Elastic Constants Prediction of Hybrid Nanocomposite

Ashish Srivastava* and Dinesh Kumar**

Received: 18 April 2016; Published online 4 February 2017

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Abstract

In this paper a complete characterization of CNT-graphene reinforced hybrid nanocomposite in terms of its elastic constants is performed. Continuum mechanics based model is used to evaluate the effective elastic properties of hybrid nanocomposite using a square representative volume element (RVE) approach. Numerical results are obtained from finite element analysis of the RVE under different periodic boundary conditions using the commercial software COMSOL Multiphysics and these results were validated with the results available in the literature and the obtained analytically using rule of mixtures. The effects of different matrix materials, ranging from soft polymer to stiff ceramics, and different volume fraction, on the elastic modulii of hybrid nanocomposite are also discussed. It was found that irrespective of volume fractions, hybrid nanocomposite offers better in-plane elastic properties than CNT nanocomposite, whereas the out-of-plane properties are better improved in the case of CNT nanocomposite.

Keywords: Representative volume element; Carbon nanotubes; Graphene; Elastic moduli; FEM

Nomenclature

\begin{array}{|c|c|}
\hline
\text{Symbol} & \text{Description} \\
\hline
\text{a and b} & \text{Sides of square RVE} \\
\text{u}_{11}, \text{u}_{22}\text{and }\text{u}_{33} & \text{Displacement in z, y and x directions respectively} \\
\text{\delta}_1, \text{\delta}_2 \text{and }\text{\delta}_3 & \text{Deformation of faces in x, y and z direction, subjected to loading conditions} \\
\text{\delta}_t, \text{\delta}_l & \text{Deformation of faces subjected to transverse and longitudinal shear loading conditions respectively} \\
\text{\sigma}_{ij}, \text{\varepsilon}_{ij} \text{and }\text{C}_{ijkl} & \text{Stress, strain and stiffness tensor respectively} \\
\overline{\text{\sigma}}_{ij} \text{and }\overline{\text{\varepsilon}}_{ij} & \text{Volumetric average of stress and strain of RVE} \\
\text{C}_{ijkl}^e & \text{Effective stiffness tensor} \\
\nu_{12}, \nu_{13} \text{and }\nu_{23} & \text{Poisson's ratios corresponding to x-y, x-z and y-z planes} \\
\text{E}_1, \text{E}_2 \text{and }\text{E}_3 & \text{Young's moduli in the x, y and z direction respectively} \\
\text{V}_{\text{RVE}} & \text{Volume of represented volume element} \\
\hline
\end{array}

*Corresponding e-mail: ashish.memech@gmail.com
**Corresponding e-mail: dkumar.mech@mnit.ac.in

1 Ph.D. Scholar, Mechanical Engineering Department, Malaviya National Institute of Technology, Jaipur, India.
2 Assistant Professor, Mechanical Engineering Department, Malaviya National Institute of Technology, Jaipur, India
1. Introduction

Carbon nanotubes (CNTs) discovered in 1991 by Iijima (1991) have attracted the attention of researchers around the world from almost all fields of engineering and science because of their superior electrical, thermal and mechanical properties. Possessing extraordinary strength, resilience, stiffness and low density, CNTs are established as an effective reinforcing nanofiller in composites with various matrix materials ranging from polymers to metals, and to ceramics (Ruoff and Lorents 1995; Salvetat et al. 1999; Demczyk et al. 2002; Ruoff et al. 2003; Sears and Batra 2004; Laurent et al. 2010). CNTs, also called as buckytubes, are sp² bonded structure of fullerene family made in cylindrical shape using one atom thick rolled sheet. These sp² bonded structures are stronger than sp³ bonded alkanes and diamond which provide them above mentioned unique properties. CNTs tends to agglomerate due to small diameter along with high aspect ratio and low elastic modulus in the radial direction, which makes them liable to agglomerate (Heshmati and Yas 2013).

Graphene sheet (GS), an opened CNT, is a 2D structure of single atom thick carbon foil/sheet having hexagonally arranged carbon atoms and that can be exfoliated from inexpensive graphite. GS is also found to posses extraordinary properties, like CNTs and hence can be another effective reinforcing nanofiller in the composites. The research article entitled ‘Graphene-based composite materials’ by Stankovich et al. (2006) attracted the attention of the scientists and engineers around the world. Subsequently in 2007, the article ‘The Rise of Graphene’ by Geim and Novoselov (2007) further boosted the interest of researchers into this important field of immense research. The discovery of graphene as a nanofiller material has opened a new scope for the production of light weight, low cost, and high performance composite materials for a range of applications such as solar, spacecraft, satellites, automobiles, bio-medical etc. Many of the electrical and mechanical properties of polymer/graphene nanocomposites are found superior to the base polymer matrix as well as other carbon fillers (CNT and graphite) based composites (Kuilla et al. 2010). Gallego et al. (2013) reported that the mechanical performance of cured functionalized graphene sheets (GS) nanocomposites outperformed the multiwall carbon nanotube (MWCNT) with enhancement of Young’s modulus and strength by 50% and 15%, respectively. GS have high surface area compared to CNT and it is required to preserve this high surface area to minimize the restacking (to form multilayered graphene sheet) issue associated with production of graphene-based nanocomposites (Patole et al. 2012).

In recent past, the concept of hybrid nanocomposite (involving CNT and GS both as reinforcements) have attracted the attention of many researchers to understand the synergistic effect brought about by the combination of high aspect ratio of CNTs and large surface area of GS. In hybrid nanocomposites bringing together CNT and graphene form a co-supporting network of both fillers (Kumar et al. 2010). Chatterjee et al. (2012) established that hybrid nanostructure have better...
flexural modulus than the single filler systems; at the same time fracture toughness is also found to be improved for all ratios of mixed nanofillers.

Patole et al. (2012) showed that the hybrid nanostructure (i.e., CNT-GS/epoxy composite) have the ability to combine the major individual advantages of the graphene and the CNT together to produce a better nanocomposite material. It was also shown that tensile modulus and tensile strength of the hybrid nanocomposite are increased, respectively, by 40 % and 36 % with respect to the neat epoxy. There are few investigations (Chen et al. 2012; Li et al. 2013) which have also demonstrated that the individual issues (i.e., non-uniform dispersion and restacking) associated with the CNT and the graphene reinforced nanocomposites are resolved by the hybridization of CNT and graphene in the matrix material. Chen et al. (2012) found that restacking of GS can be reduced by sandwiching CNTs between GSs. In subsequent year, Li et al. (2013) reported a significant improvement in load transfer effectiveness by embedding CNT-GS hybrids into pristine epoxy that endows optimum dispersion of CNTs and GSs as well as better interfacial adhesion between the carbon fillers and matrix. Load transfer mechanism of the GS/CNT/polyethylene hybrid nanocomposite under uniaxial tension is simulated by Zhang et. al (2014) using molecular dynamics.

At the nanoscale, analytical models are either difficult to establish or too complicated to solve. At the same time, there are enormous challenges in the experimental development and characterization of CNT- and GS-based nanocomposites (Bower et al. 1999; Qian et al. 2000; Potts et al. 2011) because of difficult and expensive processes involved. Therefore, cost-effective and less-time-consuming computational approaches play a significant role in the development and characterization of CNT- and GS-based nanocomposites to provide simulation results for better understanding, analysis and design of such nanocomposites. Presently, two computational approaches based on molecular dynamics (MD) and continuum mechanics are used for characterizing individual CNT/graphene as well as nanocomposites. There are many investigations (Cho and Sun 2007; Al-ostaz et al. 2008; Bu et al. 2009) on application of MD approach for simulation of individual CNTs/GSs or nanocomposites for understanding their behavior and hence, providing some initial guidelines to the experimental work.

Continuum mechanics based 3-D representative volume element (RVE) approach, as applied successfully in the micromechanics study of conventional fiber-reinforced composites and extended by Liu & Chen (2003) for nanocomposites, have been widely used by many researchers to evaluate the mechanical properties of nanocomposites. In another study, Chen & Liu (2004) concluded that cylindrical RVEs tend to overestimate the effective Young's moduli of nanocomposites as compared to square RVE as reported in their earlier study (Liu and Chen 2003) because of the overestimation of the volume fractions of the CNTs in a matrix in the case of cylindrical RVE. Joshi et al. (2010) used the hexagonal RVE to predict the mechanical properties of CNT based nanocomposite. Joshi and Upadhyay (2014a; 2014b) used cylindrical RVE to predict the elastic constants of multi-walled carbon nanotube (MWCNT) reinforced nanocomposite with perfect and imperfect bonding between the nanofiller and the matrix materials.

It is evident from the above literature survey that there are no investigations on predicting the elastic behavior of CNT-GS reinforced hybrid nanocomposites. Therefore, the aim of the present paper is to predict the elastic properties of the CNT-graphene reinforced hybrid nanocomposite
using finite element (FE) analysis based on continuum mechanics approach. A multi-reinforced 3-D nanoscale square representative volume element (RVE) is considered with periodic distribution of nanofillers in the matrix material with perfect bonding between the nanofillers and matrix material. The FE analysis of the RVE is carried out using finite element method based commercial package COMSOL Multiphysics. The effect of volume fraction of the reinforcements and different matrix materials, (ranging from soft polymer to stiff ceramics) on the effective elastic moduli of Hybrid nanocomposites are also investigated.

2. Present Study

2.1 Selection of representative volume element (RVE)

Although nanofillers (i.e., CNTs and GSs) are randomly distributed throughout the volume of the nanocomposite, but to simplify the simulation for the mechanical response of these nanocomposites, CNTs and GSs are assumed to be distributed throughout the matrix in a periodic pattern in square-packed array, refer Fig. 1. Further the present study is limited to the defect-free nanocomposites having perfectly straight CNT and flat GS with perfect interface between the nanofillers and the matrix. The concept of unit cells or representative volume elements (RVE), as applied successfully in the studies of conventional fiber-reinforced composites at the microscale is extended to study the mechanical responses of CNT/GS based hybrid nanocomposites at nanoscale (Sun and Vaidya 1996). As demonstrated in Fig. 1, a RVE is selected from the hybrid nanocomposite having periodic arrangement of CNT and GS. A 3D view of the selected RVE is shown in Fig. 2.

2.2 Boundary conditions applied to RVE

The boundary conditions play a vital role in accurate computation of elastic constants of nanocomposites through volumetric averages of stresses and strains by simulating the actual deformation within the nanocomposite under a given loading condition, and are thus required to be specified precisely. In the present analysis, the boundary conditions on the RVE for various loading conditions, as derived by Sun and Vaidya (1996) by judicious use of symmetry and periodicity conditions and used for the prediction of mechanical properties of conventional composite from RVE approach, are utilized and applied to the finite element model of RVE of Hybrid nanocomposite. These boundary conditions for different loading conditions, such as normal, transverse shear and longitudinal shear, for calculating various elastic constants are described subsequently.

2.2.1 Boundary conditions for normal loading

Following periodic displacement boundary conditions on the RVE are applied to calculate longitudinal and transverse moduli and Poison’s ratios:

For calculating $E_1$, $v_{12}$ and $v_{13}$ (refer Fig. 3):

\[ u_{11}(0,y,z) = u_{22}(x,0,z) = u_{33}(x,y,0) = 0, \quad u_{11}(L,y,z) = \delta_1 \]  

where $u_{11}$, $u_{22}$ and $u_{33}$ represent displacement components in $x$, $y$ and $z$ directions, respectively, and $\delta_1$ is the constant value of displacement applied in $x$-direction on $x=L$ face of the RVE.

For calculating $E_2$ and $v_{23}$:
$$u_{11}(0,y,z) = u_{22}(x,0,z) = u_{33}(x,y,0) = 0; \quad u_{22}(x,a,z) = \delta_2$$ \hspace{1cm} (2)

where $\delta_2$ is the constant value of displacement applied in $y$-direction on $y=a$ face of the RVE.

Similarly, for calculating $E_3$:

$$u_{11}(0,y,z) = u_{22}(x,0,z) = u_{33}(x,y,0) = 0; \quad u_{33}(x,y,b) = \delta_3$$ \hspace{1cm} (3)

where $\delta_3$ is the constant value of displacement in $z$-direction on $z=b$ face of the RVE.

2.2.2 Boundary conditions for transverse shear loading

For calculating $G_{23}$ (refer Fig. 4):

$$u_{11}(x,y,0) = u_{22}(x,y,0) = u_{33}(x,y,0) = 0; \quad u_{22}(x,y,b) = \delta_t$$ \hspace{1cm} (4)

where $\delta_t$ is the constant value of displacement in $y$-direction on $z=b$ face of the RVE, as shown in Fig. 4.

2.2.3 Boundary conditions for longitudinal shear loading

For calculating $G_{12}$ (refer Fig. 5):

$$u_{11}(x,0,z) = u_{22}(x,0,z) = u_{33}(x,0,z) = 0; \quad u_{11}(x,a,z) = \delta_l$$ \hspace{1cm} (5)

where $\delta_l$ is the constant value of displacement in $x$-direction on $y=a$ face of the RVE, as shown in Fig. 5.

Similar to $G_{12}$, the boundary conditions for calculating $G_{13}$ would be as follows:

$$u_{11}(x,y,0) = u_{22}(x,y,0) = u_{33}(x,y,0) = 0; \quad u_{11}(x,y,b) = \delta_t$$ \hspace{1cm} (6)

where $\delta_t$ is the constant value of displacement in $x$-direction on $z=b$ face of the RVE.

In the present study, the constant value of displacements (i.e. $\delta_1, \delta_2, \delta_3, \delta_t$ & $\delta_l$) in x, y and z-directions is taken to be 1% of the respective edge length.

![Diagram representing selection of RVE](image-url)
Fig. 2. Representative volume element

Fig. 3. Typical RVE under normal loading in x-direction (for calculating $E_1$, $v_{12}$ and $v_{13}$)
2.3 Homogenization method for evaluating average stress and strain over the RVE

Actually, the selected RVE at nanoscale is a heterogeneous composite medium containing a matrix material reinforced with CNT and GS system, but this RVE is to be used for evaluating effective (i.e., average) elastic properties of the resulting hybrid nanocomposite that is considered to be homogeneous at larger scales (i.e., micro, meso or macro scale). Therefore, it is required to use
homogenization techniques to find a globally homogeneous medium equivalent to the original heterogeneous composite medium at nanoscale and to reduce the non-homogeneous stress and strain fields within the heterogeneous material obtained from the finite element analysis of RVE to the volume-averaged stress and strain. Following paragraphs contains homogenization procedure to determine the effective modulii that describe the 'average' material properties of the actual heterogeneous nanocomposite.

Individual phases have isotropic material properties, and it is assumed that the constitutive law in the matrix and the reinforcement is given by the following generalized Hooke's Law, written in summation convention:

\[ \sigma_{ij} = C_{ijkl} \varepsilon_{kl}, \quad i, j, k, l = 1, 2, 3 \]

where \( \sigma_{ij} \) and \( \varepsilon_{kl} \) are the coefficients of the stress tensor, the linear strain tensor and the stiffness tensor, respectively.

The FE analysis of the RVE would yield the above mentioned stress and strain fields within the heterogeneous material. The effective (i.e., averaged) stiffness coefficients of nanocomposite (at micro or macro scale) can be calculated from

\[ \bar{\sigma}_{ij} = C^e_{ijkl} \bar{\varepsilon}_{kl} \]

where \( C^e_{ijkl} \) refers to the effective stiffness tensor, and \( \bar{\sigma}_{ij} \) and \( \bar{\varepsilon}_{kl} \) are the volume-averaged stress and strain tensors calculated over the volume of the RVE using following volumetric integral expressions:

\[ \bar{\sigma}_{ij} = \frac{1}{V_{RVE}} \int_{V_{RVE}} \sigma_{ij}(x, y, z) \, dV \]
\[ \bar{\varepsilon}_{kl} = \frac{1}{V_{RVE}} \int_{V_{RVE}} \varepsilon_{kl}(x, y, z) \, dV \]

where \( V_{RVE} \) represents the volume of representative volume element.

In the present study, COMSOL Multiphysics tool is used to carry out the FE analysis of the RVE, and all finite element based calculations, required to determine homogenized material properties of nanocomposites such as volumetric-average of the stresses and the strains, are also done using this tool. After calculating the volume-averaged stress and strain components, the relevant nanocomposite modulii (i.e., effective/averaged stiffness coefficients) can be obtained from average stresses and average strains. For three pure normal strain states and for three pure shear states, the stiffness tensors can be written as:

\[ C^e_{ijkl} = \frac{\bar{\sigma}_{ij}}{\bar{\varepsilon}_{kl}}, \quad i = j = k = l; \text{ (for pure normal strain states)} \]
\[ C^e_{ijkl} = \frac{\bar{\sigma}_{ij}}{2\bar{\varepsilon}_{kl}}, \quad (i = k) \neq (j = l); \text{ (for pure shear strain states)} \]

The Poison's ratios are given by:
\[ \nu_{ij} = -\frac{e_{ij}}{\varepsilon_{ii}}, \]  \hspace{1cm} (13)

Therefore, Eqs. (11-13) are used, respectively, to calculate the effective Young's modulii, shear modulii and Poisson's ratios of the hybrid nanocomposite.

3. Analytical Approach

Strength of materials based rule of mixtures (ROM), also called Reuss model, that assumes same strain tensor in matrix, reinforcement and composite system, is a very good method for estimation of the elastic modulus in axial direction and the in-plane Poisson's ratio (i.e., \( \nu_{12} \)), '1' being the axial direction) of a composite system. Because of its simplicity and accuracy, ROM has been used frequently by many researchers (Liu and Chen 2003; Chen and Liu 2004; Joshi et al. 2010) to validate their results. Because of dependency of ROM method only on volume fraction of the reinforcement with no consideration to reinforcement dimensions and geometry, this method doesn't predict good results for transverse Young's modulii that require non-uniform strain condition for transverse direction loading that in turn would violates the assumption of Reuss model (Hyer 1998).

For comparison purpose, ROM based formulae used for the calculation of various elastic constants (i.e. \( E_1 \) and \( \nu_{12} \)) of nanocomposite are given below.

\[ E_1 = V_f E_f + (1 - V_f) E_m \]  \hspace{1cm} (14)

\[ \nu_{12} = \nu_f V_f + \nu_m (1 - V_f) \]  \hspace{1cm} (15)

In Eqs. (14-17), subscripts 'm' and 'f' correspond to the matrix and the reinforcement (i.e., CNT and graphene), respectively, and accordingly \( E \) and \( \nu \) denote the Young's modulus and Poisson's ratio of matrix or reinforcement, respectively;

Volume fractions of CNT and graphene in nanocomposite are given as:

\[ V_f^C = \frac{2\pi (r_o^2 - r_i^2)}{a^2 - 2\pi r_i^2} \]  (for CNT)  \hspace{1cm} (16-1)

\[ V_f^G = \frac{2w t}{a^2 - 2\pi r_i^2} \]  (for GS)  \hspace{1cm} (16-2)

where \( r_i \) and \( r_o \) are the inner and outer radii of the CNT, respectively; \( w \) and \( t \) represent width and thickness of the graphene sheet, respectively, and; \( a \) denotes the side of the square RVE. It is to be noted that the lengths of the RVE and the reinforcements (CNT and GS) are taken to be same.

Further, it is to be mentioned that for a given volume fraction \( \left( V_f = V_f^C + V_f^G \right) \) of the reinforcement in the hybrid nanocomposite, CNT and graphene are considered to occupy equal share of that volume fraction (i.e., \( V_f^C = V_f^G = V_f/2 \)). For a fixed value of \( V_f \) and given values of inner and outer radii \( (r_i \text{ and } r_o, \text{ respectively}) \) of CNT and thickness \( t \) (equal to \( r_o - r_i \)) of GS, Eqs. (18.1 & 18.2) are used to calculate the side of square RVE and the width of GS.
4. Verification

To verify the FE based procedure followed in the present study, elastic constants (only axial modulus and in-plane Poisson's ratio) of CNT reinforced and hybrid nanocomposites obtained in the present study are validated with the results obtained by analytical approach, i.e., rules of mixtures (as described in Section 3) and the reported results in the literature (Chen and Liu 2004). A square RVE containing matrix and reinforcement(s) (CNT or CNT & GS) with nano-filler's volume fraction $V_f = 0.03617$ is considered. The finite element mesh models of square RVEs reinforced only with CNT, and reinforced with CNT and GS are shown in Figs. 6 and 7, respectively. The dimensions and properties of matrix, CNT and GS considered for the validation purpose are given below.

Matrix: Length, $L = 100$ nm; Young's modulus, $E_m = E_f/10$; Poisson's ratio, $\nu = 0.3$.

Carbon nanotube (CNT): Length, $L = 100$ nm; Young's modulus, $E_f = 1000$ GPa; Poisson's ratio, $\nu = 0.3$; Outer radius, $r_o = 3.34$ nm; Inner radius, $r_i = 3$ nm.

Graphene sheet (GS): Length, $L = 100$ nm; Young’s modulus, $E_f = 1000$ GPa; Poisson's ratio, $\nu = 0.3$; Thickness, $t = 0.34$ nm

![FE model of CNT reinforced RVE, for $V_f = 0.03617$, $E_f/E_m = 10$](image)

A comparison of values of elastic constants predicted by the present FEM based study with those evaluated from rule of mixtures and that reported in Ref. (Chen and Liu 2004) is shown in Table 1.
It can be noticed from Table 1 that there is good agreement in the values of axial elastic modulus ($E_1$) and in-plane Poisson’s ratio ($\nu_{12}$) predicted by the finite element procedure of the present investigation, the analytical method and the available results in the literature (Chen and Liu 2004).

![FE model of the hybrid RVE containing CNT and GS, for $V_f = 0.03617$, $E_f/E_m=10$.](image)

**Table 1** Comparison of Elastic constants of CNT reinforced and Hybrid nanocomposite

<table>
<thead>
<tr>
<th>Elastic Constants</th>
<th>CNT Nanocomposite</th>
<th>Hybrid (CNT+GS) Nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref (Chen and Liu 2004)</td>
<td>Present study</td>
</tr>
<tr>
<td>$E_1$</td>
<td>132.5500</td>
<td>132.5518</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>0.3000</td>
<td>0.2999</td>
</tr>
</tbody>
</table>

5. Present Study

In this paper, hybrid nanocomposite comprising of a matrix material reinforced with two different kind of reinforcements (i.e. CNT and graphene) with a periodic distribution is modeled using a square representative volume elements (RVE). Dimensions and material properties of CNT, graphene and matrix materials considered are same as discussed in Section 4. Although the bonding between the CNT/graphene and the matrix is not perfect, but in the current study a perfect
bonding is assumed between the reinforcements and the matrix. The RVE is analyzed using FE based tool COMSOL Multiphysics. The RVE is meshed with tetrahedron elements using physics-controlled meshing feature of COMSOL with fine enough mesh near to CNT/GS (as shown in Figs. 6 & 7) to deliver converged FEM results. Various periodic displacement boundary conditions for different loading cases, as discussed in Section 2 and shown in Figs. (3-5), are applied to yield the stress and strain fields within the actual heterogeneous RVE. The corresponding average quantities ($\bar{\sigma}_{ij}$ and $\bar{\varepsilon}_{kl}$) are obtained by taking volumetric integral of stresses and strains, as given by Eqs. (9 & 10). By using the calculated values of average stress and average strain, the effective nanocomposite modulii can be evaluated using Eqs. (11-13) as the ratio of average stress (or average transverse strain, for Poisson’s ratio) to the average strain.

A hybrid nanocomposite with a combined volume fraction of CNT and graphene equal to 3.617 % (1.8085% each) is considered first to predict its elastic properties. Thereafter, for the same volume fractions of graphene and CNT in the hybrid nanocomposite, effects of matrix materials ranging from stiff ceramics to soft polymers (i.e. $E_i/E_m$ varying from 2 to 100) on the effective elastic moduli are observed. In addition, effects of volume fractions (varying from 1% to 4%) on elastic modulii of hybrid nanocomposites are also investigated. For comparison purpose, corresponding results of CNT reinforced nanocomposite with same volume fraction as that of hybrid nanocomposite are also presented along with the results of hybrid nanocomposite.

6. Results and Discussion

<table>
<thead>
<tr>
<th>Elastic constants (GPa)</th>
<th>CNT Nanocomposite (percentage change*)</th>
<th>Hybrid Nanocomposite (percentage change*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$</td>
<td>132.5527(32.5)</td>
<td>132.5526(32.5)</td>
</tr>
<tr>
<td>$E_2$</td>
<td>112.5711(12.6)</td>
<td>118.1274(18.1)</td>
</tr>
<tr>
<td>$E_3$</td>
<td>112.5711(12.6)</td>
<td>110.5279(10.5)</td>
</tr>
<tr>
<td>$G_{12}$</td>
<td>45.2526(17)</td>
<td>47.9998(24.8)</td>
</tr>
<tr>
<td>$G_{23}$</td>
<td>45.0086(17)</td>
<td>39.8103(3.5)</td>
</tr>
<tr>
<td>$G_{13}$</td>
<td>45.2526(17.7)</td>
<td>42.4526(10.4)</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>0.2999(-0.03)</td>
<td>0.2999(-0.03)</td>
</tr>
<tr>
<td>$\nu_{23}$</td>
<td>0.3672(22.4)</td>
<td>0.3682(22.7)</td>
</tr>
<tr>
<td>$\nu_{13}$</td>
<td>0.2999(-0.03)</td>
<td>0.2999(-0.03)</td>
</tr>
</tbody>
</table>

* Percentage change is evaluated with reference to matrix material

Results of elastic constants of hybrid nanocomposite (with $E_i/E_m = 10$ and $V_f = 3.617$ %) evaluated from FEM analysis of a nanoscale 3D square RVE after applying periodic displacement boundary conditions for different loading cases [as mentioned in Section 2.2 and Figs. (3-5)] are presented in Table 2. For comparison purpose, corresponding results for CNT based nanocomposite having same volume fraction as that of hybrid nanocomposite are also given in Table 2.
It can be noted from Table 2 that hybrid and CNT nanocomposites show orthotropic and transversely-isotropic behavior, respectively, with all stiffness properties increased as compared to that of the matrix material. A significant increase (about 32.5%) in stiffness in axial direction (i.e., $E_1$) as compared to matrix material is almost same for both kinds of nanocomposite. In-plane transverse modulus (i.e., $E_2$) along the $y$-axis of hybrid nanocomposite is also increased by 18% as compared to pure matrix, and this increase is more than CNT based nanocomposite. Therefore, the hybrid nanocomposites offers better bi-directional in-plane stiffening effects than CNT nanocomposites which can be attributed to the biaxial in-plane stiffness properties of 2-D GS. On the contrary, transverse modulus $E_3$ of hybrid nanocomposite along $z$-axis direction is observed to be less than that of the CNT nanocomposite. It can also be noted from Table 2 that the in-plane ($xy$-plane) shear modulus $G_{12}$ of hybrid nanocomposite is more (increased by 24.8%) than that of the CNT nanocomposite; whereas, CNT nanocomposite offers enhanced values of $G_{23}$ and $G_{13}$ relative to the hybrid nanocomposite.

Fig. 8. von-Mises stress distribution (sectioned at $y = a/2$) under axial normal loading in $x$-direction.

Although the whole load of CNT nanocomposite is taken by CNT (Liu and Chen 2003; Chen and Liu 2004; Joshi et al. 2010) but it would be shared by CNT and GS both in the case of hybrid nanocomposite. To visualize the load sharing, under different constant-displacement loading conditions, between different reinforcing constituents of a hybrid nanocomposite, distribution of von-Mises stress are presented in Figs. (8-13). It can be observed from Fig. 8 that for axial normal loading in $x$-direction, the CNT and the graphene both share the load in equal proportion, whereas Fig. 9 shows that for transverse normal loading in $y$-direction CNT takes maximum load, at the same time GS also contribute marginally in load carrying capacity of hybrid nanocomposite. Further as depicted in Fig. 10 that there is insignificant load carried by GS in comparison to CNT in the case of transverse normal loading in $z$-direction. Similarly, load shared by GS in the cases of transverse
Fig. 9. von-Mises stress distribution (sectioned at $x = L/2$) under normal loading in $y$-direction.

Fig. 10. von-Mises stress distribution (sectioned at $x = L/2$) under normal loading in $z$-direction.
Fig. 11. von-Mises stress distribution (sectioned at $x = L/2$) under transverse shear loading in $y$-$z$ plane applied at face $z=a$.

Fig. 12. von-Mises stress distribution (sectioned at $x = L/2$) under longitudinal shear loading in $x$-$z$ plane applied at face $z=a$. 
Fig. 73. von-Mises stress distribution [(a) sectioned at $z = a/2$ & (b) sectioned at $x = L/2$] under transverse shear loading in $x$-$y$ plane applied at face $y = a$. 

$G_{\max} = 4.4 \times 10^{10}$ Pa

$G_{\min} = 1.84 \times 10^7$ Pa

$\sigma_{\max} = 4.32 \times 10^{10}$ Pa

$G_{\min} = 3.31 \times 10^9$ Pa
shear loading in y-z plane and longitudinal shear loading in x-z plane, as shown, respectively, in Figs. 11 and 12, is less significant as compared to the CNT; whereas, GS contribute marginally in carrying load in the case of longitudinal shear loading in x-y plane, as shown in Fig. 13.

Normalized values of the effective extensional and shear modulii of the hybrid nanocomposite (with $V_f = 0.03617$), for different matrix materials (having $E_f/E_m = 2, 5, 10, 20, 50$ and $100$) varying from stiff ceramics to soft polymers, are given in Tables 3 and 4, respectively. For comparison purpose, corresponding values of CNT reinforced nanocomposite with same volume fraction are also provided in Tables 3 and 4. To better visualize the effects of variation of $E_f/E_m$ on various elastic stiffness properties of CNT and hybrid nanocomposites, the normalized values of effective extensional and shear modulii presented in Tables 3 and 4 are also plotted in Figs. 8 and 9, respectively.

It can be observed from Tables 3 & 4 and Figs. 14 & 15 that the values of extensional and shear modulii of CNT as well as hybrid nanocomposites are improved as compared to that of the corresponding matrix material. It is also important to note that this improvement in extensional and shear modulii of CNT as well as hybrid nanocomposites is marginal for stiff, such as ceramics, matrix material (i.e., for $E_f/E_m = 2$) and it is substantial for soft, such as polymer, matrix material (i.e., for $E_f/E_m = 100$). Table 3 and Fig. 14 also show that for a particular volume fraction, the effect of hybridization (of CNT and graphene) on the value of extensional modulus $E_2$ becomes more prevalent with the increase in $E_f/E_m$ ratio, whereas there is no much change in other extensional modulii (i.e., $E_1$ and $E_3$) because of hybridization (inclusion of graphene along with CNT) in nanocomposite for all values of $E_f/E_m$ ratio.

Table 3 Normalized effective extensional modulii of CNT- and hybrid nanocomposites with different matrix materials (for $V_f = 0.03617$).

<table>
<thead>
<tr>
<th>$E_f/E_m$</th>
<th>CNT Nanocomposites</th>
<th>Hybrid Nanocomposites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1/E_m$</td>
<td>$E_2/E_m = E_3/E_m$</td>
</tr>
<tr>
<td>2</td>
<td>1.03617</td>
<td>1.02856</td>
</tr>
<tr>
<td>5</td>
<td>1.14468</td>
<td>1.08060</td>
</tr>
<tr>
<td>10</td>
<td>1.32553</td>
<td>1.12571</td>
</tr>
<tr>
<td>20</td>
<td>1.68722</td>
<td>1.17075</td>
</tr>
<tr>
<td>50</td>
<td>2.77232</td>
<td>1.22451</td>
</tr>
<tr>
<td>100</td>
<td>4.58080</td>
<td>1.25872</td>
</tr>
</tbody>
</table>

Note: $E_i$ is the Young’s modulus of reinforcement material (GS/CNT)

It can be observed from Table 4 and Fig. 15 that there is significant effect of hybridization on various shear modulii. The value of $G_{12}$ for hybrid nanocomposite is improved as compared to CNT nanocomposite, except for $E_f/E_m = 2$, and this improvement show increasing trend with the increase in $E_f/E_m$ ratio. For all types of matrix material, the values of $G_{13}$ and $G_{23}$ of hybrid nanocomposite is decreased in comparison to CNT nanocomposite. It is also important to note from Table 4 and Fig. 15 that there is negligible effect of matrix material on $G_{23}$ of hybrid nanocomposite.
Fig. 14. Variation of normalized extensional modulii for different matrix materials for $v_f = 0.03617$

Table 4 Normalized effective shear modulii of CNT- and hybrid nanocomposites with different matrix materials (for $V_f = 0.03617$)

<table>
<thead>
<tr>
<th>$E_f/E_m$</th>
<th>CNT Nanocomposites</th>
<th>Hybrid Nanocomposites</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$G_{23}/G_m$</td>
<td>$G_{12}/G_m = G_{13}/G_m$</td>
</tr>
<tr>
<td>2</td>
<td>1.05089</td>
<td>1.03316</td>
</tr>
<tr>
<td>5</td>
<td>1.12428</td>
<td>1.10535</td>
</tr>
<tr>
<td>10</td>
<td>1.17022</td>
<td>1.17657</td>
</tr>
<tr>
<td>20</td>
<td>1.20313</td>
<td>1.24702</td>
</tr>
<tr>
<td>50</td>
<td>1.23269</td>
<td>1.31717</td>
</tr>
<tr>
<td>100</td>
<td>1.25219</td>
<td>1.34942</td>
</tr>
</tbody>
</table>

Note: $E_f$ is the Young’s modulus of reinforcement material (Graphene/CNT)
Fig. 15. Variation of normalized shear modulii for different matrix materials for $v_f = 0.03617$

The effect of change in volume fraction (varying from 1 % to 3.617 %) of reinforcements inside the matrix material (with $E_f/E_m=10$) on the elastic normal and shear modulii of the hybrid and CNT nanocomposites is plotted in Figs. 16(a-f). It can be noted from Figs. 16(a-f) that theoretically all elastic modulii of nanocomposite increase with the increase in volume fraction. For all volume fractions, there is no difference in the axial normal modulus (i.e. $E_1$) of the hybrid and the CNT nanocomposites, and the increase in the value of $E_1$ is very significant (about 32.5 %) for a change in volume fraction from 1 % to 3.617 %. It can also be seen from Figs. 16(b & d) that irrespective of the amount of reinforcement, hybrid nanocomposites offer better in-plane stiffness properties (i.e., $E_2$ and $G_{12}$) than CNT nanocomposites. On the contrary, Figs. 16 (c, e & f) show that out-of-plane stiffness properties (i.e., $E_3$, $G_{13}$ and $G_{23}$) of hybrid nanocomposites are lower than that of CNT nanocomposites, irrespective of the volume fractions. It is also important to note from Fig. 16(f) that the effect of change in volume fraction on transverse shear modulus $G_{23}$ is less significant for hybrid nanocomposite as compared to CNT nanocomposite.
7. Conclusion

Effective elastic constants of CNT-GS reinforced hybrid nanocomposite are calculated using continuum mechanics approach based finite element (FE) analysis of a 3-D nanoscale square representative volume element (RVE). The multi-reinforced RVE is considered with periodic distribution of nanofillers (graphene and CNT) in the matrix material with perfect bonding between the nanofillers and the matrix material. The FE analysis of the RVE constrained with different periodic boundary conditions is carried out using FE based commercial software COMSOL Multiphysics. Before carrying out the present study, the results for axial modulus and Poisson's ratio are validated with the corresponding results available in the literature and obtained analytically using mechanics of solid based rule of mixtures. A complete characterization in terms of various elastic constants of hybrid nanocomposite is made. The effects of different matrix materials, ranging from soft polymer to stiff ceramics, and different volume fraction, on the elastic modulii of hybrid nanocomposite are also discussed. A comparative study is done between the elastic properties of CNT based nanocomposite and hybrid nanocomposite. It is observed that hybrid nanocomposite depicts an orthotropic behavior because of 2D structure of graphene sheet which is in contrast to the transversely isotropic behavior of CNT reinforced nanocomposite. Irrespective of
volume fractions, hybrid nanocomposite offers better in-plane elastic properties (i.e., $E_1$, $E_2$ and $G_{12}$) than CNT nanocomposite, whereas the out-of-plane properties (i.e., $E_3$, $G_{13}$ and $G_{23}$) are better improved in the case of CNT nanocomposite. CNT and GS in the hybrid nanocomposite share load in different proportion depending upon the loading conditions. It is also found that because of the nanofiller reinforcement in a matrix material, the increase in the stiffness properties of the resulting nanocomposite is more significant for soft matrix materials, like polymers, than stiff materials, like ceramics.

Acknowledgements

The present research work is carried out by utilizing the computation research facilities at the Material Research Center (MRC), Malaviya National Institute of Technology (MNIT) Jaipur. The authors would like to kindly acknowledge the MRC, MNIT Jaipur.

Funding Source

None

Conflict of Interest

None

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