A Study of the Mechanical Properties of Chemically Functionalized Carbon Nanotubes Reinforced Epoxy

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Abstract

In this work, a novel functionalization method has been employed, with the aim of achieving less entangled CNT and greater dispersion into the polymer matrix. The functionalization method, which was initially proposed by Suri et al. proved it to be successful however more mechanical testing had to be conducted to see the overall improvement [1]. Raman spectra analysis will be conducted to study the response of the CNT to the functionalization process. Also Tensile strength test and impact test will be conducted, to estimate the improvement in mechanical strength. TGA and DSC are employed to study the thermal behavior of the composite material, and effect of ethanol as a dispersion solvent.

Keywords: CNT, Functionalization, MWCNT, Solvent influence, Nanocomposite, Epoxy

Nomenclature

- CNTs Carbon Nanotubes SW - Single Wall (CNTs) DW - Double Wall (CNTs) MW - Multi Wall (CNTs) RCNTs - Pristine CNTs FCNTs - Functionalized CNTs
- TGA Thermo Gravimetric Analysis
- DSC Differential Scanning Calorimetry
- FTIR Fourier Transform Infrared Spectroscopy
- eth Ethanol

1. Introduction

Cabon nanotubes (CNTs) being first discovered in 1991 has shown great potential and application in various fields [2]. This includes fields such as drug delivery systems, biosensors and composite materials [3, 4, 1]. The great interest in CNTs is inherently due to its great electrical and thermal properties. Moreover, they exhibit great mechanical properties as they have an exceptionally high modulus of elasticity up to 1 TPa and tensile strength in the scale of 10 GPa [5, 1]. Ultimately this makes CNTs very promising as a reinforcement material for polymer composites.

One of the main challenges concerning CNTs as a reinforcement material in polymers, is the dispersion of CNTs as they tend to agglomerate into bundles[6].

The agglomeration is ultimately due to the Van der Walls interaction between the individual CNTs, which furthermore limits the load carrying effect of the CNTs from the matrix [1, 7].

In order to overcome this obstacle of entanglement and utilize the beneficial properties of CNTs as a reinforcement material, several approaches have been employed. This includes covalent functionalization and noncovalent functionalization, both being well studied. Jacobs et al. utilized Nitric acid as a functionalizing agent for the reinforcement of CNTs in epoxy. The pre-treatment of the CNTs with the acid, successfully introduces polar functional groups on the surface of the CNTs interacting better with the polar epoxy medium. However, covalent functionalization has the downside of altering the intrinsic properties of pristine CNTs[8].

A study by Jiang Zhu et al. successfully managed to chemically functionalize SWCNTs by means of strong oxidizing acids followed by a flourination. The effect of the functionalization was verified by means of Raman spectroscopy, with appearing peaks corresponding to C-F bond and sp_3 bonds indicating covalent bonding. Despite the success, the study also reveals that the chemical procedure and the ultrasonic procedure necessary for sufficient dispersion shortens the average length of the CNTs by a factor of 10. The functionalization proved itself to be successful as the group obtained an increase in tensile strength of 24 % compared to the pristine SWCNTs [9]. Another group utilized strong oxidizing inorganic acids to introduce functional amine groups on the outer surface of the CNTs. By means of Transmission Electron Microscope, the group was able to deduce an enhanced interfacial compatibility between the epoxy matrix and CNTs. However severe damages were also introduced to the CNTs impacting their mechanical properties [10].

As observed by a group led by Lau, the dispersion solvent plays a major role in the final mechanical properties of the composite[11]. It was shown that the ethanol solvent resulted in a lowered Vickers hardness value compared to pure cured epoxy. Also the flexural strength revealed detrimental results upon the use of ethanol as a dispersion solvent[11].

Recently a group led by Anil Suri managed to successfully functionalize SWCNTs in an epoxy matrix by means of a simple scale-able chemical treatment, and disperse them by sonication [1]. The group washed the pristine CNTs in a concentrated bath of NaOH followed by a washing in ethanol for 24 hours. It was verified by means of Raman spectroscopy that the CNTs did not suffer any alteration compared to the pristine CNTs. The group obtained an increase of 36 % in fracture toughness in terms of K_Ic [1].

In the presented paper the same functionalization procedure used by Suri et al. has been followed to modify MWCNTs. The feasibility of a shear mixing method has been assessed, with an objective to propose a more safe and scale-able dispersion method compared to ultra bath sonication.

2. Materials and Methods

The epoxy resin utilized for this project was Proset INF-114 with the hardener INF-213. The CNTs were provided by Cheap Tubes Inc., Cambridgeport, VT 05141 USA. The tubes have a diameter of 20-30 nm, and were obtained by means of Combustion Chemical Vapour Deposition (CCVD). The NaOH and ethanol used for the washing and as a solvent respectively, were obtained from Sigma-Aldrich.

2.1 Chemical Treatment of CNTs

The chemical treatment used followed the same procedure used by Suri et al [1]. and consist of the stirring the CNTs in a concentrated solution of NaOH in absolute ethanol at room temperature for 24 hours.

Subsequently, the CNTs are collected by vacuum filtration on a poly-carbonate membrane filter, followed by repeated washing in ethanol. Lastly, the samples were dried until the desired final concentration is reached (2g/50 ml). To evaluate the influence of the solvent, a control batch without the presence of ethanol solvent was also made.

2.2 Preparation of Samples

Samples of neat epoxy and epoxy reinforced with multiple compositions of CNTs, and epoxy reinforced with multiple compositions of functionalized CNTs, with and without the presence of ethanol, were produced, characterized and tested.

Firstly, neat epoxy samples, used primarily as a reference material, were produced by mixing the resin material with the hardener. Then, epoxy samples mixed with 3 wt% of ethanol were produced in order to track the influence of ethanol.

Epoxy-CNTs nanocomposite samples were also produced in batches with and without ethanol, by using multiple wt% of MWCNTs as seen in table I.

One of the challenges in production of the samples is the presence of defects caused by air trapped inside the samples. A vacuum degassing procedure proved to be an effective solution.

The CNTs are dispersed in the hardener by shear-mixing for a total of 50 minutes at 40 RPM.

More details on sample production are available in the appendix.

2.3 Characterization Methods

The dispersion of the CNTs in the epoxy matrix were investigated using optical microscopy.

Furthermore TGA and DSC analysis were performed for both the pristine and functionalized CNTs using Netzsch 449 and TAQ2000 respectively. The TGA was run to a maximum temperature of 900 $^{\circ}C$ in Nitrogen atmosphere.

Raman spectrometer provided by Renishaw inVia was utilized to characterize both the pristine CNTs and the functionalized CNTs. It should be noted that both the pristine and functionalized CNTs were in powder form. A laser excitation of 532 nm was used on different

	CNTs (wt%)	Ethanol (wt%)
Epoxy	0.000	0.00
Epoxy+eth	0.000	3.00
RCNTs	0.025	0.00
	0.050	0.00
	0.075	0.00
	0.100	0.00
	0.200	0.00
FCNTs	0.025	0.00
	0.050	0.01
	0.075	0.01
	0.100	0.01
	0.200	0.03
RCNTs+eth	0.025	0.33
	0.050	0.67
	0.075	1.00
	0.100	1.33
	0.200	2.67
FCNTs+eth	0.025	0.40
	0.050	0.81
	0.075	1.21
	0.100	1.61
	0.200	3 23

Tab. I Samples list

areas of the samples to evaluate the fuctionalization.

Analysis of the matrix material was done by means of Fourier - Transform Infrared Spectroscopy (FTIR) on Perkin Elmer Instruments - Spectrum One FTIR Spectrometer.

Mechanical properties of both the epoxy samples and CNTs-epoxy samples were obtained using ZWICK z100/TL3S. The specimens were dogbone shaped, and subjected to uniaxial extension.

Impact testing was further performed on Instron Ceast 9050 to asses the presence of toughening phenomena.

Creep-behaviour of the samples was studied using a home-made setup. The Dogbone shaped samples were attached to clamps at both ends, with one end attached to a screw and the opposite side to a load. The creep-behaviour is observed during several weeks and is monitored using a logitech c170 webcam.

3. Results

3.1 Microscopy Analysis

Dispersion of the CNTs in the epoxy matrix was analyzed by optical microscopy. The main objective was to identify how the functionalization influences the dispersion, and how the increase of the wt% of

CNTs in epoxy matrix affect agglomeration. Moreover, the influence of ethanol as a thinning agent on the effectiveness of the shear-mixing have been assessed.

Based on the microscopy analysis, the functionalization had a positive influence on the dispersion, which can be seen in figures 1, 2 and 3, for samples with 0.050% CNTs in the epoxy matrix.

Furthermore, it can be observed in figures 1, 2 and 3, that ethanol positively affected the dispersion, as the amount of agglomerations is drastically decreased. Moreover, the thinning effect of the ethanol also improved the effectiveness of the shear-mixing.

Additionally, it can be concluded from the microscopic analysis that increasing the amount of CNTs in the matrix results in increased agglomeration.



Fig. 1 Pristine MWCNTs in epoxy matrix



Fig. 2 Functionalized MWCNTs in epoxy matrix

3.2 TGA

Thermogravimetric analysis was obtained for both pristine and functionalized CNTs. Two TGA profiles were done for the pristine CNTs, whereas one profile was obtained for the functionalized CNTs.



Fig. 3 Functionalized MWCNTs in epoxy matrix, without ethanol

Comparing the two profiles of the pristine CNTs, it is possible to determine that there are several differences. For the first sample a peak is observed at around $125^{\circ}C$ - $195^{\circ}C$, which may be due to the presence of amorphous CNTs and their oxidation. This peak is not present for the second sample, which was not expected as the presence of amorphous CNTs is almost inevitable. For the second sample a break is observed as the slope increases for a small range of temperature and changes back again.

The residual weight of the samples also provide an important insight into the purity of the material at hand. According to [12] the residual weight after a TGA of the CNTs can vary from 0% to 50%. Although this is observed, a strange behaviour of the weight going below zero and increasing again is noticed. This may have been caused by the fluffiness of the material in hand, as it may have elevated the pan when the low weight are approached. However the residual weight rises at temperatures above $800^{\circ}C$.

For the second sample a larger amount of material was used . It proved successful at eliminating the strange behaviour at elevated temperatures.

As for the functionalized CNTs, the TGA profile looked different as expected. In contrast to the first sample for the pristine CNTs, no observable peak was present around $125^{\circ}C$ - $195^{\circ}C$. Also, any functionalization or introduction of defect onto the pristine structure of the CNTs reduces the oxidation temperature [12]. This effectively mean that the onset temperature for the functionalized CNTs should be lower than that for the



Fig. 4 TGA results of 1.32 mg pristine MWCNT



Fig. 5 TGA results of 1.9 mg pristine MWCNT

pristine CNTs. For the functionalized CNTs, the onset of the thermal degradation begins at $470.9^{\circ}C$ and stops around $521.9^{\circ}C$.

Comparing this to the value obtained for the pristine CNTs, there is a fall in the onset temperature of the thermal degradation of the samples after functionalization. For the pristine CNTs the onset of degradation began at $570^{\circ}C$ and was terminated around $836.6^{\circ}C$. Thus the functionalization effectively reduced the thermal degradation temperature of the CNTs.



Fig. 6 TGA results of 2.6 mg functionalized MWCNT

3.3 Raman Spectroscopy

Sample preparation for Raman spectroscopy consisted of dispersing the CNTs in ethanol and drying them out before performing the test. Raman spectra for both pristine and functionalized CNTs can be seen in the figures 7, 8 and 9.

The main objective of Raman spectroscopy was to identify the type of nanotubes, determine the quality and purity and the effect of functionalization procedure.

Purity and quality of the CNTs was determined by the ratio between the intensities of D and G band (I_D/I_G) . Since the intensity values of G and D band is quite similar (I_D/I_G) equal to 1.12), based on the literature it can be concluded that the defect density is high and structural quality of pristine CNTs, quite low [13, 14, 12].

On the contrary to the spectra of pristine CNTs, I_D/I_G ratio for functionalized CNTs is equal to 0.96. Comparing that with the pristine CNTs, it can be stated that functionalization improved the quality and purity of nanotubes.

It has to be noted that while doing the Raman spectroscopy for the functionalized CNTs, a nonhomogeneous surface of the microscopic sample image was noticed, covered with black and white spots. Therefore, an analysis was performed on both the black and white zones, and the results of the Raman spectra are given in figure 8 and 9, respectively.

The main difference between the spectra of functionalized nanotubes with the laser focused on the white and black spots is a very sharp, high intensity peak at 1080 cm^{-1} in the spectra taken from the white spot of the sample, and it is attributed to the residual Sodium Ethoxide (C_2H_5ONa) from the functionalization process. Some indication of the same peak can be found in the spectra taken from the black spot as well, but significantly lower in intensity value.



Fig. 7 Raman spectra of pristine MWCNTs with a green laser, wavelength of 532 nm and power of 25 mW



Fig. 8 Raman spectra of functionalized MWCNTs with the laser beam focused on the black spot with a green laser, wavelength of 532 nm and power of 25 mW



Fig. 9 Raman spectra of functionalized MWCNTs with the laser beam focused on white spots with a green laser, wavelength of 532 nm and power of 25 mW

Furthermore, Raman shift, for functionalized CNTs is moved to the higher wavenumber for each band, which is related to the shortening of the chemical bonds, but is also a result of poor calibration of the machine [15].

Absence of the low-frequency Radial Breathing Mode (RBM) goes hand in hand with the identification that the CNTs that were used are actually MWCNTs.

3.4 FTIR

The exact chemistry of the epoxy and hardener are not disclosed by the manufacturer. However, by the FTIR analysis performed the resin appears to be of the Bisphenol-A diglycidyl ether group (figure 10).



Fig. 10 Bisphenol-A diglycidyl ether chemical structure[16] The identified OH group can interact with the ethanol

to form hydrogen bonds that can contribute to the intermolecular interactions within the polymer chain, as supported by the research done by Teh et al[17].

3.5 DSC

In order to evaluate the effect of ethanol on the epoxy matrix, DSC measurements were obtained. As can be seen in figure 11, the DSC profile for cured epoxy with and without ethanol solvent present looks very different. For the epoxy with no ethanol present a distinctive endothermic process is initiated around $59^{\circ}C$.



Fig. 11 DSC spectra of both cured epoxy with ethanol mixed into it, and cured epoxy without ethanol mixed into it.

Despite the absence of the distinctive peak around $59^{\circ}C$ for the cured epoxy with ethanol solvent, a gradual decrease is observed around $60^{\circ}C$.

Depending on the degree of curing, the T_g and the ΔH are subjected to change. The more cured the epoxy sample is, the higher temperature the T_g occurs upon, the and the lower the ΔH value becomes [18].

As can be observed in both figure 12 and figure 13 a clear shift in the T_g value is observed for the cured epoxy with ethanol solvent compared to the cured epoxy with no ethanol.



Fig. 12 DSC spectra of cured epoxy with ethanol mixed into it

The higher value for the T_g , may indicate a greater cure of the epoxy sample in hand. This may have been caused by the intrinsic properties of the epoxy resin. The bisphenol-A epoxy resin has an alcohol group which



Fig. 13 DSC spectra of cured epoxy without ethanol mixed into it.

makes is susceptible to forming hydrogen bonds with the ethanol present in the system.

3.6 Tensile Test

The mechanical properties of the fabricated samples were evaluated by means of a tensile test. In order to evaluate the effect of the functionalization process on the dispersion and exfoliation of the MWCNTs, the obtained results were contrasted with samples which had equal wt% of pristine MWCNTs.



Fig. 14 Young's modulus of pure epoxy, pristine CNT and functionalized CNT

As shown in figure 14 which is the the epoxy without any ethanol solvent, the highest Young's modulus is observed for 0.025 wt% functionalized MWCNTs with an increase of around 21% in stiffness compared to cured epoxy reference sample. However, this tendency should also be reflected by the ultimate strength (UTS) values obtained for the samples. This was not the case as a UTS of 60 MPa was obtained for the functionalized MWCNTs with a composition of 0.025 wt%, compared to a UTS value of approximately 80 MPa for reference cured epoxy. This results suggests that the spike observed for the stiffness for 0.025 wt% functionalized MWCNTs composition may have been caused by an experimental error.



Fig. 15 Young's modulus of pure epoxy, pristine CNT and functionalized CNT both with ethanol solvent present

However, a general tendency of increasing stiffness is observed for figure 14 as the wt% of functionalized MWCNT is increased. This same tendency is not observed for the pristine CNTs, whereas a "flat" profile is observed for the samples presented in figure 15 with the ethanol solvent present.

Observing the ultimate tensile strength of the different samples presented in figure 16, reveals interesting features. Apart from the aforementioned fact that the 0.025 wt% of functionalized MWCNTs had a 25% lower UTS value compared to the reference cured epoxy sample, an trend of increasing UTS value is observed for the pristine MWCNTs with a peak for 0.025 wt%.



Fig. 16 UTS of pure epoxy, pristine CNT and functionalized CNT

It can be seen in figure 16 and figure 18 that regardless the presence of ethanol, the functionalized samples present a decrease of 25% in UTS value compared to the reference cured epoxy with no ethanol.



Fig. 17 UTS of pure epoxy, raw carbon nanotubes and functionalized carbon nanotubes both with ethanol solvent present

The elongation rupture profile for the samples with no ethanol solvent is presented in figure 18.

Fig. 18 %-Elongation at rupture for pure epoxy, pristine CNT and functionalized CNT both with ethanol solvent present

A greater elongation is observed for the pristine CNTs, with a peak elongation occurring for 0.1 wt% with an elongation of around 9%. Judging from the values obtained for the functionalized CNTs, the functionalization process merely is not enough to induce reinforcing properties.

Gkikas et al. obtained an increase in UTS value of epoxy by the addition of MWCNTs. However, the group did not observe any significant change to the stiffness of the samples by means of the addition of MWCNT [19]. No trend of increasing UTS value were observed for the functionalized samples with ethanol and those without for this article. Despite the fact that the functionalized samples were hypothesized to reveal improved dispersion of MWCNTs in the epoxy matrix, it was observed that the pristine MWCNTs yield greater UTS values.

An increased Young's modulus for the functionalized samples was achieved in this paper in contrast to Gkikas et al. However this was also obtained by Cha et al, as they observed an increase in the Young's modulus as a function of increasing wt% of MWCNTs in the epoxy matrix [20]. The increase in the modulus as a function of the CNTs filler amount was theoretically expected, however the group reached a wt% in which they experienced re-agglomeration [20].

3.7 Impact Testing

The results of the impact testing are presented in figure 19.

What can be observed from the graphical representation in the figure 19 is that the neat epoxy exhibits the biggest impact strength with an average value of $6.6 \ Kj/m^2$. This can be explained by the fact that the MWCNTs act as micro defects instead of an reinforcement. However, there is a very high standard deviation that has to be taken into account.

Samples reinforced with pristine MWCNTs show better impact strength than samples reinforced with functionalized MWCNTs. This was not expected, as the functionalization should result in a better dispersion of the MWCNTs compared to the pristine MWCNTs. According to Cha et al. an increase in toughness as high as 62% for 0.1% functionalized MWCNTs and even 95 - 100% for 0.5% and higher compositions was observed by the group [21].

Plausible causes for the contradictory result obtained in this paper may be caused by insufficient effect of the functionalization process on the distribution of the MWCNTs. Agglomeration of the MWCNTs have detrimental effect on the impact strength of the epoxy.

Additionally, analyzing the ethanol effect, from the graph in figure19 it can be seen that the ethanol weakened the impact strength both in the case of pristine and functionalized MWCNTs. However due to the relatively large standard deviation of the results, the real influence of ethanol is probably insignificant to the final impact strength of the MWCNTs.

3.8 Creep

Fig. 19 Graphical representation of impact strength of neat epoxy sample, and epoxy sample reinforced with 0.05% MWCNTs, both with and without ethanol

Samples containing 0.05 wt% of MWCNTs both functionalized and pristine have been compared to references of pure epoxy. The same test have been done for dry samples and samples containing traces of ethanol in percentage presented in table I.

From the creep strain rate measured in the secondary creep stage visible in figure 20 it is possible to see how the improved dispersion and matrix interaction obtained with the modification positively influence the creep behaviour.

By comparing the performances of pure epoxy and epoxy plus ethanol is possible also to see the plasticizing effect of the ethanol, that act as a lubricant and increase the free volume in the polymer, thus lowering the creep [17].

4. Conclusion

The objective of this article was to study the dispersion efficiency of a novel method proposed by Suri et al. [1]. It was by means of microscopy analysis revealed

Fig. 20 Creep strain rate in the secondary creep stage (measured between 50 and 150 hours)

that the agglomeration phenomenon was reduced following the functionalization step. Furthermore the ethanol solvent positively affected the dispersion of the MWCNTs, as less agglomerates were observed in the case of functionalized MWCNTs in ethanol solvent compared to dried functionalized MWCNTs. As the mixing procedure chosen in this article was shear-mixing, the use of ethanol as a solvent proved to be useful due to its thinning effect aiding the effectiveness of the mixing. Also it it notes worthy that no harmful chemicals were used for the dispersion of the CNTs. This along with the use of a shear mixer instead of a ultrasonic bath provides an easy scalable method for the dispersion of CNT in a polymer medium.

For the functionalization process, the CNTs were repeatedly washed in ethanol. By means of the Raman analysis presented in figure 7 and figure 8, the effect of the washing on the purity of the samples can be seen as decreasing the amount of impurities. This was expected, and corresponds to the removal of impurities such as amorphous carbon. From the TGA analysis, the shift of the onset temperature for the functionalized CNTs compared to the pristine CNTs indicate an increase in the amount of defects present. This is theoretically expected as the functionalization procedure of washing in concentrated NaOH and ethanol is expected to alter the intrinsic structure of the CNTs.

As previously mentioned, it was obtained by Lau et al. that the use of ethanol as a dispersion solvent had detrimental effect on the mechanical properties of the epoxy components [11]. It was by means of FTIR analysis verified that the epoxy resin utilized was bisphenol-A. This epoxy resin has the characteristic feature of OH groups along its chain, making it susceptible to forming hydrogen bonds with the present ethanol solvent. As obtained from the DSC profile for both cured epoxy with ethanol solvent and cured epoxy without ethanol solvent, a shift in the T_g value is observed. This shift may have been caused by the catalyzing effect provided by the hydroxil compounds such as ethanol which increases the rate of curing [22, 23].

With regards to the mechanical properties, tensile test, creep and impact tests were evaluated to determine both the effect of ethanol solvent and CNTs on the

epoxy components. The creep results revealed that the functionalization had a positive effect on the creep behaviour. The plasticizing effect of ethanol was also very apparent, which is due to epoxy network becoming more flexible[24]. The impact testing revealed a decreasing tendency with the inclusion of ethanol solvent. Also it is evident from the impact test results that the CNTs failed to reinforce the epoxy resin as was expected. This may have been caused by insufficient mixing, resulting in the CNTs having a detrimental role as agglomerates. As the impact strength is mostly determined by the matrix material, the consistent decrease in impact strength as a result of the presence of ethanol solvent may be caused by chemical structure changes[11].

From the tensile tests results, a tendency of increasing Youngs modulus is observed, along with a lower UTS value for functionalized CNTs compared to pristine CNTs. The increasing tendency in Young's modulus observed for the functionalized CNTs may indicate that we can further increase the wt% of the CNTs filler. However the results obtained for the UTS, indicate re-agglomeration of the CNTs thus the detrimental effect.

For future work, a shear mixing process will be employed for a longer duration along with a change of epoxy resin. Microscopy images revealed greater dispersion by ethanol solvent, which is the desired outcome. Greater wt% of MWCNT filler is also a possible area of study, as no processing problems were encountered with 0.2 wt% of MWCNTs. In order to enhance the mechanical properties, a modification step has to be undertaken in which the inter-facial adhesion is improved by chemically bonding the matrix and CNTs.

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