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Elastic modulus measurement of polymer matrix nano-composites reinforced by platelet nano-clays

S. Saber Samandari*

New Technologies Research Centre, Amirkabir University of Technology, Tehran, PO Box 1591633311, Iran.

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ABSTRACT

Polymer-clay nano-composite materials, in which nano-meter thick layers of clay dispersed in polymer matrix, have generally higher mechanical properties than normal polymeric materials. A new three-dimensional unit cell model has been developed for modeling three constituent phases including inclusion, interphase and matrix. The total elastic modulus of nano-composite is evaluated. Numerical results are in good agreement with the previous proposed theoretical modeling. Higher matrix and inclusion elastic modulus both can dramatically increase the total elastic modulus.

Keywords: *Elastic modulus; Nano-composites; Polymer; Nano-clay; Modeling.*

INTRODUCTION

The reinforcement of polymers using inclusions is commonly undertaken in the production of high-performances plastics. In general, composites combine two or more distinct materials in such a way that neither material completely merges with the other, generating properties far more superior to those of the individual components [1]. For this reason, they have been widely used in areas of transportation, construction, electronics and computer products. Nano-composites are a relatively new class of composite materials with inclusions having ultra small dimensions, typically with one dimension smaller than 100 nm. One of the most important platelet reinforcing material is clays. Reinforced polymers with layered clays are generally referred to as polymer clay nano-composites [2-3]. The clay mineral is usually of a layered type or a fraction of silicates with high surface area [4]. Desirable polymer clay nano-composites are highly exfoliated (where individual silicate layers are uniformly dispersed in the polymer matrix and have higher phase homogeneity [5]) after fully intercalation (where polymer chains are sandwiched in between silicate layers), Figure 1.

* Corresponding author:
Saeed Saber-Samandari
New Technologies Research Centre, Amirkabir University of Technology, Tehran, PO Box 1591633311, Iran.
Tel +98 21 6696 4418
Fax +98 21 66402044
Email saeedss@aut.ac.ir

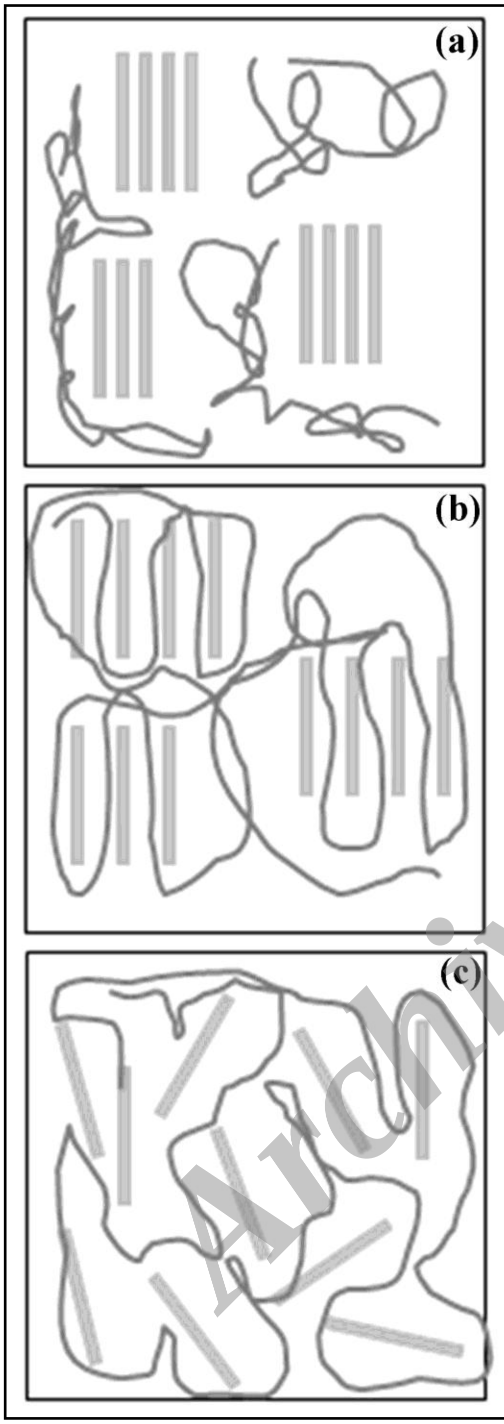

Fig. 1. Schematic representation of A) a conventional phase separated, B) an intercalated, and C) a disordered exfoliated polymer clay nano-composite.

The first commercialized polymer clay nano-composites reported by Toyota Central Research Laboratories [6-7]. Since Toyota research, few thousands research papers have been published with concept of clay as an inclusion for polymer matrices [8-11]. Nowadays, polymer clay nano-composites are studied for their improved mechanical properties such as elastic modulus [12-14]. Doubled elastic modulus value at a loading of only 4.2 wt% of nylon-6 was reported by Toyota researchers.

Computational modelling of material mechanical properties is becoming a more reliable tool to investigate and to complement theoretical and experimental approaches. Considerable efforts have been made in recent years to determine the mechanical properties of composites by using FEA (Finite Element Analysis) [15]. The objective of this work is to numerically measure the elastic modulus of polymer clay nano-composites. To achieve this objective, a three-dimensional unit cell was built in order to investigate and illustrate the effect of platelet shape inclusions and the role of the interphase as a third phase on total nano-composite's elastic modulus.

EXPERIMENTAL

Finite Element Analysis (FEA)

A sweep meshing technique with hex (inclusion and matrix) and wedge (interphase) element shape in the case of three-phase unit cell was carried out, Figure 2. The FEA outcomes should be more accurate as the model is subdivided into smaller elements (the process of dividing a large amount of finite element mesh into sub-regions). The only confident way to know if one has a sufficiently dense mesh is to make several models, changing the seed number and check the discrepancy of one mechanical property such as displacement at the two different seed numbers. From Table 1, it can be concluded that the difference between the results of the last meshes (seed numbers 0.3 and 0.2) are less than 0.4%, thus the further subdivision appears unnecessary. A commercial finite element package, ABAQUS 6.4, was used in this study. Reinforced nano-composites with platelet inclusions were modelled by around 25,500 elements (1980 for inclusion, 6666 for interphase and 16896 for matrix). The following assumptions were also made in this numerical study: the nano-composite is microscopically homogenous, matrix and nano-platelets are isotropic and all three phases are completely tied together. Nano-platelets are uniformly distributed in the matrix, since uniform dispersion constructs interfacial coupling between the individual layers and the polymer matrix facilitating the stress transfer to the reinforcement phase. This reduces the weak points present in conventional polymer composites [9].

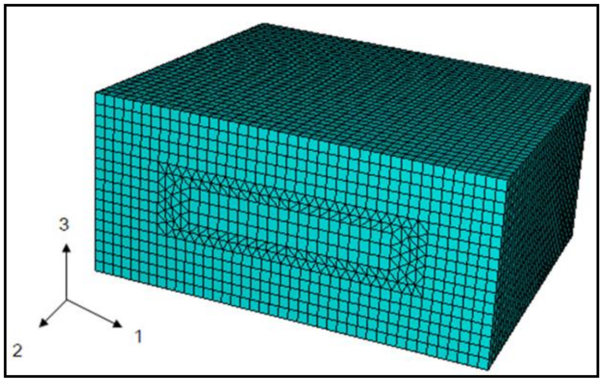

Fig. 2. Typical mesh used in the finite element analysis. Matrix dimensions were taken 5x12x10 nm

Table 1. Minimum displacement with a three-phase platelet model

Seed	Inclusion	Interphase	Matrix
2	2.38E-04	1.07E-06	3.00E-06
1	2.08E-04	1.31E-06	2.89E-06
0.9	2.08E-04	1.32E-06	2.87E-06
0.8	2.30E-04	1.22E-06	2.94E-06
0.7	2.30E-04	1.23E-06	2.94E-06
0.6	2.51E-04	1.35E-06	2.86E-06
0.5	2.42E-04	1.30E-06	2.87E-06
0.4	2.52E-04	1.32E-06	2.91E-06
0.3	2.53E-04	1.34E-06	2.91E-06
0.2	2.54E-04	1.35E-06	2.89E-06

Tensile load is applied via a prescribed displacement onto the front face in the 2-direction; Figure 3, while there are no tractions in other directions thus, the applied shear stresses on all faces of the unit cell is zero. There are six different boundary conditions to calculate by the FEA. Top and right faces will remain parallel to the original position after being displaced in the 2-direction, F1= 0 =F2 and F2= 0 =F3 for these two faces, respectively. Fs represent the normal force acting on faces and are set to zero to simulate a simple unidirectional tension test in the 2- direction.

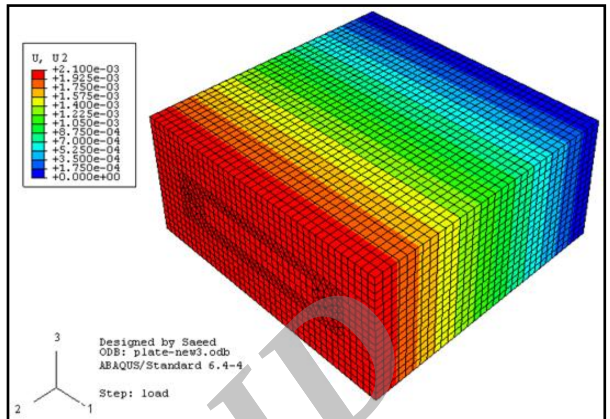

Fig. 3. Simulated displacement distribution in a three-phase nano-composite reinforced by a nano-platelet.

Moreover, all shearing stresses on all boundaries were set to zero. In order to satisfy this requirement, an arbitrary point, which does not belong to any part of the model and is allowed to freely move in any direction was created and related to all nodes on the right face. It was found that displacement of all element nodes on this face in 1- direction are the same and equal to that of the arbitrary point [16]. Thus, one can conclude that no external force is applied onto this face.

The back face is fixed in 2-direction, U2=0=UR1=UR2=UR3 so the displacement on this face is zero. On the both faces, the symmetry boundary, the left face: U1= 0 = F2 = F3 and also the bottom face: U3 = 0 = F1 = F2 were imposed everywhere. These boundary conditions ensure that the cells which are rectangular blocks of material around the inclusion remain rectangular and will stack to completely fill the material space. Thus, compatibility requirements between cells are satisfied.

Poisson's ratio of nano-clay, polymer and interphase were assumed 0.2, 0.45 and 0.4, respectively [17]. Matrix dimensions were taken 5x12x10 nm. The following analysis was carried out in order to calculate the nano-composite elastic modulus "E".

$$E = \frac{\sigma_2}{\varepsilon_2} \quad (1)$$

Where, σ_2 and ε_2 are the stress and the strain in 2-direction. The average value of stress σ_2 is given by:

$$\sigma_2 = \frac{1}{A}\int_A \sigma_y(x,z)d_x d_z \quad (2)$$

Where, A is the cross section. ε_2 is the strain in 2-direction and can be obtained by:

$$\varepsilon_2 = \frac{\Delta L}{L} \quad (3)$$

Where, ΔL and L are prescribed displacement and initial length respectively.

RESULTS AND DISCUSSION

The FEA results of this study are in good agreement with the previously proposed theoretical results [17]. The agreement between all results leads to conclusion that material properties such an elastic modulus could be successfully predicted numerically.

Effect of inclusion properties

From the FEA results in Figure 4, the total elastic modulus is seen to increase with increasing inclusion elastic modulus as expected from the previously proposed theoretical model. The elastic modulus of different types of clay has reported from 20 to 200 GPa [18]. In this study, we have also chosen the range of 20 to 200 GPa for the inclusion elastic modulus. The FEA result has shown a limitation regarding inclusion property that is a discrepancy between FEA and theoretical values when inclusion elastic modulus is less than 20 GPa (not shown here), however, results revealed that FEA is a powerful tool to predict the behaviour of effect of inclusion properties on total elastic modulus.

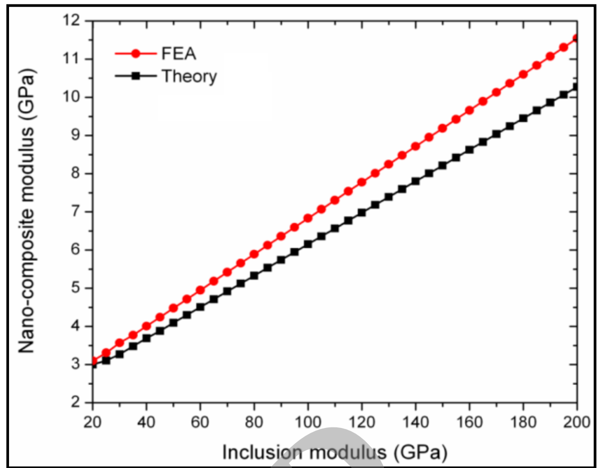

Fig. 4. Effect of inclusion elastic modulus on total elastic modulus of nano-composite.

Effect of matrix properties

In order to study the effect of matrix elastic modulus on total nano-composite elastic modulus, one must be able to carry out computations with a large range of finite elements. For this purpose, we have chosen the range of 1 to 5 GPa for the polymer matrix. Figure 5 shows that finite element results are consistent with the theoretical results. It is expected that total elastic modulus increases with increasing matrix modulus.

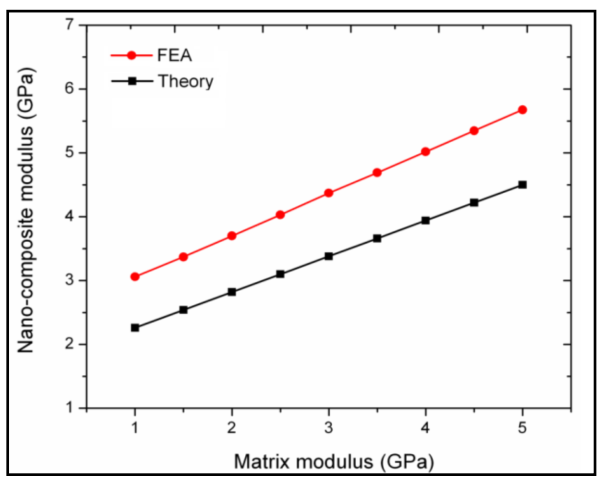

Fig. 5. Effect of matrix elastic modulus on total elastic modulus of nano-composite.

Effect of interphase thickness

An interphase of 1 nm thick represents roughly 0.3% of the total volume of polymer in the case of micro- particle filled composites, whereas it can reach 30% of the total volume in case of nano-composites [19]. Therefore, volume of interphase plays a central role in nano-composite materials. However, different inclusion shapes exhibit different reinforcement. If inclusions size d surrounded by interphase size D (see Figure 6) then the area becomes βd^2 where β is large due to high aspect ratio.

Volume of inclusion is $v_f = \beta d^3$ and

volume of interphase is $v_i = \beta d^2 (D - d)$. If there are n inclusions per m^3 then

inclusion volume fraction becomes $V_f = n * v_f = n * \beta d^3$ and also

interphase volume fraction becomes $V_i = n * v_i = n * \beta d^2 (D - d)$

therefore, $V_i = V_f \left[\left(D/d \right) - 1 \right]$.

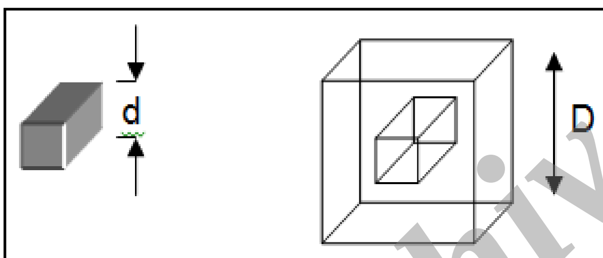

Fig. 6. Schematic of an inclusion and surrounded matrix.

Effect of inclusion volume fractions

Figure 7 presents the theoretical and finite element values of elastic modulus from 0.05% to 15% inclusion volume fraction. Unfortunately, it is well established that adding more than 20% inclusion volume fraction cause reduction in mechanical properties and improvement fails to occur due to chemical interaction between particles or low intercalation percentage. Subsequently, neither reduction in elastic modulus was observed from FEA, nor from theoretical studies. Thus, analyses were carried out up to 15% reinforcement volume fraction. Finite element values showed that elastic modulus increase with increase in reinforcement volume fraction as expected from theoretical studies. As a result, from the FEA and theoretical results, it can be concluded that mechanical properties in general and elastic modulus in particular increase dramatically below 20 wt% clay addition. It is worthwhile to mention that in this study the FE models have platelets stacked in neat geometric arrays. This is not so in the real nano-composite and the effect of inclusion randomness is difficult to simulate in FE models and difficult to include in theoretical models.

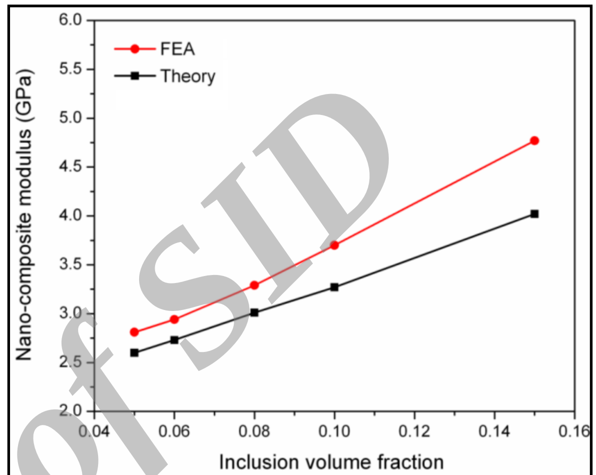

Fig. 7. Effect of inclusion volume fraction on total elastic modulus of nano-composite.

CONCLUSIONS

This study leads to the conclusions that:

- Good agreement has been obtained between previously proposed theoretical models and the current FEA results of total elastic modulus of nano-composite materials.
- Finite element results support the view that the interphase plays a role on the elastic modulus and cannot be neglected.
- Theoretical and FEA studies show that total elastic modulus increases with increasing reinforcement volume fraction, contrasting with experimental studies for more than 20 wt% which display decreases.
- Analytical magnitudes are quite close to FEA solutions, based on 3-D elasticity, with a difference of only 1.5%. Therefore, the earlier analytical model may serve as a quick tool to estimate the elastic modulus of composite materials, which are reinforced by nano-platelet.

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