Study of Functionalized Carbon Nanotubes Polymer Composites

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Abstract
The production of CNT reinforced polymer based composites has been hindered due to two main reasons. The reasons being; incompatible interfaces between the CNTs and the polymer matrix and poor dispersion of CNTs in the polymer matrix. A simple and scalable functionalization method proposed by Suri et al. proved to be successful in overcoming the above-mentioned obstacles, however more tests had to be carried out to know its degree of effectiveness [1]. In this work, this functionalization method is employed and its effect on the MWCNTs and in turn the mechanical properties of the composites is investigated. The pristine and functionalized CNTs were characterized using Raman, TGA and SEM analysis. Composites with 0.4 wt% and 0.8 wt% pristine and functionalized MWCNTs were produced and then characterized using DSC, tensile test and SEM.

Keywords: CNT, Functionalazation, MWCNT, Dispersion, Epoxy

Nomenclature

CNT	Carbon Nanotubes
SW	Single Walled (CNTs)
MW	Multi Walled (CNTs)
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
UTS	Ultimate Tensile Strength
SEM	Scanning Electron Microscopy

1. Introduction

Carbon Nanotubes [CNTs] have since their discovery in 1991 been a catalyst for research within the field of Nanotechnology [2, 3]. The great interest can be attributed to their excellent mechanical properties as well as great thermal and electrical properties [4, 5, 1]. In addition, their large surface area and small dimensions make CNTs an ideal reinforcement material in polymer composites. However, despite their promising properties and considerable research of the topic, the development of commercial CNT-composites has been stagnated due to poor dispersion in the matrix material and weak interfacial bonding [6, 4].

An aspect of the problem with bad dispersion is that commercially supplied CNTs are already found in bundles entangled together. Agglomerates lead to a decrease in mechanical properties, and to solve this, a successful dispersion is needed. This can be achieved by separation of the bundles and ensuring stability by avoiding re-agglomeration.

Furthermore due to the chemical structure of CNTs they are chemically stable and inert, bound only due to Van der Waals forces. Thus, a proper load transfer is not achievable. To overcome these issues several researchers have tried to functionalize the CNTs in order to make them less inert. This involves chemically altering the surface of CNTs by attaching functional groups to them [7] [8].

Cha et al. conducted a study to improve the dispersion of MWCNTs in epoxy matrix for the fabrication of composites with enhanced mechanical properties. Polystyrene sulfonate (PSS) and poly(4-aminostyrene) (PAS) were the functional groups that were attached to the surface of CNTs by non-covalent functionalization. The functionalization procedure began with dissolving the two functional molecules in N,N-dimethylforamide (DMF) by stirring. This was followed by sonication of the DMF solution with CNTs for 1 h. The functionalized CNTs were obtained by vacuum filtration. On fabricating composites with epoxy matrix and 1 wt.% of the functionalized CNTs, they found that the mechanical properties of the composites were superior to those of neat epoxy. The tensile strength and Young's modulus of the composites saw an increase of 34% (increased to 82.57 82.57 MPa) and 41% (increased to 3.89 GPa). They attributed this enhancement to effective CNTs dispersion in the epoxy matrix, as well as strong interfacial interaction between PAS and the epoxy [9].

Paiva et al. carried out functionalization of CNTs with low molecular weight polyvinyl alcohol (PVA) by the N,N'-dicyclohexyl carbodiimide-activated esterification reaction to use them as reinforcement in PVA matrix nanocomposites. The functionalized CNTs were added to a PVA solution, briefly sonicated and then stirred overnight. Nanocomposites containing pristine and functionalized CNTs were produced using wet-casting. On conducting tensile tests, they found that the incorporation of SWCNTs in the PVA matrix resulted in an increase in Young's modulus for all the composite systems. The tensile strength increased for the composites with functionalized SWCNTs, but decreased for the composites with pristine SWCNTs, compared with the pure PVA. They carried out a SEM investigation which indicated good wetting of the nanotubes by the PVA matrix. They concluded that the functionalization resulted in good dispersion and better interfacial bonding, which consequently improved the mechanical properties of the composites [10].

Yang et al. opted a covalent functionalization method by grafting triethylenetetramine (TETA) onto the surface of the MWCNTs. However, for the functionalization to take place, prior acid modification was carried out to generate Carboxylic groups on the surface of the MWCNTs. The acid treatment method employed a 3:1 (v/v) mixture of concentrated H_2SO_4/HNO_3. After addition of MWCNTs to the mixture, it was sonicated at $40\,°\mathrm{C}$ for $10\,\mathrm{h}$. After acid treatment, MWCNTs were washed using deionized water, filtered until the pH value reached 7 and then dried at $80\,°\mathrm{C}$ for $24\,\mathrm{h}$. After adding these modified MWCNTs into a $SOCl_2$ solution, the mixture was stirred at $70\,°\mathrm{C}$ for $24\,\mathrm{h}$ by using a magnetic bar. Then, obtained MWCNT-COCl was further reacted with TETA at $120\,°\mathrm{C}$ under magnetic stirring for $96\,\mathrm{h}$. The final product was the functionalized TETA-MWCNTs. The impact strength, bending strength and bending modulus of 0.6 wt% content TETA-MWCNT/epoxy composite was found to be $20.83\,\mathrm{kJ\,m^{-2}}$, $110.67\,\mathrm{MPa}$ and $2.7\,\mathrm{GPa}$, respectively. Therefore, the three performance indices increased by 84%, 29% and 22%, respectively, compared with those of the pure epoxy matrix.

Recently an environmentally and industrial scaleable functionalization method was developed by Suri et al. The group showcased via Raman Spectroscopy that no changes in the functionalized SWCNTs had occurred when compared to the pristine ones. The group produced epoxy-composites that showed a 36% increase in K_IC [1].

The present paper will utilize the aforementioned functionalization method by Suri et al. for MWCNTs. A different epoxy resin will be used as matrix and shear mixing will be utilized as the dispersion method in order to minimize damage to the MWCNTs. The effectiveness of this functionalization method will be studied by characterization of the MWCNTs and the composites produced. The primary objective is to propose a safe and simple production method for MWCNT-composites.

2. Materials and Methods

The epoxy resin used in this project is the PRO-SET INF-114, cured with hardener INF-213 in the ratio 3.65:1 by weight. MWCNTs provided by Cheap Tubes Inc. Cambrideport, VT 05141 USA were produced by Combustion chemical vapor deposition. The functionalization involved mixing of the CNTs in a solution of extra pure NaOH provided by Acros Organics and 96 $\%$ ethanol provided by VWR CHEMICALS.

2.1 Composites production

MWCNTs were submerged in a solution of NaOH and 97% ethanol at room temperature and magnetically stirred for $24\,\mathrm{h}$. The CNTs, NaOH and ethanol were mixed in the ratio $0.5\,\mathrm{g}$: $12.5\,\mathrm{g}$: $1\,\mathrm{L}$, respectively. They were then washed using ethanol and vacuum filtered using PTFE membrane filter of pore size 0.22 micron. As a last step, for evaporation of the remaining ethanol, the obtained MWCNTs were left to air dry before making the composites.

When air dried, composites of 0.4 wt% and 0.8 wt% MWCNTs were made. The MWCNTs were dispersed in the epoxy resin by shear mixing using a Silverson L5M shear mixer for $30\,\mathrm{min}$ at 25 RPM. The hardener was manually mixed in the solution using an aluminium rod and the final solution was then poured in a dogbone mould and left to cure.

2.2 Characterization

TGA analysis was performed on both pristine and functionalized MWCNTs in TA SDT650 and analysed using TRIOS software. The measurements was done in oxygen atmosphere from $0\,°\mathrm{C}$ to $1000\,°\mathrm{C}$ at a rate of $10\,°\mathrm{C\,min^{-1}}$.

DSC measurements were performed for neat epoxy and the composites. All measurements were carried out using TA Q2000 DSC with a heating from 35°C to 300°C and a heating rate of 10°C per min.

For analysing the carbon structures of the pristine and functionalized MWCNTs, Raman Spectroscopy was carried out. It was done using a Renishaw InVia 2013 model with a $532nm$ green laser with a power of $25mW$ in the range $100 - 3200\ cm^{-1}$.

FTIR was applied to the neat epoxy for further identification and investigation of the sample's functional groups and molecular structure. All the measurements were done on a Brukes Lumos.

Tensile test was performed on neat epoxy and the different composites using an Instron 5568 with a load speed of $5\ mm * min^{-1}$ and initial gauge length of $60\ mm$. The tensile testing was carried out for evaluation and comparison of different obtained mechanical properties.

SEM was carried out for investigation of purity of the MWCNTs and fractography of the composites. This was done using A Zeiss 1540 X at different magnifications.

3. Results

3.1 Raman Spectroscopy

The samples were left to air dry for at least 24 hours prior to investigation in Raman spectroscope.

The spectra obtained for pristine and functionalized MWCNTs can be seen in Figures 1 and 2.

Raman spectroscopy was utilized to investigate the purity, disorder and the effect of the functionalization.

In both spectra a variety of different peaks were seen other than the expected D, G and 2D bands indicating the presence of impurities and other carbon species [11] [12] [13] [14].

Utilizing the I_D/I_G ratio as an measurement for disorder, a slightly larger ratio could be observed for the functionalized samples [15]. However, no significant difference could be attributed to the functionalization based on the Raman spectroscopy similar to Suri et al. [1].

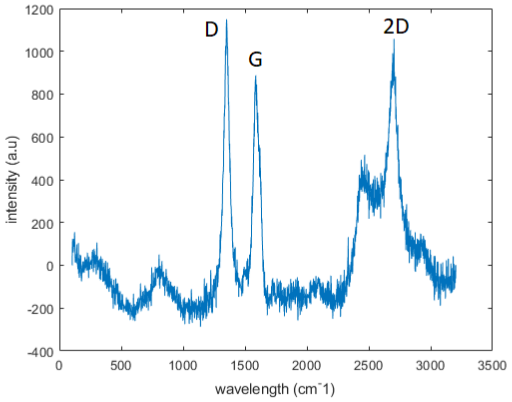

Fig. 1 Respective Raman spectrum for pristine CNTs

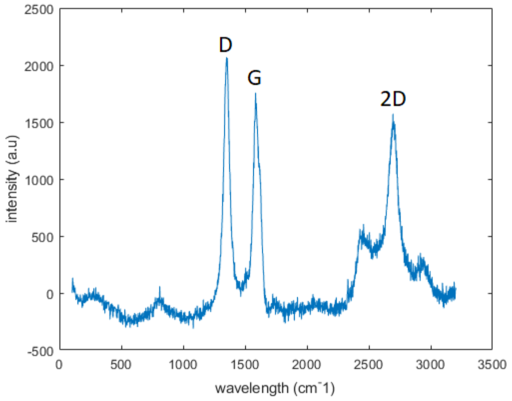

Fig. 2 Functionalized CNTs

3.2 Thermogravimetric Analysis

TGA was performed for both pristine and functionalized MWCNTs. The objective was to investigate the purity of the CNTs [16]. The obtained graphs can be seen in Figures 3 and 4. Comparing with literature an onset temperature of 700 °C is expected for MWCNTs [17]. Yet for pristine a lower average value of 596 °C is observed, indicating impurities present in the sample. In addition, the average onset temperature for functionalized MWCNTs was found to be 477 °C. This implies that functionalization reduces the thermal stability of the MWCNTs. Around 11 % residual mass was found for functionalized samples, while an insignificant residual mass was found for the pristine samples. The residual mass is assumed to be NaOH left over from the functionalization process.

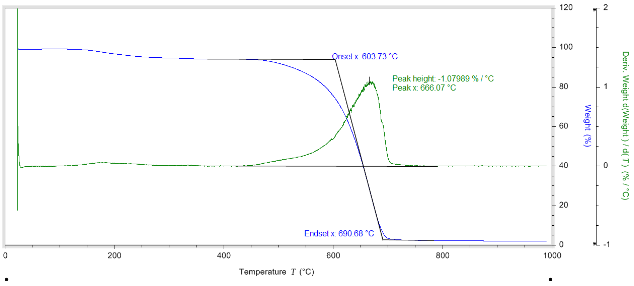

Fig. 3 TGA of pristine MWNTs shows an onset onset temperature of 603 °C and primary oxidation temperature of 666 °C

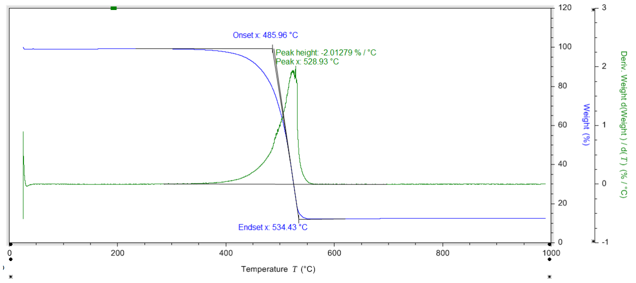

Fig. 4 TGA of functionalized MWNTs shows an onset temperature of 485 °C and primary oxidation temperature of 528 °C

3.3 Scanning Electron Microscopy

3.3.1 Purity analysis

The SEM images for pristine and functionalized samples can be seen in Figures 5 and 6, respectively. It can be seen for both samples that the MWCNTs are agglomerated into bundles, it was not possible to identify any visual difference due to the functionalization. Nonetheless, for the pristine samples it was possible to observe soot-like particles as seen in Figure 7. Thus indicating the presence of impurities as given by the TGA graphs and the Raman spectrum.

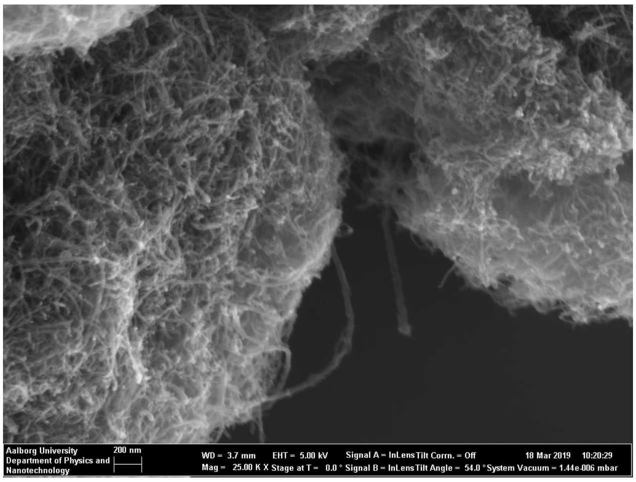

Fig. 5 SEM image of pristine MWCNTs at 25K magnification

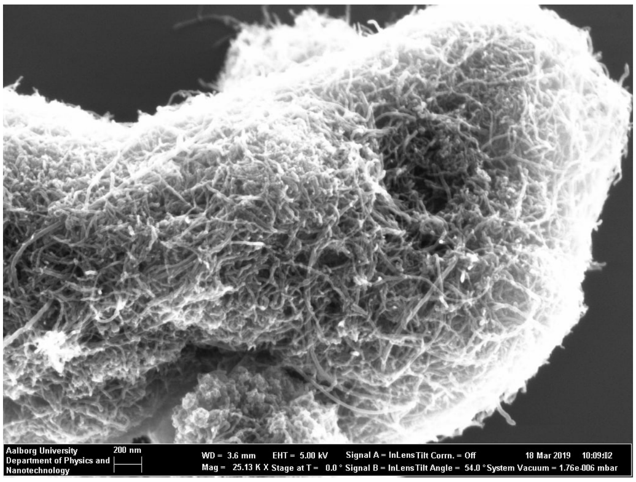

Fig. 6 SEM image of functionalized MWCNTs at 25,13 K magnification

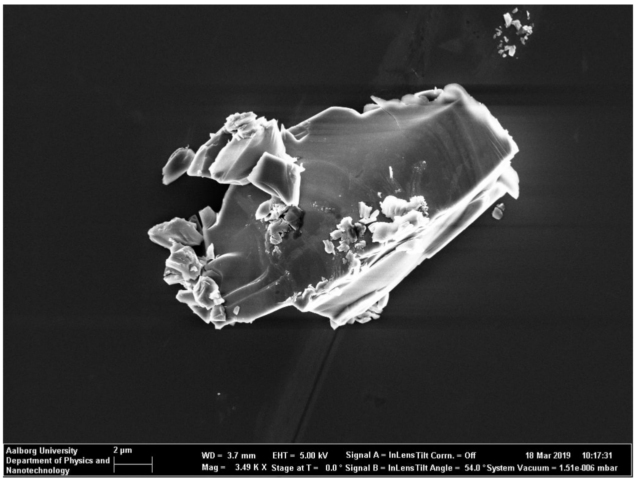

Fig. 7 Soot seen in sample at 3.49K magnification

3.3.2 Fractography

Fractography was done on samples that underwent cryofracture. By immersing neat epoxy samples and composites with 0.4 wt% MWCNTs, both pristine and functionalized, in liquid nitrogen, a cryogenically fracture could be carried out.

By examination of the SEM images of the three samples, as seen in Figures 8, 9 and 11, a contrast between the fractured surface of the neat epoxy and composites can be noticed. The fracture surface of the neat epoxy displays a smaller amount of cracks compared to those of the composites with pristine and functionalized MWCNTs. The cracks seem to have deflected as they get closer to these MWCNT agglomerates. According to Alamand Yunus [2016], this is a toughening effect [18]. Smaller cracks can be seen originating from these agglomerates which is an indication of agglomerates acting as stress concentrations. The MWCNTs that are a part of the agglomerates are closer together for the pristine compared with the functionalized ones.

In Figures 10 and 12 it is evident that the contrast between the nanotubes and the surrounding matrix materials differ for the two composites. The pristine MWCNTs composites show a higher contrast, indicating a higher degree of fiber pull out and hence a weaker interfacial bonding than for the functionalized [19].

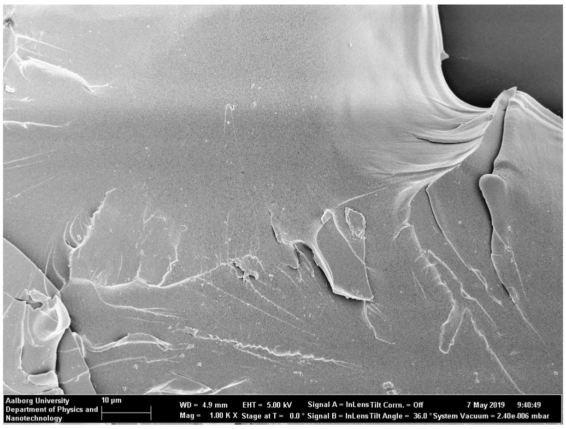

Fig. 8 SEM image of neat epoxy surface

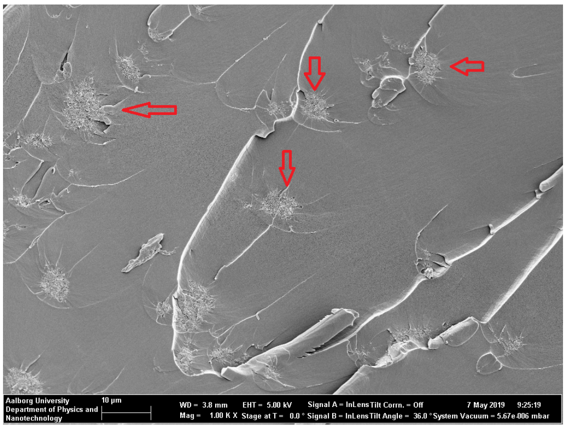

Fig. 9 SEM image of composite with 0.8 wt% raw CNTs

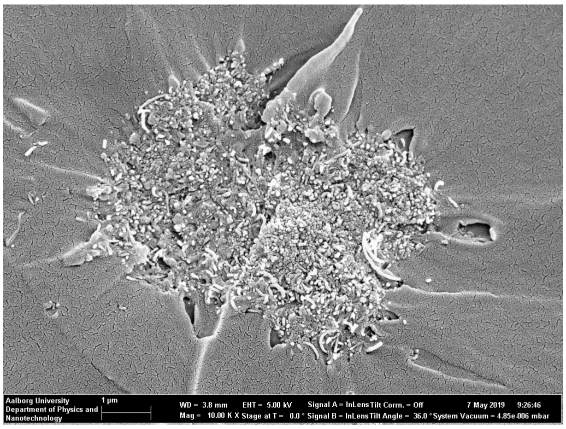

Fig. 10 SEM image of composite with 0.8 wt% raw CNTs zoomed in on CNT bundle

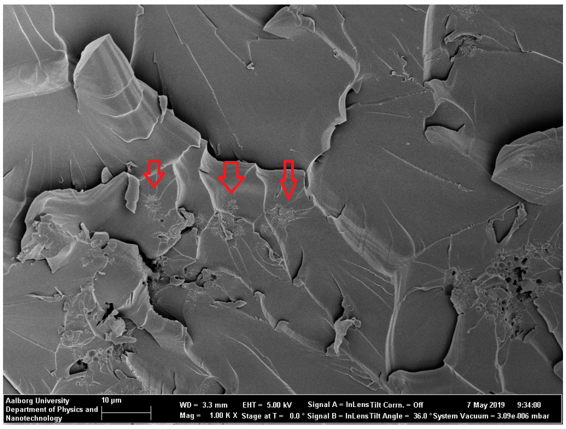

Fig. 11 SEM image of composite with 0.8 wt% functionalized CNTs

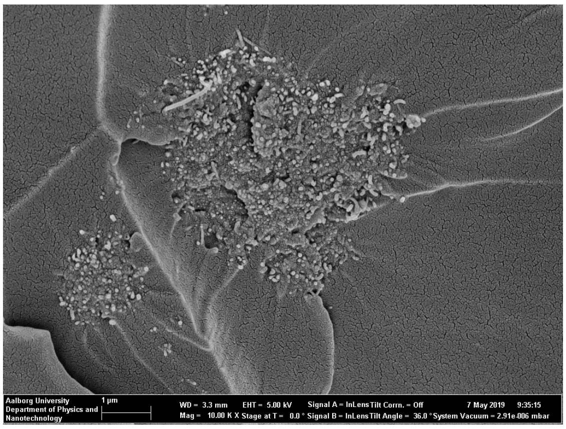

Fig. 12 SEM image of composite with 0.8 wt% functionalized CNTs zoomed in on CNTs bundles

3.4 Fourier-transform Infrared Spectroscopy

The cured Epoxy resin was analyzed by FTIR. Utilizing the database in OPUS and tables from [20], it was found to be a bisphenol A type epoxy. The chemical structure can be seen in Figure 13.

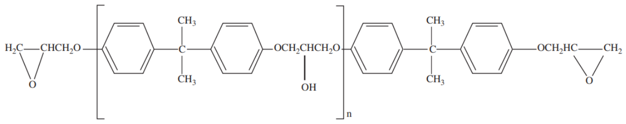

Fig. 13 Schematic of bisphenol A diglycidyl ethers [21]

3.5 Differential Scanning Calorimetry

The DSC curves obtained for the samples can be seen in Figure 14. The largest difference in Glass transition temperature (T_g) is for neat epoxy with 67.72 °C and Composites of 0.8 wt% functionalized MWCNTs with a T_g of 72.02 °C. This is in agreement with literature [22] [23].

The endothermic peaks observed in the curve after the Glass transition can be explained by structural relaxation of the epoxy [24] [25] [26].

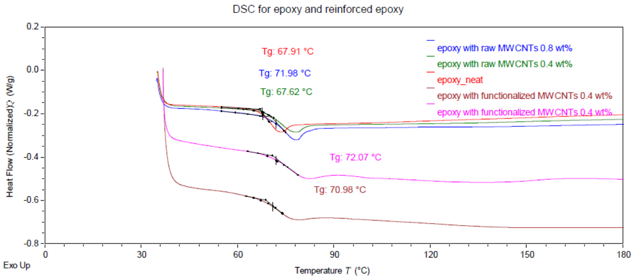

Fig. 14 Curves of DSC of neat epoxy and with MWCNT reinforcements

3.6 Tensile test

UTS and Young's modulus of the neat epoxy and composites were determined from their stress strain plots. It was seen that composites with pristine MWCNTs had superior mechanical properties as compared to the composites with functionalized MWCNTs and neat epoxy.

The composites with 0.8 wt.% of functionalized MWCNTs were the only composites which showed lower ultimate tensile strength than that of the neat epoxy. The composites reinforced with, 0.4 wt.% pristine MWCNTs had a 31% increase in its UTS, composites with 0.8 wt.% pristine MWCNTs had a 12% increase and composites with 0.4 wt.% functionalized MWCNTs had a 10% increase, when compared to neat epoxy. The values of UTS of the samples can be seen in Figure 15. It can be observed that the use of functionalized MWCNTs as reinforcement lowered the composites' strength when compared to the composites with pristine MWCNTs.

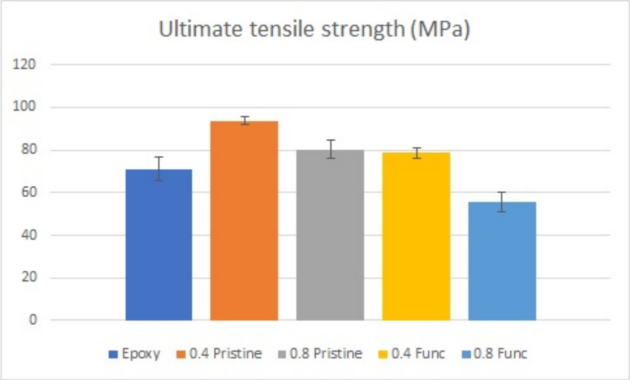

Fig. 15 Ultimate tensile strength data shown for neat epoxy and composites

The Young's modulus of all composites was higher than that of neat epoxy. The composites reinforced with 0.4 wt.% pristine MWCNTs had the highest increase of 45%. Composites with 0.4 wt.% of functionalized MWCNTs showed an increase of 20%. The composites with 0.8 wt.% of pristine MWCNTs had an increase of 21% while those with 0.8 wt.% of functionalized MWCNTs had an increase of 23%. Figure 16 shows the values of Young's modulus for neat epoxy and composites. It can be seen that the 0.4 wt.% pristine MWCNTs reinforced composites have a considerably higher Young's modulus than the other tested samples.

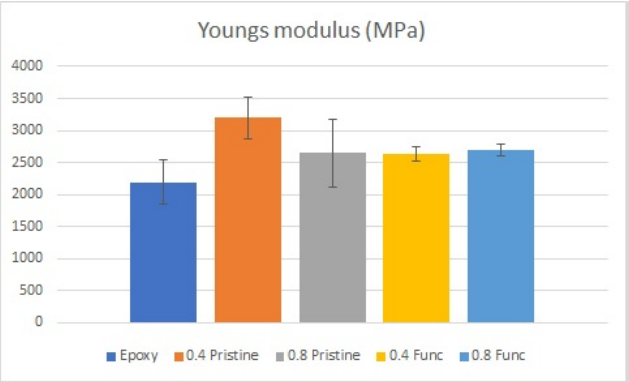

Fig. 16 Young's modulus data shown for neat epoxy and composites

Tensile test was carried out on composites which contained less dispersed and re-agglomerated MWCNTs. The re-agglomeration took place since the mixture of MWCNTs and epoxy resin was left unused. Thus, composites produced from this mixture showed larger agglomerates due to re-agglomeration. The stress-strain curves of these composites are shown in figure 17.

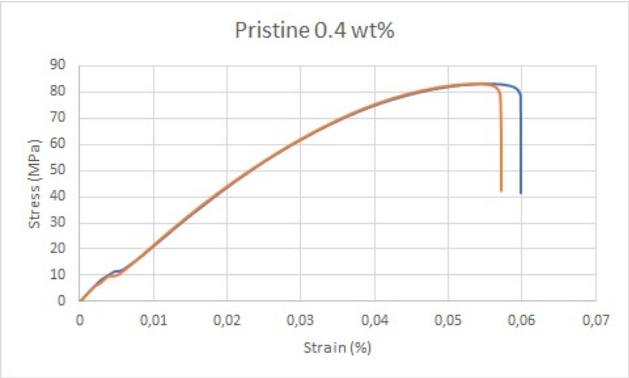

Fig. 17 Stress-strain curves of the re-agglomerated composites

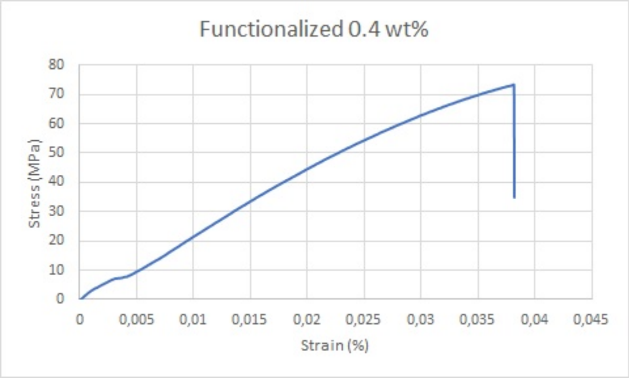

Fig. 18 Stress-strain curve of the composite with 0.4 wt.% functionalized MWCNTs

An interesting observation was made regarding the stress-strain curves of these composites. The stress-strain curves shows two different slopes divided by a small horizontal line. The first slope corresponds to a Young's modulus similar to that of the composites with 0.4 wt.% of pristine MWCNTs while the second slope to that of neat epoxy. The stress-strain curves of the composites reinforced with well dispersed functionalized MWCNTs are similar to those of these re-agglomerated composites. This similarity can be seen by comparing Figures 17 and 18 This implies a slippage of the functionalized MWCNTs. It was rationalized that a likely cause would be either a weak interfacial bonding, or as described by literature, breaking of MWCNTs in a sword-in-sheath manner [2].

4. Conclusion

The objective of this paper was to propose a simple and safe production method of MWCNTs-composites by using the foundation laid by Suri et al. [1].

In order to gain insight into the disorder, purity and quality of the MWCNTs used and the effect the functionalization had on these parameters, Raman, TGA and SEM analysis was used.

Raman spectroscopy showed no significant changes in the spectrum after functionalization, yet a slightly higher disorder was indicated by the spectrum of the functionalized MWCNTS, implying some damage to the structure. The spectrum showed the presence of impurities in the form of other carbon species.

TGA was performed on the pristine and functionalized MWCNTs. A low onset temperature of the pristine MWCNTs verified the presence of impurities indicated by the Raman analysis. Furthermore, it was found that modification of the MWCNTs decreased their onset temperature and as a result, their thermal stability.

SEM images showed the presence of soot-like particles in the pristine samples, whilst not in the functionalized samples indicating the filtration process was successful. Yet no visual difference could be seen between the pristine and functionalized MWCNTs.

Thus, based on the aforementioned analysis methods, it can be said that the MWCNTs used in this project were of low quality. The lack of soot observed indicates that the increase in disorder along with the decrease in onset temperature is a result of the functionalization process having a degrading effect on the MWCNTs.

The epoxy resin was found to be a bisphenol A epoxy type by FTIR.

DSC showed no significant changes in the glass transistion temperature of the composites across loading and composition. Endothermic peaks were observed which was deemed to be due to structural relaxation.

The tensile test showed that the composites with MWCNTs have better mechanical properties than neat epoxy. However, it was found that the functionalized MWCNTs did not prove to be acceptable reinforcements. The composites reinforced with functionalized MWCNTs showed lower values of ultimate tensile strength than those reinforced with pristine MWCNTs. The Young's modulus of the composites reinforced with functionalized MWCNTs showed lower values as well. 0.4 wt.% was observed to be a decent loading of MWCNTs since composites reinforced with 0.4 wt. % of pristine MWCNTs showed the highest values of ultimate tensile strength and Young's modulus. An interesting similarity was observed in the stress-strain behaviour of the composites with functionalized MWCNTs and those with re-agglomerated MWCNTs.

Fractography of cryofractured samples showed that for both composites, MWCNT agglomerates acted as regions of stress concentration as cracks initiated from these. Due to less dispersion observed in the pristine samples, a larger stress concentration would be expected. For the individual agglomerates, the functionalized MWCNTs didn't possess as much fiber pull out as the pristine, indicating better interfacial bonding.

To summarise, it can be proposed that functionalization of the MWCNTs caused them to disperse better in the composite matrix. On the other hand, it also lead to degraded mechanical properties of the composites which could be attributed to restricted load transfer between the matrix and reinforcement. While the proposed production method is safe and simple one, further research is needed to make the this method a competent means of production.

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