Electrically conductive nano adhesive bonding: Futuristic approach for satellites and electromagnetic interference shielding

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Abstract. This investigation highlights rationale of electrically conductive nano adhesives for its essential application for Electromagnetic Interference (EMI) Shielding in satellites and Lightning Strike Protection in aircrafts. Carbon Nano Fibres (CNF) were functionalized by electroless process using Tollen's reagent and by Plasma Enhanced Chemical Vapour Deposition (PECVD) process by depositing silver on CNF. Different weight percentage of CNF and silver coated CNF were reinforced into the epoxy resin hardener system. Scanning Electron Microscopy (SEM) micrographs clearly show the presence of CNF in the epoxy matrix, thus giving enough evidence to show that dispersion is uniform. Transmission Electron Microscopy (TEM) studies reveal that there is uniform deposition of silver on CNF resulting in significant improvement in interfacial adhesion with epoxy matrix. There is a considerable increase in thermal stability of the conductive nano adhesive demonstrated by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Four probe conductivity meters clearly shows a substantial increase in the electrical conductivity of silver coated CNF-epoxy composite compared to non-coated CNF-epoxy composite. Tensile test results clearly show that there is a significant increase in the tensile strength of silver coated CNF-epoxy composites. Consequently, this technology is highly desirable for satellites and EMI Shielding and will open a new dimension in space research.

Keywords: nanocomposite; spacecraft structural design; carbon nanotubes; unmanned aerial vehicles; carbon fibre composites

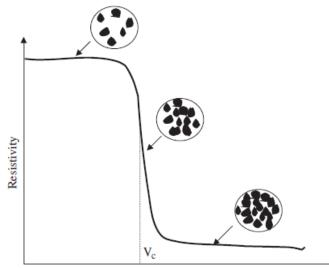
1. Introduction

In the aerospace industry, composites are used extensively in manufacturing of aircraft and satellite parts. Currently, aircrafts with up to 50% of composites are being manufactured (Eurofighter and A350XWB). This percentage is expected to increase further in the next decade.

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Volume Fraction of Filler

Fig. 1 Effect of filler volume fraction on the resistivity of isotropically conductive adhesives systems (Vietri and Guadagno 2014)

The major problems faced by composite structures in aerospace domain are Lightning strike protection and EMI shielding for satellites. The objective of electromagnetic, electric and magnetic shielding is to provide a significant reduction or elimination of incident fields that can affect sensitive circuits.

It also prevents the radiation emitted by the components of the system from radiating outside the shield boundaries. The effectiveness of a shield depends on the shield material. Lightning strike can cause severe damage to the aircraft structure. Composite aircrafts which are less conductive are damaged more compared to the metallic parts of aircrafts. This is because metal aircrafts are conductive by virtue and causes less damage as the electric charges are distributed.

To protect the non-conducting or semi-conducting composite aircraft from lightning strikes, the currently followed technique is to use a conductive metallic mesh, which serves as a pathway for the electric charges from the lightning to flow across the composite body to the discharge locations, without damaging the composite structure. The drawback of this method is that usage of such metallic meshes increases the overall weight of the aircraft, thus affecting its efficiency. (Gagné and Therriault 2014).

In order to address the above-mentioned issues of lightning strike protection and design against weight increase, electrically conductive composites are needed. However, the interface between two composite panels also needs to be conductive. This can be resolved by using electrically conductive adhesives. This has been one of the recent developments in composite industry. Electrically conductive adhesives perform two functions; first they form joints with sufficient strength to bond the surfaces and they also provide an electrical interconnection between them (Sancaktar 2011). The advantage of using electrically conductive adhesives is it potential to fulfil the desired conductivity requirement and yet not cause an increase in weight of the aircraft. Though using fillers such as silver nanoparticles provide good conductive properties in adhesives, they are expensive to synthesise (Chen and Qiao 2010). Thus, it is also necessary to develop adhesives that are economically feasible to use. The main objective of this investigation is to

develop conductive adhesives without compromising the thermo-mechanical properties. Conductive adhesive is a combination of both resin and fillers. These conductive adhesives facilitate a good conduction between two electrically conductive composite panels. Conductive adhesives with conductivity of 10^{-3} to 10^{-1} (S/cm) and 10^{-1} (S/cm) are required for EMI shielding and Lightning strike protection respectively (Burton, NA). The other properties expected for electrically conductive adhesive are high strength of 35 MPa (Billias 1984), low coefficient of thermal expansion (Simone and Angeliu 2007) and ability to withstand temperatures from -200°C to +350°C.

When conductive fillers are added to the insulating polymer matrix, linkages are formed between the fillers and hence, polymers are made conductive. No significant changes are observed until a critical concentration 'V_c' is reached. This point is called the percolation threshold and it gives a threshold value. This value gives significant information on the percentage weight fraction of the fillers which causes a sudden drop in resistivity. Volume fraction of approximately 25-30% is the percolation threshold in many Electrically Conductive Adhesives (ECA) as shown in Fig. 1.

Fillers generally used are micro or nano sized metal particles such as Silver, Gold, Nickel, Copper or Aluminium, Carbon nano tubes (CNT), Silver with Graphene, Carbon Black and Metal nano wires. Typical polymer matrices used are Epoxy, Silicone, Polyamide and Poly Urethane (Sancaktar 2011). Epoxy which has properties of as being a thixotropic mixture and a eutectic binder isthe most widely used resin (Simone and Angeliu 2007, Shaheen and Quintana 1979).

Several researches have shown the impact of various nano fillers on the electrical conductivity of epoxies. Using silver nano particles as fillers, a resistivity of 0.00024 ohm-cm was achieved (Chen and Qiao 2010) and using 28% volume fractions of CNT, Silver Coated CNT (SCCNT) and Silver micro particles as fillers, resistivity in the scale of 10⁻³ ohm-cm, 10⁻⁴ ohm-cm and 10⁻⁴ ohm-cm respectively were achieved (Amoli and Trinidad 2015).

In addition to type of nanofillers, the processing technique also plays an important role in the electrical behaviour of adhesives. It was shown that heat treatment of multi-walled-CNT (MWCNT) induces a morphological change such as straightening of graphene layer and reduction in interlayer spacing on it which increases the conductivity for lower filler content and decreases the percolation threshold from 0.75% to 0.3% (Guadagno 2014) (Guadagno 2013). A similar decrease in percolation threshold was witnessed while using graphene fillers, where an increase in degree of exfoliation decreases the threshold by 50% (Guadagno 2015).

Based on these considerations, in this investigation, emphasis is given to study the influence of nano fillers such as CNF and SCCNF (Silver Coated Carbon Nano Fibre) on the electric, thermal and mechanical properties of a high temperature resistant insulating material, epoxy Renlam LY 5210. Successful outcome of this study with SCCNF dispersed epoxy showing better conductive properties than CNF dispersed epoxy, will potentially pave way for a cheaper alternative to adhesives filled with silver nanoparticles and a lighter alternative to the lightning strike protection system that uses conductive metal meshes. 4-probe conductivity measurement is used to characterise the electrical property of the epoxy laminate. TGA and DSC are used to characterise the thermal property of the epoxy laminate. Tensile testing is used to characterise the mechanical property of the epoxy laminate.

Surface modification of CNF is carried out to convert it to SCCNF. Electroless process (Li and Lu 2010) and Plasma Enhanced Chemical Vapour Deposition (PECVD) are the two methods used for this purpose. While electroless process is used to synthesise SCCNF in small scale, PECVD is necessary for large scale production of SCCNF. Electroless process also produces harmful chemical wastes. Thus, PECVD is the method used in this investigation for synthesis of SCCNF.

2. Materials and methods

2.1 Materials

A high temperature resistant epoxy Renlam LY 5210 procured from Mouldlife Ltd. is the matrix used in the synthesis of this polymeric adhesive. This pale beige coloured epoxy resin has a viscosity of 3000 mPas and a density of 1.2 g/cm³. The hardener used in the synthesis of the resin is Lapox K24, procured from Mouldlife Ltd. CNF were procured from Nano shell industries with an outer diameter of 60 nm and length of 700-800 nm.

2.2 Modification of CNF using PECVD

PECVD is a process used to deposit thin films from a gas state (vapour) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after creation of plasma of the reacting gases. The plasma is created by Radio Frequency (RF) electromagnetic waves. The precursor gas and the carrier gas are mixed in reaction chamber. RF electric field is used to ionise these gases to plasma. Energetic electrons dissociate precursor molecules to free radicals. The particles then move to the substrate and the radicals are adsorbed onto substrate (Tan and Qiao 2006).

2.3 Development of polymeric nanoadhesive

CNF and silver coated CNF were reinforced into the mixture of epoxy resin (LY 5210) and hardener (K 24). Different weight fractions of CNF and SCCNF are mixed with the resin hardener system, with resin and hardener mixed in a 1:1 ratio. 0.5%, 1%, 2% and 5% wt fractions of CNF and SCCNF were reinforced with epoxy hardener mixture. To ensure uniform dispersion of nano particles, ultrasonication was performed for a period of two hours. Also, as CNFs have lesser Van der Waal's forces compared to CNTs, they have a better dispersion as fillers (Nobile 2015). The mixture is further kept under vacuum for one hour to remove the trapped air bubbles.

The resin reinforced with CNF and SCCNF were poured into moulds. To ensure uniform thickness, doctor's blade was used. The curing was performed in an oven for 48 hours at a temperature of 130°C. The cured composite samples were released from the mould. This procedure gives laminates of predetermined length (50 mm), width (10 mm) and thickness (2 mm).

2.4 Four-probe conductivity measurement

Four-probe conductivity measurement technique was used to determine the bulk conductivity of the epoxy adhesive. The experiment was carried out at room temperature (25°C) with current values ranging from 10^{-6} A to 10^{-12} A.

2.5 Thermogravimetric analysis (TGA)

TGA was performed using the SDT Q600 instrument. The experiment was performed from temperature of 20°C to 800°C with the rate of heating as 20°C/min in a Nitrogen atmosphere.

2.6 Differential scanning calorimetry (DSC)

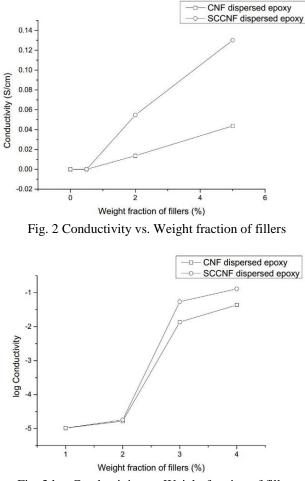


Fig. 3 log Conductivity vs. Weight fraction of fillers

DSC analysis was performed using the DSC Q20 instrument. The experiment was performed from temperature of 10°C to 390°C with the rate of heating as 10°C/min in a Nitrogen excessive atmosphere.

2.7 Scanning electron microscopy (SEM)

The instrument used for this characterisation procedure is JEOL JSM 6490 LA. The surface topography images of the samples having different weight fractions are studied using this method.

2.8 Tensile testing

Zwick/Roell Z101 was used to characterise the mechanical property of the epoxy laminate. The tensile testing was performed on the samples until failure occurred. The rate of extension was set as 10 mm/min. A set of 5 samples (per weight fraction of filler fractions) were taken for testing and the mean value is presented in the results section with the standard deviation.

2.9 TEM analysis

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons are transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. Transmission electron microscopy was performed on polymeric samples using a FEI Tecnai High-Contrast microscope with an acceleration of 120 kV and maintaining a magnification of 3,50,000X. TEM is a powerful technique for imaging fine structures of materials up to 1 nm in size. The polymeric composites were subjected to TEM to understand the dispersion of nano particles in polymers.

3. Results

3.1 Four-probe conductivity measurement

Four probe conductivity measurement was carried out for the virgin epoxy, 0.5% CNF dispersed epoxy, 2% CNF dispersed epoxy, 5% CNF dispersed epoxy, 0.5% SCCNF dispersed epoxy, 2% SCCNF dispersed epoxy and 5% SCCNF dispersed epoxy. The data obtained from the experiment is in the form of Ohms per square (Ω/\Box). Multiplying these values with thickness of the sample gives bulk resistance (Ω cm), and its inverse gives the values of bulk conductivity (Ω^{-1} cm⁻¹ or S/cm). The results from this experiment are shown in Figs. 2 and 3 respectively.

From the graphs shown in Figs. 2 and 3, it can be noticed that the bulk conductivity of the samples increase for higher weight fractions of fillers. While the bulk conductivity of Virgin epoxy laminate is 10^{-5} S/cm, bulk conductivity for 0.5%, 2% and 5% weight fractions of CNF dispersed epoxy laminates are 1.6×10^{-5} S/cm, 1.3×10^{-2} S/cm and 4.4×10^{-2} S/cm respectively; and bulk conductivity for 0.5%, 2% and 5% weight fractions of SCCNF dispersed epoxy laminates are 1.8×10^{-5} S/cm, 5.5×10^{-2} S/cm and 13×10^{-2} S/cm respectively. Increase in conductivity from Virgin epoxy laminate to 0.5% weight fractions dispersed epoxy laminates is very less. But, for 2% and 5% weight dispersion, the conductivity shows an effective increase. Also, the difference of conductivity between samples having 2% and 5% weight fractions show that the percolation threshold has not yet been reached.

The transformation of the epoxy based adhesive from an insulator to conductor is due to the cross linkages formed by the nano fillers inside the matrix. Cross linkages increase for higher weight fractions of fillers. Thus, higher weight fractions of fillers facilitate higher conductivity in the sample. This trend continues until the percolation threshold is reached, beyond which, increase in quantity of fillers does not show any significant changes in electrical conductivity of the samples (Li and Lu 2010).

The electrical properties of the Isotropically Conductive Adhesives (ICA) primarily depend on the content, size, shape, and the surface treatments of the fillers and the curing state of the adhesive binder. High aspect ratio and highly conductive materials such as CNT and CNF are used as conductive fillers, since they can provide electrical percolation at very low concentrations for filler dispersion (Wu and Ge 2007).

Conductivity of the adhesive depends on the homogeneity of the CNF and SCCNF fillers, links formed among them inside the matrix and the interaction of the fillers with the matrix. At higher weight fractions, there is a higher probability of forming large number of links, thus, the conductivity increases for higher weight fractions of fillers. Though there is a possibility of agglomeration of fillers at higher weight fractions, it does not have significant effect on the

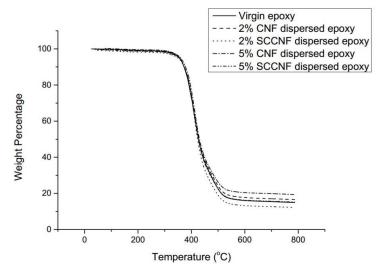


Fig. 4 Thermogravimetric analysis of epoxy and reinforced epoxy laminates

conductivity of the sample. Comparing with lower weight fractions of fillers dispersed epoxy sample, there is higher number of fillers per unit volume of the higher weight fractions of fillers dispersed epoxy sample, which increases its the conductivity; despite the fact that homogeneity is lesser for higher weight fractions of fillers.

Another interesting phenomenon to be noted here is the difference in conductivity for samples dispersed with CNF compared with samples dispersed with SCCNF. While the trend of the conductivity shows a continuous increase with increase in weight fractions of fillers, the epoxy laminates with SCCNF fillers show exceedingly high conductivity compared to the epoxy laminates with CNF fillers. The reason for this phenomenon is that the electronic interactions between the fillers and the matrix are higher for SCCNF dispersed epoxy adhesive, compared to CNF dispersed epoxy adhesive. It can be inferred that when epoxy is dispersed with SCCNF fillers, there are higher number of free electrons available when compared with CNF dispersed epoxy. It is the presence of these free electrons that increases the conductivity of the sample.

A conductivity of 1.3×10^{-1} S/cm has been achieved for 5% weight fraction addition of the SCCNF filler. This conductivity satisfies the necessary condition to be used for being used for EMI shielding and lightning strike protection, as the conductivity required is 10^{-3} to 10^{-1} S/cm and 10^{-1} S/cm respectively. The most significant achievement of this analysis is that, with respect to electrical conductivity, SCCNF is better filler compared to CNF in increasing the conductivity.

3.2 Thermogravimetric analysis (TGA)

TGA was carried out for the virgin epoxy, 2% CNF dispersed epoxy, 5% CNF dispersed epoxy, 2% SCCNF dispersed epoxy and 5% SCCNF dispersed epoxy, and the results are shown in Fig. 4.

The decomposition temperature of the epoxy remains unchanged for all samples ranging from Virgin epoxy to Epoxy dispersed with up to 5% weight fraction of both CNF and SCCNF. The samples start decomposing at around +270°C and are completely decomposed at around +550°C for all the different types of samples. A similar observation was reported by Zhou *et al.* (2008) while working with Multi-Walled Carbon Nano Tubes (MWCNT) as the nanofiller.

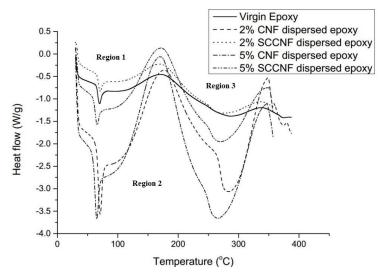


Fig. 5 Differential scanning calorimetry for epoxy and reinforced epoxy laminates

Area under DSC curve

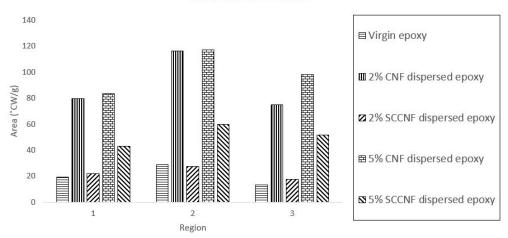


Fig. 6 Area under DSC graph for various regions

The phenomenon to be noted here is the absence of changes in decomposition temperatures for samples having CNF and SCCNF as fillers. It can be inferred that bonds formed between the matrix and the fillers do not have any effect on the decomposition temperatures of the samples.

3.3 Differential scanning calorimetry (DSC)

DSC was carried out for the virgin epoxy, 2% CNF dispersed epoxy, 5% CNF dispersed epoxy, 2% SCCNF dispersed epoxy and 5% SCCNF dispersed epoxy. The observations of this characterisation techniques are shown in Figs. 5 and 6. Fig. 6 shows the area under the DSC curve, where region 1, 2 and 3 correspond to Glass Transition Phase, Crystallisation Phase and Melting Phase respectively.

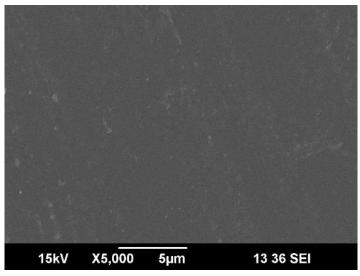


Fig. 7 SEM image of virgin epoxy

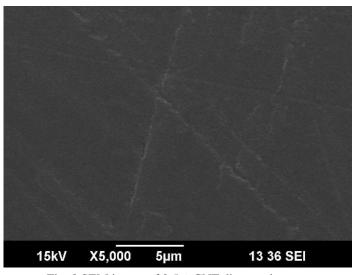


Fig. 8 SEM image of 0.5% CNF dispersed epoxy

From the graph shown in Fig. 5, it can be noted that the transition temperatures for various phase changes remain roughly the same for all the samples. This phenomenon shows that addition of the fillers, both CNF and SCCNF, does not affect the temperatures at which the samples start decomposing. This phenomenon supports the results of the TGA.

A similar analysis performed by Tan *et al.* showed a similar result. It was noticed the addition of fillers had negligible difference in the Glass Transition Temperatures of the samples (Tan and Qiao 2006).

The area under the graphs gives the heat flux during a particular phase change as shown in Fig. 6. It can be noted that the heat flux during the phase changes for CNF dispersed epoxies are very high compared to the heat flux during the phase changes for SCCNF dispersed epoxies and Virgin

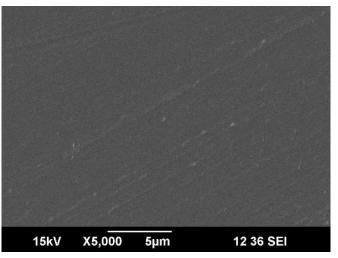


Fig. 9 SEM image of 0.5% SCCNF dispersed epoxy

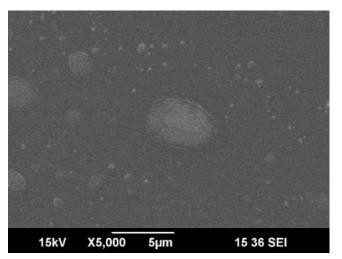


Fig. 10 SEM image of 5% CNF dispersed epoxy

epoxies. Also, the heat flux during the phase changes for SCCNF dispersed epoxies is marginally higher than the heat flux during the phase changes for Virgin epoxies (Hohne and Hemminger 1996).

The fillers form bonds with the matrix when they are dispersed inside the matrix. During phase changes, the bonds between them break when sufficient energy is provided to the system. From the above graph, it is deduced that more energy is required to break the bonds formed between CNF and the matrix, compared to that between SCCNF and matrix. Thus, the intermolecular forces between CNF and the matrix is higher than that of SCCNF and matrix. Though the bond energy is higher when CNF is used as filler, the tensile strength test and conductivity test shows that the matrix with SCCNF dispersed as the filler has better properties. The above-mentioned statement is true as strength and conductivity of the samples are not dependent on bond energies alone, but also other factors such as homogeneity of the sample, agglomeration of fillers, filler density et cetra.

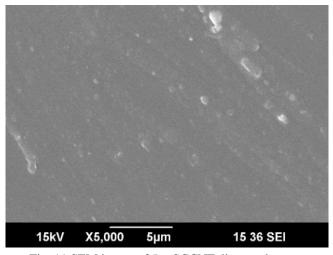


Fig. 11 SEM image of 5% SCCNF dispersed epoxy

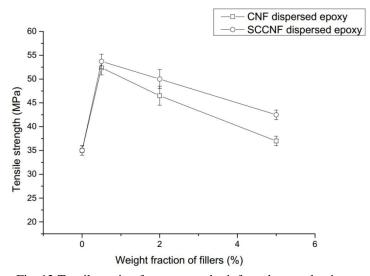


Fig. 12 Tensile testing for epoxy and reinforced epoxy laminates

3.4 Scanning electron microscopy (SEM)

The 5000X magnified images of Virgin epoxy laminate, 0.5% CNF dispersed epoxy laminate, 0.5% SCCNF dispersed epoxy laminate, 5% CNF dispersed epoxy laminate and 5% SCCNF dispersed epoxy laminate are shown in Figs. 7 to 11 respectively.

The changes in the surface topography of various laminates having various weight fractions of fillers are shown in these figures.

From these figures, it is seen that Virgin epoxy has a smooth surface (Fig. 7). However, for 0.5% weight fractions, contours of fibres can be seen on the surface of the samples (Figs. 8 and 9). For 5% weight fractions, the fibres are seen piercing through the surface of the laminate (Figs. 10 and 11).

The higher weight fractions of fillers ensure that there is higher number of fillers per unit volume compared to the matrix with lower weight fractions of fillers. It is due to presence of higher filler density that a few of filler fibres can be seen on the surface of the sample for 5% weight fractions of fillers. However, for 2% weight fractions of fillers, there is a lesser fibre density, thus filaments are not always present on the surface. However, it can be seen from the above figures that the contours of the fillers are slightly visible for 2% weight fractions of fillers. The above witnessed phenomena show the effect of weight fractions in dispersion of fillers.

3.5 Tensile testing

Tensile testing was carried out for the Virgin epoxy, 0.5% CNF dispersed epoxy, 2% CNF dispersed epoxy, 5% CNF dispersed epoxy, 0.5% SCCNF dispersed epoxy, 2% SCCNF dispersed epoxy and 5% SCCNF dispersed epoxy, and the results are shown in Fig. 12. Tensile loading was performed along the length direction.

It can be seen that there is an increase in strength of the polymeric adhesive laminates for addition of 0.5% weight fraction fillers. But the strength deteriorates for higher weight fractions of fillers. However, comparing the strength of the samples, it is noticed that the polymeric adhesive laminate having SCCNF as fillers show higher strength compared to the polymeric composites.

For 0.5% weight fraction fractions of the fillers, there is a high level of homogeneity and very less agglomerations. Thus, the samples show an increase in tensile strength. The tensile strengths are 53 MPa and 54 MPa for 0.5% weight fractions of CNF and SCCNF dispersed epoxy respectively, which are higher than the tensile strength of Virgin epoxy (35 MPa). The dispersed fillers aid in increasing the strength of the sample by stopping crack propagation and reinforcing the matrix.

However, for higher weight fractions of fillers, there is a decrease in the strength of the sample. The tensile strength for 2% and 5% weight fractions of CNF dispersed epoxy adhesive laminatesare 46 MPa and 37 MPa respectively, and the tensile strength for 2% and 5% weight fractions of SCCNF dispersed epoxy adhesive laminatesare 50 MPa and 42.5 MPa respectively. This witnessed phenomenon is due to the agglomeration of the nano fillers and formation of voids in the matrix at higher weight fractions of fillers. Agglomeration occurs due to the Van der Waals forces between the CNF fibres. For higher weight fractions of fillers, the fibres are at close proximity to each other and so they attract each other. This attraction leads to agglomeration in few localities, thus causing stress concentrations at that particular region. This leads to decrease in the strength of the sample.

The tensile strength of the SCCNF dispersed epoxy is marginally higher than CNF dispersed epoxy in all weight fractions. It can be inferred that coating of silver over CNF has decreased the effective Van der Waals forces between the fillers, thus decreasing the possibility of forming agglomerations. Thus, it is possible that SCCNF dispersed epoxies have marginally lesser number of agglomerations, resulting in marginally higher tensile strength of the sample, compared to CNF dispersed epoxy.

It also can be deduced that the ultrasonication of the epoxy resin along with the filler has not ensured homogeneity in the mixture at higher weight fractions of fillers. Density of the resin also has played a major role in the non-homogeneity of the resin. The agglomeration and voids thus formed, created regions of stress concentrations in the samples and causes it to fail at lower stress values. Also, it is due to this phenomenon that the crack propagation distance increases and causes mechanical failure.

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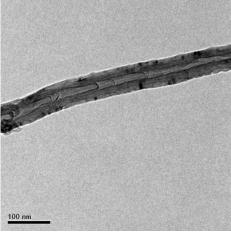


Fig. 13 TEM image of CNF

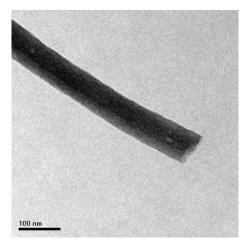


Fig. 14 TEM image of SCCNF

However, the increase in tensile strength of the adhesive laminates for lower weight fractions of fillers is probably due to the improved adhesion between the matrix and the fillers. This enables the mechanical energy to transfer conveniently between the matrix and the fillers.

A similar phenomenon was observed by Vietri *et al.* in their analysis of testing the tensile strength of various adhesives. It was noticed that addition of higher weight fractions of fillers, decreased the tensile strength of the adhesive. The strength decreased from 65 MPa for epoxy with 1.3% weight fraction of filler (CNF) to 49 MPa for epoxy with 5% weight fraction of fillers (Vietri and Guadagno 2014).

3.6 TEM analysis

TEM was performed to understand the effect of coating on the surface of CNF. Figs. 13 and 14 shows the TEM micrographs of CNF and SCCNF. Fig. 15 shows the dispersion of nano particles in the polymers.

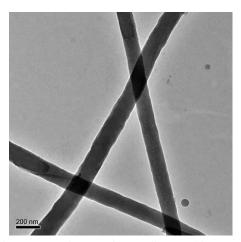


Fig. 15 TEM image of CNF dispersed in epoxy

It is also reported that during with treatment, the surface energy of CNT's increases and the functional radicals introduced by plasma physically or chemically results the CNT's tip coalescent and form into CNT bundles. Therefore, it can be concluded that low pressure plasma results in coalescence of MWCNT's and formation of large size lumps (Gohel and Zhu 2005). Trulli et al (Datsyuk and Dagreou 2005) reveals that the best dispersion improvement was obtained when CNTs were treated with O_2 , as they remain dispersed for long duration, demonstrating a large increase in wettability.

The figures clearly indicate that there is a significant change in the surface morphology of CNF. This is attributed to the coating of silver on the CNF.

4. Discussion and summary

The main objective of this investigation is to develop an electrically conductive adhesive which is capable of being used in aircrafts, satellites and spacecrafts, for the purpose of EMI Shielding and Lightning Strike Protection.

The extensive characterisation techniques performed on the epoxy laminates with various weight fractions of fillers show the properties and variation of properties that are encountered. Conductivity measurement experiment shows that conductivity of the laminates increases up to 1.3×10^{-1} (S/cm) for a 5% weight fraction of modified CNF i.e., SCCNF. Mechanical testing shows that the strength is always higher for the laminate having SCCNF compared to laminate having CNF. The strength increases up to 54 MPa for 0.5% weight fractions dispersion of CNF and SCCNF, but then decreases for higher loads of weight fractions. Thus, higher weight loads of fillers compromises on mechanical strength to give very high conductivity. For industrial application, based on the requirement, weight fractions of fillers can be added after a necessary balance between electrical conductivity and mechanical strength are reached. SEM images of various laminates shows the changes in surface topography due to the addition of different weight fractions of different fillers. TGA analysis shows no significant changes in the decomposition temperature for the samples. It can be seen that addition of higher weight fractions of fillers hardly has any impact on the thermal stability of the laminate. The graph from DSC analysis (Fig. 5)

shows the changes in heat absorbed or released by the samples while transitioning from one phase to another. The fillers do not affect the glass transitioning temperature of the sample. DSC analysis (Fig. 6) shows that very high quantity of heat is absorbed for Glass transitioning and Melting of SCCNF dispersed epoxy laminate compared to the virgin epoxy laminate. However, CNF dispersed epoxy laminate absorbs higher heat for the same compared to SCCNF dispersed epoxy laminate. A similar trend is followed for the heat release during crystallisation phase.

The epoxy based adhesive thus developed could as such be used in aircrafts for lightning strike protection, provided that more sophisticated dispersion methods are used. The novelty of this investigation is a successful proof showing that SCCNF is a better filler compared to CNF. The desirable outcomes from this work can potentially be used to develop low-cost electrically conductive adhesives. It must be noted that using SCCNF as filler, percolation threshold is attained for a very low volume content of just 5%. Further investigation is needed to study the reason behind this phenomenon.

This epoxy based adhesive could be used in satellites as such; however, this application may require the adhesive to withstand temperature of -200°C to +350°C, gamma rays, neutron radiations and UV radiation. For the above-mentioned purpose, further research could be carried out in this field by using ultra-high-performance polymer based adhesives. The filler SCCNF could also be used along with ultra-high-performance polymer matrix to develop conductive adhesives which is capable of being used for satellite and space vehicles applications.

5. Conclusions

• Conductivity of 1.3×10^{-1} S/cm had been achieved for 5% weight fraction dispersion of SCCNF in the epoxy matrix.

• Decomposition of the adhesive starts at +270°C and is completely decomposed at +550°C. Decomposition temperature remains unchanged for all the samples.

- Glass Transition temperature remains the same for all the samples.
- CNF dispersed epoxy shows higher enthalpy than SCCNF dispersed epoxy.

• Tensile strength of the samples increase to 35 MPa for Virgin epoxy. Tensile strength increases to 53 MPa and 54 MPa for 0.5% weight fraction of CNF and SCCNF dispersed epoxy samples respectively. Tensile strength decreases to 46 MPa and 50 MPa for 2% weight fraction of CNF and SCCNF dispersed epoxy samples respectively. Tensile strength decreases further to 37 MPa and 42.5 MPa for 5% weight fraction of CNF and SCCNF dispersed epoxy samples respectively.

• Significant deposition of silver is noted on the surface of CNF, as evident from TEM analysis.

References

- Amoli, B.M., Trinidad, J., Hu, A. and Zhou, B. (2015), "Highly electrically conductive adhesives using silver nanoparticle (Ag NP)-decorated graphene: The effect of NPs sintering on the electrical conductivity improvement", J. Mater. Sci. Mater. Electr., 26(1), 598-600.
- Billias, M.G. and Borders, M.E. (1984), Patent US 4428867 A, Lockheed Corporation.

Burton, D., Lake, P. and Palmer, A. Carbon Nanofiber Applications & Properties.

Chen, D., Qiao, Z., Qiu, X., Tan, F., Chen, J. and Jiang, R. (2010), "Effect of silver nanostructures on the resistivity of electrically conductive adhesives composed of silver flakes", J. Mater. Sci. Mater. Electr.,

21(5), 487-490.

- Datsyuk, V., Dagreou, S., Billon, L., Dupin, J.C. and Flahaut, E. (2005), "Double walled carbon nanotube/polymer composites via in situ nitrooxide mediated polymerization of amphiphilic block copolymers", *Carbon*, **43**(4), 853-894.
- Gagné, M. and Therriault, D. (2014), "Lightning strike protection of composites", *Progr. Aerosp. Sci.*, 64, 1-16.
- Gohel, A., Zhu, Y.W., Sow, C.H. and Wee, A.T.S. (2005), "Field emission properties of N2 and Ar plasma treated multi wall carbon nanotubes", *Carbon*, **43**(15), 2530-2535.
- Guadagno, L., Raimondo, M., Vertuccio, L., Mauro, M., Guerra, G., Lafdi, L., De Vivo, B., Lamberti, P., Spinelli, G. and Tucci, V. (2015), "Optimization of graphene-based materials outperforming host epoxy matrices", *RSC Adv.*, 5(46), 36969-36978.
- Guadagno, L., Raimondo, M., Vittoria, V., Vertuccio, L., Lafdi, L., De Vivo, B., Lamberti, P., Spinelli, G. and Tucci, V. (2013), "The role of carbon nanofiber defects on the electrical and mechanical properties of CNF-based resins", *Nanotechnol.*, 24(30), 305704.
- Guadagno, L., Raimondo, M., Vittoria, V., Vertuccio, L., Naddeo, C., Russo, S., De Vivo, B., Lamberti, P., Spinelli, G. and Tucci, V. (2014), "Development of epoxy mixtures for application inaeronautics and aerospace", *RSC Adv.*, 4(30), 15474-15488.
- Höhne, G.W.H., Hemminger, W. and Flammershein. (1996), *Differential Scanning Calorimetry: An Introduction for Practitioners*, 1st Edition, Springer.
- Li, Y., Lu, D. and Wong, C.P. (2010), *Electrically Conductive Adhesives with Nanotechnologies*, 1st 17th Edition, Springer.
- Nobile, M.R., Raimondo, M., Lafdi, K., Fierro, A., Rosolia, S. and Guadagno, L. (2015), "Relationships between nanofiller morphology and viscoelastic properties in CNF/epoxy resins", *Polym. Compos.*, 36(6), 1152-1160.
- Sancaktar, E. and Bai, L. (2011), "Electrically conductive epoxy adhesives", Polym., 3, 1-3.
- Shaheen, J.M. and Leo, Q.J. (1979), Patent US 4147669 A, Rockwell Int. Corp.
- Simone, D., Angeliu, T., Tonapi, S., Gibson, D. and Zhang, J. (2007), Patent US 20070131912 A1.
- Tan, F., Qiao, X., Chen, J. and Wang, H. (2006), "Effects of coupling agents on the properties of epoxybased electrically conductive adhesives", J. Adhes. Adhes., 26(6), 409-413.
- Vietri, U., Guadagno, L., Raimondo, M., Vertuccio, L. and Lafdi, K. (2014), "Nanofilled epoxy adhesive for structural aeronautic materials", *Compos. Part B: Eng.*, **61**, 73-83.
- Wu, H.P., Wu, X.J., Ge, M., Zhang, G.Q., Wang, Y. and Jiang, J. (2007), "Properties investigation on isotropic conductive adhesives filled with silver coated carbon nanotubes", *Compos. Sci. Technol.*, 67(6), 1183-1186.