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Material characterization of polymer nanocomposites for aerospace applications

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ABSTRACT

Nanocomposites have been used as suitable substitutes for metal matrices and alloys for quite some time. In industrial applications, carbon fiber reinforced polymers (CFRP) and other fiber reinforced polymers (FRP) are more prevalent as compared to polymers reinforced with one dimensional nanofillers. It becomes important to analyze the effects on the mechanical properties of polymer matrix when reinforced with nanofillers. The nanocomposites are prepared using epoxy resin as the polymer matrix. Two nanofillers, namely carbon nanotubes (CNT) and halloysite nanotubes (HNT) are used to compare the impact of each on the polymer matrix. Three different weight percentages for each nanofiller composite are fabricated: 0.5 wt%, 1 wt% & 1.5 wt% for CNT and 1 wt%, 5 wt% & 10 wt% for HNT is considered. The microstructural characterization through Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) provided an in-depth understanding of the dispersion of nanofillers in the polymer matrix and the quality of its fabrication. The images obtained from the SEM show the presence of micro voids and some agglomerations in the specimens. The XRD plots with peak broadening confirm the smaller size of crystallite in nanocrystalline materials of the specimens. The mechanical characterization, which includes hardness, tensile and flexural showed the effect of nanofillers in the epoxy. However, it can be concluded that the application of 1 wt% nanofillers leads to an optimum dispersion and improved the polymer mechanical capabilities. A fractography analysis can be considered as a future scope of this study.

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1. Introduction

Composites are made of two constituent materials, the matrix (binder) and the reinforcement. The matrix surrounds and preserves its reinforcement relative location and properties; therefore, it provides support to the reinforcement. Since, the reinforcement incorporate their extraordinary mechanical, chemical, and physical qualities into the matrix, the matrix properties need to be improved. Rathod et al. [1] reviewed the polymer and ceramic matrix composites for aerospace applications. The authors provided a detailed discussion on the influence of mechanical properties due to the dispersion of nano-fillers into the polymer matrix and also, they addressed the cost, processing difficulties and future perspectives of nanocomposites. Njuguna et al. [2] provided a wide range of materials, which are being used in the structural and thermal applications. The review work extracts valuable information on fundamental elements involving field emission, thermal stability, electrical, optical as well as mechanical properties of polymer nanocomposites for aerospace applicability. It is concluded that the aerospace industry could be the potential user of polymer nanocomposites. Prabhakar et al. [3] reviewed the tribological properties of polymer composites, and addressed the challenges of the characterization of nanocomposites.

Natural nanocomposites are multiphase solids with one, two, or more dimensions within 100 nm and repeat distances between the distinguishable states in the nanoscale that make up the material. From a fundamental perspective, the nanocomposite is based on

Abbreviations: CNT, Carbon Nanotubes; HNT, Halloysite Nanotubes; SEM, Scanning Electron Microscopy; XRD, X-Ray Diffraction; FTIR, Fourier Transform Infrared; TEM, Transmission Electron Microscopy.

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the concept of instilling enhanced characteristics to the matrix with the use of reinforcement at a nano-level. In the concept of nanocomposites, there are two parts; the matrix and reinforcement.

Ain et al. [4] studied the tribological behavior of polymer nanocomposites as they find applications in automotive, high-barrier food packing films, and extremely hard and wear-resistant coatings. In this work, the authors discussed the key mechanisms governing the effects of reinforcement on the mechanical and tribological behavior of polymer nanocomposites. Husaen [5] investigated the effect of carbon nanotubes having various weight percentage of 0.01, 0.05, and 0.1 % in epoxy matrix and its effect on the mechanical properties such as tensile, bending, and hardness. From the results, it is observed that the flexural and tensile modulus of the epoxy nanocomposites was found to be higher than the neat epoxy, which could be due to the high mechanical strength of the carbon nanotubes. Njuguna et al. [6] provided a detailed review of nanocomposites and primarily focused on the characterization techniques such as HRSEM, FTIR, XRD, TEM, and other methods. Dinca et al. [7] reported that the structural composites are the most important application of nanocomposites in aerospace industry and also it can be used as anti-lightning, anti-radar protectors and paints. The authors studied the effects of sonic dispersion of carbon nanotubes and montmorillonite clay on the mechanical, electrical, rheological and tribological properties of epoxy polymers and laminated composites, with carbon or glass fiber reinforcement, with nonadditive epoxy matrix. Kamal et al. [8] reviewed the various fabrication techniques for polymeric nanocomposites. Fu et al. [9] discussed the basic aspects of polymer nanocomposites and its various processing methods and characterization techniques. Askar et al. [10] explained the benefits of multifunctional nanocomposites such as wear resistance, optical transparency, stimuli responsiveness, surficial wettability, recyclability, and biodegradability. In this work, the authors incorporated halloysite nanotubes (HNT) and cellulose acetate butyrate (CAB) as nanotubes (fillers) and dispersive molecules. respectively. Kamble et al. [11] explained the benefits of halloysite nanotubes. It is noted that the mechanically advantageous nanomaterials such as carbon nanotubes, nanofluids, nanoparticles, nanoemulsions, nanocapsules, etc., are hazardous to environment. In order to overcome this issue, halloysite nanotubes are preferred, which is naturally available nano material and eco-friendly in nature.

In recent years, a lot of research work have been carried out in natural fiber reinforced composites due to their easy availability, low cost, sustainability, eco-friendliness, biodegradability and recyclability. Kumar et al. [12] presented a review study on the mechanical properties of bamboo fiber, bamboo fiber-based composites, and hybrid bamboo fiber-based composites. Goyat et al. [13] carried out a detailed review on the mechanical properties of untreated coir and chemically treated coir composites. Das et al. [14] presented a detailed review of biocomposites made from various wastes and their related mechanical and fire properties. Based on the recent studies, it is concluded that the nanofillers can also be added as secondary reinforcement with natural fiber reinforced polymers to improve its mechanical properties.

Polymer composites have been researched for the past few decades and it is extensively used in the construction, automobile, and aerospace industries. Significant changes in the compositions of aerospace parts would make them lighter without compromising structural strength. By incorporating proper manufacturing techniques, this small-scale evaluation can be incorporated in solving real-world mechanical and aerospace problems. In this current study, an attempt is made to enhance the mechanical properties of epoxy matrix by incorporating one-dimensional nanofillers as reinforcement. The main objective of the current work is to understand the influence of carbon nanotubes (CNT) and halloysite nanotubes (HNT) on the mechanical properties of epoxy system and to identify the optimum loading of carbon and halloysite nanotubes.

2. Experimental details

2.1. Materials

It is known that there are primarily two types of polymer-curing methods, which classify the resin as thermoplastic or thermoset resins. Uncured thermoplastic resins at room temperature are in solid state and it makes the impregnation of nanofillers into the resin system become difficult. The manufacturing procedure of thermoplastic composites is very tedious in comparison with traditional thermoset composites. Due to this problem, the current study focusses on thermoset polymer resins, which can be cured at room temperature. One such thermoset polymer resin is epoxy, which is being used as a matrix in the current study.

Uncured thermoset resins at room temperature are in a liquid state and it makes the impregnation of reinforcing the nanofillers into the resin system become convenient. During the curing process, the resin molecules are cross-linked through a catalytic chemical reaction. This exothermic reaction facilitates the resin to create extremely strong bonds with one another, thereby changing from a liquid to a solid. Apart from the ease of manufacturing process, thermoset resins also exhibit excellent properties at a low material cost. The resin used for the research is Araldite CY 205, an aliphatic glycidyl epoxy resin with Araldite hardener HY 951 (N'-[2-(2-aminoethylamino) ethyl] ethane-1,2-diamine). It is important to understand the effects of curing on the mechanical capabilities of the polymer nanocomposite.

Based on the literature survey, carbon nanotubes and halloysite nanotubes were considered as the reinforcing one-dimensional nanofillers for the current study. Microstructural characterizations were carried out using SEM and XRD and mechanical characterization was carried out to understand the influence of nanofillers in the mechanical properties of the epoxy system.

2.2. Composition and fabrication

The experimental setup is composed of a mold having two glass plates with two mylar sheets and rubber beading. Glass plates of 300 × 300 mm were used as a supporting member and the wax coated mylar sheets were used to get better surface finish and to release the specimen easily from the mold.

In order to fabricate the epoxy nanocomposites, three different weight percentages for each nanofiller composite were considered as follows: 0.5 wt%, 1 wt% and 1.5 wt% for CNT and 1 wt%, 5 wt% and 10 wt% for HNT is considered. The required weight percentage of nanofiller is incorporated into a calculated 200 g of epoxy. Therefore 1 g, 2 g & 3 g of CNT was used and 2 g, 10 g, and 20 g of HNT was used to prepare the specimens. A mechanical stirrer was used for a duration of 7 h to facilitate good dispersion of the nanofillers in the resin. The addition of CNT increased the viscosity of the epoxy and hence a speed of 200 rpm was set to disperse the nanofillers in epoxy system. In the case of HNT, the epoxy viscosity was unchanged. Thus, a speed of 300 rpm was set to disperse the nanofillers in epoxy system. After dispersion of nanofillers into epoxy system, a required amount of hardener was added and the mixture was poured into the mold. The weight of nanofiller, epoxy and hardener were measured carefully using a high-resolution weight balance. It usually takes the epoxy and hardener 8 h to cure, but due to the addition of nanofiller 24 h was set as the curing time.

After curing process, the specimens were machined using water jet cutting machine to get desired geometry. The dimension of the specimens was considered according to ASTM standards. So, the cutting method incorporated was water-jet cutting.

2.3. Microstructural characterization

X-ray diffraction (XRD) is a non-destructive analyzing technique used to understand the crystallographic structure of a material. In this testing, the specimen is placed in the X-ray diffractometer and illuminated with a beam of X-rays. The X-ray tube and the detector move in a synchronized way. The constructive interference with the incident X-ray is called diffraction, which is the principle behind the instrument. The angle between the incident ray and the scattered beam is called 2θ. The X-ray diffraction performed in this current study helps to understand the quality of the dispersion of the nanofillers in the specimen.

Scanning electron microscopy (SEM) is a technique used to examine the surface images of specimens using a focused beam of electrons. The electrons penetrate through the specimen till a certain extent and then get reflected by the specimen molecules. The reflected electrons are captured and then processed to get micrographs. In general, the SEM images provide an insight to the level of dispersion and quality of the fabricated nanocomposites. Dikin et al. [15] discussed the factors influences the scanning electron microscopy, such as acceleration voltage, conductivity of the materials of the composites, thickness of the specimen etc.

2.4. Mechanical characterization

Mechanical characterization was conducted by performing hardness, tensile and flexural tests on the composite specimens. A hardness test is used to test wear resistance, toughness etc. of the material. Hardness is determined by performing indentation for a specified period of time. The indenting instrument used is called a 'durometer'. It includes a calibrated spring which is meant to apply a defined and constant load. The indentation hardness is inversely proportional to the penetration and is dependent on the elastic modulus and viscoelasticity of the material. The hardness test used in the current study is "Shore D hardness scale". It measures the hardness of hard rubbers, semi-rigid polymers, and hard polymers. The shore D test involves a spring-loaded indenting machine for measuring the material's hardness. The type of indenter varies with respect to each material to be tested. Shore D hardness test employs a sharp conical point as indenter tip and a high stiffness spring to make it ideal for testing harder polymers such as cured epoxies or highly cross-linked materials. The specification of the indenter is as shown in Table 1.

Tensile testing is used to determine the elongation, ultimate tensile strength and Young's modulus of the composite material. Tensile testing is one of the destructive tests carried out to understand the mechanical characteristics of the fabricated nanocomposites. ASTM D638 is used to test plastics reinforced with particles and it is one of the primary tests used to characterise the tensile properties of composite materials. Fig. 1 shows the tensile specimens of epoxy and its nanocomposites. During the testing process, each specimen is held between two crossheads and clamped. The load is applied gradually and the specimen elongates while the testing process continues until the specimen breaks. The graph between elongation with respect to the force applied is recorded. The suggested test speed is given as a strain rate of 0.01 min^{-1} or constant crosshead speed of 2 mm/min (0.05 in/min). The general practice is to conduct the test at a constant crosshead speed.

Table 1
Specifications of Shore D hardness.

Property	Value
Hardness scale	Shore D
Indenter type	Conical type
Tip angle	30°
Tip size	0.1 mm radius
Range	20–90
Resolution	0.1
Testing load	44.64 N

Flexural test or bending test is used to determine the flexural strength and stiffness of the composite material. Since composites are anisotropic, the setting of test needs to be carried out carefully and the flexural tests must be properly conducted to ensure proper specimen alignment and load application to the test specimen. A three-point or four-point loading configuration is employed to carry out the flexural test. ASTM D790 is used to determine the flexural properties of composite materials. Flexural strength, as well as flexural modulus, is the ability and quantitative value of a material's capability to resist cracking or breaking under bending stress. A material with high flexural strength has the ability to resist deformation when a load is implemented in tension or compression; it inherently withstands bending, stretching, twisting, and other types of stress. By using theory of bending, the flexural strength of the specimens can be evaluated.

3. Results and discussion

3.1. Microstructural characterization

The X-ray diffraction was performed to characterize the quality of dispersion of fabricated nanocomposites. The results show an exfoliated structure of nanocomposites. From the XRD results, it is noted that the specimens possess a uniform dispersion. Fig. 2 shows the micrographs obtained from scanning electron microscopy. From the micrographs, it is noted that lower weight fraction of nanofillers show a uniform distribution of the nanofillers with slight presence of agglomerations and higher weight fraction of nanofillers show a lot of micro voids. But the micro voids were inevitable due to the absence of vacuum setup.

3.2. Mechanical characterization

Hardness is described as a result of empirical testing owing to the indentation of a specimen using a durometer. The hardness value of the specimens was measured in the machine and the results are shown in Fig. 3. It is noted that the addition of nanofillers has not impacted the hardness criterion of epoxy. Shore D hardness 1 wt% CNT with epoxy and 1 wt% HNT with epoxy shows an improvement in comparison with neat epoxy. Since the hardness is a surface property, it can be speculated that due to imperfections in the specimen, the regions of indentation in the CNT and HNT specimens might have micro voids.

The tensile testing was performed and the addition of nanofillers considerably increases the tensile strength of epoxy. From Fig. 4, it is noted that the neat epoxy system shows the lowest value of ultimate tensile strength and 1 wt% CNT and 1 wt% HNT show the highest ultimate tensile strength. The addition of nanofillers at more than a specified level led to poor dispersion of nanofillers into the epoxy system.

The flexural testing was performed and the results of both CNT and HNT is shown in Fig. 5. The reason for the decrement in flexural strength could be due to the existence of inevitable micro voids or agglomeration of nanofillers.

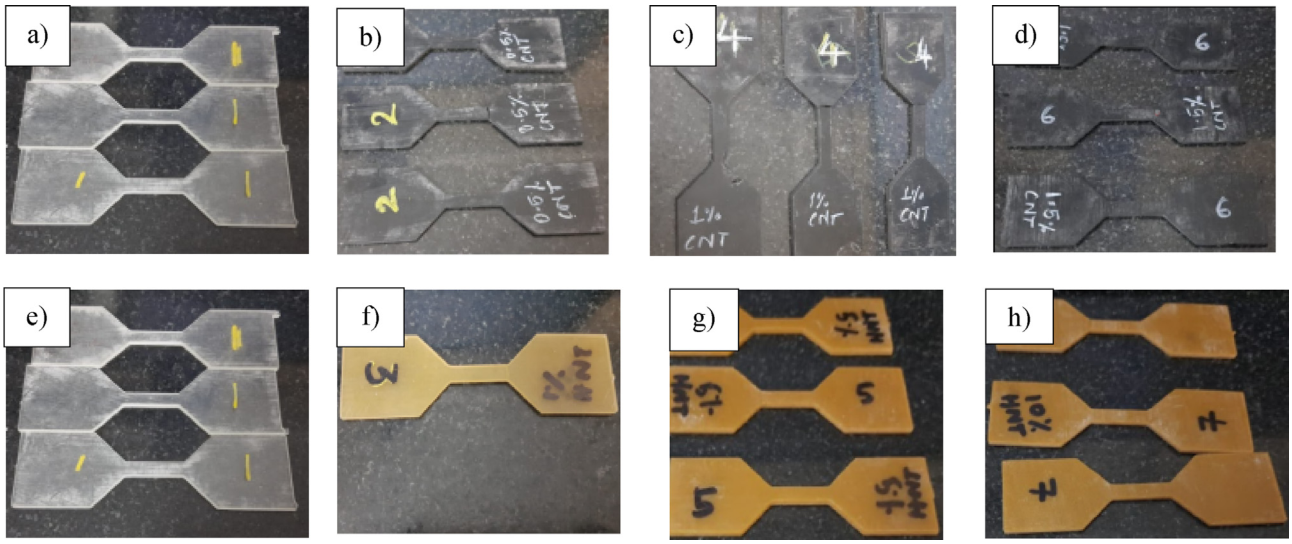

Fig. 1. Specimens for tensile testing of epoxy and its carbon nanotubes (a)-(d) and halloysites (e)-(h) nanocomposites (a) Neat epoxy (b) 0.5 wt% CNT (c) 1 wt% CNT (d) 1.5 wt % CNT (e) Neat epoxy (f) 1 wt% HNT (g) 5 wt% HNT (h) 10 wt% HNT.

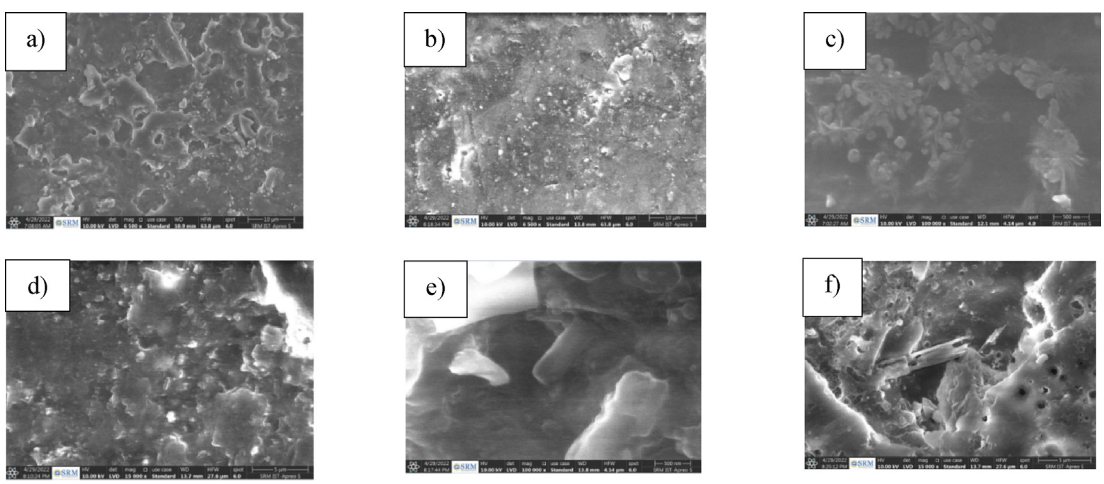

Fig. 2. SEM micrographs of epoxy and its nanocomposites (a) Neat epoxy (b) 0.5 wt% CNT (c) 1.5 wt% CNT (d) 1 wt% HNT (e) 5 wt% HNT (f) 10 wt% HNT.

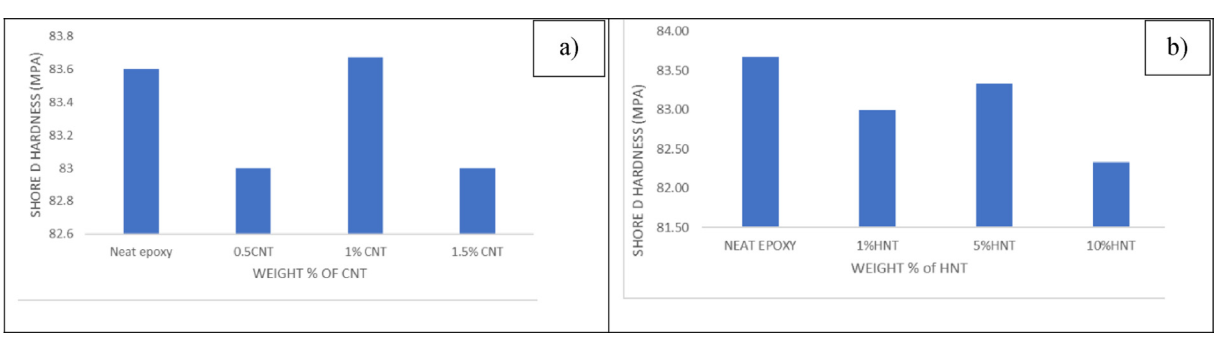

Fig. 3. Variation of Shore D Hardness (a) CNT (b) HNT.

4. Conclusion

The epoxy/CNT and epoxy/HNT specimens containing various weight fractions were fabricated using hand mold technique. The quality of the dispersion of nanofillers in the epoxy matrix was characterized through SEM and XRD techniques. The results reveal that it is noted that lower weight fraction of nanofillers show a uniform distribution of the nanofillers with slight presence of agglomerations and higher weight fraction of nanofillers show a lot of micro voids. Various mechanical characterization, which includes hardness, tensile and flexural tests were carried out to understand the influence of nanofillers in the epoxy system. From tensile testing, it is observed that the addition of 1 wt% CNT and 1 wt% HNT

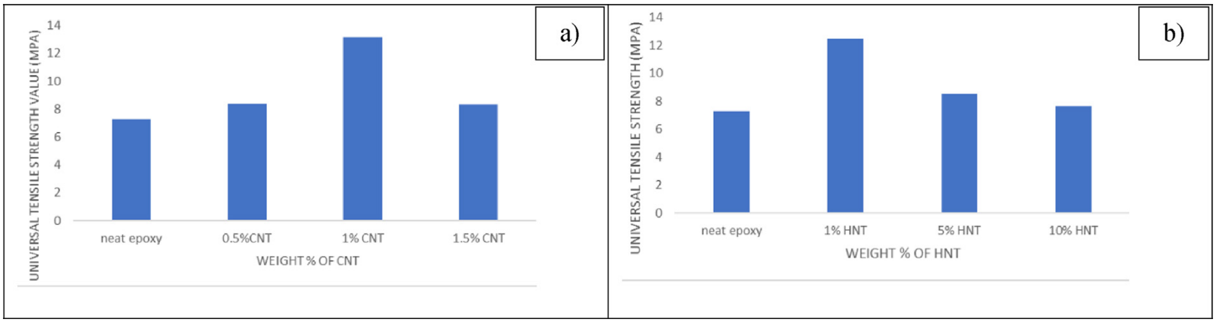

Fig. 4. Variation of Tensile Strength (a) CNT (b) HNT.

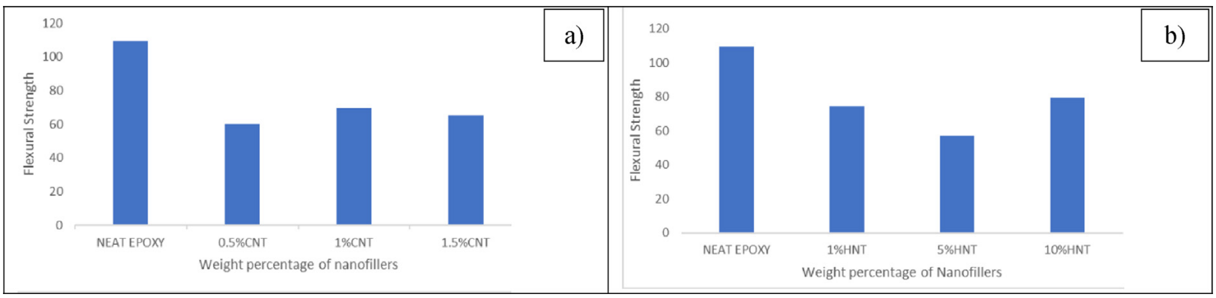

Fig. 5. Variation of Flexural Strength (a) CNT (b) HNT.

showed an enhanced strength in comparison with neat epoxy system. From hardness and flexural tests, it is noted that the neat epoxy specimens show the highest value of hardness and flexural strength, which could be due to the presence of agglomerations and micro voids.

Polymer nanocomposites have a lot of scope in the impending future and the current study may be extended and the following area may be focused: Fractography and thermal characterization. Further improvements can also be implemented in fabrication methods to get good specimens. The nanofillers can also be used as a secondary reinforcement with traditional fiber reinforced polymers. The limitations of polymer nanocomposites need to be incorporated in large scale aerospace industries with further exploration into polymer fiber based composites.

CRediT authorship contribution statement

Nandita Roy: Conceptualization, Investigation, Validation, Writing – original draft. **S. Gurusideswar:** Methodology, Project administration, Resources, Supervision, Visualization, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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