CQUNIVERSITY RESEARCH

CQUniversity AUSTRALIA

RESEARCH WITH IMPACT

EFFECT OF DILUENT ON THE RHEOLOGICAL AND MECHANICAL PROPERTIES OF EPOXY-CARBON NANOTUBES COMPOSITE

T. T. OO, A.H. ABDULLAH, M. ANWAR, N. A. N. KHANDOKER, S. ISLAM, S. DEBNATH

Bibliographic citation

Effect of Diluent on the Rheological and Mechanical Properties of Epoxy-Carbon Nanotubes Composite—IOPscience. (n.d.). Retrieved October 25, 2022, from https://iopscience.iop.org/article/10.1088/1757-899X/495/1/012094/meta

Link to Published Version: https://doi.org/10.1088/1757-899X/495/1/012094

If you believe that this work infringes copyright, please provide details by email to acquire-staff@cqu.edu.au

aCQUIRe CQU repository

This is an open access article under Creative Commons license.

Downloaded on 21/11/2022

Please do not remove this page

aCQUIRe

CRICOS: 00219C

IOP Conf. Series: Materials Science and Engineering **495** (2019) 012094 doi:10.1088/1757-899X/495/1/012094

Effect of Diluent on the Rheological and Mechanical Properties of Epoxy-Carbon Nanotubes Composite

T. T. Oo, A.H. Abdullah, M. Anwar, N. A. N. Khandoker, S. Islam, S. Debnath*

Department of Mechanical Engineering, Faculty of Engineering and Science, Curtin University Malaysia. CDT 250, Miri 98009, Sarawak, Malaysia

*Corresponding Author: d.sujan@curtin.edu.my

Abstract. The incorporation of carbon nanotubes (CNTs) with polymer material has been the focus of research for many years, due to relatively simple processing procedure and high potential application. However, it is found to be difficult to get very good CNT dispersion, due to the viscosity built-up during the CNTs dispersions. This project investigated the effect of viscosity of the polymer resin through rheological and mechanical characterization. The key ingredient applied for the modification of the epoxy-CNTs viscosity properties is the ethanol diluent. The effect of ethanol diluent on epoxy-CNTs composites was studied through addition of 5% and 10% weight ratio of ethanol to the epoxy-CNTs suspension with increasing CNTs content up to 0.5% weight proportion. The produced specimens were studied and compared with non-diluent specimens through viscometer, optical microscope and tensile strength testing. The addition of ethanol was found to reduce the viscosity of epoxy-CNTs composite through shear-thinning behaviour, in which results due to a high shear rate condition and was found to be beneficial in reducing the CNTs agglomerations and clusters formation within the composite structure. Moreover, improvement in tensile strength of epoxy-CNTs suspension with diluent was observed over non-diluent epoxy-CNTs specimens. The highest gain in tensile strength among the epoxy-CNTs sample was the one containing 0.5% CNTs and 5% ethanol weight ratio, the highest CNTs content tested in this experiment. The experimental results proved that ethanol diluent is beneficial to epoxy-CNTs composites in reducing agglomeration, improving flow-ability and tensile strength.

1. Introduction

Epoxy is utilized widely in various industries as alternatives for metals and wooden material due to its easy accessibility in commercial market and simple fabrication methodology. However, the application of polymers had some disadvantages such as high brittleness, UV deterioration etc. Various filler materials and techniques have been considered to improve the mechanical properties of structural polymer composites [1]. In further improving epoxy matrices' poor mechanical properties in these areas, researchers had found that Carbon Nanotubes reinforced epoxy have greater mechanical strength and fracture toughness than neat epoxy matrices. However, High viscosity of the nanocomposite and processing constraints become significant limitations to the incorporation of reinforcement particles into epoxies. Carbon Nanotubes addition to epoxy increases the viscosity of the resin by several times, making the mixing processing difficult. Moreover, as the content of CNT composition becomes higher, the high viscosity of the composites leads to poor dispersion of CNT, resulting in poor performance.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

Because of their excellent elasticity and good impact strength, a number of reactive diluents had been considered as a good choice to lower viscosity and extended pot life. Diluents increase the resin wetting action and the level of filler loading without a substantial decrease in cure rate and thermal stability of epoxy resin [2] In addition to the viscosity lowering effect on the epoxy system, diluents improve the resistance to brittle fracture behaviour of the nanocomposites [3]. These properties make diluents suitable for modification of an epoxy matrix to obtain improved mechanical and impact strengths, and to facilitate processing of nano particle reinforced composites.

Shear-thinning behaviour is not unique to carbon nanotubes suspensions, carbon nanotubes suspensions tended to show a much stronger shear thinning effect compared with traditional reinforcement filler suspensions at similar concentration levels. Thus shear-thinning effect, due to the consequence of increase viscosity, has various implications on the process ability of carbon nanotubes suspensions. Since the addition of a small amount of carbon nanotubes could result in an increase of several orders of magnitude in shear viscosity, possibly making processing more difficult [4].

Modifying the epoxy resins by incorporating diluents is one such method to reduce the highly viscous cross-linking structure of Carbon nanotubes epoxy system which imposes rigidity for CNT dispersion. Diluents reduce the resin viscosity, helping to boost shear rate of the composite suspension. Moreover, the addition of diluent effectively improves the resin flow behaviour, improving handling during processing and moulding stages [5].

Moreover, the functionalized CNT-epoxy composites were found to have significant improvement on mechanical properties and is regularly utilized in research concerning with CNT-polymer's mechanical properties. Thus, the experiment will be utilization functionalization process in improving the reactivity between CNTs' surface and epoxy polymer cross-linking network. Therefore, the experiment tested the effectiveness of diluent on the mechanical properties of CNT-epoxy composites, with focus on the influence of viscosity during the curing process.

2. Experimental method

2.1. Material

The epoxy resin, EpoxAmite 100 and 103 slow epoxy hardener, supplied by Smooth-on, Inc. was used as thermoset polymer base in this experiment. The mixing ratio of epoxy hardener to resin is 28.4:100 by weight with the pot life of 55 minutes. Diluent used is ethanol and added to resin at 5% and 10% weight content. Carbon Nanotubes (CNTs) is added to resin mixture is in weight percent of 0.1, 0.3 and 0.5.

2.2. Sample fabrication

The CNTs, at first, went through silanization to provide functionalization of CNTs' interface with epoxy matrix. A 100 ml of ethanol: distilled water (95:5 v/v) solution was prepared. 2 grams of CNTs with 6 grams of 3-aminopropyltriethoxysilane was mixed with ethanol-water solution. The mixture was stirred for 4 hours using mechanical stirrer. Silanized CNTs were filtered using paper filter and washed with distilled water and further dried at 80°C for 12 hours using oven. Aluminium moulds, conforming to ASTM D638-10 with dimensions of 165 x 19 x 3.8 mm, were applied in this experiment. The aluminium moulds were applied with mould release wax and CNT-epoxy solutions was poured into the tensile mould. The moulds were degassed under vacuum pump desiccator for 10 minutes. The casted moulds were undergone curing process at 30°C for 4 hours. The samples then undergo second stage curing process for 120°C for another 4 hours.

2.3. *Characterization*

Brookfield viscometer having tube type viscometer with probe model LV02 as shown in figure was deployed to investigate the CNTs-epoxy suspension with varying content of carbon nanotubes and ethanol. Test were performed at room temperature in a 30 ml beaker specimen sizes. The probe was

allowed to complete five revolutions before data can be recorded from the probe speed of 0.3 RPM to 60 RPM. The optical microscopy images were taken using Leica EZ4E microscope with built-in software installed in the computer. All the microscopic images were taken with both top and bottom light fully switched on at magnification range from 8x to 35x. The mechanical properties of the epoxy and epoxy-CNTs sample were demonstrated using tensile test characterization of the cured samples. The mechanical properties such as tensile stress, strain, young's modulus and stress-strain curve behaviour were tested on epoxy and epoxy-CNT samples with various diluent additions.

3. Results and Discussion

3.1. *Viscosity Properties*

The Figure 1 shows the viscosity properties of pure epoxy and epoxy-CNTs samples with CNTs contents of 0.1, 0.3 and 0.5%. The values obtained allow understanding the change in epoxy suspension behavior from Newtonian to non-Newtonian behavior with the inclusion of CNTs. The pure epoxy samples showed the least change in viscosity values with all data between the 500 to 600 mPa.s with standard deviation of 10%. The behavior proved the fact that the epoxy suspension is a Newtonian fluid in which the viscosity properties are not effected by shear rate or probe speed, and the ability to remain in constant rheological behavior under any shear stress. However, the increases in viscosity properties were observed in all samples with carbon nanotubes mixed in. The samples with smallest CNTs (0.1%) content were found to increase viscosity by up to 10% in average throughout all the speed level.

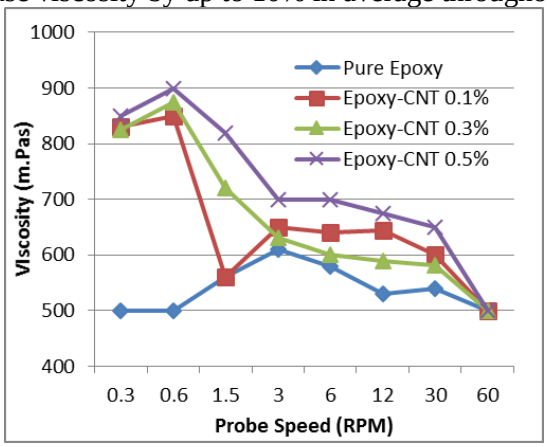


Figure 1. Viscosity Properties of Epoxy and CNT-Epoxy suspensions at different probe speed

The effect of CNTs and ethanol diluent on the viscosity properties and shear-thinning behavior can be observed from Figure 2. At 0.3% and 0.5% CNTs suspension, viscosity values were found to nearly twice compare to neat samples, indicating effect of CNTs network in the epoxy solution. Due to this behavior, at 0.5% CNT weight fraction, CNTs are able to increase the suspension viscosity of epoxy-CNTs by twice. The clear shear thinning behavior, which is the decreasing trend of viscosity at increasing probe speed, can be observed at all three epoxy-CNTs suspension. The significant decreases in viscosity were observed at samples with ethanol diluent at all three CNTs content. This behavior change marks the transition from Newtonian to non-Newtonian fluid of the epoxy solution after CNTs are mixed in.

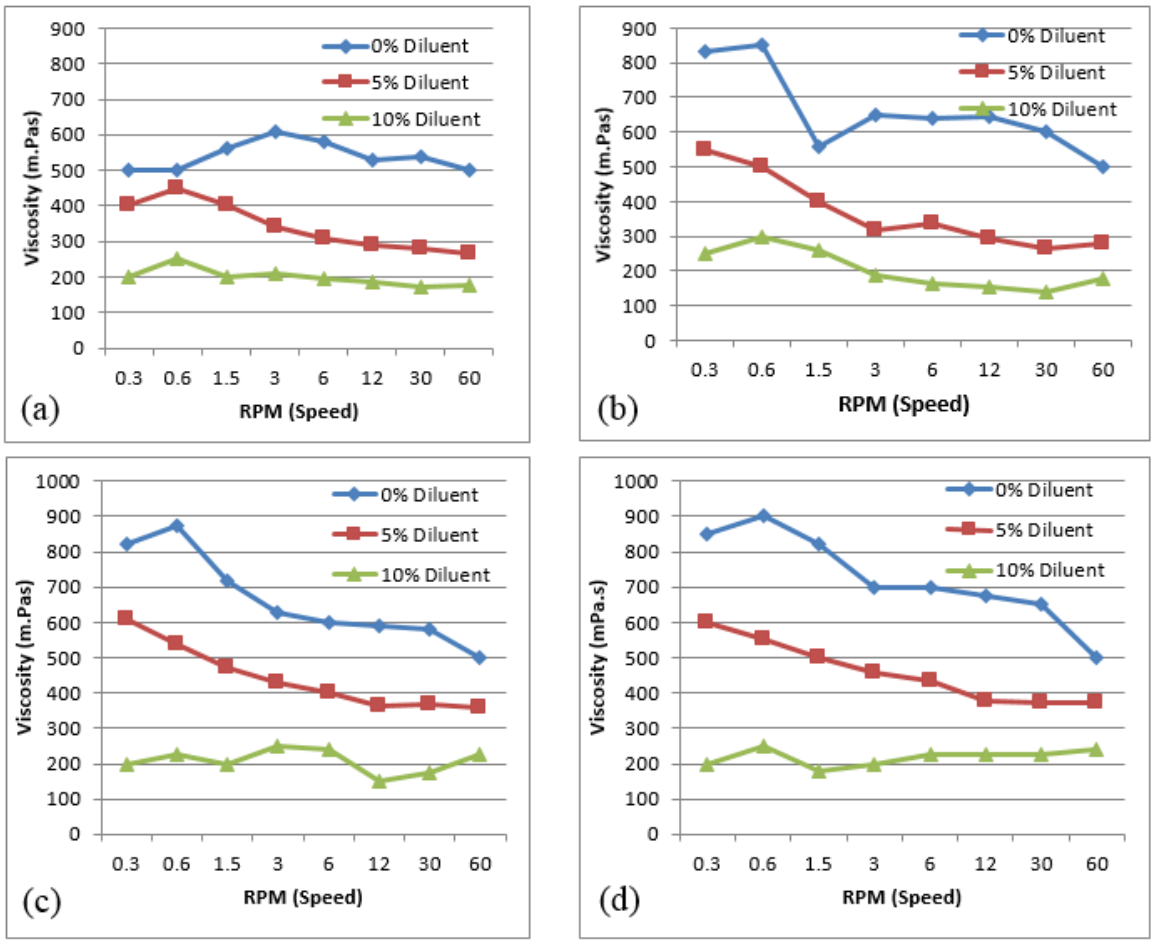


Figure 2. Properties of (a) Neat Epoxy (b) CNT 0.1% (c) CNT 0.3% and (d) CNT 0.5% with 0, 5 and 10% ethanol addition

Interestingly, viscosity properties of composites samples with different CNTs content, levelled to that of pure epoxy when added with 5% weight ratio of ethanol diluent. With the addition of 10% of ethanol, the solution velocity reaches lower than that of pure epoxy system. At 5% ethanol suspensions, all the CNTs contained samples still exhibit the shear-thinning behavior, though in a less distinct manner compared to pure CNTs specimens. However, at 10% ethanol addition, the viscosity values reaches to the range of 200-300 mPa.s and remain stable in that range. The shear-thinning behavior is found to be non-existent at this stage, almost mimicking a Newtonian fluid trend, even at high CNTs content of 0.5%. This is due to diluents reducing the viscosity of epoxy mixtures by weakening the interaction between the resin molecules and CNTs network [6].

3.2. Morphology

Dispersion condition of CNTs within epoxy matrix as well as the fracture point and surface texture were observed using Leica EZ4E optical microscope. The optical microscopic images with varying ethanol and CNTs ratio were captured and compared. From Figure 3(a), significant existent of CNTs agglomeration in the 0.1% CNT sample without ethanol can be observed. Moreover, the cluster of these agglomerations can be seen distinctly, confirming the strong interaction of CNTs network with in the epoxy-CNT composite structure. The largest CNTs agglomeration sizes were around 0.1 mm in diameter

and single cluster with up to three of such agglomerations were observed. These agglomerations become stress points within the sample as well as due to high viscosity of the mixture, large porosity of similar sizes can be observed as well. These factors are severe defects of the samples which degrades the performance of such samples.

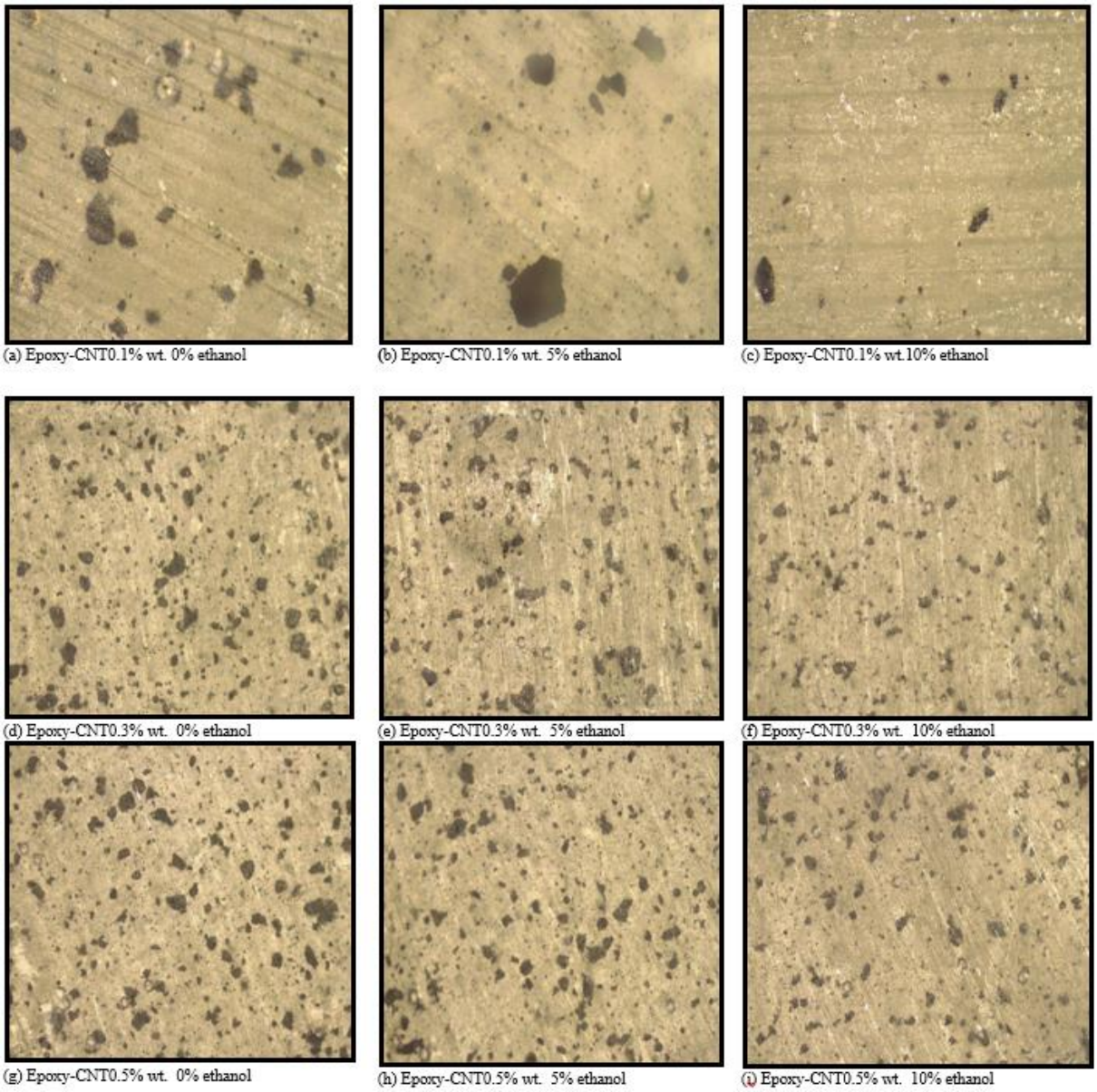


Figure 3. Optical Microscope Image of CNTs Dispersion of Epoxy-CNT 0.1%, 0.3% and 0.5% Samples

From Figure 3(b), reduced cluster formation of CNTs agglomerations can be clearly observed, as well as porosity formed were found to be less small compared to Figure 3(a). However, large agglomeration can still be observed, which reaches the size of 0.2 x 0.1 mm. In Figure 3(c) sample which contains 10% ethanol, significant size reduction of CNTs agglomeration can be observed as well as elimination of clusters. From observation of samples with 0.3% of CNTs, significant formation in agglomerations and multiple clusters can be seen. (Figure 4) Most of the agglomeration sizes are around 0.1 x 0.1 mm and clusters containing up to 10 agglomerations can be observed. Due to increased CNTs

content, increased in number of agglomerations were observed though the sizes are found to be consistent in all samples with different CNTs content. From Figure 3(e) and 3(h), with inclusion of diluent, the cluster formation becomes to break up as well as the reduction in number of large size agglomerations can be seen. As stated earlier, the inclusion of diluent reduces the interaction bonds of CNTs agglomeration, the microscopic image proved such claim. For the ethanol 10% samples, agglomeration pattern were found to be highly similar to ethanol 5% sample, but most of the agglomeration sizes were reduced by almost half.

For the samples with 0.5% CNTs, the reduction in agglomeration and cluster formations between the neat and 5% ethanol was observable but very less so, compared to 0.1% and 0.3% CNTs sample. At the non-diluent epoxy-CNT specimens, some large agglomeration size of 0.2 x 0.1 mm were found, however, in ethanol included samples, the agglomeration sizes were reduced though the dispersion pattern are very similar. At the 10% ethanol sample, the agglomeration sizes were found to be further reduced, the dispersion pattern were much more spread out. From Figure 3(f) and 3(i), improvement in dispersion and reduction in agglomerations were observable with the increasing amount of ethanol diluent.

3.3. Fracture Point

The negative impact of CNTs agglomeration can also be observed by studying the fracture point of the CNTs sample. Many CNTs contained samples were found to have crack propagated along the CNTs agglomeration border with epoxy. Proper adhesion between epoxy matrix and CNTs results in better crosslink interaction improving the crack propagation trap.

From Figure 4(a), a pattern of cracks propagation can be seen passing through a CNTs network bundles. After propagation of crack from the edge, the smooth fracture pattern was arrested by the CNTs network, forcing the pattern to change direction, though the crack still pushed through the CNTs bundle due to nanotubes slippage. From Figure 4 (b), however, an arrest of crack propagation from a CNTs structure can be observed. When crack propagates in nanocomposites through a nanotube, crack tips cannot break the strong CNTs due to bridging by crosslinking. The energy of the tips is significantly reduced by the large quantity of nanotubes pulled out. As a result, crack initiation and propagation become difficult within the matrix as compared to samples with no CNTs, resulting in higher energy absorption capability.

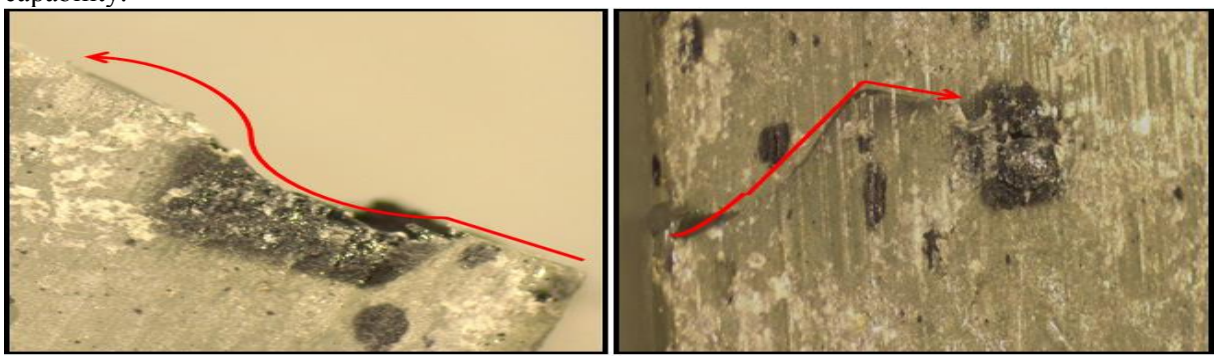


Figure 4. Optical Microscope Image of crack propagation pattern of Epoxy-CNT0.1% samples.

3.4. *Mechanical Properties*

Tensile Strength

The ultimate tensile strength properties of samples with varying ethanol content at different CNTs filler range is illustrated in Figure 5-8. From Figure 5, it can be observed that the neat epoxy with zero ethanol showed the highest results, with decreasing in value as the ethanol content increases. This is due to ethanol reducing interaction bond between the epoxy matrixes, reducing structural bonding of the epoxy resin during the curing process. Moreover, the plasticizing effect of diluent addition reduces the

bonding strength as noted in literature by Firdaus and Mariatti, 2015. Addition of 5% ethanol reduces the tensile strength though not significantly, retaining 85% of the neat sample strength. However, 10% ethanol inclusion was found to significantly reduce the tensile strength of the sample.

In samples with CNTs with no ethanol addition, reduction in tensile strength properties can be noted in the Figure 5, though not significant in manner. The tensile strength of 0.1% and 0.3% CNTs sample recorded around 40 MPa, 80% of the neat epoxy system. With the addition of 0.5% CNTs, a slight increase to 42 MPa was recorded. With addition of ethanol, in contrast to pure epoxy system, increases in tensile strength properties were recorded for all three CNTs contained samples. The 0.1% CNTs sample with 5% ethanol content gained 5% compared to sample without ethanol inclusion, while 0.3% and 0.5% CNTs sample showed 22% and 19% increases respectively. This conforms to earlier viscosity and microscopic observations that reduced agglomeration and cluster formation leads to better mechanical performance.

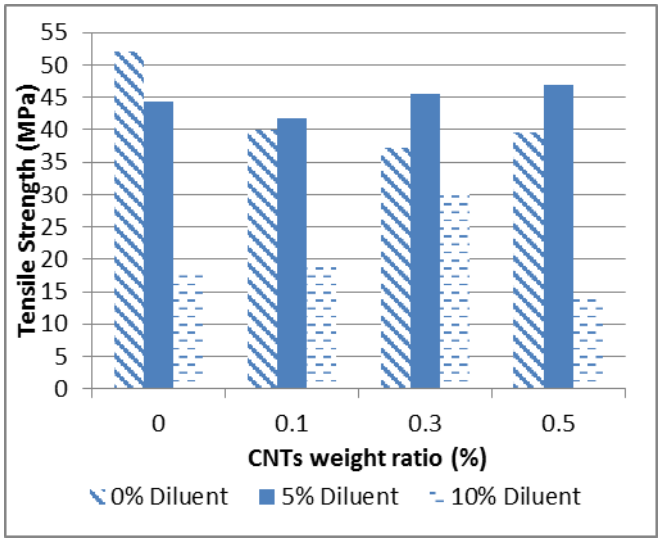


Figure 5. Tensile Strength of CNTs samples with varying CNTs content at 0, 5 and 10% ethanol.

However, it can be observed that these results suggest that there exists a critical ethanol content over which the strength of the CNTs-epoxy bonding began to degrade. This could be explained due to though most properly dispersed CNTs network was observed in samples with 10% ethanol, reduced interaction bonding of epoxy and weaker van der Waals bonding of the CNTs become too significant [1].

Young's Modulus

The modulus of elasticity or Young's modulus is a material property, that describes its stiffness and is therefore one of the most important properties of solid materials. From the Figure 6, interestingly, the neat CNT 0.1% showed the highest Young's modulus due to its low strain and deformation length. The Young's modulus is reversely proportional to the strain value, in which CNT 0.1% showed relatively low. This has been recorded by some literature that the low dispersion of nanoparticles in polymer matrix and the poor interphase properties are the main factors which cause the minor improvement of modulus in polymer nanocomposites [8] Apart from this sample, it can be observed that at 5% ethanol added sample, the modulus properties improves minor as the CNTs content increases from 0 to 0.3% weight ratio. At 0.5% CNTs sample, the Young's modulus value was recorded to be improved by 5% compared to neat sample due to improved CNTs dispersion and load transfer efficiency.

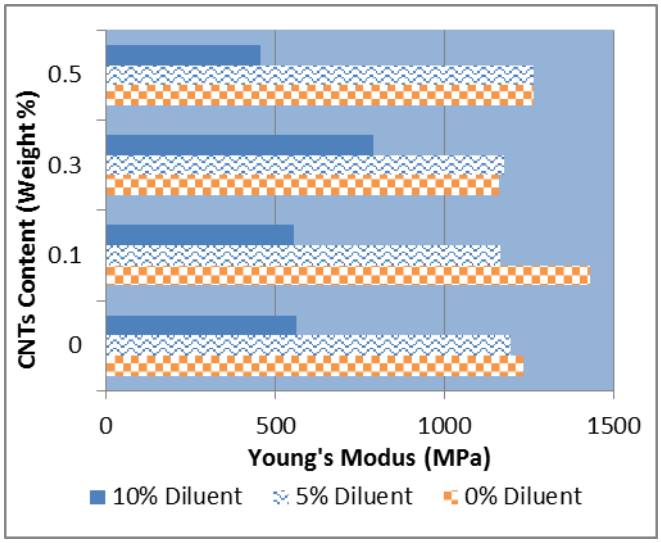


Figure 6. Young Modulus Properties of CNTs samples with varying CNTs content at 0, 5 and 10% ethanol diluent

References

[1] Wernik, J.m., and Meguid, S.a.. "On the mechanical characterization of carbon nanotube reinforced epoxy adhesives." Materials & Design 59 (2014): 19-32. doi:10.1016/j.matdes.2014.02.034.

[2] Downey, Markus A., and Drzal, Lawrence T.. "Toughening of aromatic epoxy via aliphatic epoxy copolymers." Polymer 55, no. 26 (2014): 6658-663. doi:10.1016/j.polymer.2014.10.052.

[3] Rahman, Muhammad M., Mahesh Hosur, Shaik Zainuddin, Kailash C. Jajam, Hareesh V. Tippur, and Shaik Jeelani. "Mechanical characterization of epoxy composites modified with reactive polyol diluent and randomly-oriented amino-functionalized MWCNTs." Polymer Testing 31, no. 8 (2012): 1083-093. doi:10.1016/j.polymertesting.2012.08.010.

[4] Ma, A. W. K., Chinesta, F., and Mackley, M. R. The microstructure and rheology of carbon nanotube suspensions. In Science and applications of carbon nanotubes (Ed. M. Chipara), 2009, in press (Blackwell)

[5] Hutera, Barbara, and Drozynski, Dariusz. An effect of aromatic diluent addition on the selected properties of epoxy resin. Accessed 2005.

[6] Ozgul, Eren Ozeren, and Ozkul, M. Hulusi "Effects of epoxy, hardener, and diluent types on the workability of epoxy mixtures." Construction and Building Materials 158 (2018): 369-77. doi:10.1016/j.conbuildmat.2017.10.008.

[7] Firdaus, S. Muhammad, and M. Mariatti. "Nano-sized boron nitride epoxy composites for underfill application: effect of diluent and filler loading." Journal of Materials Science: Materials in Electronics 26, no. 2 (2014): 774-83. doi:10.1007/s10854-014-2463-4.

[8] Zare, Yasser. "The roles of nanoparticles accumulation and interphase properties in properties of polymer particulate nanocomposites by a multi-step methodology." Composites Part A: Applied Science and Manufacturing 91 (2016): 127-32. doi:10.1016/j.compositesa.2016.10.003.