INTRODUCTION

Hybrid nanocomposites usually refer to composites containing more than one type of filler and/or more than one type of matrix in which at least one of the constituent must be in nanosize range. In an epoxy composite when one of the filling materials is glass fibers and the other filler is nano-silica particles. The addition of a second type of filler such as nano-silica particles can serve to increase the strength of the hybrid nanocomposite².

Silica, with simple chemical formula SiO₂, exists in many different shapes and crystalline structures. Silica exists in ten different crystalline forms and polymorphs with the three main forms viz., quartz, which is the most common form, tridymite and cristobalite. It also occurs in a number of cryptocrystalline forms. Fibrous forms have the general name chalcedony and include semi-precious stone versions such as agate, onyx and carnelian. Granular varieties include jasper and flint. There are also anhydrous forms - diatomite and opal¹.

High purity silica (up to 99% SiO₂) is called Industrial sand. It is a more precise product than common concrete and asphalt gravels. Found most commonly in the crystalline state, it also occurs in an amorphous form resulting from weathering or plankton fossilization. The addition of nanoscale fillers to polymers can have a dramatic effect on
the mechanical properties\textsuperscript{3,4} compared to micron scale fillers. Silica nano particles have showed great usage in the formation of nanocomposites with various polymeric materials\textsuperscript{5}.

Silica (SiO$_2$) is a multi-functional ceramic material that is being used in various industries to improve surfaces and mechanical properties of diverse materials. It is used as a filler, performance additive, rheological modifier or processing aid in many product formulations, such as paints & coatings, plastics, synthetic rubber, adhesives, sealants, or insulation materials. In particular silica fume (amorphous silicon dioxide) or micro silica is being added to concrete in order to improve the concrete strength and durability. Silica fume is also being used in refractory concretes to reduce porosity and to enhance strength by improved particle packing.

Epoxy resins are the preferred matrix material since they possess better mechanical and thermal properties. Further, they wet many substrate materials, absorb less moisture. The other advantages worth mentioning are that they possess excellent chemical resistance coupled with good electrical properties\textsuperscript{6}.

When the filler has a nanometer thickness and a high aspect ratio (30–1000) plate-like structure, it is classified as a layered nanomaterial (such as an organosilicate)\textsuperscript{7}. In general, nanomaterials provide reinforcing efficiency because of their high aspect ratios\textsuperscript{8}. The effect of nano-silica addition improves the mechanical properties of epoxy polymer and glass fiber-reinforced epoxy-silica hybrid composites.

X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials. The method has been traditionally used for phase identification, quantitative analysis and the determination of structure imperfections. In recent years, applications have been extended to new areas, such as the determination of crystal structures and the extraction of three-dimensional micro structural properties. The method is normally applied to data collected under ambient conditions, but \textit{in situ} diffraction as a function of external constraints (temperature, pressure, stress, electric field, atmosphere, etc.) is important for the interpretation of solid state transformations and materials behavior. Various kinds of micro- and nano-crystalline materials can be characterized from X-ray powder diffraction, including inorganic, organics, drugs, minerals, zeolites, catalysts, metals and ceramics. The physical states of the materials can be loose powders, thin films, poly crystalline and bulk materials. For most applications, information possible to extract depends on the nature of the sample microstructure (crystallinity, structure imperfections, crystalite size, and texture), the complexity of the crystal structure (number of atoms in the asymmetric unit cell, unit cell volume) and the quality of the experimental data (instrument performances, counting statistics).

Rocks, sediments, and precipitates are examples of geologic materials that are composed of minerals. Numerous analytical techniques are used to characterize these materials. One of these methods, X-ray powder diffraction (XRD), is an instrumental technique that is used to identify minerals, as well as other crystalline materials. In many geologic investigations, XRD complements other mineralogical methods, including optical light microscopy, electron microprobe microscopy, and scanning electron microscopy. XRD provides the researcher with a fast and reliable tool for routine mineral identification. XRD is particularly useful for identifying fine-grained minerals and mixtures or intergrowths of minerals that may not lend themselves to analysis by other techniques. XRD can provide additional information beyond basic identification. If the sample is a mixture, XRD data can be analyzed to determine the proportion of the different minerals present. Other information obtained can include the degree of crystallinity of the minerals present, possible deviations of the minerals from their ideal compositions (presence of element substitutions and solid solutions), the structural state of the minerals (which can be used to deduce temperatures and (or) pressures of formation), and the degree of hydration for minerals that contain water in their structure. Some mineralogical samples analyzed by XRD are too fine grained to be identified by optical light microscopy. XRD does not, however, provide the quantitative compositional data obtained by the electron
Several micromechanics models are available for predicting the elastic modulus of the polymer nanocomposites. Mori–Tanaka model\textsuperscript{12} was used in the Jia-Lin et al. work for predicting the elastic modulus of the composite at different silica contents. Micromechanics analysis was used to predict the elastic properties of the four composite systems using the Mori–Tanaka approach with the elastic properties of the pure polyimide matrix and silica materials determined with the molecular modeling.

In the present work the elastic modulus of the composite was calculated by the Mori–Tanaka model\textsuperscript{12} and which predicts that the elastic modulus increases with the increase of silica content. But the experimental values showed that the elastic modulus of the composite increases for 1%, 2% and 3% weight fraction of silica and the longitudinal tensile strength increased for 1% and 2% and decreased for 3%.

The main objective of the work is to improve the mechanical properties such as elastic and tensile properties of the fiber reinforced composites by adding silica nanoparticles at different proportions. These types of composites may be called as hybrid nanocomposites. Nanoparticles influence the various properties of the epoxies. The nanoparticles are directly involved with the dislocations movements of the grains of the materials thereby increases the strength of the materials. It can improve the mechanical properties as well as electrical properties. These types of composites can be used in making the electrical boards, sockets, casings, etc.

**EXPERIMENTAL**

**Materials Used**

The matrix used in the present study was an epoxy resin (LY556) system from ECMAS Pvt. Ltd, Hyderabad, an araldite hardener (HY951) was mixed in proportions of 100:12 from ECMAS Pvt. Ltd, Hyderabad.

The reinforcing nano silica particle from CHEMAPOL INDIA Pvt. Ltd, Mumbai. It is organically modified with a 3-aminopropyltriethoxysilane by sonication process.

- Woven roving glass fiber mat is taken from Saint-Gobain-Vetrotex India Ltd.

**Ultrasonic Dispersing of Silica (\(\text{SiO}_2\))**

Silica is used in various industries for its abrasion resistance, electrical insulation and high thermal stability. Ultrasonic dispersing helps the potential of silica by improving the dispersion quality. Silica is available in a wide range of hydrophilic and hydrophobic forms and is typically used in extremely fine particle size. Typically, silica is not well dispersed after wetting. It also adds a lot of micro bubbles to the product formulation\textsuperscript{9}.

For most silica applications, a good and uniform dispersion is important. In particular when being used in coatings and lacquers, the silica particles need to be small enough to improve scratch resistance and not to interfere with the visible light to avoid haze and maintain transparency. For most coatings silica need to be smaller than 40nm. For other applications, particle agglomeration hinders each individual silica particle to interact with the surrounding media. Ultrasonic processing has been proven to be more effective in dispersing silica than other high-shear mixing methods. The Fig. 1 shows a typical result of ultrasonic dispersing of fumed silica in water. The measurements were obtained using a Malvern Mastersizer 2000\textsuperscript{10,11}.

It is also reported that the degree of exfoliation depends on the structure of the clay, curing agent. Vaia et al. have suggested that the degree of exfoliation can be improved through conventional shear devices such as extruders, mixers, ultra sonicators.

In this study, an ultra sonicator was used to disperse and exfoliate the 3-aminopropyltriethoxysilane treated silica nano particles in the epoxy matrix.

**Synthesis of Epoxy-Silica nanocomposites and Glass Fiber-Reinforced Epoxy-Silica Hybrids**

The synthesis of glass fiber reinforced epoxy-silica hybrids consists of mixing of resin-silica and E-glass fibers by the hand-layup process. The 50wt% of fiber and 50wt% of epoxy resin are used
Silica nanocomposites are prepared by mixing hardener with treated silica nano particles and poured into wooden mould of 10mm diameter and 100mm length. E-glass fibers are embedded in longitudinal direction in epoxy. The XRD and the tensile specimens are cut as per the dimensions.

**Working principle of XRD**

The three-dimensional structure of non-amorphous materials, such as minerals, is defined by regularand repeating planes of atoms that form a crystal lattice. When a focused X-ray beam interacts with these planes of atoms, part of the beam is transmitted, part is absorbed by the sample, part is refracted and scattered, and part is diffracted. Diffraction of an X-ray beam by a crystalline solid is analogous to diffraction of light by droplets of water, producing the familiar rainbow. X-rays are diffracted by each mineral differently, depending on what atoms make up the crystal lattice and how these atoms are arranged. In X-ray powder diffractometry, X-rays are generated within a sealed tube under vacuum. A current is applied that heats a filament within the tube, the higher the current the greater the number of electrons emitted from the filament. This generation of electrons is analogous to the production of electrons in a television picture tube. A high voltage, typically 40 kilovolts, is applied within the tube. This high voltage accelerates the electrons that hit the target made of copper to produce X-rays.

The wavelength of these X-rays characterises the target. These X-rays are collimated and directed onto the sample, which has been ground to a fine powder particles of size less than 10 microns. A detector detects the X-ray signal that is processed electronically to generate a count rate. X-ray scan changes the angle between the X-ray source, the sample, and the detector at a controlled rate between preset limits. When an X-ray beam hits a sample and is diffracted, by applying Bragg's Law the distances between the planes of the atoms that constitute the sample can be measured.

In this configuration, the X-ray tube and the detector both move through the angle theta (θ) and the sample remains stationary. $n l = 2 d \sin \theta$, where $n$ is the order of the diffracted beam, $\lambda$ is the wavelength of the incident X-ray beam, $d$ is the distance between adjacent planes of atoms (the $d$-spacing), and $\theta$ is the angle of incidence of the X-ray beam. Since $\lambda$ is known and $\theta$ is measured, the $d$-spacing can be calculated. The characteristic set of $d$-spacing generated in a typical X-ray scan provides a unique “fingerprint” of the mineral or minerals present in the sample. Comparing with standard reference patterns and measurements, this “fingerprint” allows identification of the material.

**RESULTS AND DISCUSSION**

The hybrid nanocomposites are prepared by hand layup method. Silica nanoparticles are mixed into the epoxy polymer by sonication to disperse uniformly. The silica nanoparticles used in...
the preparation of composites were treated with 3-aminopropyltriethoxysilane. A unidirectional glass fiber is reinforced into the nano-silica mixed epoxy. Composite is prepared by alternate layers of epoxy and fiber by maintaining 50% weight fraction. By varying the nano-silica content 1%, 2% and 3% weight fraction composites are prepared. The prepared composites are then used for both characterization and tensile strength testing.

Fig. 4 represents the non-crystalline (amorphous) nature of the pure epoxy. This XRD pattern is having only one broad maxima from 10 deg to 35 deg approx. Generally this type of patterns represents the non-crystalline nature i.e. amorphous
Fig. 6: Multiple record graph

Fig. 7: Planes representation of XRD pattern of 3 wt% silica nanocomposite

Fig. 8: Composite longitudinal tensile strength (with unidirectional fiber reinforced) Vs Weight percent of silica
A comparison between 1 wt%, 2 wt% and 3 wt% can be made in the Table 2 and 3 given below.

Table 1: Structural data of 3% weight fraction of nano-silica based hybrid composite

| Crystal Structure | Orthorhombic |
|-------------------|--------------|
| 2 Theta (degrees) | 14.131       |
| FWHM (degrees)    | 0.183        |
| d-spacing of [110] plane (nm) | 0.62782 |
| Particle size (nm) | 63.74       |

A comparison between 1 wt%, 2 wt% and 3 wt% can be made in the Table 2 and 3 given below.

Table 2: Comparison of structural data obtained from XRD patterns

| Wt % | Phase Identified | Lattice Parameters | Density (g/cm³) |
|------|------------------|--------------------|-----------------|
|      |                  | Sides (Å)          | Angles (degrees) |                  |
|      |                  | a      | b     | c     | A    | β    | γ    |                  |
| 1    | Silica (SiO₂)    | 11.103 | 7.8989| 4.9771| 90   | 112.265 | 90 | 1.976           |
| 2    | Silica (SiO₂)    | 18.576 | 13.995| 7.391 | 90   | 90    | 90 | 1.869           |
| 3    | Silica (SiO₂)    | 10.217 | 7.9579| 4.9565| 90   | 90    | 90 | 1.981           |

Table 3: Comparison of structural data between 1%, 2% and 3% silica nanocomposite

| Parameters \ Wt. Content | 1 wt % silica | 2 wt % silica | 3 wt % silica |
|--------------------------|---------------|---------------|---------------|
| Crystal Structure        | Monoclinic    | Orthorhombic  | Orthorhombic  |
| 2 Theta (degrees)        | 14.131        | 14.238        | 14.131        |
| FWHM (degrees)           | 0.188         | 0.192         | 0.183         |
| d-spacing of [110] plane (nm) | 0.62624 | 0.61651 | 0.62782 |
| Particle size (nm)       | 60.88         | 58.79         | 63.74         |
| Intensity (CPS) at maximum peak | 2462 | 2190 | 2051 |

Note: CPS means counts per second

The intensity of the maximum peak decreases with the increase in the content of nano-silica powder of the composite and increase in crystallinity of the nanocomposite. The intensity of the maximum peak lies at approximately 14º for all the three compositions of the composite. The intensity of the peaks is slightly reduced with the increase of composition. The average particle size of the silica is 60 nm.
intensity of the XRD pattern decreases in pure resin to 1 wt% nano-silica with the inclusion of nano-silica powder. The crystallinity of the composite increases with the inclusion of crystalline material, silica nanoparticles, in the non-crystalline material, epoxy.

The XRD patterns of 1%, 2% and 3% silica nanocomposites show similar patterns in the multiple record graph shown in the Fig. 6. This shows that similar dispersion phase (i.e. Silica phase) is present in the present nanocomposites.

Fig. 7 represent different diffracted planes at corresponding angles for 1%, 2% and 3% weight fraction of silica based hybrid nanocomposites. In the Fig. 6 three XRD patterns at [1 1 0] plane show a maximum diffraction at approximately 14.1 degrees and that angle is considered as 2theta angle for calculating the crystallite size of the silica present in the nanocomposite.

The other planes [1 1 1], [3 1 0], [0 2 1], [2 0 0], show lower diffracted peaks (lower intensity) when compared to [1 1 0] plane. This means that the [1 1 0] plane is more common plane (basal plane) present in the silica than other planes. The main advantage of the basal plane is used to identify the crystal structure and chemical phase of the material in X-ray diffraction. From these basal planes, it is also possible to identify the periodicity of the material to identify the chemical formula.

The longitudinal tensile strengths of the hybrid nanocomposites are observed in the UTM (Universal Testing Machine).

The results imply that the longitudinal tensile strength increases slightly from pure epoxy (with unidirectional fiber reinforced) to 1% weight fraction of silica mixed epoxy composite to 2% and decreases from 2% to 3%. The decrease of the tensile strength may be due to the increase of silica composition which is more than the dislocations of the epoxy and agglomerates at the dislocations (Fig.8).

Mori tanaka model for predicting the elastic modulus

The Mori-Tanaka approach was used to predict the elastic properties of two-phase composites (matrix and effective particle phases) as a function of the effective particle volume fraction and geometry.

The overall elastic-stiffness tensor of the composite is

\[ C = (c^m C^m - c^p C^p T^p)(c^m I + c^p T^p)^{-1} \]  \( \ldots (1) \)

where
- \( C^p \), stiffness tensor of the effective particle
- \( C^m \), stiffness tensor of the matrix
- \( c^p \), volume fraction of the effective particle
- \( c^m \), volume fraction of the matrix
- \( I \), Identity tensor
- \( S^p \), Eshelby tensor
- \( T^p \), dilute strain-concentration tensor of the effective particles and it is given by

\[ T^p = [I + S^p(C^m)^{-1}(C^p - C^m)]^{-1} \]  \( \ldots (2) \)

For spherical effective particle and an isotropic matrix, the components of the Eshelby tensor are

\[
\begin{bmatrix}
S_{111} & S_{122} & S_{133} & 0 & 0 & 0 \\
S_{222} & S_{222} & S_{222} & 0 & 0 & 0 \\
S_{333} & S_{333} & S_{333} & 0 & 0 & 0 \\
0 & 0 & 0 & S_{1212} & 0 & 0 \\
0 & 0 & 0 & 0 & S_{2323} & 0 \\
0 & 0 & 0 & 0 & 0 & S_{3131} \\
\end{bmatrix}
\]

where
- \( \nu \) is the Poisson’s ratio of the matrix.

To find out the \( S^p \), Eshelby tensor

Poisson’s ratio of the epoxy matrix, \( \nu = 0.35 \)
Stiffness tensor matrix of the epoxy, \( C^m \) is

\[
C^m = \begin{bmatrix}
0.3305 & 0.0769 & 0.0769 & 0 & 0 & 0 \\
0.0769 & 0.3305 & 0.0769 & 0 & 0 & 0 \\
0.0769 & 0.0769 & 0.3305 & 0 & 0 & 0 \\
0 & 0 & 0 & 1.2330 & 0 & 0 \\
0 & 0 & 0 & 0 & 1.2330 & 0 \\
0 & 0 & 0 & 0 & 0 & 1.2330
\end{bmatrix}
\]

Stiffness tensor matrix of the effective particle, \( C^p \) is

\[
C^p = \begin{bmatrix}
73 & 41 & 0 & 0 & 0 & 0 \\
41 & 73 & 41 & 0 & 0 & 0 \\
41 & 41 & 73 & 0 & 0 & 0 \\
0 & 0 & 0 & 16 & 0 & 0 \\
0 & 0 & 0 & 0 & 16 & 0 \\
0 & 0 & 0 & 0 & 0 & 16
\end{bmatrix}
\]

By substituting the values of \( S^p \), \( C^m \) and \( C^p \) then the \( T^p \) is

\[
T^p = \begin{bmatrix}
0.0095 & -0.0133 & -0.0133 & 0 & 0 & 0 \\
-0.0133 & 0.0095 & 0.0095 & 0 & 0 & 0 \\
0.0133 & -0.0095 & 0.0095 & 0 & 0 & 0 \\
0 & 0 & 0 & 0.4945 & 0 & 0 \\
0 & 0 & 0 & 0 & 0.4945 & 0 \\
0 & 0 & 0 & 0 & 0 & 0.4945
\end{bmatrix}
\]

Substitute \( T^p \) in equation-1 to calculate the overall elastic-stiffness tensor for various weight fractions of silica mixed in the epoxy resin. From this equation, the elastic modulus of the composite can be calculated for various fraction of silica content mixed in the polymer resin.

For 1 wt% silica mixed epoxy

- Weight fraction of the silica nanoparticles = 1%
- Density of the silica = 2.2 g/cm³
- Volume fraction of the silica nanoparticles, \( c^p = \frac{\text{Weight fraction}}{\text{Density of silica}} \times 0.004545 \)
- Volume fraction of the epoxy matrix, \( c^m = 1 - 0.004545 = 0.995455 \)

Young’s modulus of the epoxy with 1% with nanosilica is 2.4276 GPa.

Based on Mori-tanaka model, the elastic modulus of the composite increases with the increase of composition of silica nanoparticles from 1 % to 3 %. The elastic modulus increased due to the inclusion of high strength crystalline material i.e. silica. The silica nanoparticles are set as obstacles to the free movement of dislocations of the epoxy thereby increase the elastic modulus and strength of the material.

Mori-Tanaka model predicts that the inclusion of nanoparticles (silica nanoparticles) improves the strength of the epoxy with increase of weight percent of the nanoparticles.

CONCLUSIONS

The crystallinity of the composite is observed by the XRD pattern and found to be increasing with the increase of silica content. The silica phase is identified in all the three composites by their XRD patterns. The crystal structure of silica in 1% weight fraction of hybrid nanocomposite is found to be monoclinic and for 2% and 3% the crystal structure is orthorhombic. The maximum intensity peak is obtained at [110] plane and the 2theta is 14.1º approximately. The average d-spacing of [110] plane is 0.62nm. The average crystallite size of the silica present in the nanocomposites is 60nm. Residual strains are found in the nanocomposite by XRD and increased from 1% to 2% weight fraction of silica and there is a slight decrease in 3%.

The elastic modulus of the hybrid nanocomposite is increased by 51 percent for 2% weight fraction of silica hybrid nanocomposite and decreased for 3% weight fraction of silica. For 1% weight fraction of silica the elastic modulus of the nanocomposite is increased by 48 percent.

The longitudinal tensile strength of the hybrid nanocomposite is increased by 25 percent for 2% weight fraction by the inclusion of silica nanoparticles as fillers in the epoxy polymer.

The experimental values of elastic modulus and longitudinal tensile strength are compared with Mori-Tanaka model and a deviation of 29 percent is observed from experimental values.
to the theoretical values. Experimental values show better results compared to theoretical values.

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