Surface Activation of Carbon Nanotubes Generating a Chemical Interaction in Epoxy Nanocomposite

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***Abstract*—**Carbon nanotubes (CNTs) are known for having high elastic properties with high surface area that promote them as good candidates for reinforcing polymeric matrices. In composite materials, CNTs lack chemical bonding with the surrounding matrix which decreases the possibility of better stress transfer between the components. In this work, a chemical treatment for activating the surface of the multi-wall carbon nanotubes (MWCNT) was applied and the effect of this functionalization on the elastic properties of the epoxy nanocomposites was studied. Functional amino-groups were added to the surface of the CNTs and it was evaluated to be about 34% of the total weight of the CNTs. Elastic modulus was found to increase by about 40% of the neat epoxy resin at CNTs' weight fraction of 0.5%. The elastic modulus was found to decrease after reaching a certain concentration of CNTs which was found to be 1% wt. The scanning electron microscopic pictures showed the effect of the CNTs on the crack propagation through the sample by forming stress concentrated spots at the nanocomposite samples.

***Keywords*—**Carbon nanotubes functionalization, crack propagation, elastic modulus, epoxy nanocomposites.

I. Introduction

THE extraordinary physical and mechanical properties and high specific surface area (SSA) of carbon nanotubes (CNTs) have encouraged scientists to incorporate them as reinforcements in composite structures looking for super new materials [1], [2]. Carbon nanotubes (CNTs) are considered as a macromolecular form of carbon with unique properties and a high potential for practical applications [3]. CNTs consist of only carbon in hexagonal shapes that can be considered theoretically as graphene sheets rolled into seamless cylinders [4]. Although the higher specific surface area of CNTs leads to higher area of interface for stress transfer, it induces strong attractive forces between CNTs causing agglomeration. Single wall carbon nanotubes (SWCNTs) have larger SSA than multi-wall carbon nanotubes (MWCNTs) which have much larger diameter and several concentric walls. Therefore, MWCNTs demonstrate better dispersibility and smaller interface for stress transfer [5]. However, the stress transfer between concentric walls is transferred by relatively weak van der Waals forces and hence they are less efficient concerning the mechanical properties [5]. Stirring and sonication have been reported as effective and widely used method for dispersing nanotubes in resins [6], [7]. The pulsed ultrasound used in sonication technique separates the agglomerated CNTs and disperse them in the matrix.

Another challenge is getting sufficient interfacial bonding between CNTs and polymer matrix which directly influence the mechanical properties of nanocomposites. Previous researches showed that this interfacial bonding can be improved by functionalizing the CNT-surface by grafting chemical groups (e.g., amino- or glycidyl-) to enable covalent bonding between nanotubes and epoxy in order to enhance the interfacial stress transfer. The effect of functionalization process on mechanical properties has been examined theoretically [8] and experimentally [9]-[11] in previous work. Therefore, due to the smoothness of the CNTs surface and the lack of functional positions on that surface, activating the CNTs became one of the important topics in recent research. Activating the surface of the CNT targets their existing defects, end caps, and sidewalls, as well as the hollow interior [1]. The functionalization of single walled carbon nanotubes (SWNT) was performed using non-covalent strategies [12], [13] as well as covalent strategies [1], [3], [14], [15]. Functionalization of the CNT through amidation and esterification of the nanotube-bound carboxylic acids found some applications in the literature [16].

One of the most common resins used to manufacture nanocomposites is epoxy due to its good chemical and corrosion resistance, good adhesion and dimensional stability [5]. In addition, it has relatively high mechanical properties compared to other thermosetting resins. These advantages elect epoxy to be a good candidate as a matrix for many composite and nanocomposite materials in various applications [17].

Wang *et al.* grafted a curing agent on the surface of nanotube achieving 25% improvement in elastic modulus with 0.5 wt% of functionalized carbon nanotube [18]. Yang *et al.* used bisphenol-A glycidol ether epoxy resin/2-ethyl-4-methylimidazole to functionalize MWCNTs. The experiments showed that the chemical functionalization decreased the crystalline content of MWCNTs without disrupting their structure. Also, the impact strength, bending strength and thermal conductivity of nanocomposites were improved [19].

This work tries to address the low dispersion problem of pristine CNTs and the lack of covalent bonding between the CNTs and the matrix. Therefore, MWCNTs are activated with carboxylic groups and functionalized with amino-groups that

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interact with the crosslinking agent during curing the epoxy resin. The functionalized CNTs are introduced to the epoxy matrix at different concentrations and their effects on the mechanical properties of the produced nanocomposite are tested. Scanning electron microscopy (SEM) is used to investigate the surface topology to explore how cracks distribute in sample's cross section.

II. Procedures

A. Materials

MWCNT was purchased from Shenzhen Nanotech. Port Co., China. The MWCNTs have a diameter range of 40-60 nm, a length range of 5–15 μm, and purity higher than 95%. The ash content is less than or equal to 0.2% wt, the amorphous carbon is less than 3% wt and the specific surface area range is 40 - 300 m^2/g.

Diglycidyl ether of bisphenol A (DGEBA), known commercially as EPON 828, was used as epoxy resin and was purchased from Miller-Stephenson. Glycolitic polypropyleneoxide triamine (Jeffamine T-403) was used as the curing agent. The curing agent was purchased from Hunsman Co. and has a molecular weight of 440 g/mol.

B. Sample Preparation

Carboxylic groups were grafted to the MWCNT surfaces following the acidification scheme shown in Fig. 1. The acidification reaction was performed by dispersing 5 g of MWNTs in 480 ml of sulfuric acid and 160 ml of nitric acid. The mixture was stirred for about 30 minutes with magnetic stirrer after which it was tip sonicated for one hour at 200 watt. The sonication process worked in four intervals of 15 minutes each, stirring with a glass rod between these intervals was performed to check the consistency of the mixture. The mixture was stirred for 2.5 hours after sonication to have 4 hours of total acidification time.

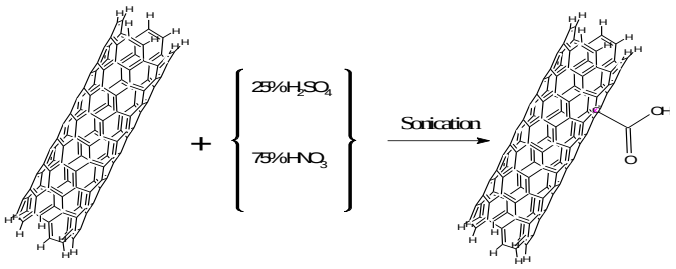


Fig. 1 Schematic representation for the acidification reaction of pristine CNT

After this acidification, the mixture was decanted in a big flask with 3 L of distilled water to dilute the mixture. After cooling down, the mixture was centrifuged using International Equipment Company (IEC) instrument at 5000 rpm for 7 min. After completing the centrifugation, a 50 ml of hydrochloric acid was added to the purified CNTs to allow more oxidization and acylation of the carboxylic acid groups on the surface of the carbon nanotubes. The mixture was stirred for 15 minutes then the mixture was diluted with water and prepared for another cycle of centrifuging for 7 minutes at the same 5000 rpm speed.

Amidification of the MWNT-COOH was carried out, as shown in Fig. 2, by placing the modified nanotubes in thionyl chloride ($SOCl_2$) for 24 h at 70℃ with continuous stirring to convert the carboxylic acid surface groups into acyl chloride groups. The mixture was left to cool down to room temperature, after which a separation process of the excess $SOCl_2$ was performed by centrifuging for 7 minutes. The precipitated solid MWNT was washed with anhydrous tetrahydrofuran (THF). Jeffamine was added to the resultant solid and the mixture was stirred at 90℃ under a nitrogen atmosphere for 72 h and the excess T-403 was washed with ethanol as eluent. The mixture was centrifuged again to remove the excess liquid. The precipitated solid was dissolved in chloroform for 5 minutes under mild sonication and left for 72 h allowing the nanotubes without enough functionality to precipitate and the dispersed ones to stay mixed in the upper solution which was taken and dried to be used in producing the nanocomposite.

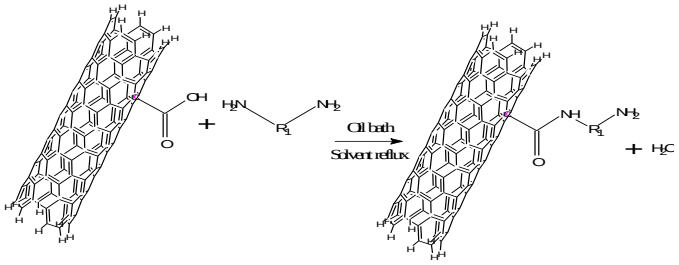


Fig. 2 Amidification reaction between the carboxylic group and Jeffamine T-403

Nanocomposites were manufactured by distributing functionalized and non-functionalized carbon nanotubes within a host polymer. Based on the target weight fraction, an amount of functionalized nanotubes was weighed taking into account that the required percentage should be from pure nanotubes. The amount was dispersed in a proportional amount of Jeffamine T-403 by continuous stirring for 15 minutes after which the appropriate amount of Epon 828 was added and stirred for another 15 minutes. The mixture was casted in a Teflon mold which was placed in an oven to cure at 85℃ for 2 h then at 125℃ for 3 h. Four weight fractions were used to manufacture the nanocomposite samples (0.5, 1, 1.5 and 2 wt. %). In addition, neat epoxy samples were prepared and tested as a reference. The samples were prepared by mixing Epon 828 and Jeffamine T-403 with 100:42 weight ratio and following the same procedure mentioned above.

III. Characterization

A. Thermal Gravimetric Analysis (TGA)

Pristine and activated CNTs samples were tested on Thermo Gravimetric Analyzer (TGA) Q500 manufactured by TA Instruments. The analyzer has a high-precision balance with a pan to carry the sample. The pan is placed in an electrically heated oven equipped with thermocouples to accurately

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measure the temperature. The analysis is conducted by gradually raising the temperature from room temperature up to 1000℃ in a rate of 10℃/min, under purging of nitrogen gas at 60 ml/min.

B. Tensile Testing

Tensile testing was carried out following ASTM D 5026. Samples were cut into coupons with 90 mm length and 10 mm width. Sample dimensions were measured at five different locations and averaged. Edges in the length direction were polished to eliminate the effect of micro-cracks typically resulting from cutting. Three samples were tested for each data point. Tensile tests were carried out on a computerized Instron tester (Instron 5565 universal testing machine) equipped with a video extensometer (AVE with 60mm FOV lens). Before conducting the tensile test, four dots were marked on each sample to allow measuring the longitudinal and lateral strains using the video extensometer. The machine cross-head speed was set at 2.5 mm/min and the gage length was 50.73 mm following the ASTM standard. The structural dimensions for each sample (gage length, average width and average thickness) were input into the machine and the stress strain curve was obtained for each sample.

C. Surface Morphology

Scanning electron microscopy (SEM) was used to observe the surface morphology of selected samples using a TESCAN VEGA TS 5130 scanning electron microscope (TESCAN s.r.o., Czech Republic). The samples were placed on a holder that allows the study of their cross section, then sputter-coated with gold using SCD 030 auto sputter coating device (Balzers Union FL 9496 Balzers).

IV. Results and Discussion

A. Functionalization of the CNTs

The procedure for activating the surface of the carbon nanotubes in this study depends on targeting the MWNT defects, end caps, and sidewalls and causing more of these defects during the sonication. Exposing the nanotubes to the strong acid mixture for a long time (4 hours in total) with sonication allows the acids to oxidize the defects and to purify the mixture from the amorphous carbon, the residues of the catalysts, and the soot that exist in the pristine CNTs. This process leads to a functionalized surface with attached carbonyl groups.

After activating the surface of the CNTs with carbonyl groups the CNTs got better dispersion in the solution with the evidence of the color change that gets the solution into dark black color. To collect the CNTs from the solution, it is required to centrifuge the mixture where the centrifugal forces allow splitting the mixture in two phases with the solid CNTs at the bottom and the liquid acid filling the rest of the volume. The collected CNTs were washed with distilled water to decrease their acidity. After their washing with water, the CNTs mixture is centrifuged and the pH of the solution was noticed to increase after each cycle of washing and centrifuging implying the removal of the acid. The CNTs went through five cycles of washing and centrifuging and the pH of the mixture increased from 0.83 at the beginning to about 3.83 after these 5 washing cycles. With the increase in the mixture's pH the CNTs were found to be harder for separation with centrifuging which implies a change in the surface nature of the CNTs after the acidification process. The obtained mixture of CNTs dispersed in water was placed in the oven at 120℃ for about 12 hours to evaporate the liquid and to have dry functionalized carbon nanotubes suitable for further processing.

After processing the obtained CNTs according to the amidification procedure described in the procedures section, the samples were tested for their activation yield using the TGA. Samples of the pristine CNTs and of the CNTs that were functionalized with Jeffamine T-403 were tested.

As Fig. 3 shows, the weight loss of the pristine CNTs sample did not significantly change until about 700℃ whereas the weight of the functionalized sample started to decrease at a temperature of around 180℃ and continued to decrease until it reached about 65% of its original weight. By comparing the two curves, the change in the behavior of the functionalized sample can be attributed to the loss of the functional groups that were added during the processing of the CNTs. The amount of the functional groups can be estimated by about 34% of the total weight of the nanotube.

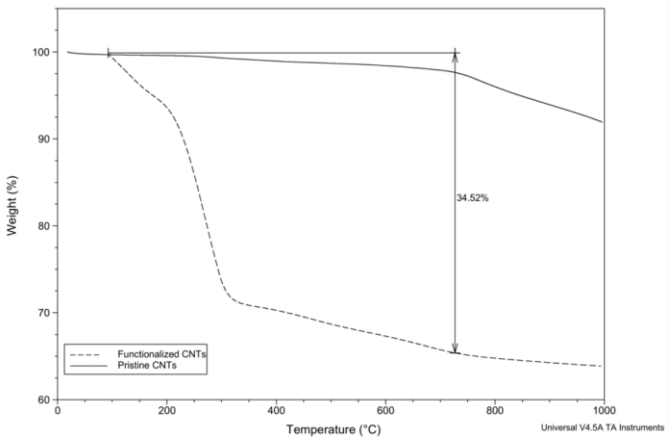


Fig. 3 TGA test results for pristine CNT and CNTs functionalized with Jeffamine T-403

B. Epoxy Nanocomposites

Samples of functionalized CNTs showed good dispersion in the epoxy matrix that was inspected visually by a monotone dark color of the sample, whereas some samples of pristine CNTs showed inhomogeneous distribution with agglomeration of the filler at different spots of the sample. Preparation of the pristine CNTs samples required more stirring and mixing to enhance their distribution in the epoxy matrix which is judged by the homogeneity of the sample color. The good dispersiblity of the functionalized CNTs in the epoxy matrix can be attributed to the polarity of the matrix [9] that has compatibility with the functionalized CNTs more than the pristine CNTs.

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The produced samples were tested for their mechanical properties using the tensile tester where the tensile modulus was calculated as the slope of the stress/strain curve in the elastic region. Fig. 4 shows the value of the elastic modulus (E) for the epoxy nanocomposites with different concentrations of the functionalized CNTs. Error bars represent the standard deviation of the results within each weight fraction. The measured modulus for the neat epoxy (0% CNTs) was about 2.7 ± 0.14 GPa which is in a close agreement with the reported values of 2.6 GPa [5]. The general trend for the elastic modulus tends to increase with the addition of the CNTs although it increases to a certain limit then starts to decrease. The maximum value of the modulus as measured for the produced samples was found at weight fraction (φ) = 0.5% of the functionalized CNTs. The elastic modulus reached a value of 3.8±0.8 GPa at this concentration which represents an increase of about 40% of the modulus of the neat epoxy. The measured elastic modulus for the nanocomposites with φ=1% is also higher than the measured value for the neat epoxy and relatively lower than the measured value at 0.5%. These results are in agreement with some published experimental findings that report an increase of the modulus until 0.5% [18] or 1% [20] weight fractions, although the papers that reported a decrease after 1% did not apply concentrations below this value. It is noticeable that the deviation of the readings at φ=1% is lower than that at φ=0.5% which allows us to conclude that the decrease of the elastic modulus of the nanocomposite generally starts after reaching a CNTs concentration beyond 1%.

As the weight fraction increases beyond the 1% wt, the tensile modulus decreased to reach a value that is almost equal to the measured modulus of the neat epoxy at CNTs concentration of 2%. Gojny et al. [5] explained this behavior by the attractive forces that increase with increasing the concentration of the CNTs and result in agglomeration of the CNTs which reduces the homogeneity of their distribution in the epoxy matrix.

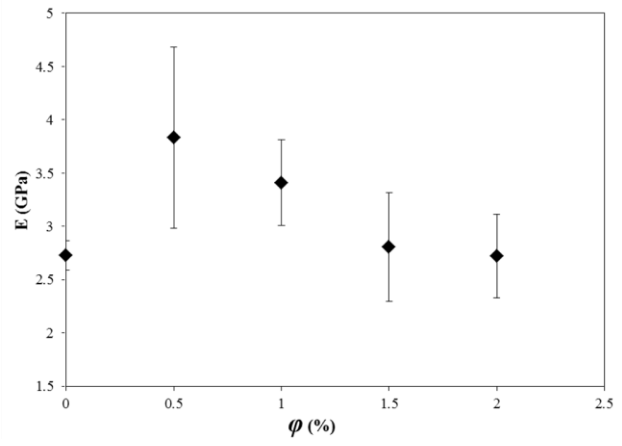


Fig. 4 Tensile modulus (E) of epoxy nanocomposites with different weight fractions (φ) of CNTs

The Poisson's ratio (ν) of the tested samples was evaluated according to the extension in the axial and the transverse directions as recorded by the video extensometer. The change of Poisson's ratio as a function of the CNTs weight fraction is shown in Fig. 5. It can be noticed from this figure that there is no specific trend for the relation between the Poisson's ratio and the concentration of the CNTs. There is also no significant change in the values and the ambient increase at high weight fractions cannot be considered significant because of the large deviation in the results of these samples.

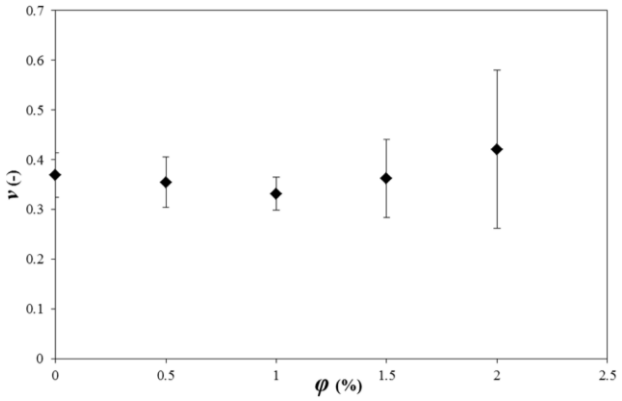


Fig. 5 Poisson's ratio (ν) of epoxy nanocomposites with different weight fractions (φ) of CNTs

The cross-sections of the broken samples (after their tensile test) were examined under the scanning electron microscope (SEM). It can be seen in the SEM photographs shown in Fig. 6 that the crack propagates through the nanocomposite (Figs. 6 (a) and (b)) samples in a different manner than the neat epoxy (Figs. 6 (c) and (d)). There are notches that can be observed frequently in the nanocomposite sample as circled in Fig. 6 (a) and they are clearer when bigger magnification is applied as shown in Fig. 6 (b). These crack notches may be attributed to the existence of the nanotubes at these positions where the stress distribution changes and higher stress concentration lead to the behavior observed in Fig. 6 (b). The neat epoxy samples, on the other hand, did not show such position for change in stress distribution as can be seen in Fig. 6 (c) or at higher magnification shown in Fig. 6 (d).

V. Conclusion

Carbon nanotubes can be functionalized under strong acid conditions with the aid of sonication that helps creating more positions on the surface that are ready for oxidation. The amidification of the activated CNTs was possible with about 34% loading of functional groups. The introduction of the polar groups to the surface of the CNTs allows better dispersion in the polar epoxy matrix which affected the mechanical properties of the produced epoxy nanocomposite samples. The elastic modulus of the nanocomposites was found to increase with about 40% of the neat epoxy modulus at a CNTs concentration of 0.5%. The modulus tends to decrease by increasing the concentration of the CNTs which might be attributed to their agglomeration at higher concentrations. The impact of the CNTs existence in the nanocomposite was observed by the SEM pictures where

notches were observed in the crack paths, revealing stress concentration spots around the CNTs.

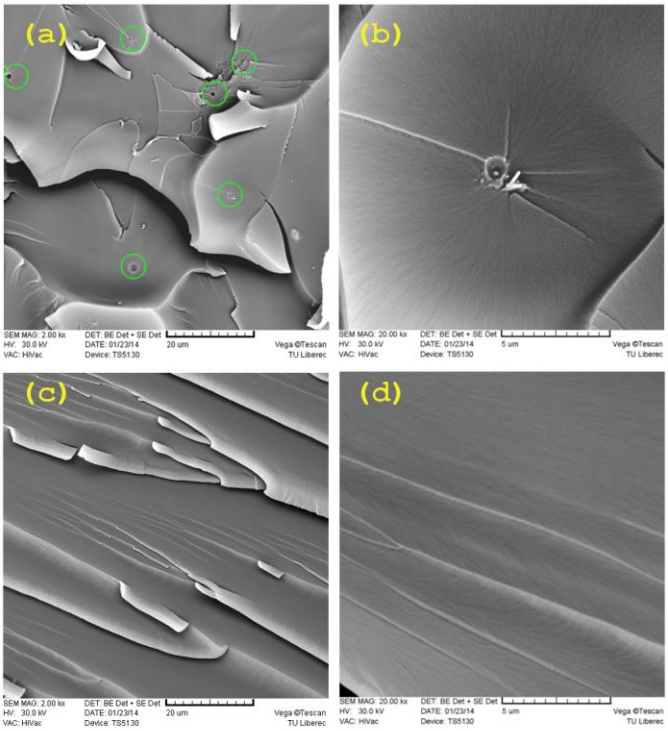


Fig. 6 SEM pictures for the CNTs/epoxy (a) (b) and for neat epoxy (c) (d) at similar magnifications

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