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MECHANICAL AND ELECTRICAL PROPERTIES OF EPOXY BASED THERMOSET RESINS REINFORCED WITH CARBON NANOTUBE (CNT)

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ABSTRACT

Aerospace industry is improving rapidly due to the wide use of high performance materials and polymer matrix composites reinforced with Carbon Nanotubes (CNTs) have positively effect on it. Thermoset polymers, especially epoxy resin which is increasingly used in aerospace applications due to the high mechanical properties and durability, have been used for this research. CNTs not only exhibit extraordinary mechanical properties such as high Young's modulus and tensile strength but also high thermal and electrical conductivities as well.

In this paper, electrical and mechanical properties of epoxy resin reinforced with Multi Walled CNTs (MWCNTs) have been analyzed. MWCNTs with different concentrations were added to epoxy resin to improve mechanical and electrical properties of the material. To compare the curing process effect on the properties, some of samples were cured at specific temperature and time when some of them were cured only at room temperature. To characterize the samples, some tests based on ASTM Standards (three point bending), hardness, electrical and thermal conductivity tests were carried out on samples. Neat epoxy resin was used as reference, tests and measurements were first applied to reference specimens to compare the results and observe improvements. It was found that electrical conductivity increased as much as 10% percent with 5% CNT addition while mechanical properties (hardness and elastic modulus) increased 23% with 2.5% CNT addition.

INTRODUCTION

Processing, properties and applications predominately focus on the use of advanced composite materials in aerospace engineering. Various aspects, including the type of fiber, matrix, structure, properties, modeling, and testing are considered, as well as mechanical and structural behavior, along with recent developments. There are several new types of composite materials that have huge potential for various applications in the aerospace sector, including nano composites, multiscale and auxetic composites, and self-sensing and self-healing composites [Fangueiro, Rana, 2016].

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Epoxy resins are a class of thermoset polymers used extensively in structural and specialty composite applications because they offer a unique combination of properties that are unattainable with other thermoset resins which are used as matrix material for composites. Available in a wide variety of physical forms from low-viscosity liquid to high-melting solids, they are amenable to a wide range of processes and applications. Epoxies offer high strength, low shrinkage, and excellent adhesion to various substrates, chemical and solvent resistance and at the same time low toxicity. They are easily cured without evolution of volatiles or by-products by a broad range of chemical species. Epoxy resins are also chemically compatible with most substrates and tend to wet surfaces easily, making them especially well-suited to composite applications [Boyle et al., 2001].
Among the many potential applications of CNTs, its usage to strengthen polymers has been paid considerable attention due to the exceptional stiffness, excellent strength, and the low density of CNTs. This has provided numerous opportunities for the invention of new material systems for applications requiring high strength and high modulus. Precise control over processing factors, including preserving intact CNT structure, uniform dispersion of CNT within the polymer matrix, effective filler–matrix interfacial interactions, and alignment/orientation of polymer chains/CNT, contribute to the composite fibers' superior properties. These properties are compared in Table 1. Commonly used metals such as aluminum and steel are also included for comparison [Green, Li, Meng, et al., 2013].

Table 1: Mechanical, thermal and electrical properties of Graphene, CNT and epoxy resin [Kim, Lee , Shim, 2013]

Materials	**Tensile strength**	**Thermal conductivity (W/mK) at room temperature**	**Electrical conductivity (σ, S/m)**
CNT	60–150 GPa	3500	3000–4000
Epoxy resin	85 MPa	0.25-0.35	insulator
Stainless steel	515-827 MPa	11.2-36.7	1.45 x 10 σ
Aluminum	150-300 MPa	237	3.5 x10 σ

High shear mixers work by spinning a high speed-mixing arm in one direction (3500rpm) while the basket rotates in the opposite direction (900 rpm) (thus, the name- Dual Asymmetric Centrifuge). This combination of forces in different planes enables incredibly fast mixing, and yet the precision construction of each equipment gives it a balance that allows amazingly quiet operation. There are some benefits of high shear mixing; highly reproducible results, no bubbles, reduced exposure to chemicals, virtually no material loss, etc.
In this study, the main purpose is to improve the mechanical and electrical properties of epoxy resin by adding CNT to produce prepreg composites that are extensively used in the aerospace industry. Another aim is to have high homogeneity of mixture with the help of the planetary shear forces. At the end of the experiments, tensile strength of the cured polymer is expected to rise to 20-25% and electrical conductivity is expected to rise about 10-15%.

METHOD

The production of nanoparticle added polymer materials represents an efficient way to improve the performances of polymers and expand their application area of activity. Due to the unique structure and remarkable mechanical, electrical, thermal and optical properties, CNT has been mostly studied as a second phase to produce high performance polymers. The experimental procedure consists of 4 main steps; mold preparation, mixture preparation-casting, curing and sample preparation for testing.

Mold Preparation

One of the most important steps in technological process is molding because correct molding preparation will affect sample preparation which at the end affect the test procedure. Mold preparation starts with the substrate selection. Stainless steels, aluminum and glass can be chosen as substrate. Glass was chosen as the substrate because of ease of use. Then, to remove the samples easily after curing process, researchers chose Mylar® polymer sheet which has two different surfaces. One surface of Mylar® polymer sheet contains Silicon (Si) coating which prevents sticking of epoxy with glass substrate and another surface which does not contain Si coating. Mylar® was adhered on glass substrate by using tape. After preparing of substrate of mold, Teflon® bars were used to complete mold. One of the Teflon® bars which has suitable mold dimensions was used as reference. Teflon bars were divided into two to increase number of samples to complete the process at one shot. A reference Teflon® bar was then used to adjust the gaps between the Teflon® bars. To stick Teflon® bars to substrate, double-sided tape was used. Then, Teflon® bars were covered with Si to prevent any leakage of epoxy from mold. Also, gaps on mold were covered with Si to prevent leakage. Final version of the mold is shown in Figure 1.

Mixture Preparation and Casting

Before casting process, mixture which contains epoxy resin and CNTs, was prepared. Duratek® 1200 (A) was used as epoxy resin and Duratek® 2110 (B) was used as hardener. First, mass of mixture was calculated for the first mold. Calculation was made according to density of epoxy and volume of mold. Then, based on 4:1 ratio, epoxy and CNTs were weighed by using precision scales. CNTs were weighed into cup based on predetermined ratios which were 0% CNTs, 0.25% CNTs, 0.50% CNTs, 0.75% CNTs, 1% CNTs, 1.5% CNTs, 2.5% CNTs, 5% CNTs and 10% CNTs. After that, polymer (A) and hardener (B) were added into cup. To prepare mixture, SpeedMixer™ DAC 150.1 FVZ was used. During the casting of mixture, viscosities were compared by naked eye with regard to changing CNT concentrations.

Curing

Curing is a process during which a chemical reaction (such as polymerization) or physical action (such as evaporation) takes place, that results in a harder or more stable linkage (such as an adhesive bond) or substance (such as concrete). Some curing processes require maintenance of a certain temperature and/or humidity level, others require certain pressure. In the third step of the experiment, all the samples were waited in the mold for 2 days at room temperature and then samples were removed from the mold and some of them were placed into a furnace. To characterize the curing process on the samples, some of the samples were cured at elevated temperature while others were cured at room temperature. Table 2 shows the curing information for samples.

Figure 1: Teflon bars fixed on the Mylar® and surrounded with silicon

Sample Preparation

Sample preparation step is the most important step before testing of samples, because sample preparation step directly affects testing results of the samples. So, this step must be carried out thoroughly. Also, surface and edge of the samples must be free from cracks and bubbles. Aim of this step is to adjust the dimensions of samples which depend on the applied standard during test.

Firstly, grinding process is applied for removing the impurities from the surface. During this process, all bubbles should be removed from the surface. 320 grinding paper was used at 280 rpm for 10 minutes for removing of all the defects from the samples. Then, the surface position was changed which must be opposite 90° direction. After using of 320 grinding paper, 1000 grinding paper was utilized at 280 rpm for 5 minutes to remove the fine impurities. Then, the polishing step was applied to samples. 3 micrometer pastes were applied on the polishing paper and hold the samples for 5 minutes. After sample preparation step, three different tests were fulfilled; measurement of hardness, three point bending test and measurement of electrical conductivity.

Table 2: Curing process details

Sample number	Additive type	% Additive	Polymer ratio	Curing temperature	Curing time
1	CNT	0	4:1	23°C	48 hours
2	CNT	0	4:1	100°C	4 hours
3	CNT	0.25	4:1	100°C	4 hours
4	CNT	0.5	4:1	100°C	4 hours
5	CNT	0.75	4:1	100°C	4 hours
6	CNT	1	4:1	100°C	4 hours
7	CNT	1.5	4:1	100°C	4 hours
8	CNT	2.5	4:1	100°C	4 hours
9	CNT	5	4:1	23°C	48 hours
10	CNT	5	4:1	100°C	4 hours
11	CNT	10	4:1	23°C	48 hours
12	CNT	10	4:1	100°C	4 hours

RESULTS AND DISCUSSION

Durometer Hardness Test

Durometer Hardness is used to determine the relative hardness of soft materials, usually plastic or rubber. The test measures the penetration of a specified indenter into the material under specified conditions of force and time. The hardness value is often used to identify or specify a particular hardness of elastomers or as a quality control measure on several materials. The specimen is first placed on a hard flat surface. The indenter of the instrument is then pressed into the specimen making sure that it is parallel to the surface. The hardness is read within one second (or as specified by the researchers) of firm contact with the specimen. [ASTM, 1997] After all samples were arranged for tests, first, hardness test was applied to the samples. To measure the hardness of samples, Hardness Tester PCE-D™ Shore D device was used. For each specimen, hardness was taken five times on various areas of samples. After that, arithmetic average value of measured results was calculated. Then, chart was plotted according to the arithmetic average hardness values that is showed in Figure 2.

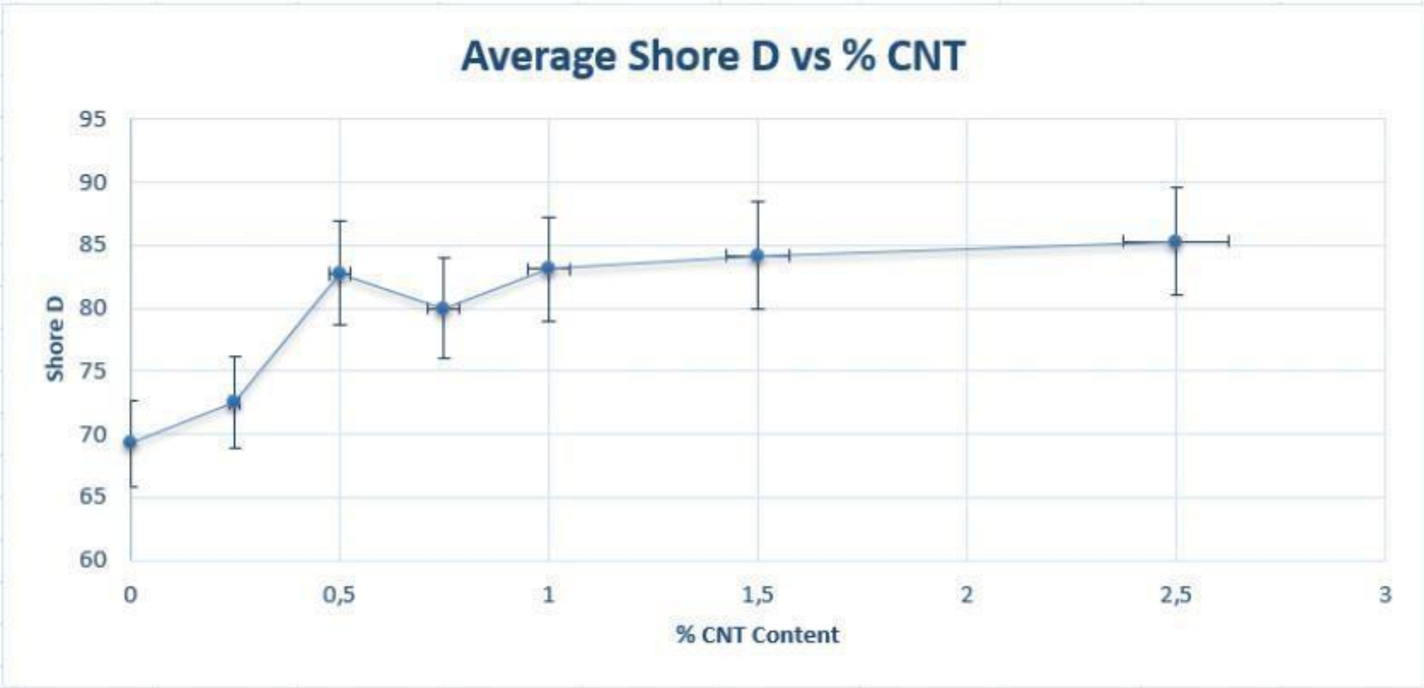

Figure 2: Shore D vs. % CNT content

Three Point Bending Test

Bend testing (also called flexural testing) is commonly performed to measure the flexural strength and modulus of all types of materials. This test is performed on a universal testing machine (tensile testing machine or tensile tester) with a 3-point bend fixture [N ´ EZERKA, 2012]. Three-point bending test was applied to samples to measure elastic modulus of samples. Before testing, samples were prepared according to the applied standard. Then, samples' dimensions were measured by using caliper. After measuring the dimensions, three-point bending test was carried out for all samples. Firstly, reference sample was tested to calibrate testing machine. Then, samples were placed on the middle point on the machine. Then, force was applied on the samples. Until the samples were broken, loads were applied. Test was finished when all samples were broken. This test was performed with Hegewald Peschke™ test equipment. DIN EN ISO 14125 standard was used as the reference standard. The test was handled by using a 50 kN servo-hydraulic testing machine. The machine was run under displacement control mode at a crosshead speed of 1.0 mm/min. All test was made at room temperature. After all tests were fulfilled, the data were extracted from the computer. Then, average result of elastic modulus was computed from testing results for all mixtures and chart was drawn by utilizing calculated average results. Computed results and diagram (Elastic modulus vs. % CNT content) are given in Figure 3.

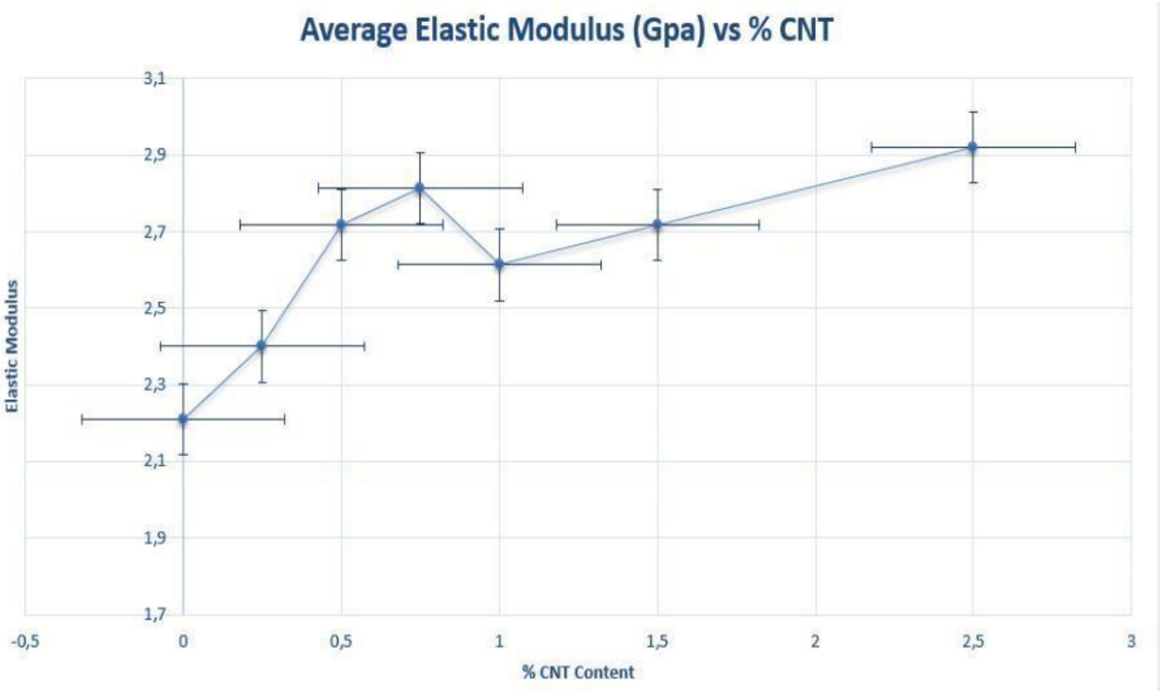

Figure 3: Chart of elastic modulus versus %CNT concentration

Measurement of Electrical Conductivity

To measure electrical conductivity, samples were chosen from each type of mixture which involves different concentration of CNT additives and they were cut with cutting machine in suitable sizes. Then, sample dimensions were measured by using caliper. Thickness of a sample must be smaller than width and length of the sample. Before measurement, sample surfaces were cleaned and silver solution was applied on both sides of samples. Samples waited for two days in room temperature in order to be dried up. After drying process, edges of specimens were cleaned up by using ethanol and grinding paper to prevent short circuit. Then, conductance (G) was measured for each specimen. Measurement was done by using an impedance analyzer. After measurement, electrical conductivity was calculated by using formula. Electrical conductivity vs. % CNT graph was drawn by using test results and σ vs. % CNT graph is given in Figure 4.

Results which are obtained from literature review indicate that adding of CNTs to epoxy resin increases the mechanical properties and electrical properties of neat epoxy resin. It is an expected result after these additions. Results which are given in this study after tests show that with 0.25% CNT, 0.5% CNT and 0.75% CNT addition, linear increasing of Young's modulus of composite material starts with 2.21GPa to 2.82 GPa until 1% CNT addition. Sudden decline was observed with addition of 1% CNT which was 2.61 GPa. This decreasing can be observed due to some reasons. First reason is creation of bubbles which happen during casting process. High speed mixer can eliminate these bubbles during mixing process but this problem can emerge during casting. Bubbles can reduce mechanical strength when tests are applied. So, importance of sample preparation becomes a part of activity in this point. Improper sample preparation is another reason of reducing of elastic modulus. Samples must be prepared thoroughly. All bubbles must be removed from sample surfaces. Also, sample edges should be crack free. Maximum elastic modulus which is 2.92 GPa, was obtained with addition of 2.5% CNT.

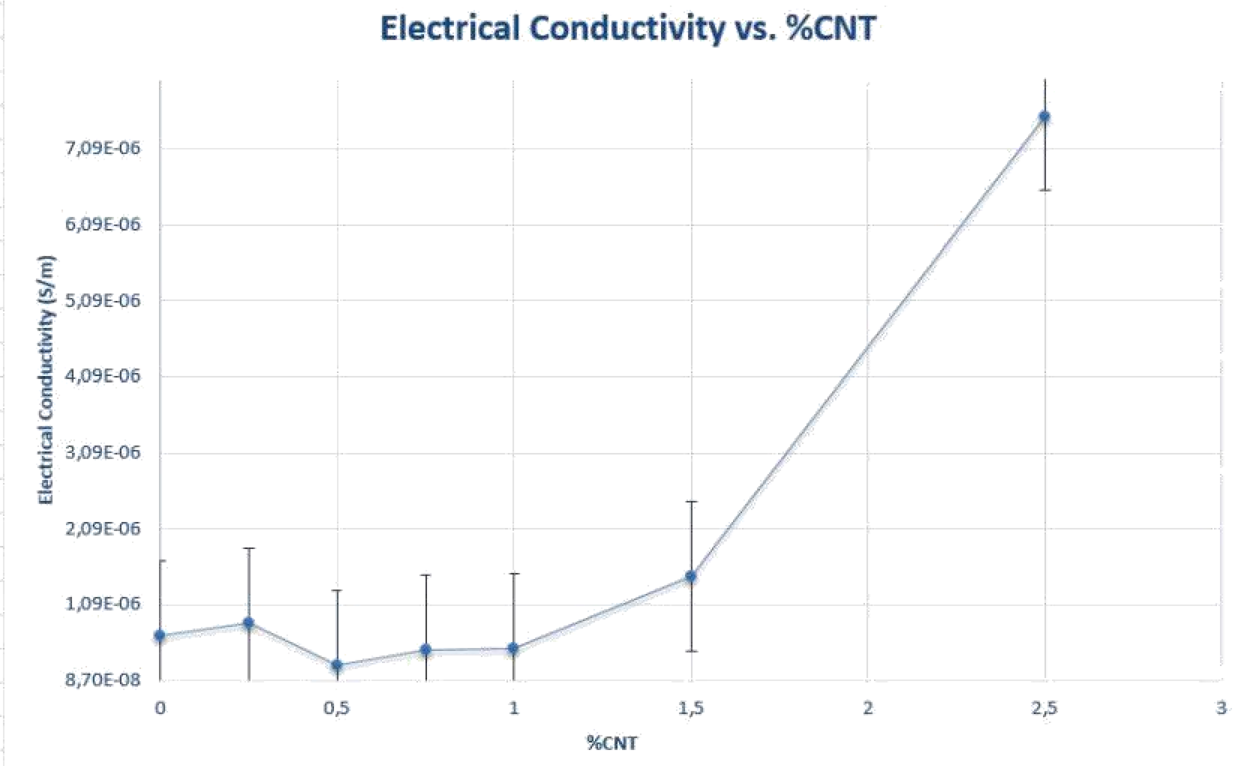

Figure 4: Electrical conductivity vs. % CNT concentration

Also, results were obtained from measurement of electrical conductivity. Electrical conductivity of composite materials which include different CNT content, go up with addition of CNTs. Maximum electrical conductivity was measured as 7.52E-06 S/m from mixture which includes 2.5% CNT. Electrical conductivity is not related to sample preparation method but it is related to type of epoxy used and type of CNT. So, results can be different from literature. Shore D hardness test was applied onto samples and results were obtained and examined. Hardness of samples increases with addition of CNT content which was different for each mixture, and maximum hardness value was obtained from mixture which includes 2.5% CNT concentration. Measured maximum value is 85.3 shore D.

During casting process, some important observations were obtained. After addition of 5% CNT to epoxy resin, visible increasing of viscosity was observed. When we added CNTs to epoxy resin, they demonstrated tendency to agglomeration for high amount addition (5% CNT) and viscosity increased which caused air voids in samples. If these voids aren’t eliminated from structure, they may cause reduction of mechanical properties. Agglomeration is due to Van der Waals forces between nanotubes.

CONCLUSION

This paper presents a study on the mechanical and electrical properties of MWCNT reinforced epoxy nanocomposites. The contribution of this project can be highlighted as follows:

1) Elastic modulus of composite materials increased with increasing CNT addition until 1% CNT concentration. In this concentration, decreasingly growing of elastic modulus was observed. Maximum elastic modulus was gained at 2.5% CNT concentration.

2) With measurement of electrical conductivity, expected results were obtained. Electrical conductivity of composite materials increased by adding CNT particles and maximum conductivity was attained at 2.5% CNT concentration.

3) Shore test results indicated that hardness of composite materials increased by addition of CNT particles. Again, maximum value was obtained at 2.5% CNT concentration.

4) For each concentration, viscosity was screened. According to observations, viscosity was low for all concentrations except for 5% CNT concentration. There is a critical concentration where viscosity begins to increment.

REFERENCES

ASTM (1997) D2240-15 Standard Test Method for Rubber Property -Durometer Hardness

Boyle, Martin, and Neuner (2001) Hexcel Corporation, Epoxy Resins

Fangueiro, Rana (2016) Advanced Composite Materials for Aerospace Engineering 1st edition

Green, Li, Meng, Minus, Song, Tajaddod and Zhang (2013) Structural Polymer-Based Carbon Nanotube Composite Fibers: Understanding the Processing–Structure–Performance Relationship

Kim, Lee , Shim (2013) Graphene An emerging material for biological tissue engineering

N'EZERKA (2012) 14 Standard Test Methods for Bend Testing of Material for Ductility