Studies on Effective Elastic Properties of CNT/Nano-Clay Reinforced Polymer Hybrid Composite

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Abstract. This paper presents a computational approach to predict elastic propertiesof hybrid nano-composite material prepared by adding nano-clayplatelets to conventional CNT-reinforced epoxy system. In comparison to polymers alone/single-fiber reinforced polymers, if an additional fiber is added to the composite structure, it was found a drastic improvement in resultant properties. In this regard, effective elastic moduli of a hybrid nano composite are determined by using finite element (FE) model with square representative volume element (RVE). Continuum mechanics based homogenization of the nano-filler reinforced composite is considered for evaluating the volumetric average of the stresses and the strains under different periodic boundary conditions.A three phase Halpin-Tsai approach is selected to obtain the analytical result based on micromechanical modeling. The effect of the volume fractions of CNTs and nano-clay platelets on the mechanical behavior is studied. Two different RVEs of nano-clay platelets were used to investigate the influence of nano-filler geometry on composite properties. The combination of high aspect ratio of CNTs and larger surface area of clay platelets contribute to the stiffening effect of the hybrid samples. Results of analysis are validated with Halpin-Tsai empirical formulae.

Keywords: Nano-clay, CNT, Hybrid composite, FEM, Halpin-Tsai, RVE.

1. Introduction

Polymers with suitable and proper nano filler have emerged as an advanced polymeric composites system which shows prospective applications in the field of automotive, aerospace, packaging and construction industries [1]. Compared to conventional and micro fillers, carbon nanotubes (CNTs) reinforced polymers have gained increased interest in both industrial and academic fields, specifically utilizing their high aspect ratio and tremendous mechanical strength of CNTs [2-4]. But practical point of view CNT reinforced polymer composite materials have limited applications because of poor load transfer through interfacial region and agglomerations of CNTs [5-6]. Surface treatment and chemical functionalization are few effective techniques to enhance the interfacial adhesion and dispersion ability of CNTs [7-8]. Similarly, polymer materials reinforced with Nano fillers such as layered silicates (clay) [9] are prominent substitute for conventional composite materials. Intuitively, polymer/clay Nano composite provide best performance with high degree of clay exfoliation. With the time, rapid advancement have taken place in material science and technology and developed new generation multi-scale, multifunctional nanostructured hybrid polymer composite reinforced by CNTs and other nano reinforcements. Therefore, it becomes necessary to investigate the reinforcing mechanism of hybrid polymer composite which provides basic foundation for modeling and design of these high performances composite. Clay-CNT/polymer matrix hybrid composite [10-14] is one of the most widely used materials due to their light weight, long durability, high strength, chemical resistant, and so forth. Great deals of analytical and

numerical works have been carried out to investigate the mechanical properties of CNTs reinforced polymer [15-16] and clay reinforced polymer [17] composite separately. Among the analytical techniques employed to obtain effective properties of composite, most of the researchers used the rule of mixture and Halpin-Tsai equations to modeling nanocomposite. However, few modifications have been employed to traditional theories to account the irregular geometry and distribution of nanostructured reinforcement at nano-scale for hybrid composite. Till to date no work found in literature related to modeling of clay-CNTs/polymer hybrid composite, however few articles are investigated numerical analysis of silica nanoparticle-MWCNT hybrid composite [18]. Jia eta al. [19] prepared a novel nanostructure hybrid (SiO2-MWCNTs) polymer composite, in which nano silica particle are grown over CNTs. Rahmanian et al.[20] demonstrate the FE modeling of carbon nanotube silica reinforced epoxy composite considering that CNTs are grown over micro silica particle. In most of work related to hybrid composite finite element method is an efficient and preferable numerical approach for investigating the reinforcing effect of different nano fillers on polymer composite. This method demonstrates the continuum representation of nano filler structure and polymer matrix.

Since CNTs/nano-clay hybrid showed prominent reinforcement on polymer matrix than pure CNTs as reported in previous work, there is a great potential in preparing new generation high performance composite. In present work, finite element method is used to predict the elastic behavior of epoxy composite reinforce by CNTs and nano-clay platelets. Specifically, to accurately describe geometry and reinforcing mechanism of CNTs and nano-clay platelets, the traditional theories of the rule of mixtures and Halpin–Tsai equations were properly corrected and a finite element approach based on nano-scale representative volume element (RVE) model was built up. To better understand the stiffening effect of CNTs and nano-clay nanoparticles in hybrid polymer composite, the tensile modulus for CNT/nano-clay/epoxy composites predicted by three phase Halpin–Tsai equations, were compared with FEM outcomes.

2. Modeling of hybrid composite

Modelling of CNT and nano clay reinforced hybrid composite is presented in two steps. In first part illustrate the micromechanical modelling and second one numerical modelling (FEM).

2.1.Micromechanical modeling

To predict the mechanical properties of three phase polymer composite, Halpin-Tsai model and theory of micromechanics were applied in hierarchy. The rule of mixture are used to obtained the effective elastic modulus of effective clay particle and effective CNT fiber (as shown in figure 1) which include clay, CNT and interphase as follow,

$$E_{CP} = E_{clay}\alpha + E_{int}(1-\alpha) \quad (1)$$

$$E_{CF} = E_{cnt}\beta + E_{int}(1-\beta) \qquad\qquad (2)$$

Where E_{CP} and E_{CF} are the effective elastic modulus of clay particle and CNT fiber. E_{clay}, E_{cnt}, α, β are the elastic modulus and volume fractions of clay and CNT respectively.
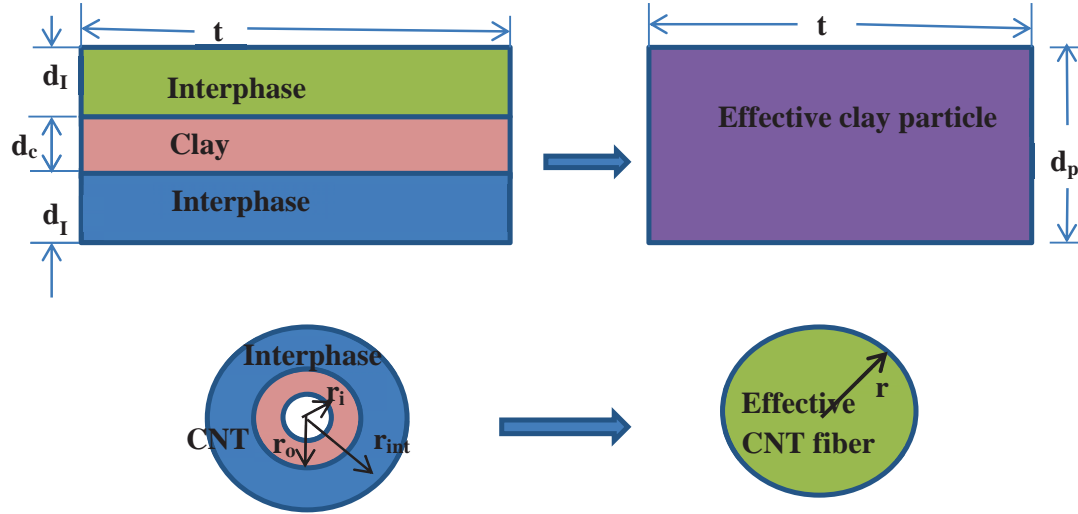
Fig. 1:- Representation of effective Clay particle and effective CNT fiber

To evaluate the elastic modulus of hybrid composite by combining effective particle and polymer (epoxy) by using modified Halpin-Tsai model as follow.

$$\frac{P}{P_m} = \frac{1 + (\varepsilon_1 \eta_{CP} V_{CP} + \varepsilon_2 \eta_{CF} V_{CF})}{1 - (\eta_{CP} V_{CP} + \eta_{CF} V_{CF})} \qquad (3)$$

Where, P is the elastic property of hybrid composite and P_m is elastic properties of polymer matrix.

$$\eta_{CP} = \frac{(P_{CP}/P_m) - 1}{(P_{CP}/P_m) + \varepsilon_1} \qquad (4)$$

$$\eta_{CF} = \frac{(P_{CF}/P_m) - 1}{(P_{CF}/P_m) + \varepsilon_2} \qquad (5)$$

$$V_m + V_{CP} + V_{CF} = 1 \qquad (6)$$

Where V_m, V_{CP}, and V_{CF} are the volume fraction of polymer matrix, clay particle and CNT fiber respectively. ε_1, ε_2 are the reinforcement efficiency parameters for clay particle and CNT fiber. For, longitudinal elastic modulus $\varepsilon_1 = (2l/d_p)$, $\varepsilon_2 = (2l/d)$ and for transverse elastic modulus $\varepsilon_1 = \sqrt{3} \log(l/d_p)$, $\varepsilon_2 = 1$. Where $d_p = d_c + 2*d_I$, $d = 2r$ are total thickness of effective clay particle and diameter of effective CNT fiber respectively. Figure 2 demonstrate the overall modeling procedure of CNT/nano-clay reinforced hybrid composite using micromechanical modeling.
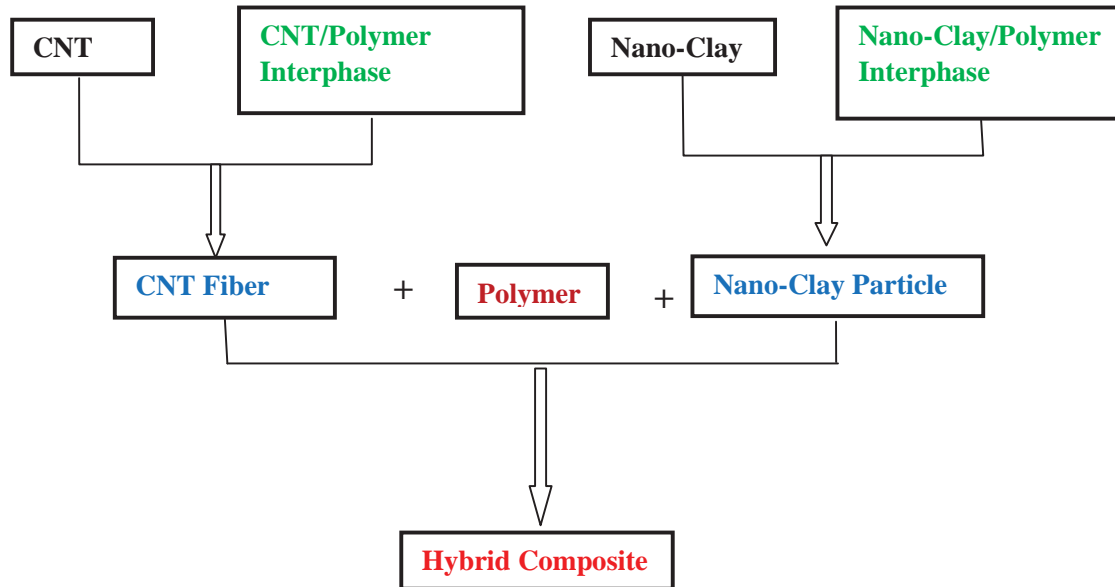
Fig. 2:- Modeling procedure of CNT/nano-clay reinforced hybrid composite

2.2. Constitutive relations and RVE model

For a transversely isotropic composite, the material behavior is based on only five independent constants. This concept is particularly ensured for regular fiber arrangement. In this work arbitrary fiber distributions are considered which results in transversely isotropic properties. By considering effective stiffness coefficient and average stress-strain value, the constitutive equations for the homogenized composite can be expressed as

$$
\begin{Bmatrix} \overline{\sigma_1} \\ \overline{\sigma_2} \\ \overline{\sigma_3} \\ \overline{\sigma_4} \\ \overline{\sigma_5} \\ \overline{\sigma_6} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{12} & C_{23} & C_{22} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(C_{22}-C_{23}) & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{66} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{Bmatrix} \overline{\varepsilon_1} \\ \overline{\varepsilon_2} \\ \overline{\varepsilon_3} \\ \overline{\gamma_4} \\ \overline{\gamma_5} \\ \overline{\gamma_6} \end{Bmatrix}
$$

(7)

A representative volume element model can be used for the calculation of effective elastic coefficients by applying the appropriate periodic boundary conditions under the assumption of periodicity of fiber arrangement. Figure 3 shows the RVE model for CNT/nano-clay reinforced polymer composite.
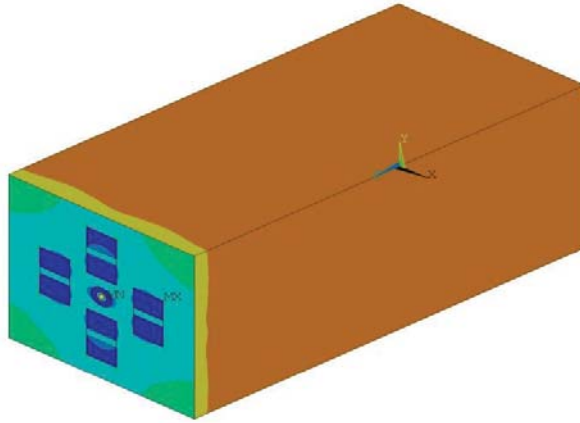
Fig. 3:- RVE of CNT/nano-clay reinforced polymer

The main advantage of the method is to replace the original composite with globally homogenized equivalent medium with same strain energy stored. To find out effective elastic coefficients such load cases with different boundary conditions must be applied that for a particular load case only one value in the strain field vector is non-zero and all other becomes zero. Then from corresponding column, the effective coefficients can be determined using calculated average stress value corresponding to unit strain.

2.3.Finite element modeling
A three dimensional multi-field elements is used for finite element calculations using FE package ANSYS. ANSYS Parametric Design Language (APDL) coding is used for modeling and applying the constraint equations. An algorithm was written in APDL for automated generation of RVE with aligns CNT and clay inside the polymer matrix. First 2-D model is generated in X_2-X_3 plane with circle as CNT and rectangle as clay and meshed with PLANE82 element. Further FE mesh is extruded in X_1 direction with SOLID185, 3-D element for meshing of RVE. Fibers surfaces are connected by Boolean operation with the aim of predicting the modulus of resin matrix reinforced with periodic nano-reinforcement of clay-CNTs. An interphase region is also considered here between CNT/polymer and clay/polymer to demonstrate the imperfect load transfer phenomenon at interfaces. The interphase region is meshed with random material properties lies between fiber and polymer matric properties. The generation of RVE can be controlled by some input parameters like size of RVE, CNT and nano-clay diameters for desired volumefraction. A certain minimum distance must be ensuring to generate suitable meshing of each part of model. From the numerical analysis, the effective elastic parameters of compositional material were estimated by relating boundary conditions.The calculation of effective coefficients in order to evaluate the overall stiffness matrix [C] of hybrid composite, RVE is subjected to an average strain. The six components of strain are applied by imposing the following boundary conditions on the displacement components.

$$-a_2 \leq x_2 \leq a_2$$
$$u_i(a_1,x_2,x_3) - u_i(-a_1,x_2,x_3) = 2a_1\varepsilon_{i1} \quad -a_3 \leq x_3 \leq a_3$$
$$-a_1 \leq x_1 \leq a_1$$
$$u_i(x_1,a_2,x_3) - u_i(x_1,-a_2,x_3) = 2a_2\varepsilon_{i2} \quad -a_3 \leq x_3 \leq a_3$$

$$-a_1 \leq x_1 \leq a_1$$

$$u_i(x_1,x_2,a_3) - u_i(x_1,x_2,-a_3) = 2a_3\varepsilon_{i3} - a_2 \leq x_2 \leq a_2 \qquad (8)$$

Here $2a_j\varepsilon_{ij}$ represents the applied displacement necessary to enforce a strain ε_{ij} over a distance $2a_j$. The strain applied on boundary results in complex state of strain inside the RVE. So, volume average strain in the RVE equals to the applied strain, i.e.

$$\overline{\varepsilon_{ij}} = \frac{1}{V}\int_V \varepsilon_{ij} dV = \varepsilon_{ij} \qquad (9)$$

Considering hybrid composite as homogeneous material, the average stress-strain relationship can be written as

$$\overline{\sigma_\alpha} = C_{\alpha\beta}\overline{\varepsilon_\beta} \qquad (10)$$

By choosing a unit applied strain in one direction and imposing periodic boundary conditions on other directions, stress field can be computed. Whose average value over the volume gives the required components of stiffness matrix, one column at a time;

$$C_{\alpha\beta} = \overline{\sigma_\alpha} = \frac{1}{V}\int_V \sigma_\alpha(x_1,x_2,x_3)dV \qquad (11)$$

Where α, β are varying 1 to 3. Gauss-Legendre quadrature can be used for evaluating the volume integrals of a finite element. Commercial ANSYS have such type of capability to evaluate the average stress over the volume, element by element. Three loading cases are imposed to evaluate the all elastic coefficient of [C] for transversely isotropic composite. Figure 4 shows the meshing of RVEs used in finite element analysis.
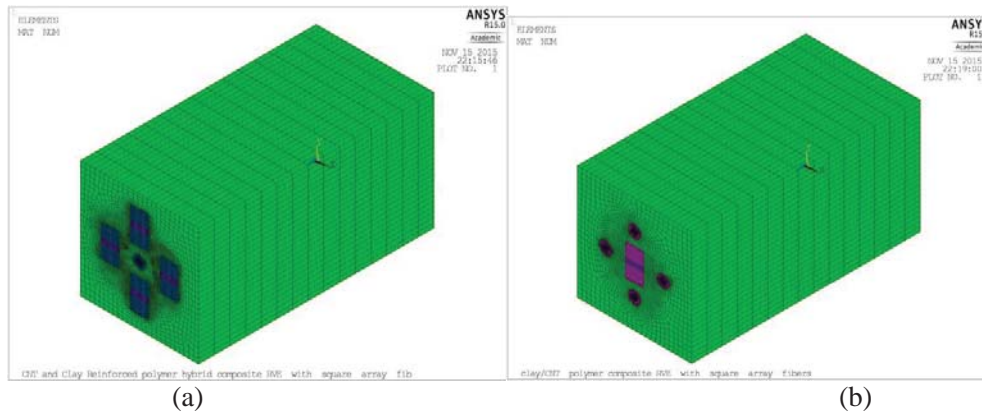

(a)   (b)

Fig. 4:- Meshing of (a) 1 CNT and 4 clay based RVE (b) 1 clay and 4 CNT based RVE

3. Results and discussion

By considering interphase parameters, elastic behavior of nanocomposite reinforced by CNTs and nano-clay plateletsis first analyzed. The advantages of nano-clay in CNT- reinforced polymer composite can be explained with reduction of interfacial reinforcing area of CNTs and enhancing the interfacial adhesion and dispersion of CNTs in polymer. In Fig.5 stress and strain distributionswere shown to explain the elastic behavior of CNT/nano-clay reinforced hybrid composite.

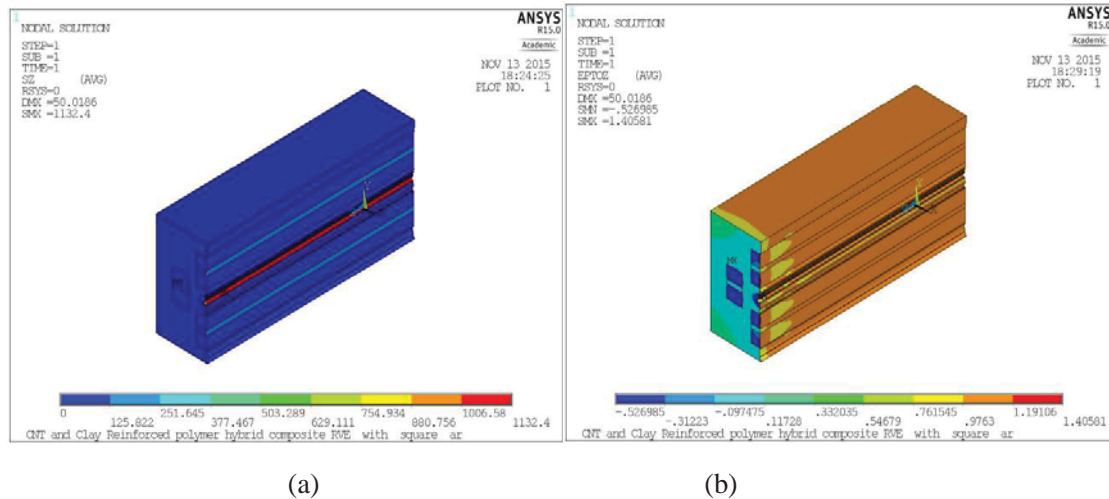(a)   (b)

Fig. 5:- (a) Stress and (b) strain distribution across cross-section of a RVE

The elastic and geometric property of each phase of RVE is listed in table 1. For simplification of calculation RVE length is considered as 50 nm.

Table 1 Material property of all phases in RVE

Material	Elastic Modulus (GPa)	Poisson's ratio (μ)	Geometry
Epoxy	2.026	0.4	25x25 nm
CNT	1054	0.25	r_i=0.315 nm, r_o=0.650
Clay (MMT)	178	0.28	t=4 nm, d_c=1 nm
CNT/polymer interphase	16.10	0.4	r_{int}=1.404 nm
Clay/polymer interphase	16.10	0.4	d_I=3 nm

A case study has been illustrated to reveal the importance of nano-clay reinforcement in CNT reinforced composite. Table 2 shows the elastic properties of CNT/clay hybrid composite considering four types RVE. The finite element modeling results are validated with micromechanical modeling results.

Table 2 Elastic properties of hybrid composite with variation of number of clay platelet

RVE with	E_L	E_T	G_T	υ_L	υ_T
1 CNT	3.667	2.2119	0.738	0.395	0.5054
1 CNT +1 Clay	5.3245	2.420	0.7868	0.3938	0.5382
1 CNT + 2 Clay	7.0019	2.626	0.8468	0.3938	0.5508
1 CNT + 3 Clay	8.6448	2.8338	0.9092	0.3928	0.5582
1 CNT +4 Clay	10.2846	3.0908	0.9929	0.3917	0.5564
Three phase Halpin-Tsai	9.8932	2.9931	0.9865	0.3899	0.5423

In Table 3, elastic moduli are investigated considering constant volume fraction of CNTs inside hybrid composite. It can be concluded from predicted results that four CNTs with one clay based RVE gives better results as compared to one CNT with four-clay RVE.

Table 3 Elastic properties of hybrid composite with variation of Number of CNTs

RVE with	E_L	E_T	G_T	υ_L	υ_T
1 Clay	3.6576	2.3079	0.7719	0.3952	0.4949
1 Clay +1 CNT	5.3236	2.4137	0.7838	0.3948	0.5397
1 Clay + 2 CNT	6.9921	2.4899	0.7963	0.3944	0.5634
1 Clay + 3 CNT	8.6552	2.5700	0.8164	0.3940	0.5753
1 Clay +4 CNT	10.3201	2.6521	0.8381	0.3935	0.5820

4. Conclusions

A nano structured hybrid composite composed of clay nano particle and carbon nanotubes were studied using finite element modeling. For numerical investigations through finite element approach, a square RVE was selected to demonstrate the hybrid composite structure. Predicted values from FE modeling were compared with three-phase Halpin-Tsai model. It was found that the elastic modulus from numerical modelling is in close agreement with micromechanics based results. This work provides basic overview of modeling of hybrid composite; furthermore studies have to be done by considering the variation of interphase properties and random distribution of nano-clay and CNTs. It is also planned to prepare CNT/nano clay polymer composite specimen and perform tensile and compressive test to validate the predicted numerical data.

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