New horizons of Space Qualification of Single-Walled Carbon Nano Tubes-Carbon Fibre Reinforced Polymer Composite

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Abstract: The requirement of lightweight components for interplanetary missions explore the possibilities of the application of composite materials. Carbon Fibre Reinforced polymers (CFRP) are most practical and widely used in space industries. Enhancement of mechanical, thermal, and electrical properties by reinforcing CFRP with Carbon Nanotubes (CNTs) is advantageous, considering the potential applications of such a modified CFRP material in space payload. CNT composites for space use opens new horizons to improve specific stiffness and electrical conductivity of the CFRP components without degrading the performance index. Composite characterization and space qualification are critical and essential, which demonstrate the capability of fulfilling functional as well as specific requirements for space. CNT Composites have to undergo severe environmental tests without degradation. This paper addresses the synthesis of CNT-CFRP composites, its Characterisation and Space Qualification aspects. Synthesis of CNT-CFRP sample with single-walled CNT (Ø1.6µm & L>5µm) 0.5%wt by solution mixing method is attempted. The characterization in terms of measurement of tensile strength, electrical resistivity, shielding effectiveness, thermal conductivity, Co-efficient of thermal expansion (CTE) is carried out. Limited Space qualification on samples and electroplated coupons has been carried out by conducting various environmental tests. The results indicate that CNT reinforced CFRP composites are a promising potential candidate for use in the space domain.

Keywords: Single-walled Carbon Nanotubes (SWCNTs), CNT-CFRP composites, Space Qualification, Material Characterisation, Tensile Strength, Thermal Property, Electrical Property, Space Applications.

Introduction

Carbon fiber reinforced polymer (CFRP) composites are widely used in the aerospace sector due to their specific stiffness and low density. Carbon nanotubes based composite materials has attracted the attention of researchers due to enhancement in mechanical, thermal and electrical properties of CFRP composites, making them suitable for specific applications[1-2]. Over the last few years, the technology for producing carbon nanotubes polymer (CNT) is being developed by advanced scale-up capabilities of industries due to CNT’s significant material properties[3-4]. Potential applications of these composite explore the feasibility for fabrication of space components[5]. The processing of reinforcement of CNT in CFRP and its characterization for space applications is challenging; as it has to satisfy specific functional requirements.
The current research work is carried out to develop the CNT composite components, which includes the design, fabrication methods, synthesis of CNT and polymer, selection of CNTs, dispersion techniques, characterization of composite and applications for space. Any new material to be used for space has to be qualified, to evaluate its physical, thermal and electrical properties after it undergoes various environmental testing like thermo vacuum, thermal cycling, humidity, EMI/EMC tests, etc[6]. After which the material is allowed to be used as a space component.

The fabrication process specific for CFRP depends on the requirement of structural strength. This can be achieved by using the unidirectional and bidirectional fabrics, the orientation of fabrics, number of layers and types of resin hardener, solvent [7-9]. The amount of CNTs(%wt.), reinforced in composite significantly affects the thermal and electrical properties required in components for the specific use[10-11]. There are many potential applications of this composite for space use like replacing high-density Kovar (Fe-Ni-Co alloy) Carrier plates (CPs) of Microwave Package, Invar (Fe-Ni alloy) Brackets for optical payloads and many more[5]. A few hundred CPs are used in microwave electronics packages of space communication payload, which can be advantageous to replace high-density alloy by this CNT composites. The CPs require thermal and electrical conductivities both for maintaining thermal balance during the assembly process and surface treatment during the electroplating process respectively[12]. The single-walled Carbon Nanotubes (SWCNTs) 0.3%-0.5% wt. reinforce with polymer to enhance the electrical conductivity significantly[13]. This paper highlights the experimental analysis of CNT-CFRP composite with 0.5% wt. of SWCNT for the space qualification and characterization of the mechanical, thermal and electrical properties.

**Materials  CNT-CFRP composite**

| Material          | Specification                                      |
|-------------------|----------------------------------------------------|
| Carbon Fabric     | Bidirectional, Plain weave, Thickness 0.250 mm, Density 1.7 g/cc. |
| Single-Walled Carbon | Mean Diameter 1.6±0.4 µm, Length >5µm, Metal impurity <15wt% |
| Nanotube (SWCNTs) | Epoxy Resin-ARL-135 LV, Hardener: AH-422, |
| Solvent           | Acetone Grade AR                                    |

1. **Methodology and Sample Preparation**

Processing of SWCNTs in a polymer matrix: This experimental study is carried out with SWCNTs in a polymer matrix, fabricated via Mix solution method as shown in fig 1. Single-walled carbon nanotubes (0.5% wt of Resin-Hardener) are added with an appropriate quantity of acetone. After sonication, Hardener is added to this epoxy resin solution and the solution is mixed with a magnetic stirrer to obtain uniform dispersion. Sample is prepared with Hand Layup method. Curing were allowed to cure at room temperature for 24 hrs later post-cured at elevated temperature for 8 hrs using a hot air oven.

![Sample Preparation - Solution Mixing Method](image)

2. **Experimental Analysis**

CNT-CFRP samples have been characterized to understand structure, Mechanical, Electrical and Thermal properties and behavior under specific conditions. Results are compared with neat CFRP sample. All test Samples are prepared and tested as per ASTM standards[14-22].
• Mechanical Characterization: Tensile strength (ASTM D3039/D3039M), Flexure Test (ASTM D7264/D 7264M)
• Thermal Characterization: Thermal Conductivity (ASTM E 1461), Co eff. of thermal Expansion (ASTM E 228), Specific Heat Capacity (ASTM E 1269)
• Electrical Characterization: Bulk Resistivity, Sheet Resistivity (ASTMD257), Shielding Effectiveness (ASTMD 4935)
• Space Environmental Test:
  o Thermal shock (-55°C to +105°C), Period: 5min, Number of Cycle: 100 cycles
  o Heat resistance test: (+150°C), Period : 2 Hrs.
  o Humidity (+60°C ± 2 °C and 95 ± 5 % RH), Soak Period: 48 Hours
  o Thermo vac (-55°C to +105°C) Dwell time: 15 min after stabilization, Vacuum: 1 X 10^-5 torr or better, Number of Cycle: 10 cycles
  o Out gassing Temp: 125°C, Time: 24 hr. Vacuum 10^-5 torr (ASTM E595)
Silver electroplating is carried out on samples to qualify the composite for space use. These samples are to withstand under space environment conditions as explained above. The peel test (ASTM D3359) is carried out before and after each environmental test using 3M Scotch bidirectional adhesive tape.

3. Results and Discussion
3.1 Microstructure and Morphological Characterisation
The composites samples are micro sectioned and the layer structure is studied at magnification of 80x. Eight layers of Carbon Fibers and Epoxy (intermediate) are seen clearly (Fig 2). There is no damage of fibres. Epoxy can be seen at intermediate layers of fiber. Further, the scanning electron microscope(SEM) indicates the bidirectional carbon fibers and homogeneously dispersed epoxy for CFRP; whereas CNTs can be seen with agglomeration in an epoxy dominant area in the CNT CFRP sample with the magnification of 21,000 X.

![Fig.2: Microstructure and Structure under SEM](image-url)
3.2 Mechanical Characterisation

The effect of thermal shock and thermo vacuum on tensile strength for both the samples CNT CFRP and Neat CFRP composite is analyzed as shown in fig 3. There is a decrement in tensile strength by 16%-23% is observed in CNT-CFRP samples than that of Neat CFRP. The cause may be due to non-uniform dispersion of CNTs, which form agglomeration in the composite. This agglomeration due to Van der Waals force can be avoided by homogeneous distribution (mixing) of CNTs in resin matrix. Fig 3 shows the tensile strength after thermal shock affects the strength of CFRP material, which depends on the type of resin polymer and its structure. Moreover, it also depends on the number of cycles in testing. These factors affect the inconsistency in structural behavior, specifically the interface of fabric and polymer matrix[23]. The use of functionalized CNTs improves the glass transition temperature, which results in better tensile strength than that of non-functionalized CNTs[24-25].

![Fig 3. Tensile Strength Measurement](image)

3.3 Electrical Characterisation

3.3.1 Resistivity and Shielding Effectiveness

Electrical conductivity and Electromagnetic interference (SE) are important parameters for the space material. Space components are surface treated (plating) to change the surface character for the optimal performance and to avoid the environmental effects like corrosion. Electroplating on the material is essential to increase the RF performance for realising microwave passive components, Shielding Effectiveness for packages and solderability for carrier plates. The DC resistivity is measured with the PRS-801 Resistance System for the samples of Neat CFRP and CNT-CFRP. Enhancement of electrical conductivity of CNT-CFRP is observed in the order of 10 times that of Neat CFRP as shown in fig. 4. The increase in electrical conductivity enables to electroplate directly on composite without activating the surface.

The material of the payload packages used for space should have better shielding effectiveness to avoid electromagnetic interference by providing adequate isolation. The adequacy to prevent emission or to withstand external interference depends on the shielding effectiveness(SE). SE is measured using free space two antenna method. The measured test result data analysis revealed an improvement in SE values for CNT CFRP as compared to neat CFRP. The typical test result data analysis revealed the improvement 5dB to 18dB in the frequency range of 18Ghz-26Ghz SE values for CNT CFRP as compared to neat CFRP. However, for testing more number of samples, sample to sample variation and test set-up variations need to be considered. The SE is mainly reflection dominated in SWCNT/polymer composite[27], which are measured against neat CFRP composite.
Fig. 4. Electrical Resistivity and Shielding Effectiveness Measurement

The electrical conductivity and Shielding effectiveness (SE) depends on the aspect ratio of CNTs [28]. The SWCNTs used for this experimental analysis have a short aspect ratio, it increases electrical conductivity significantly, however it is poor in the case of shielding property. The greater scattering of phonon results to increment of electrical conductivity exponentially in case of a short aspect ratio, However, this leads an improvement of thermal resistivity marginally.

3.4 Thermal Characterisation

3.4.1 Thermal Expansion: The thermal expansion (CTE) results in Neat and CNT-CFRP laminate is evaluated by measuring the change in length to the corresponding temperature as shown in Fig.5.

Fig.5: Change in length Vs Temp for (a) Neat CFRP Samples (b) CNT-CFRP Samples
To avoid instrument induced uncertainty in results, initially standard fused silica rod loaded in the fused silica push rod dilatometer is used. The desired temp range and heating rate(-100°C to 150°C and 2°C/min), the obtained dataset is corrected with standard quartz dataset. This corrected dataset of standard fused silica used for the correction of the dataset of CFRP samples to avoid instrument bias. The neat CFRP sample shows CTE 0.783 ppm/°C, whereas the CNT-CFRP sample shows CTE 0.550 ppm/°C for temperature range -100°C to 150°C. This temperature range is taken into consideration for the materials to be qualified for the interplanetary missions. The results indicate that an addition of 0.5 % CNT in CFRP reduces the CTE of the sample by 29.77%. This phenomenon is observed due to CNT matrix fiber interfacial interaction, which resists the expansion due to CNTs. Moreover, The solvent used with CNT for dispersion can reduce the glass transition Tg, which acts as an impurity that rises the thermal motion of the molecular of the polymer. CTE behaves linearly up to Tg then starts to decline. The addition of CNT decreases in the expansion of CNT- CFRP compared to the neat CFRP which is considered as a positive effect for the thermal stability of the material.

3.4.2 Specific heat capacity and Thermal conductivity
Specific heat capacity of Neat CFRP sample 491.95 J/(kg °C) is observed at temperature 0°C and it gradually increases up to 1483 J/(kg °C) at temperature 150°C whereas in the case of CNT-CFRP sample 476.15J/(kg °C) observed at temperature 0°C and it gradually increases up to 1426.5 J/(kg °C) at temperature 150°C as shown in the Fig.9. Results indicate that the addition of 0.5% CNT in CFRP reduces the average specific heat capacity of CFRP by 2.393% ± σ1.569 for temperature range of -100 to 150 °C. The specific heat capacity of CNT decreases with the temperature compared to that of neat material. This occurs due to the resistance of the molecular movement of the polymer, which decreases the kinetic energy of the system[29].

Thermal conductivity can be calculated based on thermal diffusivity and density of Neat CFRP 1.361 gm/cm³ and CNT CFRP 1.313 gm/cm³. The thermal conductivity increases for both the samples and reduces marginally after 101°C (near to Tg) up to 152°C as shown in fig.6. Results indicate that the addition of 0.5% CNT in CFRP enhances the thermal conductivity by 2.783 % ± σ1.019 for temperature range -100 to 150°C. CNT concentration from 0.1 to 1% results in the different influences on electrical and thermal conductivity[30]. Thermal conductivity reduces slightly after the glass transition limit of the composite. It is concluded that the presence of CNTs in the epoxy matrix causes discontinuities in polymer leading to reduction of mean free oscillation of polymer molecules and electron scattering results into decrement of the thermal conductivity.

![Fig. 6 Variation of Specific heat Capacity and thermal conductivity with a temperature of Neat CFRP and CNT-CFRP](image-url)
4. Limited Space Qualification

The process of qualification of the product that assures the withstanding against space environmental is called space qualification testing. It is the basic requirement of any process or product before use in space. The outgassing test results in a total mass loss (TML) and collective volatile condensable mass (CVCM) are well within the limits of 1% and 0.1%

Samples from Neat CFRP and CNT CFRP size 50 x 50 mm are prepared for silver electroplating as shown in Fig 7. Silver plating on Neat CFRP is difficult to achieve without surface activation, results in discontinuous plating, whereas direct electroplating is achievable in CNT-CFRP samples due to enhancement of electrical conductivity. These samples are passed through a heat resistance test, thermal shock, humidity, thermo vacuum tests. The peeling test is carried out on the silver-plated surface after each test. The peel test shows good adhesion of silver plate on the samples. This is to be done for qualifying the silver plating process directly on the CFRP without surface activation to qualify the process.

Fig 7. Silver Plating on CFRP samples (above row) and CNT samples (below row)

5. Discussion

The experimental analysis confirms that there is a significant improvement (reducing the resistivity $445\Omega$ to $14\Omega$) in the electrical conductivity of CFRP by adding SWCNT (0.5%wt). The enhancement of electrical conductivity (10 times that of neat CFRP) improves SE values in the range of 5dB to 18dB. This improves surface treatment on the material used for the space components, which is basic requirements for the space environment and functionality index. The major advantage of this is the enhancement of electrical conductivity that can directly electroplate the surface. Direct electroplating on CFRP helps avoid the otherwise essential step of surface activation process using a reducing agent. CNT-CFRP composite qualifies the silver electroplating.

Thermal properties are enhanced marginally (2-3%), however, it can further be enhanced by the change of resin and modification in the curing cycle. The slight decrement (16%-23%) of tensile strength depends on the dispersion of CNT but it is fairly within a limit for space requirement. The mechanical and thermal properties depend on the aspect ratio of the CNTs and their types. However, these properties can be enhanced significantly by exploring the different dispersion techniques to achieve a homogeneous dispersion of CNT.
6. Conclusion

Applications of CNT composite are a challenge for space industries, because of material and process parameters, which affect the mechanical and thermal properties. Optimization of these parameters is essential to fabricate the composite for space applications as per the requirement. The electroplated silver CNT CFRP samples undergo all environmental tests and it confirms no degradation of the plating on samples. This satisfies the process of qualification required for CNT CFRP material. These results give confidence for life testing on the composite. Such detailed analysis is useful for fabricating carrier plates, feed horns and Radio Frequency (RF) cavities for future space missions and their benefits can be quantified at the subsystem levels.

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