Synergistic Effect of Nano-α-Al_2O_3 Particles on Mechanical Properties of Glass-fibre reinforced Epoxy Hybrid Composites

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ABSTRACT

The mechanical properties of hybrid nanocomposites made of epoxy/glass fibre dispersed with nano-α-Al_2O_3 powder at different weight percentages were studied.The effect of nano-α-Al_2O_3size and wt% on mechanical properties like tensile, flexural, interlaminar shear stress and hardness enhanced because of their higher surface area and interfacial polymer-metal interaction. The nanoparticle embedded laminates have shown improvement in flexural strength,and hardness when compared to laminate without nano-α-Al_2O_3. The properties varied with the loading and size of the nanoparticles. The tensile strength was highest for 0.5 wt% of 200nm nano-α-Al_2O_3, which is 167.80 N/m2.The highest flexural strength was observed for 1.5 wt% of 60nm nano-α-Al_2O_3 based laminates which was 378.39 N/m_2 and the highest interlaminar shear strength (ILSS) was observed for 0.5 wt% of 60nm nano-α-Al_2O_3, which is 31.21 MPa and the highest Vickers hardness was found to be 86.72 for 1.5 wt% of 60nm nano-α-Al_2O_3.

KEYWORDS: *Alumina, GFRC, SEM, XRD, Epoxy resin, Hardener, Mechanical properties.*

1. INTRODUCTION

Development of novel reinforced composite materials or alteration of existing composite material to face the reality is very challenging for most of the materials scientists1.Compared to other resins, epoxy resins have diverse

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advantages, like, increased mechanical and fatigue strength, impact-resistant, excellent moisture resistance and chemical resistance, good electrical properties and low shrinkage during cure. Addition of fibres to the polymer matrix is proven to increase the mechanical properties of the composite material as compared to the neat polymer, especially glass fibres [2].

It was observed from the literature that there is a significant improvement in mechanical properties with epoxy matrix modification [3]. One approach to modify the polymer matrix with nil or less covalent interaction or supramolecular interaction is to incorporate metals in their nanoscale either as free metal or metal oxide[4].Some of the nanoparticles which are reported to enhance the properties in presence of fibre-reinforced plastic (FRP) are nano clay, Al_2O_3, SiO_2 and TiO_2[5,6].Iron nanoparticles (NPs) embedded in glass fibre/ epoxy composite enhanced the mechanical and magnetic properties[7]. Addition of nanoclay particles also resulted in improvement of the tensile properties which is due to higher interaction of the polymer matrix with the metal oxides in the clay structure via hydrogen bonding[8].Few studied the effect of nanoalumina particles on physical and mechanical properties of UV cured epoxy acrylate via nano-indentation[9] and observed that the scratch resistance and self-healing of the film improved in the presence of nanoalumina particles. Nano SiO_2 fillers showed higher elastic moduli for the nano SiO_2/epoxy composite to that of neat epoxy resins[10] and effectively increased both the toughness and strength of epoxy resin even at low loadings[11].It was reported well in all the work that final properties are affected by the change in particle size, shape, and size distribution of the loaded filler i.e., nanoparticle along with the resin crosslink density.Other promising fillers such as SiC, AIN and BN were also found to improve the mechanical properties[12,13]. Among these, ceramic fillers are considered as an ideal candidate for improving thermal properties. Alumina is an engineering ceramic material[14] with many interesting properties such as wear resistance, good dielectric application[15], resistance to acid and alkali at elevated temperatures, excellent thermal conductivity and can be obtained in high purity upto 99.5%[16,17].Some found that alumina improved wear resistance of the compositebut its mechanical strength decreased with an increase ina weight proportion[18] of the reinforcement.

In this work, we have investigated the mechanical properties of S-fibre glass-reinforced epoxy resin composite by embedding nano-α-Al_2O_3 (60 and 200nm) with three different weight percentages (0.5, 1.0, 1.5 wt%). The nanoparticles were synthesized by high energy ball milling technique (60 and 200nm), a greener approach. Subsequently, these materials were characterised by SEM and XRD for their surface morphology. Mechanical properties of nano-α-Al_2O_3 embedded glass fibre/epoxy hybrid composites were evaluated.

2. EXPERIMENTAL

To attain the various nanocomposites, 2 different sizes of nano-⟨-Al_2O_3(60nm and 200nm) were embedded with fibreglass/epoxy bolstered laminates as composites. The nanocomposite samples are taken in triplicate, with 0.5%, 1% and 1.5% by weights of nano-α-Al_2O_3 along

with blank without nano alumina, for concordance and a better understanding of their mechanical properties after the addition of nano-α-Al_2O_3 to the epoxy composites.The testing of composites materials wasdone strictly following the ASTM standards[19,20].

2.1 Materials

In this study, commercially available Al_2O_3(bulk) particles were purchased from Qualitech Systems; Ludhiana. Al_2O_3 nanopowder fillers were prepared using a high energy ball milling technique (Ikon instruments, New Delhi, India) having 14 stainless steel balls.Two different sizes of nanomaterials were predominantly obtained, (60±5nm and 200±5nm) by the milling process. The main characteristics of the synthesised Al_2O_3 nanopowder are listed in Table 1.

Commercially available S-fibre glass woven cloth(Style-6533, 200 GSM (6oz) Plain Weave 30", Aerialite compatible with polyester, vinyl ester and epoxy resin system was used in this work. The glass fibre sheets chosen for the study are weaved in two directions.

2.2 Fabrication of hybrid nanocomposites

Hybrid nanocomposite materials with different weight percentages of nano-α-Al_2O_3 fillers were fabricated by well-known hand lay-up method. The ratio of glass fibre to binder was 1:1.5 in weight % and preliminary experiments were conducted to assess the dispersibility of alumina nanoparticles with varying size in epoxy glue using a mechanical stirrer. Commercial grade Epoxy resin (LY556) and hardener (HY951), was taken in the weight ratio of 10:1 respectively to make the composite material. Before the addition of hardener, the nanomaterial in total weight % (resin plus glass fibre) is added to the matrix and dispersed evenly using a mechanical agitator for a period of 30 min.

The prepared controlled composite samples (without nanosilica) are designated as A-X-0 and A-Y-0. On the other hand, the prepared composite samples are designated as A-X-1, A-X-2 and A-X-3 with 0.5wt%, 1.0wt% and 1.5wt% of nano Al_2O_3 of 60nm diameter; while A-Y-1, A-Y-2 and A-Y-3 for the nano Al_2O_3 of 200nm diameter. The Epoxy resin (LY556) and hardener (HY951) were taken 10:1 ratio.

TABLE 1. Main parameters of synthesised Al_2O_3 nanopowder

Crystal Phase	Purity (%)	Average size (nm)	Specific surface Area, BET (m^2/g)	Density (g/cm^3)
α	≥99.90	60±5	42±5	3.11
α	≥99.85	200±5	7.6±2	3.27

The mould was cleaned well and the base is set with a Teflon sheet to facilitate easy removal of the composite.The first layer of the composite is made by spreading the epoxy resin over a sheet of glass fibre inside the mould by carefully applying using a brush. Seven layers of composite with S-glass fibre were prepared to make a thickness of about 4mm. After each layer, mild steel roller is rolled over the composite to remove the entrapped air and to maintain a uniform thickness all over the composite material.The prepared composites are allowed to cure in the mould by placing it in the oven at a temperature of 35°C for a period of 72hrs. The cured composite was smoothened and cut into ASTM standard dimensions using a diamond cutter to measure tensile strength, flexural strength and Vickers hardness.

3. CHARACTERISATION

The surface morphological features of the materials synthesised were studied using high-resolution scanning electron microscopy (SEM). The samples were characterised for their crystallinity and the crystal parameters by using X-ray diffractometer (Shimadzu Scientific Instruments (SSI), Shimadzu Lab-X XRD-6000; X-ray tube: Cu Kα radiation (1.54060Å), voltage: 40.0 keV and current: 30.0 mA). The XRD-6000 boasts an integrated design featuring high speed and a high precision

vertical goniometer suitable for diverse applications and data processing software supporting the Windows XP user interface. The 2θ scanning range was between 10 and 900, at 5°/min scan rate.

4. RESULTS AND DISCUSSIONS

The influence of nanoparticle on the enhancement of material properties of epoxy-based fibreglass reinforced composites were analysed by using nano α-alumina, synthesised by greener ball milling approach. The size of the as synthesised nanoparticle was around 60 and 200nm, which was confirmed by SEM analysis (Figure1a). The purity of the nanopowders was confirmed using XRD, where the peaks corresponding to the crystalline phase of α-alumina (Figure1b) matches with the XRD patterns reported in the literature[21].

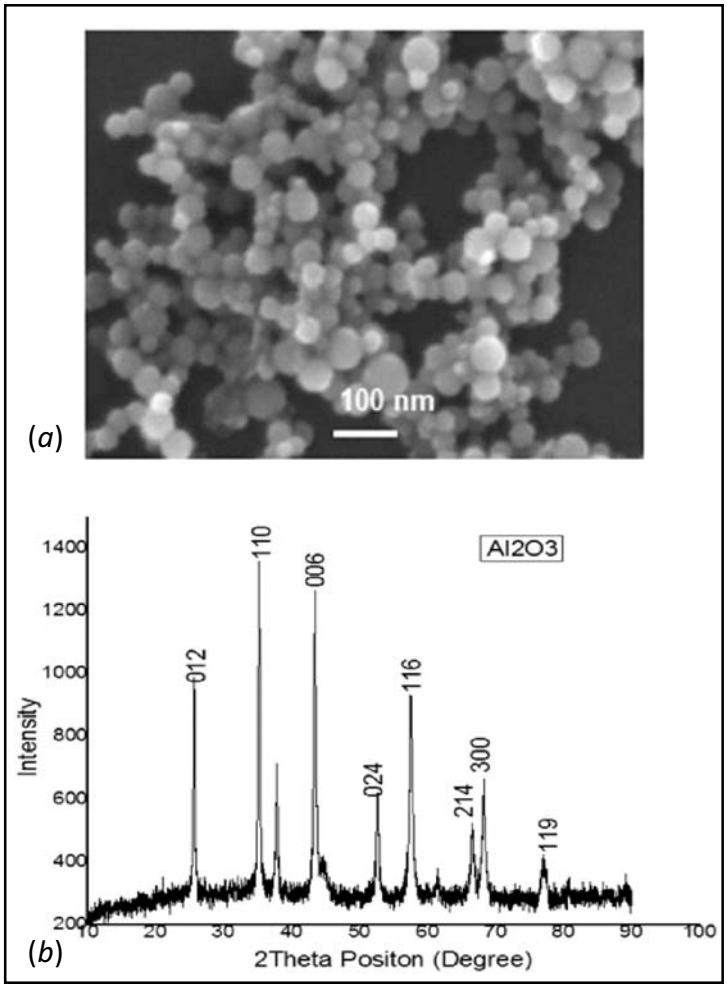

Fig. 1a) SEM image of the nano-α-Al_2O_3powder, 1b) X-ray diffraction pattern of nano-α-Al_2O_3

4.1: Tensile strength

The quality of engineering materials is usually assessed by its ability to withstand applied stress. The maximum force or stress that can be tolerated while being stretched or pulled before breaking is defined as Tensile Strength. For this study, the composites were prepared as per ASTM D-638 standards with and without nanofiller and the tensile tests were measured using Universal Testing Machine. Using the stress-strain data from UTM, the tensile strength was estimated for alumina nanoparticle embedded epoxy-GF composites of two different sizes (60nm and 200nm) as a function of its wt% (Figure 2). It is observed from the results that the tensile strengths for 60nm laminate showed a decreasing trend with the increase of % addition of nanoalumina. Whereas for 200nm nanoalumina samples; the highest tensile strength of 167.8 N/m^2 was recorded for 0.5 wt% nanoalumina and with further increase in alumina % the strength decreased. It is clear from the above tensile strength data that the wt% of the particles and their particle size has a major influence on the mechanical properties of the composites.

When compared to the blank nanocomposite (136 N/m^2), 60nm hybrid materials showed a gradual decrease in strength from 128 to 96 N/m^2, which can be attributed to either non-uniform dispersion of the nanomaterial in the composite or higher % of nanomaterial (i.e. the 60nm composite might exhibit a maximum tensile strength below 0.5 wt% of alumina).The decreasing trend with increasing % of alumina might also be due to the lesser interaction of the epoxy with the nanofiller. Despite the smaller size and high surface area (45 m^2/g), the strength of the laminate was not increased when compared to the blank, due to agglomeration of the nanoparticle before it dispersed into the matrix or a decreased % of surface hydroxy over alumina. Since increasing % did not improve the strength in comparison

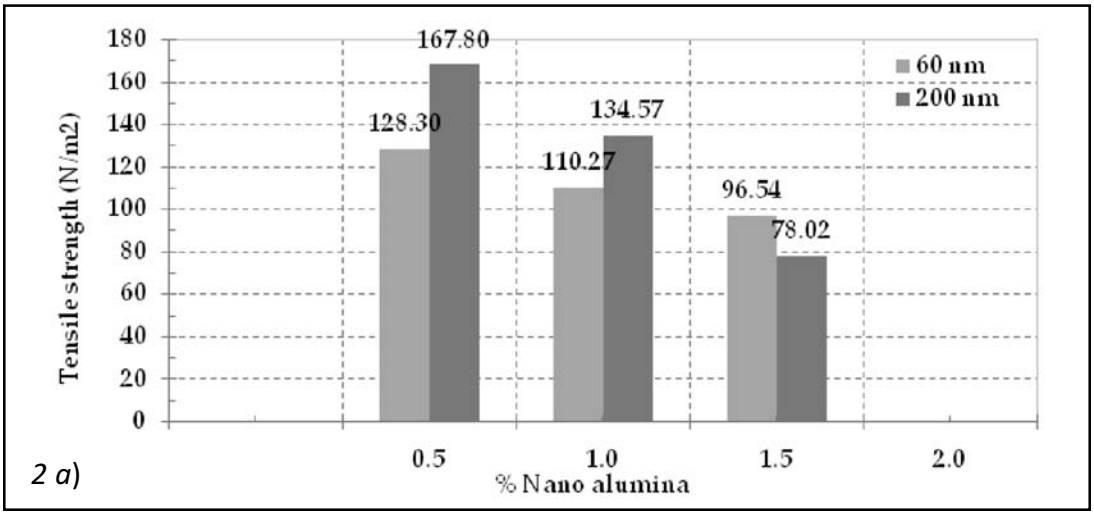

Fig. 2a Tensile strength for nano-α-Al_2O_3based Epoxy-Glass fibre hybrid laminates at 60nm and 200nm as a function of wt%

to the blank, it is understood that 60nm alumina fillers were not the optimum nano size to improve the tensile strength, in the case of alumina-based epoxy-GF laminates.

In the case of 200nm particle composites, the tensile strength value increased 20%, from 136 to 168N/m^2 for just 0.5 wt% alumina, which might be due to higher interaction of the metal nanoparticle surface with the epoxy-glass filler matrix.With increasing wt% of alumina, the strength decreased drastically up to 78N/m^2 for 1.5% alumina, where the chance of nanoparticle agglomeration increases with increasing wt%, which reduces the number of surface anchoring hydroxy (-OH) groups (higher the size lesser will be the surface area) and ultimately the strength of the laminate.

4.2 Flexural strength

Flexural strength (FS) was calculated by performing short beam shear (SBS) test; conducted as per the ASTM- D2344/D2344M-00 standards at room temperature. Samples with dimensions of 25 x 11 x 5.5 mm and a span length of 22mm are used for the analysis. The flexural strength is calculated according to equation 1

$$FS = \frac{3\,PL}{2bt^2} \qquad \text{..... equ. (1)}$$

Where, FS flexural strength (MPa), P force at fracture (N), L length of the sample (mm), b thickness (mm), and t width (mm). Flexural strength gives the amount of force or stresses a material can withstand before it breaks. Depending on the shape of the sample various equations are used and for a rectangular sample under a load in a three-point bending setup, the equation used in given above. The relation between tensile strength and flexural strength is dependent on the homogeneity of the material, with increasing inhomogeneity the flexural strength will be higher than the tensile strength. The converse will happen when the surface only has some defects and not the bulk. For the hybrid composites prepared, the surface inhomogeneity is lesser than the bulk inhomogeneity, because of this reason for all the alumina inclusion the flexural strength was much higher than the tensile strength.

The flexural strength of the prepared hybrid laminates was calculated using equation 2, for varying wt% of nano-α-$Al_2O_3$for both 60nm and 200nm particle sizes.It is observed that the flexural strengths for 60nm laminate showed an increasing trend with the increase % addition of nano-α-Al_2O_3(from 252.69 to 378.39 N/m2).Though the Tensile strength values are not convincing for 60nm, the flexural strength values show that the particles were homogeneously spread and a lesser value in tensile strength is only due to more agglomeration of nanoparticle at 0.5 wt%.The increasing trend is due to a higher amount of homogeneous materials in the system which makes the composite adhere very strongly and results in higher flexural strength. The addition of nanofiller with high surface area increases the polymer/nanofiller interface area and increases the strength. This increased interfacial strength reduces the stress concentration at the interface and enhances the load transfer efficiency effectively, which is observed in the case of 60nm laminates with increasing wt%.

In the case of 200nm nano-α-Al_2O_3hybrid laminates, Flexural strength showed a decreasing trend from 252.69 to 193.31 N/m^2, which is shown in Figure 3.With the increasing size of the nanomaterial, the possibility of more

aggregation will induce imperfection at the surface and the bulk material. This makes the flexural strength decrease with increasing wt% of nanoalumina.The flexural strength at 1 wt% of 200nm alumina is the least as both the size and amount increased the imperfection and decreased the strength drastically.

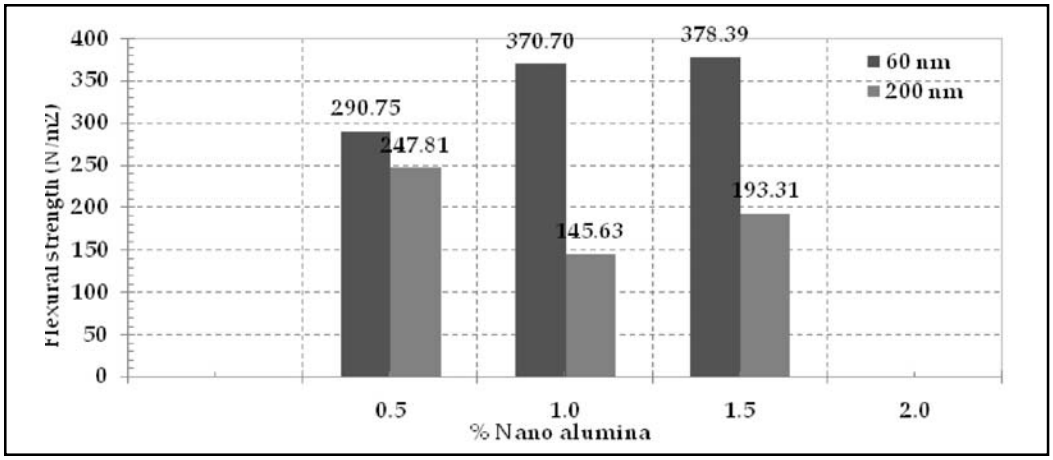

Fig. 3. Flexural strength for nano-α-Al_2O_3 based epoxy-glass fibre hybrid laminates at 60nm and 200nm as a function of wt%

4.3 Interlaminar shear stress

One of the major problems in laminate composites is their delamination characteristics. Delamination is the damage happening at the interface of the composites and happens due to high interlaminar stress at the interface which is very important in designing a laminated composite. ILSS measures the in-situ shear strength between the polymer matrix and the nanofiller/fibre. The emergence of delamination induces a drastic reduction in the mechanical and thermal properties of the composites.The interlaminar shear strength was calculated by performing short beam shear (SBS) test; conducted as per the ASTM- D2344/D2344M-00 standards at room temperature. Samples have the dimensions of 25 x 11 x 5.5 mm, with a span length of 22mm.

$$ILSS = \frac{3P}{4bt} \qquad \text{equ. (2)}$$

Where, ILSS is interlaminar shear strength (MPa), P force at fracture (N), b thickness (mm), and t width (mm).

The ILSS for the laminate with 0, 0.5, 1.0, 1.5 wt% addition of nano-α-$Al_2O_3$for 60nm showed a gradual increase from 22.84 MPa for blank to 31.21 M Pa for 0.5 wt% of nano-α-Al_2O_3 addition. The delaminating property got decreased with 0.5wt% inclusion, which slightly decreased with an increase in alumina incorporation, as shown in Figure 4. For nano-α-Al_2O_3 of 200nm, the ILSS values for 0.5% slightly increased to 23.94 MPa from 22.84 MPa (blank) and stabilised the laminate against delamination with stress. The strength decreased below the blank when alumina wt% higher than 0.5% is used. The minimum value

was obtained for 1 wt% which was 16.03 MPa. From Figure 4, it was understood that for interlaminar shear strength compared to 200nm particle size, 60nm particle laminates withstand the stress against delamination which is supported by the ILSS data.

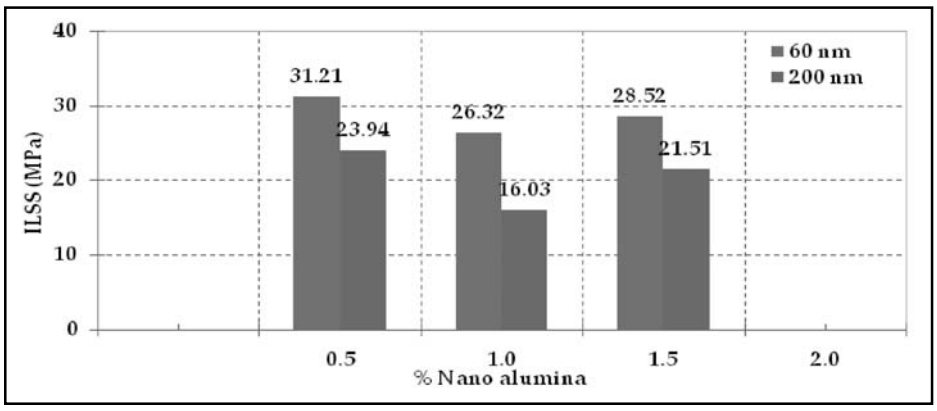

Fig. 4. Interlaminar shear stress for nano-α-Al_2O_3 based Epoxy-Glass fibre hybrid laminates at 60nm and 200nm as a function of Wt%

4.6 Vickers hardness

Vickers hardness test was performed by using hardness (Shore D) and according to (ASTM DI-2240) standard at room temperature. Samples have been cut into a diameter of 40mm and a thickness of 5mm. Results have shown not much of change in hardness for the laminate with 0.5, 1.0, 1.5 wt% addition of nano-α-Al_2O_3 for both 60nm (from 86.50 to 86.72), but when compared to the blank the values are drastically improved from 27.24 to around 86. For, 200nm nano-α-Al_2O_3 the hardness didn't improve much in comparison to the blank from 27.24 for 0% to 35.244 for 1.5%. For both the particle size, the highest value was observed for 1.5 wt% addition of nano-α-Al_2O_3in cases,

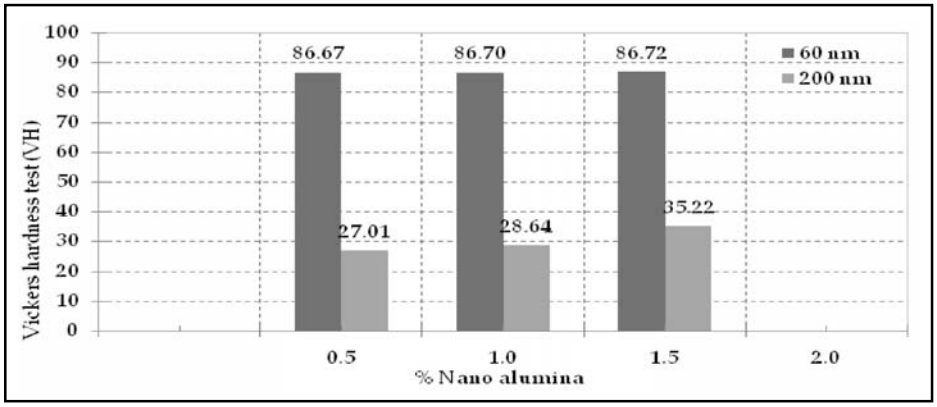

Fig. 5. Hardness for nano-α-$Al_2O_3$for sizes 60nm and 200nm

60nm and 200nm, with hardness values as 86.72 and 35.22 respectively (Figure 5). Though there is no much change in the hardness value over the varying wt% of nanoparticle when compared to 60nm the hardness of the 200nm composite was very low, which might be due to poor adhesion of the nanoparticle with the epoxy matrix due to reduced surface area of the nanoparticle.

5. CONCLUSIONS

In this work, the fibreglass nanocomposites were prepared and investigated for their mechanical properties as a function of different wt% (0, 0.5, 1, 1.5 wt%) and sizes (60 and 200nm) of nano-α-Al_2O_3. The mechanical parameters studied were tensile strength, flexural strength, interlaminar shear strength and Vickers hardness. The effect of the surface area over the binding efficiency of the epoxy was interpreted based on the results, which showed for 60nm filler; the flexural strength, ILSS and hardness was much higher than the 200nm sample as the surface area of 60nm alumina are higher.The wt% of the nanofiller also contributes to the mechanical properties, where a higher % will lead to agglomeration of the nanoparticle which decreases the strength due to lower surface area and poor adhesion. Among all the wt%'s of varied sizes of nano-α-Al_2O_3; the tensile strength was highest for 0.5 wt% of 200nm nano-α-Al_2O_3, which is 167.80 N/m^2; the highest flexural strength was observed for 1.5 wt% of 60nm nano-α-Al_2O_3, which is 378.39 N/m^2; the highest interlaminar shear strength was observed for 0.5 wt% of 60nm nano-α-Al_2O_3, which is 31.21 MPa and the highest Vickers hardness was found to be with for 1.5 wt% of 60nm nano-α-Al_2O_3, which is 86.72.

In case of feasibility towards aero applications based on the above test results; for tensile properties, 1wt% addition of nano-α-Al_2O_3 to the composite shows the best results compared to the standard composite. The percentage of increase is of 37.82% for 1% nano-α-Al_2O_3 with 200nm.The flexural strength increased by 42% for 1% nano-α-Al_2O_3 as compared with standard material, shows a better increment compared to the remaining. In the case of ILSS property, the samples that possess nano-α-Al_2O_3have shown better properties when compared to the standard material. All the samples have shown an increase in the strength, but the best was with 0.5% nano-α-Al_2O_3 then followed by 1% nano-α-Al_2O_3 and for 0.5% nano-α-Al_2O_3, there is 3.63% increase in strength.The observed results were in support of the higher interaction between the nanoparticle and polymer resin, which gives the possibility of using these hybrid materials in various applications.

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