size 10 mm × 5 mm × 5 mm were cut and one of the surfaces were made smooth and gold coated. FESEM images and EDX spectra were obtained for both the types of FGPNC.

Density ($\rho_{th}$) of composite was calculated following the rule of mixture (ROM). Density of composites was calculated using equation (1).

$$\rho_{th} = \left( \frac{W_p}{\rho_p} + \frac{W_m}{\rho_m} \right)$$

where $W_p$, $W_m$, $\rho_p$, and $\rho_m$ are the weight fraction and density of alumina nanoparticles and epoxy matrix respectively.

Density of epoxy alumina nanocomposites and FGPNC samples were determined experimentally using Archimedes’ principle. Density of composites was calculated using equation (2).

$$\rho_c = \frac{W_g}{(W_g - W_w)}$$

where $\rho_c$ is density of composite, $W_g$ and $W_w$ are weights of the sample in air and in water respectively.

Tensile properties of nanocomposites (monolithic samples) were determined following ASTM standard D638–03 [33]. Tests were performed on servo hydraulic universal Testing Machine supplied by Bangalore Integrated System Solutions (BISS), India with a load cell capacity of 25 kN. Dog bone specimen, used in the tensile testing is shown in figure 1. The cross head speed was 5 mm min$^{-1}$ and axial extensometer was used to determine elongation in the gauge region for measurement of strain. At least five valid tests were performed to calculate tensile properties with 95% confidence level.

In case of FGPNC, flexural test was conducted in place of tensile test. In FGPNC samples gradation is provided in the thickness direction i.e. property (stiffness) is varying in the thickness direction. Thus tensile test

![Figure 1. Specimen for tensile test (dimensions are in mm).](image-url)
following ASTM standard D638 will not be valid for FGPNC samples. Flexural properties of neat epoxy (layered) and FGPNC were determined using three point bending test. Samples were loaded from epoxy side and nanocomposite side on universal testing machine (UTM). UTM with a load cell of 10 kN capacity was purchased from Tinius Olsen, India.

Dimensions of the flexural test specimen are shown in figure 2. Figure 2(a) shows the schematic of specimen for loading from nanocomposite side and figure 2(b) represents the schematic of specimen for loading from neat epoxy side. Length (L), width (W) mm and thickness (B) of the specimen were 80 mm, 12.7 mm and 5 mm respectively. Flexural strength and flexural modulus were calculated from the equations (3) and (4) respectively [34].

$$\sigma_f = \frac{3PL}{2WB^2}$$  \hspace{1cm} (3)

$$E_b = \frac{mL^3}{4WB^3}$$  \hspace{1cm} (4)

where ‘\(\sigma_f\)’ is flexural stress, ‘\(E_b\)’ is the flexural modulus, ‘\(P\)’ is the maximum load and ‘\(m\)’ is slope of the tangent to the initial linear part of the load-deflection curve. At least five samples were tested for each type of sample and loading condition and flexural properties with 95% confidence level were calculated.

4. Results and discussion

4.1. Dispersion of nanoparticles

TEM images of nanocomposites having 0.25, 0.5, 0.75 and 1 wt% of alumina nanorods and spherical alumina nanoparticles are shown in figures 3 and 4 respectively. It is clear from figure 3 that orientation of alumina nanorods is random. Thus the nanocomposite layers will not have directional property and it will be isotropic in nature. Non-uniform dispersion of nanoparticles is also seen at some places in figure 3(d) for alumina nanorods (1 wt%). However for the lower wt% (0.25% & 0.5%), both the types of nanoparticles are uniformly distributed in epoxy matrix. At higher wt% of nanocomposites (1 wt%) spherical nanoparticles are more uniformly dispersed than the nanorods. Non-uniform distribution at higher wt% of nanoparticles is caused by agglomeration at some locations shown by arrow in figures 3(d) and 4(d). Nanorods have higher tendency to form agglomerates as they have higher aspect ratio and surface area.

4.2. SEM/EDX of FGPNC

Individual nanocomposite layers (0.25, 0.5, 0.75 and 1.0 wt% of nanoparticles) of FGPNC was analysed in Scanning electron microscopy (SEM) with in situ EDX. EDX map of aluminum and oxygen along with EDX
spectra for FGPNCs (nanorods and spherical) are shown in figures 5 and 6. EDX spectra give the quantity of the elements (aluminum and oxygen) in terms of weight percentage in epoxy. From figures 5 and 6 it is clear that the wt% of aluminum increases in the scanning area with the increase in wt% of the alumina nanoparticles in the layers (see EDX spectra and mapping). Further, the EDX maps in figures 5 and 6 show uniform dispersion of alumina nanoparticles in epoxy matrix.

4.3. Density of nanocomposites and FGPNCs

Densities of nanocomposites of spherical and rod shape nanoparticles are compared in figure 7. Density of neat epoxy was found to be 1.2057 g cm\(^{-3}\) experimentally. Density of nanocomposites increases with the increase of wt% of nanoparticles for both the particles. A slight increment in the density of the nanocomposite having 1 wt% of rod shape nanoparticles (1.2164 g cm\(^{-3}\)) was observed compared to that of nanocomposite having 1 wt% of spherical nanoparticles (1.2161 g cm\(^{-3}\)) due to the fact that the densities of nanoparticles (spherical and nanorods) are almost in the equal range. Similar trend in density is obtained when it was calculated using ROM.

Figure 3. TEM micrographs of nanocomposites showing the distribution of nanorods at (a) 0.25 wt%, (b) 0.5 wt%, (c) 0.75 wt% and (d) 1 wt% of nanoparticles (arrows are showing agglomeration of nanorods).
Densities of nanocomposites calculated using ROM, are almost equal to the density determined experimentally (see figure 7).

Density of FGPNC samples is compared with that of neat epoxy and nanocomposites having 1 wt% of nanoparticles in figure 8. Figure 8 shows that FGPNC having rod shape nanoparticles have slightly higher density (1.2134 g cm$^{-3}$) than that of FGPNC having spherical nanoparticles (1.2124 g cm$^{-3}$) and layered neat epoxy (1.2051 g cm$^{-3}$). It can be seen clearly from figure 8 that FGPNC of both the particles are having lower density than their respective monolithic nanocomposites having 1 wt% of nanoparticles. Thus it can be said that for a given size of sample, gradation in wt% of particles can lower the weight of the FGPNC compared to that of monolithic nanocomposites.

**Figure 4.** TEM micrographs of nanocomposites showing the distribution of spherical nanoparticles at (a) 0.25 wt% (b) 0.5 wt%, (c) 0.75 wt% and (d) 1 wt% of nanoparticles (arrows are showing agglomeration of spherical nanoparticles).
4.4. Tensile properties of epoxy-alumina nanocomposites

Stress-strain curves obtained from tensile test of monolithic samples of neat epoxy and nanocomposites (1wt%) are shown in figure 9. Slope of the initial linear part of the curve was used to determine the elastic modulus of samples. Figure 9 suggests that epoxy filled with alumina nanoparticles has higher modulus due to the fact that nanoparticles offer better resistance to the growth of cavity in epoxy matrix [35]. The nonlinear region in the stress-strain curve of nanocomposites of spherical alumina nanoparticles is more than that of nanocomposites of alumina nanorods. The increased non-linearity in the stress-strain curve is an indication of larger plastic
region. Nanocomposites of spherical nanoparticles have sustain higher plastic deformation before fracture than that of nanocomposites of alumina nanorods. The initial slope of stress-strain curve of nanocomposites of spherical alumina nanoparticles is lower than that of nanocomposite of alumina nanorods. The lower slope indicates less stiffness of composites.

Elastic modulus of nanocomposites as a function of wt% of nanoparticles is shown in figure 10. It is clear from figure 10 that the elastic modulus of nanocomposites increases with increase in wt% for both the types of nanoparticles. At 1 wt% of nanoparticles, an increment of 14% and 19% in elastic modulus was recorded over that of neat epoxy for nanocomposites having spherical and rod shape nanoparticles respectively. Rigid alumina

Figure 6. EDX spectra and mapping showing the distribution of spherical nanoparticles in (a) 0.25 wt% (b) 0.5 wt%, (c) 0.75 wt% and (d) 1 wt% of layer.
nanoparticles restrict the deformation of local matrix under applied load causing enhancement in the stiffness of nanocomposites. Compared to spherical nanoparticles, nanorods imparts higher increment in elastic modulus because alumina nanorods have higher aspect ratio (5–7) compared to that of spherical nanoparticles (almost unity) causing higher resistance to the stretching and alignment of polymer chains under the application of axial load [35–37].

Tensile strength of neat epoxy and epoxy-alumina nanocomposites was calculated by taking the ratio of maximum load taken by the sample and the original area of cross-section in the gauge region of the specimen. Tensile strength of nanocomposites (nanorods and spherical) is compared in figure 11. It is clear from figure 11 that tensile strength increases with the increase in wt% of alumina nanoparticle in epoxy. At 1 wt% of alumina nanoparticles, the tensile strength is significantly increased.
nanoparticles nanocomposites having spherical nanoparticles have higher load carrying capacity than that of nanocomposites having alumina nanorods and neat epoxy. Further it is clear that nanocomposites (spherical) have higher tensile strength at all wt% of nanoparticles used in the present work than that of nanocomposite (nanorods). The increased tensile strength of nanocomposite (spherical) is due to superior interfacial interaction between matrix and spherical nanoparticles causing better stress transfer in the composites. When tensile or axial load is applied on the nanocomposites, polymer chains can align the spherical nanoparticles easily than that of nanorods due to its shape. As a result spherical nanoparticles share higher stress without the breakage of polymer chains, which causes larger nonlinear region in the stress-strain curve. Thus the tensile strength of nanocomposite (spherical) remains higher than that of neat epoxy and nanocomposite (nanorods) at all the wt%.

4.5. Flexural properties of FGPNC
Load displacement curves obtained from three point bending test of neat epoxy (layered) and FGPNC samples are shown in figures 12 and 13 for loading from neat epoxy side and nanocomposite side respectively. Failure of FGPNC in flexural mode was governed by the crack propagation. Complete fracture of specimens happened due
to the propagation of crack from tensile side to compression side. Similar behaviour was reported elsewhere as well [18]. Samples were broken from the middle and delamination was not observed indicating proper bonding between the layers.

Figure 12 and 13 suggest that slope of the load-displacement curve of FGPNC having nanorods is higher than that of neat epoxy and FGPNC having spherical nanoparticles irrespective of direction of loading. Higher slope in case of FGPNC of alumina nanorods for both the direction of loading indicates that FGPNC of alumina nanorods is stiffer than the FGPNC of spherical nanoparticles. From figure 12 it is clear that when load is applied from epoxy side, FGPNC (spherical) have greater displacement at an applied load which indicates that FGPNC (spherical) is more compliant compared to FGPNC (nanorods). Further, FGPNC (spherical) have higher load carrying capacity (load at fracture) in comparison to that of FGPNC (nanorods) and neat epoxy. Whereas when load is applied from nanocomposite side, FGPNC (nanorods) have greater displacement at fracture and load carrying capacity (see figure 13). Thus depending on loading condition the load carrying capacity of FGPNC is changing due to the morphology of nanoparticles.
Flexural strength of FGPNCs and neat epoxy (layered) are shown in figure 14. Figure 14 shows that FGPNC samples have higher flexural strength than that of neat epoxy (layered) irrespective of direction of loading. When FGPNC samples were loaded from neat epoxy side, higher flexural strength was recorded for FGPNC (spherical) in comparison to that of FGPNC (nanorods). Whereas, when load was applied from nanocomposite side FGPNC (nanorods) have higher strength than that of FGPNC (spherical).

In flexural test layer at which load is applied, experiences compressive stress while layers at the opposite side will be under tensile stress. In other words, in three point bending layers below the neutral axis will experience tensile stresses while layers above the neutral axis i.e. towards the loading side will experience compressive stresses. With the help of density and elastic modulus of individual layers of nanocomposites the location of neutral axis of layered FGPNC was determined and was found to be placed almost at the mid plane of the layered composite in thickness direction i.e. 2.57 mm above the outer surface of neat epoxy layer i.e. in the nanocomposite layer having 0.5 wt% of nanoparticles (see figure 15). Thus the gradation did not shift the
location of neutral axis significantly from the centroidal axis due the fact that variation in density of nanocomposites for different wt% of nanoparticles is very small. It was observed in section 4.3 that nanocomposites having 1 wt% of spherical nanoparticles exhibited higher tensile strength than that of nanocomposites having 1 wt% of nanorods which is an indication that higher flexural strength will be obtained for the FGPNC (spherical) over FGPNC (nanorods) when load is applied from epoxy side as the layer having 1 wt% of alumina nanoparticles will be under tensile stress. Whereas when load was applied from nanocomposite side, FGPNC having nanorods had slightly higher flexural strength than that of FGPNC having spherical nanoparticles due to the fact that layer of nanocomposite having 0.25 wt% of nanoparticles and layer of neat epoxy will be under tensile stress as these layers are below the neutral axis. For equal wt% of nanoparticles, number of nanorods will be higher than that of spherical nanoparticles in the composite layer due to lower volume of nanorods. Moreover for this loading condition, nanocomposite layers of higher wt% of nanoparticles (layers of 0.75 wt% and 1 wt%) will be under compressive stress as these are above the neutral axis (see figure 15). It has been reported that compressive strength of nanocomposites decreases with the increase in wt% of nanoparticles in comparison to that of matrix material [38, 39]. Thus the propagation of crack, that initiated in the layer under tensile stresses will become easier than that of in the layer under compressive stresses. Experimental values of flexural strength of FGPNC samples and neat epoxy (layered) are shown in table 1. Results from experiments showed an improvement of 18% and 16% in flexural strength over that of neat epoxy (layered) for FGPNC (spherical) and FGPNC (nanorods) respectively for loading from neat epoxy side. Whereas in case of loading from nanocomposite side, an improvement of 8% and 9% in flexural strength for FGPNC (spherical) and FGPNC (nanorods) was observed over that of neat epoxy (layered) respectively.

Flexural modulus of FGPNCs and neat epoxy (layered) is shown in figure 16. Figure 16 shows that FGPNC samples have higher flexural modulus in comparison to that of neat epoxy (layered) for both the direction of loading. FGPNC having nanorods exhibited higher flexural modulus than that of FGPNC having spherical nanoparticles, because nanorods have higher aspect ratio which restricts the motion of polymer chains under application of load in better way than the spherical nanoparticles. Flexural modulus of the FGPNC samples and neat epoxy (layered) is listed in table 2. Results show an increment of 19% and 20% in flexural modulus over that of neat epoxy (layered) for FGPNC having spherical nanoparticles and FGPNC having nanorods respectively for loading from epoxy side. Whereas when load was applied from nanocomposite side, an improvement of 13% in flexural modulus over neat epoxy was obtained for both the types of FGPNC. When load was applied from neat

![Figure 15. Location of neutral axis in FGPNC sample.](image-url)

| Table 1. Flexural strength of neat epoxy (layered) and FGPNC samples. |
|---------------------------------------------------------------|
| **Loading from nanocomposite side** | **Flexural strength (MPa)** | % increase over neat epoxy | Standard deviation | **Loading from neat epoxy side** | **Flexural strength (MPa)** | % increase over neat epoxy | Standard deviation |
|-------------------------------------|----------------------------|---------------------------|-------------------|-------------------------------------|----------------------------|---------------------------|-------------------|
| Neat epoxy (layered)                | 81.29                      | —                         | 3.97              | 81.29                               | —                         | 3.97                      |
| FGPNC (spherical)                  | 87.69                      | 8                         | 8.28              | 96.08                               | 18                        | 4.86                      |
| FGPNC (nanorods)                   | 88.60                      | 9                         | 2.96              | 94.52                               | 16                        | 7.60                      |

Figure 15. Location of neutral axis in FGPNC sample.
epoxy side, higher flexural modulus was obtained for FGPNC samples because the outer most layer of sample i.e. 1 wt% of nanocomposite layer went through the maximum tensile stress. In the previous section, it was seen that nanocomposites having 1 wt% of nanoparticles were having highest tensile strength as well as Young’s modulus for both the types of nanoparticle under uniaxial tensile force because of the presence of maximum amount of alumina nanoparticles.

On the contrary, when load was applied from nanocomposite side, lower improvement in flexural modulus was obtained. In this case the outer most layer i.e. layer of neat epoxy was under maximum tensile stress. Reduced value of flexural strength and modulus of FGPNC is obtained due to the lower tensile strength and elastic modulus of neat epoxy layer. Thus for three point bending test outer most layer i.e. the layer opposite to the surface of applied load plays an important role in the increment of flexural properties of FGPNCs. Layered FGPNC having stronger and stiffer outer layer will have better flexural property.

Comparison of flexural failure strain of FGPNCs with that of neat epoxy is shown in figure 17. Figure 17 shows that FGPNC having spherical nanoparticles have higher flexural failure strain compared to neat epoxy irrespective of the direction of loading. An increment of 15% in flexural failure strain of FGPNC (spherical) was obtained over that of neat epoxy (layered) when the load was applied from neat epoxy side, while a slight increment in flexural failure strain was obtained over that of neat epoxy for loading from nanocomposite side. Whereas FGPNC having nanorods had lower flexural failure strain in comparison to that of neat epoxy (layered) for both the loading conditions. A reduction of 8% in failure strain was recorded for FGPNC (nanorods) over that of neat epoxy when loaded from neat epoxy side whereas 2% decrease in failure strain was observed over that of neat epoxy for loading from nanocomposite side. This further confirms that alumina nanorods offers higher restriction to the alignment and elongation of polymer chains compared to spherical alumina nanoparticles which positively supports the movement of polymer chains.

### Table 2. Flexural modulus of neat epoxy (layered) and FGPNC samples.

|                              | Loading from nanocomposite side | Loading from neat epoxy side |
|------------------------------|--------------------------------|------------------------------|
|                              | Flexural modulus (GPa) | % increase over neat epoxy | Standard deviation | Flexural modulus (GPa) | % increase over neat epoxy | Standard deviation |
| Neat epoxy (layered)         | 2.95                         | —                            | 0.096            | 2.95                         | —                            | 0.096            |
| FGPNC (spherical)            | 3.33                         | 13                           | 0.154            | 3.51                         | 19                           | 0.145            |
| FGPNC (nanorods)             | 3.34                         | 13                           | 0.106            | 3.55                         | 20                           | 0.153            |

![Figure 16. Flexural modulus of neat epoxy (layered) and FGPNCs.](image-url)
5. Conclusions

FGPNC of epoxy and alumina nanoparticles were fabricated using in situ polymerization technique. Gradation was attained in the thickness direction by varying the wt% of alumina nanoparticles. It can be concluded on the basis of results obtained in the present work that the reinforcement and gradation of alumina nanoparticles in the layered form can be an interesting route to improve the flexural properties of epoxy-alumina FGPNC. Flexural strength and modulus is greatly affected by the direction of applied load. FGPNC have higher flexural properties when load is applied from neat epoxy side. FGPNC having spherical nanoparticles has higher flexural strength whereas FGPNC having nanorods had higher flexural modulus compared to that of neat epoxy (layered). Thus for layered FGPNC having stronger and stiffer outer layer will have better flexural property.

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