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## Molecular Dynamics Simulation of Functional and Hybrid Epoxy Based Nanocomposites

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### KEYWORDS

Molecular dynamics  
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### ABSTRACT

In this paper, the effects of filler type, filler content, functionalization, and the use of hybrid nanofillers on nanocomposite mechanical properties are investigated. For this purpose, several nanocomposite types were modeled and analyzed using Molecular Dynamics method. In the molecular dynamic's simulations, crosslinking and nanofiller/matrix interface effects were considered. First thermoset epoxy resin with 75% crosslinking ratio between DGEBA resin and DETA hardener were simulated to determine pure resin properties. Then nanocomposites consisting of single walled carbon nanotubes (SWCNT), nanographene (NG), carbon nanoparticle (CNP), functional single walled carbon nanotubes (SWCNT-COOH), and functional nanographene (nanographene oxide) in thermoset epoxy were modeled and analyzed using Materials Studio software. In addition, filler weight fraction was increased from 2.5 to 10 percent in order to investigate the effects of filler content on nanocomposite mechanical properties. The results indicated that increasing nanofiller weight fraction from 0 to 7.5% resulted in an increase in nanocomposite elastic modulus for three non-functional nanofiller types. Moreover, functionalization improving nanocomposite properties as the highest increase in resin elastic modulus were obtained for the SWCNT-COOH reinforced epoxy for filler contents up to 7.5 weight percent. Also, agglomeration occurred at filler contents higher than 7.5 weight percent in the NG/epoxy, SWCNT/epoxy nanocomposites. Finally, the use of hybrid nanofillers reduced/prevented agglomeration for filler contents even up to 10 weight percent.

### 1. Introduction

In many of today's engineering applications, the combination of material properties to meet the needs of various industries is becoming more demanding. For example, aerospace industries demand materials with high strength, low density, high abrasion resistance, high UV resistance, and resistance to withstand high service temperatures. Nanocomposite materials have many of the needed characteristics/properties required by advancing industries. Moreover, in nanocomposites, unlike conventional composites, the improvement of one property does not mean a loss/degradation in other properties. In many cases, several properties can be improved simultaneously with the addition of nano reinforcements to the material matrix. In addition, due to the nanometer dimensions of the nanofillers,

interactions between the nanofiller and the matrix are more effective than those in conventional composite materials. Thus, properties, which depend on surface characteristics, could be modified more efficiently in nanocomposites. Polymer-matrix nanocomposites seem to be excellent candidates due to their desirable properties such as: high chemical resistance, low density, high strength, thermal stability, and low electrical conductivity. Due to these attractive properties, the development of new polymer nanocomposites has grown considerably over the past decade [1-19]. Nanoparticles, nanotubes, nanofibers, and nanosheets have all been used as reinforcements in polymer matrices. However, most of the research has been conducted on carbon nanotubes in the past. But, graphene nanosheets and nanoparticles have recently attracted attention due to their excellent mechanical, thermal, and

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electrical properties [20, 21]. For instance, Meskh et al. [20] predicted the macroscopic tensile strength and fracture toughness of fully exfoliated nano silicate clay epoxy composites accounting for the interphase behavior between the polymeric matrix and clay reinforcement. Their results indicated that the interphase thickness had the most influence on tensile strength. Also, the critical strain energy release rate of the interphase zones had an effect on the dissipation energy depending on the interphase zone thickness. In another study, Hamdia et al. [21] measured the ability of polymeric nanocomposites in resisting crack growth. Their results showed that the variance in the fracture energy was mostly influenced by the maximum allowable principal stress and Young's modulus of the epoxy matrix.

On the other hand, high aspect ratio and strong Van der Waals forces between nanotubes and nanosheets results in agglomerated reinforcements, therefore limiting their strengthening effect. Hence, much research has been performed on finding ways to obtain uniform distribution of these nanofillers in polymer matrices [19, 22-25]. Recently, functional and hybrid nanocomposite with two or more nanofillers have been used simultaneously to make improved mechanical properties [26-43].

In a recent study by Moosa et al. [26], they measured mechanical and electrical properties of epoxy / carbon nanotube / graphene hybrid nanocomposite, experimentally. According to their results, adding carbon nanotubes led to a better dispersion of graphene in the matrix and prevented the agglomeration of graphene plates. They reported an increase in the nanofiller/matrix interface strength, thus making improvements in nanocomposite mechanical and electrical properties. Al-Saleh [27] determined electrical and mechanical properties of graphene and carbon nanotube hybrid nanocomposites experimentally. This investigator determined properties of graphene/propylene and graphene/CNT/propylene. His results showed a significant increase in thermal conductivity for the hybrid nanocomposite. He also concluded that, at a constant nanofiller volume fraction, the tensile strength of graphene/CNT/propylene hybrid nanocomposite increased with increasing carbon nanotube content more than that of the two-phase nanocomposite.

In other research, Kumar et al. [28] investigated the effects of using hybrid nano reinforcement on nanocomposite properties, experimentally. They prepared and tested two-phase and hybrid nanocomposite samples and compared the results. They tested three different types of nanocomposites consisting of multi-layered nanotubes, titanium dioxide nanopowders, and hybrid nanocomposites. Their results showed an

improvement in the anti-corrosion properties, elastic modulus, hardness, and tensile strength for the hybrid nanocomposite compared to two-phase nanocomposites. Bakhtiar et al. [29], used a combination of carbon nanotubes and clay to reinforce epoxy resin. They determined tensile strength, tensile modulus, and hardness of the nanocomposite experimentally. Their results indicated an increase of 87% in tensile strength, 135% in the elastic modulus, and 14% in hardness with the addition of 1 to 5 wt % nanofiller. Ayatollahi et al. [30] measured the properties of epoxy-based hybrid nanocomposites consisting of carbon nanotubes and nanoclay. Their experimental results indicated that thermal conductivity, Young's modulus, and tensile strength of the hybrid nanocomposite were significantly higher than those of the two-phase nanocomposites. In addition, Navidfar et al. [31] in their experiments, determined the properties of polyurethane reinforced with double-walled carbon nanotubes and silica nanoparticles. They added 0.25 wt % silica nanoparticle in order to prevent nanotube agglomeration. Therefore, they could increase the nanotube content to about 0.5 wt % and obtain improved mechanical properties for the hybrid nanocomposite. According to their results, adding 0.25 wt% nanotube increased the tensile strength of nanocomposite by 15%. In another article, Jouyandeh et al. [32] used Hydroxyl-rich halloysite nanotube (HNT)/silica nanosphere (SiO<sub>2</sub>) core/ shell particles were functionalized with multi-arm hyperbranched polyethylenimine macromolecule to develop epoxy superadhesives for metal/polymer composite interfaces. Their findings suggested that amine groups of the functionalized core/shell nanoparticles were exchanged with imide ones through the reaction with pyromellitic acid dianhydride to make the system thermally stable. Incorporation of the developed reactive bushy-surface hybrid nanoparticles into epoxy resulted in a highly crosslinkable super adhesive with exceptional thermal and mechanical properties.

In other research, Liu et al. [33] studied the functionalizing CNT film on interfacial bonding strength between CNT film and epoxy resin. They found that the interfacial bonding strength could be altered by surface functionalization of the CNT film using atmospheric pressure helium/oxygen plasma. The peeling strength between the CNT film and epoxy was increased by 156.6%. The tensile strength of the functionalized CNT film/epoxy composites were reported to be 74.4% higher than that of original CNT film. Another publication by Naeb et al. [34] determined thermal and mechanical properties of graphene nano platelets for covalently functionalized graphene/epoxy nanocomposites. Their microscopy observations showed that functionalized

graphene nano platelets via Bingel reaction improved nano platelet dispersion and interfacial bonding with epoxy resin. Saeb et al. [35] studied the cure characteristics of epoxy nanocomposites containing unmodified and amino functionalized MWCNTs. These investigators examined the potential of the developed epoxy nanocomposites to cure using non-isothermal differential scanning calorimetry. They found that NH and NH<sub>2</sub> functional groups on MWCNTs have improving effects on cure characteristics of epoxy nanocomposites. Saeb et al. [36] provided an overview to emphasize the role of functionalization of multiwalled carbon nanotubes (MWCNTs) in manipulating cure kinetics of epoxy nanocomposites. Their results suggested that the type of functional groups covalently located on the surface of MWCNTs directly affected the degree of polymer-nanotube interaction followed by enhancement of curing reaction. Saeb et al. [37] investigated the interaction between epoxy, hardener and fillers using Molecular Dynamics (MD) simulation and experiments. Computational studies demonstrated that curing of epoxy resin with aminoamide hardener was governed by the interaction between epoxy and functionalized Fe<sub>3</sub>O<sub>4</sub>. Bahlakeh et al. [38], investigated, the effects of different types of iron oxides on the interfacial interaction between epoxy coating and carbon steel substrate. Their results showed that the interaction behavior of cured epoxy with hydroxylated iron oxide surfaces was quantified mechanistically. Saeb et al. [39] studied cure kinetics of epoxy/anhydride systems containing very low concentrations of pristine and amine-functionalized multiwalled carbon nanotubes (MWCNTs) using Isoconversional methods. They measured times of gelation and vitrification of epoxy using storage and loss modulus data provided by isothermal rheokinetic analysis. Their results confirmed facilitation of cure kinetics resulting from amine groups attached to MWCNTs. Bahlakeh et al. [40] investigated the effect of cerium oxide treatment on the corrosion protection properties and interfacial interaction of steel/epoxy. Their results indicated that Ce film composed of CeO<sub>2</sub> uniformly covers the steel surface and enhances surface free energy. Also, pull-off strength of epoxy coating applied in the Ce treated sample was much higher than that of bare steel.

Moreover, in most of the previous investigations, experimental methods have been used to measure nanocomposite properties. Since, laboratory procedures require advanced equipment and testing, these investigations are very expensive and time consuming. As a result, Talebi et al. [44] presented an open-source software framework called PERMIX for multiscale modeling and simulation of fracture in solids. Vu-Bak et al. [45] also provided a sensitivity analysis toolbox

consisting of a set of Matlab functions that offer utilities for quantifying the influence of uncertain input parameters on uncertain model outputs. For this purpose, Molecular Dynamics (MD) simulations could overcome these limitations. In addition, with MD methods, unlike experimental methods, the effects of different parameters can be investigated more easily at lower costs. For example, Aghadavoodi et al. [46] investigated the effects of resin cross-linking ratio on mechanical properties of epoxy-based nanocomposites using molecular dynamics. Their MD results suggested that nanocomposite Young's modulus increased with resin crosslinking ratio.

In this paper, the possibility of improvement in nanocomposite properties by using the functionalization and hybridization of nanofillers in the nanocomposite was investigated using molecular dynamics simulation. For this purpose, single walled carbon nanotubes, nanographene, carbon nanoparticles, single walled carbon nanotube-COOH and nanographene oxide were used as reinforcements. Thermoset epoxy resin with 75% crosslinking ratio between DGEBA resin and DETA hardener was simulated first to determine pure resin properties. Next, molecular dynamics simulations were carried out on five different nanocomposite samples containing functional, hybrid and three nanofiller types/shapes. In addition, models were created to investigate the effects of nanofiller content on nanocomposite mechanical properties. It should be noted that, in our models the effects of resin crosslinking ratio and nanofiller/matrix interface were also considered.

## 2. Atomistic modeling procedure

Since molecular systems generally contain a large number of particles, it is not possible to obtain the properties of complex systems analytically. As a result, Molecular Dynamics simulations could help overcome this limitation [47]. In this method, the interaction between atoms and molecules in time intervals is simulated using a computer software and the motion of atoms are determined. Molecular dynamics is used as an intermediate step between laboratory experiments and theory and is considered as a virtual laboratory. Some of the advantages of this method are: updating thermodynamic quantities instantaneously, accessing details of the system, and relatively low cost of execution.

In this investigation, periodic boundary conditions were imposed on all simulation boxes to eliminate the surface effects. In this paper, Condensed-phase Optimized Molecular Potentials for Atomistic Simulation (COMPASS) force field were used in the MD simulations. More details on this force field and the corresponding equations can be found in the reference section [48].

The simulation process was as follows:

Geometry optimization and energy minimization were applied to the molecular structures using a smart algorithm which was a combined algorithm of the steepest descent, adopted-basis Newton-Raphson (ABNR), and quasi-Newton methods to reach the nearest local minimum with convergence tolerance of 0.0001 kcal/mol.

The system was equilibrated using NPT ensemble (Berendsen & Nose methods) to achieve the nearest local equilibration for 100 ps with a time step of 1 fs at a pressure of 1 atm and a temperature of 298 K to bring the system to the final density.

Based on Hooke's law for elastic materials, using Voigt notation, the stiffness matrix components,  $C_{ij}$ , was calculated using:

$$\sigma_i = C_{ij}\varepsilon_j \quad (i, j = 1, 2, 3) \quad (1)$$

For a specific strain vector, the stress components were calculated using molecular dynamics simulations and were substituted in Eq. 3 to determine the stiffness matrix components,  $C_{ij}$ .

In this research, thermosetting polymer DGEBA resin and DETA hardener were used as the matrix material. The crosslinking process of this resin is shown in the Fig. 1.

The C-O bond in epoxide groups needed to be broken in order to form a reactive -CH<sub>2</sub> site, capable of cross-linking with DETA molecule. The crosslinking procedure had been presented in an earlier investigation performed by two of the authors [49]. In this paper, the thermoset polymer with 75% crosslinking was used as the matrix material. The term crosslinking ratio was used to describe the ratio of the total number of crosslinks created to the maximum number of possible crosslinks. The molecular dynamics model of this resin is shown in Fig. 2. First, pure resin was simulated in Materials Studio software to determine resin mechanical properties as the first step in MD simulation of the nanocomposite samples.

Next, nanocomposite samples reinforced with five different nano reinforcements were modeled. The nano reinforcements consisted of: i) single walled carbon nanotubes (CNT (4, 4) with 5.42 Å diameter and 164.79 Å length), ii) nanographene (21.85 Å × 21.85 Å), iii) carbon nanoparticle (11 Å diameter), iv) single walled carbon nanotubes-COOH (CNT (4, 4) with 5.42 Å diameter and 164.79 Å length), and v) nanographene oxide (21.85 Å × 21.85 Å). Simulation boxes consisting of the three nanofiller types used as reinforcements in the nanocomposites are shown in Figs. 3-a through 3-c. Note that each simulation box shown in this figure contains a single nanofiller, 2.5 wt % reinforcement. Models were also created containing 5, 7.5, and 10 wt % reinforcements in order to investigate the effects of reinforcement weight fraction on properties of each

nanocomposite under investigation. In addition, models were created consisting of functional reinforcements in order to investigate the effects of functional reinforcements on nanocomposite properties.

The functionalization of the nanotube and the nanographene are described in the references [50-52]. The molecular structures of these functional nanofillers are shown in Fig. 4. Functional SWCNT-COOH and NG oxide simulated in Materials Studio software are shown in Fig. 5.

Finally, the effects of hybrid reinforcement on nanocomposite properties were investigated. For this purpose, models of SWCNT/CNP/epoxy and functional SWCNT/NG/epoxy were created and analyzed. The two hybrid nanocomposites investigated are shown in Fig. 6. The results of these investigations are presented in the next section.

### 3. Results and Discussion

Molecular Dynamics models of pure epoxy and five different nanocomposite samples were created to determine the effects of nano reinforcement type, filler content, and functionalization on nanocomposite mechanical properties.

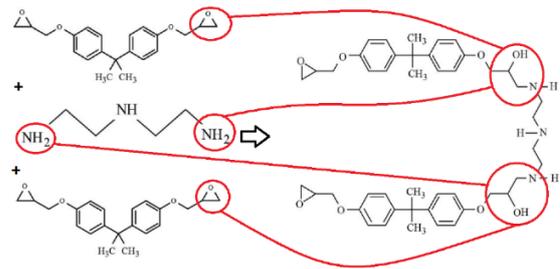


Fig. 1. DGEBA and DETA crosslinking process [23]

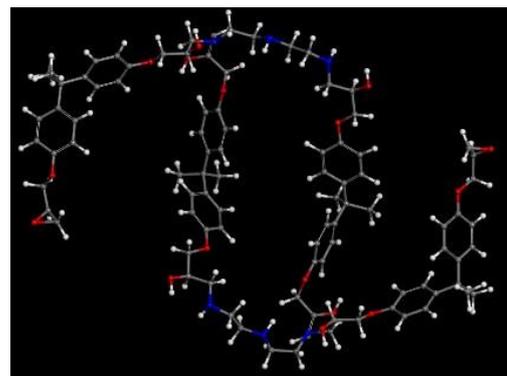


Fig. 2. MD model of the thermoset polymer with 75% crosslinking ratio

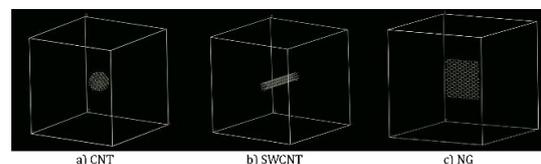


Fig. 3. Simulation boxes containing the three types of nanofillers used in this investigation

In addition, models of hybrid nanocomposites were created in order to investigate the effects of hybrid reinforcement. The results of these analyses are presented in the following sub-sections separately.

### 3.1. Pure Epoxy Results

First, models were created to determine the properties of pure epoxy with a degree of cure of 75%. Furthermore, density variation during the simulation time must be monitored in order to ensure that the modeling procedure is correct [46]. This variation is shown in Fig. 7. As can be observed, polymer density reached the macro scale resin density (1.1 g/cm<sup>3</sup>) in about 40 ps. In this investigation, a cut off time of 100 ps was used to ensure that the system has reached equilibrium.

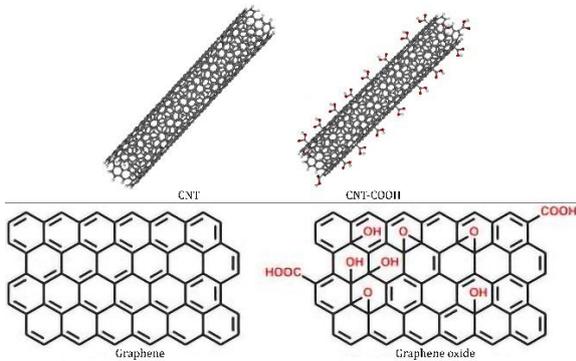


Fig. 4. Molecular structure of functional nanofillers used in this investigation

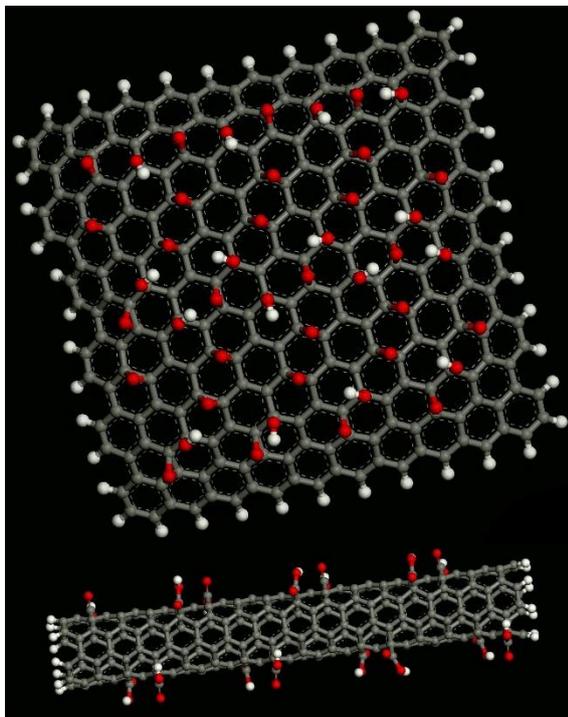


Fig. 5. Functional nanofillers in the MD simulation boxes

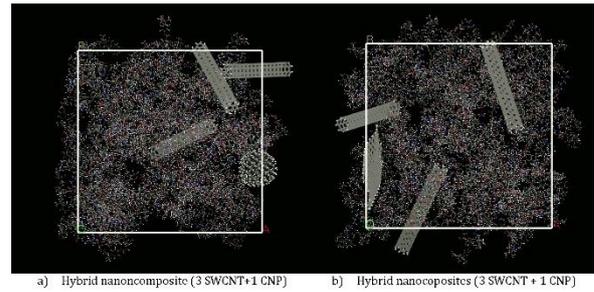


Fig. 6. Two MD models of the hybrid nanocomposites

A strain of 0.01 was applied to the resin molecular structure and pure resin mechanical properties were determined. The resulting stiffness matrix components for the thermosetting polymer, with 75% crosslinking ratio, are as follows:

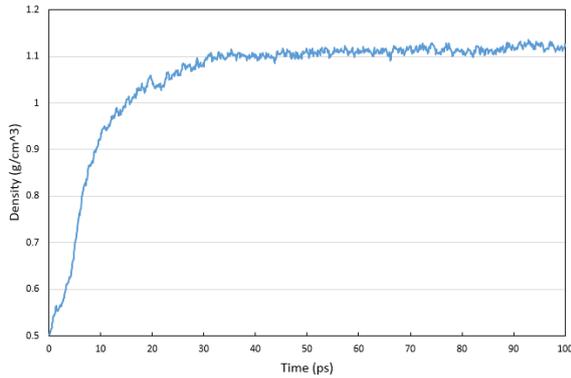
$$C_{ij} \text{ (GPa)} = \begin{bmatrix} 4.7842 & 1.9717 & 2.1085 & -0.1468 & -0.1249 & 0.1927 \\ 1.9717 & 4.6135 & 2.3224 & -0.0330 & 0.0546 & 0.1008 \\ 2.1085 & 2.3224 & 4.9769 & 0.0091 & -0.0299 & -0.0484 \\ -0.1468 & -0.0330 & 0.0091 & 1.0735 & 0.0111 & -0.0122 \\ -0.1249 & 0.0546 & -0.0299 & 0.0111 & 1.1192 & -0.0773 \\ 0.1927 & 0.1008 & -0.0484 & -0.0122 & -0.0773 & 1.1347 \end{bmatrix}$$

Note that the pure resin stiffness matrix was symmetrical and the largest values corresponded to the diagonal elements  $C_{11}$ ,  $C_{22}$ , and  $C_{33}$ . Also, note that these three components were almost equal indicating that the polymer was isotropic. These observations proved that the analysis procedure was correct.

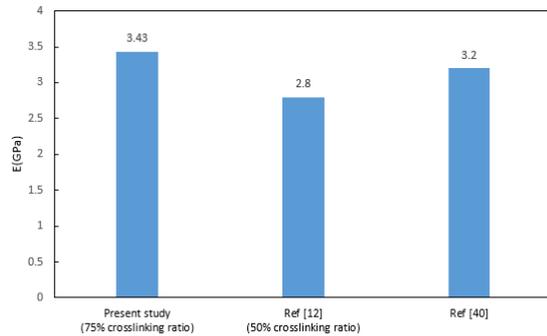
Using the MD results, the elastic modulus of the pure resin was determined to be 3.43 GPa. The results of the current investigation were compared with those presented in the literature [46, 53] in Fig. 8. Note in this figure that our models predicted a somewhat higher modulus value than that reported by Aghadavoudi et al. [46]. It is noteworthy that Aghadavoudi et al. determined resin modulus for epoxy resin with 50% crosslinking ratio whereas the crosslinking ratio considered in this investigation was much higher, at 75%. Also note that, the predicted resin modulus was close to the value reported by Alian et al. [53]. Resin crosslinking ratio was not reported by these investigators. These observations proved that our predicted modulus was in good agreement with previously published data.

### 3.2. Effects of Nanofiller Type a Content

Next, models were created to investigate the effects of nanofiller type and content on nanocomposite mechanical properties. To achieve our goals, nanocomposites consisting of 1, 2, 3, and 4 nanofillers were modeled. Note that, nanofiller contents have been kept the same (2.5, 5, 7.5 and 10 wt %) in all models for a proper comparison. The results of this investigation are presented in this sub-section.



**Fig. 7.** Density variation of the thermosetting polymer with simulation time



**Fig. 8.** Comparison of predicted resin elastic modulus with those presented in the literature

Variation of CNP-reinforced epoxy elastic modulus with nano particle weight fraction is presented in Fig. 9. Also, note that nanocomposite elastic modulus increased with CNP weight fraction. The largest increase corresponded to CNP nanocomposite with 4 CNPs (10 wt %) by about 8.7% relative to neat epoxy. Note also that no agglomeration, reduction of modulus, was observed in this nanocomposite type. This indicated that high contents of CNP could be used in epoxy resin.

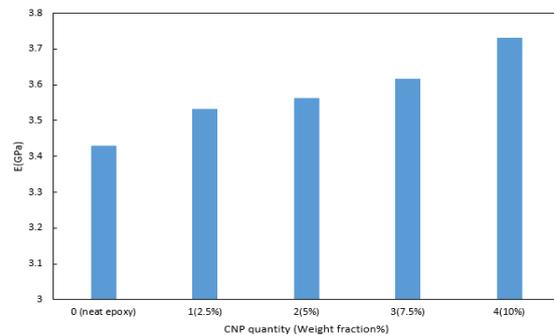
Figure 10. shows the results of single walled carbon nanotube reinforced polymer. Note in this figure that nanocomposite modulus increased with SWCNT content up to nanotube weight fraction of 7.5 weight percent. Elastic modulus of the nanocomposite containing 10 wt % nanotubes, however, was even lower than the 2.5 wt % CNT nanocomposite. This decrease in nanocomposite modulus was due to the agglomeration of carbon nanotubes. The largest elastic modulus increased, 11% relative to pure epoxy, corresponding to the nanocomposite containing 7.5 wt % CNTs.

Figure 11. shows the variation of NG nanocomposite elastic modulus with nanofiller content. The same filler content was used in these models as well.

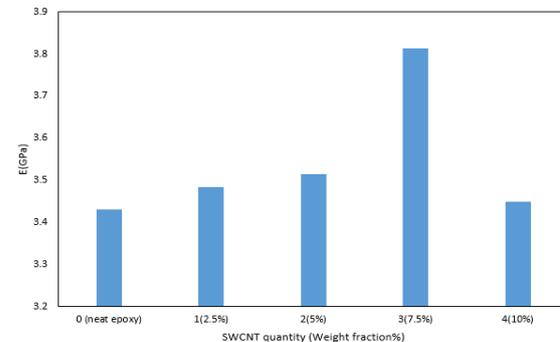
The NG nanocomposite results also show that nanocomposite elastic modulus increased with nanofiller weigh fraction up to 7.5 wt % nano graphene. At 10 wt % nano graphene,

nanocomposite modulus decreased by 1.7% compared with the 7.5 wt % nano graphene nanocomposite modulus. This was similar to the observations made on the results obtained for the SWCNT/resin nanocomposite. Note also that the largest increase of about 2.7% relative to neat epoxy corresponded to the 7.5 wt % NG nanocomposite.

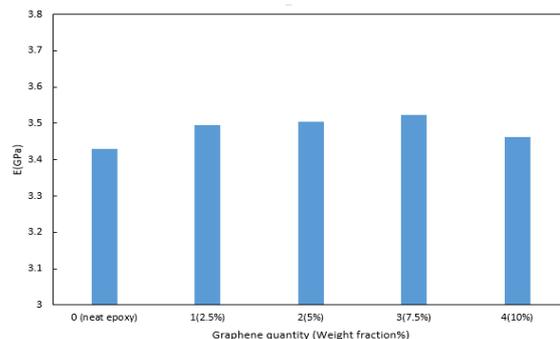
The presented results on the three nanocomposite types suggest that SWCNT has the largest effect on improving resin modulus. The increase in resin modulus at 7.5 wt. % SWCNT was about 11 percent. Next is the CNP with a 4.2 % improvement in resin modulus at 7.5 wt. % filler content. Finally, NG had the lowest efficiency in improving resin modulus (2.7% increase at 7.5 wt. %). The reasons for the differences could be due to the fact that CNT longitudinal modulus was much larger than the NG and CNP.



**Fig. 9.** Variation of CNP/epoxy elastic modulus with filler content



**Fig. 10.** Variation of SWCNT/epoxy elastic modulus with filler content



**Fig. 11.** Variation of NG/epoxy elastic modulus with filler content

### 3.3. Effects of Nanofiller functionalization

In order to investigate the effects of nanofiller functionalization on nanocomposite properties, models were created consisting of SWCNT-COOH and NG oxide reinforced polymer. Nanofiller content was kept below 7.5 wt % in these models in order to avoid agglomeration and to obtain optimum reinforcement efficiency of the reinforcements.

The results of SWCNT-COOH/epoxy nanocomposite were compared with those of SWCNT/epoxy nanocomposite in Fig. 12.

These results indicate that elastic modulus of SWCNT-COOH/epoxy was higher than untreated SWCNT/epoxy, at equal nanofiller weight fractions. Comparing the results of the 7.5 wt % reinforcement content nanocomposites, suggest that SWCNT-COOH nanocomposite modulus was about 5 percent higher than the modulus obtained for nonfunctional SWCNT/epoxy nanocomposite. This was due to improved nanofiller dispersion and interfacial bonding of functional SWCNT. Thus, functionalizing CNTs had a large effect on nanofiller efficiency in improving resin properties. This was also observed experimentally by Liu et al. [33].

The results of NG oxide/epoxy nanocomposite were compared with NG/epoxy nanocomposite in Fig. 13.

Note in this figure that, NG oxide/epoxy modulus was much higher than nonfunctional NG/epoxy modulus for filler contents less than 5 wt %. This was observed in experimental results presented by Naeb et al. [34]. However, in NG oxide nanocomposite, the elastic modulus decreased at nanofiller weight fraction of 7.5 percent.

The above results could be explained as follows: 1) functional SWCNTs improved resin modulus more due to the fact that functionalization enhanced surface wettability of the CNTs. This resulted in an increase in the CNT/matrix interface strength resulting in improved load transfer between the two phases. 2). The functional NG, however, behaved differently once added to the resin. It was observed in the simulation process that functional NGs bend inside the simulation box. This bending reduces the NG efficiency in improving resin properties at higher NG contents.

### 3.4. Hybrid Nanocomposite Results

The results of the SWCNT/epoxy and SWCNT-COOH/epoxy nanocomposites indicated that the elastic modulus of these nanocomposites decreased at 10 wt % nanofiller content compared to the 7.5 wt % SWCNT nanocomposite due to agglomeration of nanotubes. In order to decrease nanofiller agglomeration, two types of nanofillers were used as the reinforcement to model hybrid nanocomposites. First, a new model consisting of

3 SWNTS (7.5% wt %) and one CNP (2.5 wt %) was created. Note that the total reinforcement content in this hybrid nanocomposite model was 10 weight percent. The results of this hybrid nanocomposite were compared with the results of the two-phase nanocomposite in Fig. 14. Pure resin modulus was also presented in this figure for a better comparison.

Note in Fig. 14 that, at the same nanofiller weight fraction, hybrid nanocomposite elastic modulus was about 10% higher than that of neat epoxy. This improvement in properties, as experimentally observed by Ayatollahi et al. [30], was due to better dispersion of nanofillers when used as a combination in epoxy resin.

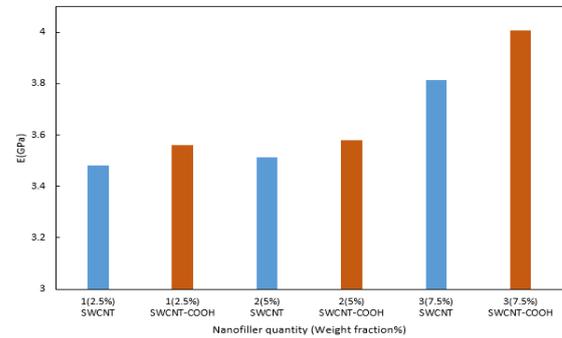


Fig. 12. Effects of CNT functionalization on SWCNT/epoxy modulus

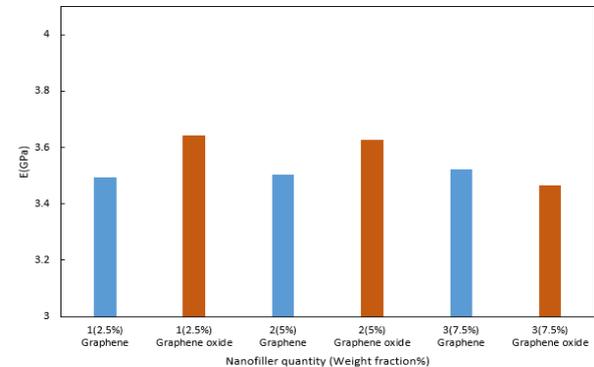


Fig. 13. Effects of NG functionalization on NG/epoxy modulus

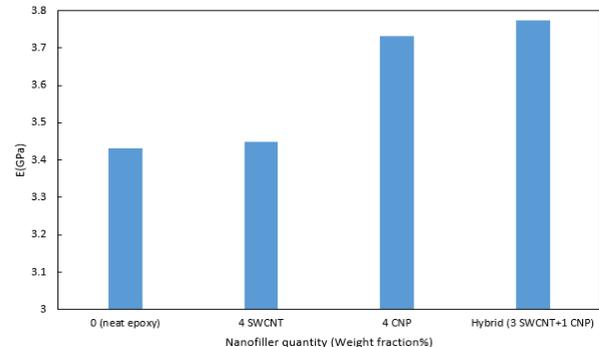


Fig. 14. Comparison of two-phase and hybrid nanocomposite modulus

Based on the above findings, it was predicted that nanofiller agglomeration could be reduced in the 10 wt % SWCNT-COOH nanocomposite by replacing one of the four SWCNT-COOH reinforcements with one NG oxide nanofiller. To prove this point, a new model was created consisting of 3 SWCNT-COOH (7.5 wt %) and 1 NG oxide (2.5 wt %). Note again that the total reinforcement content in this model was 10 weight percent. The results of this investigation are presented in Fig. 15.

According to these results, the highest elastic modulus increase was obtained by using hybrid reinforcements. The hybrid reinforcement resulted in about 19.8% increase in epoxy modulus. Whereas, resin modulus improved by about 15 percent with the addition of SWCNT-COOH at the same filler content of 10 weight percent. Addition of NG oxide has led to a better dispersion of SWCNT-COOH in the matrix and has prevented agglomeration of SWCNT-COOH. These observations are in line with experimental results reported for SWCNT/NG/epoxy hybrid nanocomposite by Moosa et al. [26].

The results of hybrid nanocomposites show higher modulus compared to two-phase nanocomposites at the same filler content. This is primarily due to the fact that the addition of two different filler types interferes with filler-filler interaction. This reduces agglomeration, thus improving nanofiller efficiency in improving resin mechanical properties.

#### 4. Conclusions

In this paper, the improvement of nanocomposite properties, as a result of using functional and hybrid nanofillers was investigated. Thermoset epoxy with 75% crosslinking ratio between DGEBA resin and DETA hardener was simulated first. The resulting resin properties were used as the matrix mechanical properties in MD models of the nanocomposites. Molecular dynamics simulations were carried out to determine the effects of nanofiller type and weight fraction on nanocomposite mechanical properties.

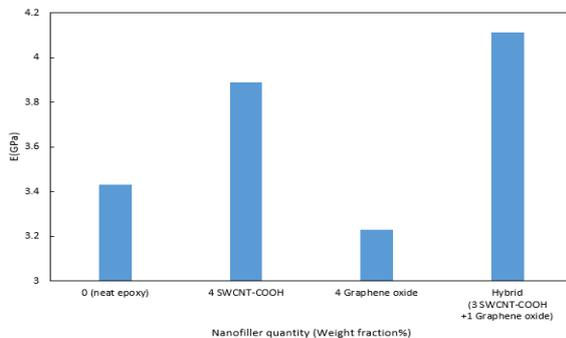


Fig. 15. Comparison of two phase and hybrid nanocomposite modulus

Single-walled carbon nanotube, nanographene, and carbon nanoparticle were used as the reinforcement to investigate the effects of nanofiller type on nanocomposite properties. In order to determine the effects of nanofiller functionalization, epoxy resin reinforced with single-walled carbon nanotube-COOH, and nanographene oxide were modeled. In addition, the effects of hybrid nano reinforcement were investigated by combining different reinforcement types in the models. The following conclusions could be drawn from the results:

Increasing nanofiller weight fraction from 0 to 7.5% resulted in an increase in nanocomposite elastic modulus for all three nanofiller types.

Nano particles did not show agglomeration even at filler contents up to 10 weight percent.

The highest improvements in elastic modulus among non-functional reinforcements corresponded to SWCNT at 7.5 wt % reinforcement content.

Nanofiller functionalization improved nanofiller/resin bonding, thus improving nanocomposite properties.

Using hybrid reinforcement prevented agglomeration. Thus making it possible to use up to 10 wt % nanofiller in epoxy resin and obtain higher improvements in resin properties.

#### Nomenclature

$C$	Stiffness, GPa
$E$	Modulus of Elasticity, GPa

#### Greek symbols

$\rho$	Density, g/cm <sup>3</sup>
$\sigma$	Stress, GPa
$\epsilon$	Strain

#### Subscript

$i, j$	1, 2, 3
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