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A numerical study on reinforced composites by spherical nano-particles

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ABSTRACT

In the current paper, finite element method is employed for numerical simulations and the study of influential parameters on elastic modulus of polymer-matrix nano-composites. Effects of different key parameters including particle elastic modulus, interphase elastic modulus, matrix elastic modulus, interphase thickness and particle volume fraction on total elastic modulus of nano-composite materials are observed in order to shed some light on experimental parameters that are difficult to measure. To this end, a three phase (i.e. particle, interphase and matrix) unit cell is modelled and results compare with previously introduced theoretical model. It is found that interphase parameters such as elastic modulus and thickness strongly influences the elastic properties of the nano-composite and cannot be neglected.

Keywords: *Nano-composites; Nano-particles; Finite Element Analysis; Elastic modulus; Polymer*.

INTRODUCTION

Nano-composites are a novel class of composite materials where one or two phases have dimensions in the range of 1 to 100 nm and have dramatically increased surface area compared to conventional-size materials. Although polymer nano-composites were developed in the late 1980s in both commercial research organizations and academic laboratories, these developments were not significant because they did not result in improvement in mechanical properties. After a decade, nano-composites have attracted much attention, particularly since the Toyota research group showed that the tensile properties of nano-composites were greatly improved [1, 2]. Later, researchers have shown that a significant improvement in a wide range of engineering properties could be achieved with a low particle volume fraction (i.e. 1-5 %) in nano-composite materials compared with conventional reinforced composites [3].

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Large numbers of researchers have conducted numerical studies using a two-phase model [4]. However, they ignored the existence of an interphase (interphase is a third phase between particle and matrix and has own mechanical properties) developing during the preparation of composite materials. Theocaris et al. have shown the important role of this third phase by investigating the effect of interphase thickness on the mechanical properties of the composites [5]. Theoretical analyses for elastic modulus can be achieved by numerical methods [6]. The effects of different interphase properties on total elastic modulus have been investigated using finite element methods [7].

The lack of understanding of the mechanisms of the enhancement effect is a major difficulty in nano-composite materials. In this study, three-dimensional unit cell is modelled to help more understanding of nano-composite fracture mechanisms. Although the elastic modulus measurement as the most interesting property has been the subject of many composite and nano-composite studies, there are still areas that are not well understood and explored. This study aims at contributing in the numerical modelling of polymer matrix nano-composites reinforced by nano-spherical particles. Several variables of interest are considered, including: particle modulus, matrix modulus, interphase thickness, interphase modulus and volume fraction.

COMPUTATIONAL METHODS

Computational modelling

The modelling 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. Figure 1 shows a three-phase unit cell of nano-composite including matrix, interphase and particle. A commercial finite element package, ABAQUS 6.4, was used. Spheres were modelled by around 15,200 elements (3024 for particle, 1296 for interphase and 10871 for matrix).

Table 1. Maximum displacement with a three-phase

Seed	Particle	Interphase	Matrix
2	9.41E-06	1.75E-05	7.16E-05
1	7.86E-06	1.51E-05	6.78E-05
0.9	8.30E-06	1.47E-05	6.67E-05
0.8	8.61E-06	1.49E-05	7.34E-05
0.7	8.41E-06	1.42E-05	6.66E-05
0.6	8.65E-06	1.51E-05	6.73E-05
0.5	9.09E-06	1.43E-05	6.67E-05
0.4	8.33E-06	1.41E-05	6.64E-05
0.3	8.30E-06	1.42E-05	6.64E-05
0.2	8.29E-06	1.42E-05	6.64E-05
0.1	8.30E-06	1.42E-05	6.64E-05

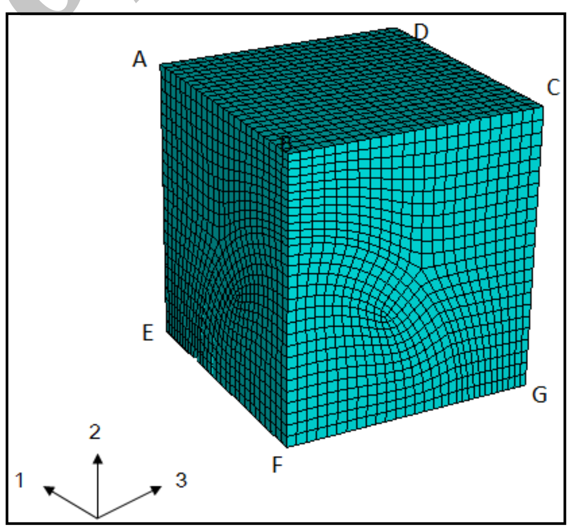


Fig. 1. Typical mesh used in the finite element analysis.

Dispersion status and boundary conditions

In the first step of dispersing the particles in the matrix, the polymer is unable to increase the distance between the particles (Figure 2a). The mechanical properties either stay in the same range as traditional composites or reduce. Thus, researchers are not satisfied with phase-separated composites. However, when polymer chains extend through the particle clusters an *intercalated* structure is obtained (Figure 2b). An *exfoliated* structure is more desirable in enhancing the properties of the nano-composites (Figure 2c). As a result, in this study, nano-particles are assumed uniformly distributed in the matrix and matrix and nano-particles are isotropic and all three phases are completely tied together.

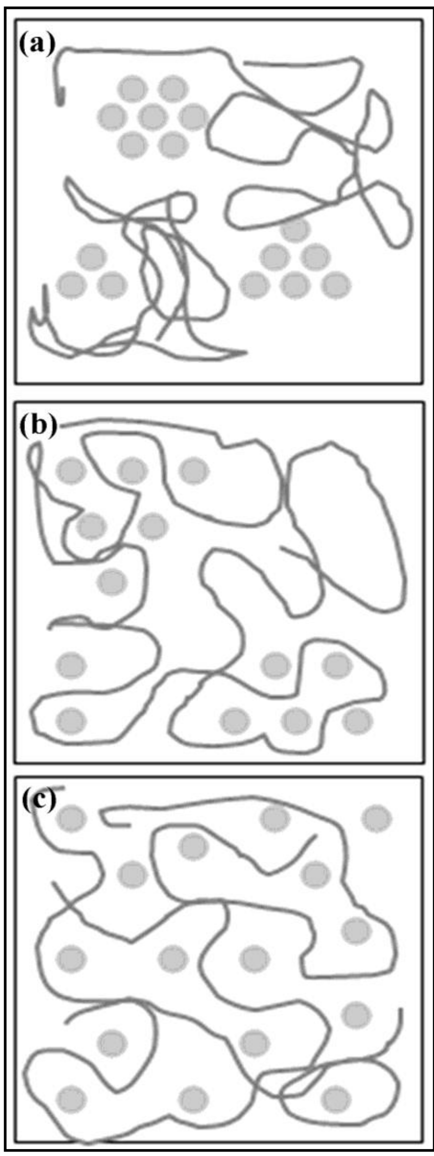


Fig. 2. Scheme of different types of nano-composites: 1.A) phase separated nano-composite, 1.B) intercalated nano-composite and 1.C) exfoliated nano-composite (Squiggly lines indicate polymer chains and geometric shapes represent particles)

Tensile load is applied via a prescribed displacement onto the face ABCD 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 modelling. Face CDHG and ADHE 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. 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 face ADHE. 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 [8]. Thus, one can conclude that no external force is applied onto this face. Face EFGH is fixed in 2-direction, U2 = 0 = UR1 = UR2 = UR3 so the displacement on this face is zero. On both the symmetry faces, the symmetry boundary, face BCGF: U1= 0 = F2 = F3 and also face ABFE: U3 = 0 = F1 = F2 were imposed everywhere since one-eighth of sphere model was analysed. These boundary conditions ensure that the cells, which are rectangular blocks of material around the particle, remain rectangular and will stack to completely fill the material space. Thus, compatibility requirements between cells are satisfied.

Theoretical background

Particle size has a dramatic effect on the resulting polymer nano-composite properties [9], and the improvement in properties when going from micron to nano sized filler particles can be large. In this study, matrix dimension was taken 10x10x10 nm^3 for sphere model. The following analysis was carried out in order to find the elastic modulus "E".

$$E = \frac{\sigma_2}{\varepsilon_2}$$

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:

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

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

$$\varepsilon_2 = \frac{\Delta L}{L}$$

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

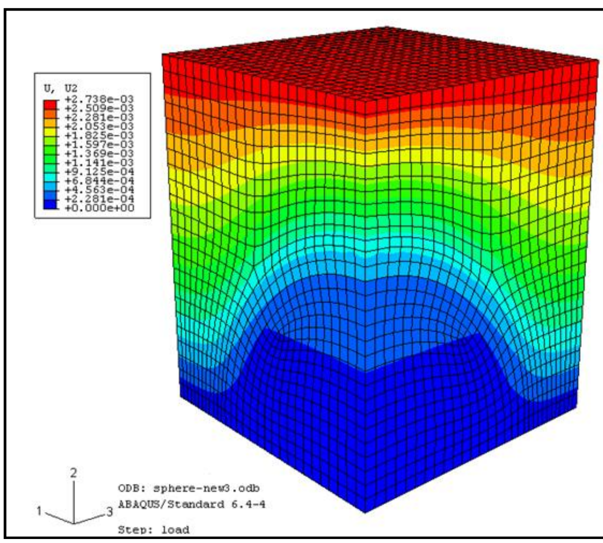


Fig. 3. Representative volume element of the axisymmetric spherical cell model after applying a tensile load.

RESULTS AND DISCUSSION

Effects of particle properties

From the numerical results in Table 2, the modulus is seen to increase with increasing particle mechanical properties as expected from the analytical equation [10]. In the case of the spherical model, results in Table 2 show good agreement between the theoretical and the numerical values.

Table 2. Effect of particle elastic modulus (GPa) on total theory and modelling elastic modulus (GPa)

Particle modulus	Nano-composite modulus	
	Theory	Modelling
25	3.74	4.56
30	4.08	4.68
35	4.43	4.76
40	4.78	4.85
45	5.12	4.88

Note: $E_m = 2$ (GPa), $r_f = 3$ (nm), $r_i = 3.5$ (nm), $d_s = 2$ (nm), $V_f = 0.1$ and intragallery enhancement factor = 40

Effects of matrix properties

In order to study the effect of matrix mechanical properties on total elastic modulus, one must be able to carry out computations with a large range of finite elements. For this purpose, the range of 1 to 3 GPa for the polymer matrix elastic modulus has been chosen. Table 3 shows that finite element results are consistent with the theoretical results. It is expected that total elastic modulus increases with increasing matrix modulus.

Table 3. Effect of matrix elastic modulus (GPa) on total theory and modelling elastic modulus (GPa)

Matrix modulus	Nano-composite modulus	
	Theory	Modelling
1.0	3.07	2.83
1.5	3.58	3.92
2.0	4.08	4.68
2.5	4.59	5.28
3.0	5.10	5.64

Note: $E_f = 30$ (GPa), $r_f = 3$ (nm), $r_i = 3.5$ (nm), $d_s = 2$ (nm), $V_f = 0.1$ and intragallery enhancement factor = 40

Effects of interphase properties

Applicability of the finite element method in predicting the effect of interphase property has been studied here. The effect of interphase properties was investigated on the basis of a simple stack pattern at a fixed particle content of 0.1 volume percentage (see Table 4). The total elastic modulus of the model, estimated by earlier theoretical solution [10], is also listed in Table 4. According to the numerical results, the interphase properties play an important role in nano-composite elastic modulus. Results indicate that nano-composite properties are sensitive to interphase property.

Table 4. Effect of interphase elastic modulus (GPa) on total theory and modelling elastic modulus (GPa)

Index	Interphase modulus	Nano-composite modulus	
		Theory	Modelling
20	4.67	4.20	4.82
30	3.88	4.13	4.73
40	3.48	4.08	4.67
50	3.22	4.06	4.63
60	3.05	4.04	4.60

Note: E_f = 30 (GPa), E_m = 2 (GPa), $r_{f\,=}$ 3 (nm), r_i = 3.5 (nm), d_s = 2 (nm) and V_f = 0.1

Effects of interphase thickness

In the previous subsections, the interphase thickness was considered to be constant at 1 nm. The effect of varying the interphase thickness in determining the total elastic modulus was investigated. A parametric study of the interphase thickness is listed in Table 5. It can be seen that finite element results are in good agreement with theoretical values. Moreover, as expected from earlier equations [10], total elastic modulus increases with increasing interphase thickness. This can be interpreted by the fact that the interphase becomes an independent part of the system. Interestingly, by adding only 2 nm to the interphase thickness, the total elastic modulus increases 6.5%. As expected, Table 5 reveals that total elastic modulus increases sharply by adding only 1 nm to the interphase thickness and then increases more gradually with thickness increase. 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 [11].

Table 5. Effect of interphase thickness (nm) on total theory and modelling elastic modulus (GPa)

Interphase thickness	Interphase modulus	Nano-composite modulus	
		Theory	Modelling
3.5	3.48	4.08	4.68
4.0	3.60	4.10	4.79
4.5	3.71	4.11	4.92
5.0	3.80	4.12	5.01

Note: E_f = 30 (GPa), E_m = 2 (GPa), $r_{f\,=}$ 3 (nm), d_s = 2 (nm), V_f = 0.1 and intragallery enhancement factor = 40

Effects of particle volume fractions

To investigate the effect of particle volume fraction on mechanical properties a three-phase unit cell nano-composites were modelled. Table 6 presents the theoretical and finite element values of elastic modulus from 0% to 15% particle volume fraction. Unfortunately, it is well established that adding more than 20% particle volume fraction cause reduction in mechanical properties and improvement fails to occur due to chemical interaction between particles or low intercalation percentage [12].

Table 6. Effect of particle volume fraction on total theory and modelling elastic modulus (GPa)

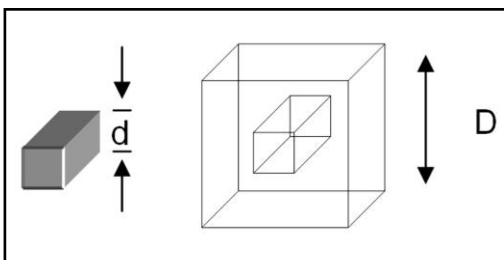
Volume fraction	Nano-composite modulus	
	Theory	Modelling
0.05	2.99	3.99
0.06	3.21	4.12
0.08	3.63	4.39
0.10	4.08	4.68
0.15	5.31	5.34

Note: E_f = 30 (GPa), E_m = 2 (GPa), $r_{f\,=}$ 3 (nm), r_i = 3.5 (nm), d_s = 2 (nm) and intragallery enhancement factor = 40

Subsequently, neither reduction in mechanical properties was observed from numerical or from theoretical studies. Thus, analyses were carried out up to 15% particle volume fraction. Finite element values showed that elastic modulus increases with increase in particle volume fraction as expected from theoretical studies [10]. As a result, from the numerical and theoretical results, it can be concluded that mechanical properties in general and elastic modulus in particular can increase dramatically below 2-20 wt% particle addition. In this study the finite element model has particles stacked in neat geometric arrays. This is not so in the real nano-composite and the effect of particle randomness is difficult to simulate in modelling and difficult to include in theoretical models.

Relationship between volume fraction and particle shape

Reynaud et al. showed that an interphase of 1 nm thick represents roughly 0.3% of the total volume of polymer in case of micro particle filled composites, whereas it can reach 30% of total volume in case of nano- composites [11]. Therefore, volume of interphase plays a central role in nano-composite materials. However, different particle shapes exhibit different reinforcement. If particles size “d” surrounded by interphase size “D” then



Regular particles: (Spherical, Cubic)

Volume of particle = $v_f = c.\ d^3$

Volume of interphase = $v_i = c.\ (D^3 - d^3)$

Where c = 1 for cubic and $\pi/8$ for spherical. If there are n particles per m^3 then

Particle volume fraction = $V_f = n.\ v_f = n.\ c.\ d^3$

Interphase volume fraction=$V_i = n.\ v_i = n\ c.(D^3 - d^3)$

Therefore $$V_i = V_f\left[\left(D/d\right)^3 - 1\right] \qquad (1)$$

Long prismatic particles: (Cylindrical)

Assume a length αd where α is large due to high aspect ratio.
Volume of particle = $v_f = \alpha d^3$

Volume of interphase = $v_i = \alpha(\ dD^2 - d^3)$

If there are n particles per m^3 then

Particle volume fraction = $V_f = n.\ vf = n.\alpha d^3$

Interphase volume fraction=$V_i = n.vi = n.\alpha(dD^2 - d^3)$

Therefore $$V_i = V_f\left[\left(D/d\right)^2 - 1\right] \qquad (2)$$

Short prismatic particles: (Platelet)

Assume an area βd^2 where β is large due to high aspect ratio.

Volume of particle = $v_f = \beta d3$

Volume of interphase = $v_i = \beta d^2\ (D - d)$

If there are n particles per m^3 then

Particle volume fraction = $V_f = n.\ v_f = n.\beta d^3$

Interphase volume fraction=$V_i = n.v_i = n.\beta d^2\ (D - d)$

Therefore $$V_i = V_f\left[\left(D/d\right) - 1\right] \qquad (3)$$

From equations (1), (2) and (3) and at the same volume of reinforcement with reasonable assumption of D = 2d
For spherical particles: $V_i = 7\ V_f$
For cylindrical particles: $V_i = 3\ V_f$
For platelet particles: $V_i = V_f$
Therefore V_i sphere > V_i cylinder > V_i platelet

CONCLUSIONS

Good agreement has been obtained between theoretical models and the current numerical results of total elastic modulus of nano-composite materials. Numerical results support the view that the interphase plays a role on the mechanical properties and cannot be neglected.

Theoretical and numerical studies show that total elastic modulus increases with increasing particle volume fraction, contrasting with experimental studies for more than 20 wt% which display decreases. Analytical magnitudes are quite close to modelling solutions, based on 3-D elasticity, with a difference of only 1.5%.

Therefore, the earlier analytical equations may serve as a quick tool to estimate the elastic modulus of nano-composite materials, which are reinforced by nano-particles. Ideal nano-composites have not been achieved yet (100% intercalation and 100% exfoliation) and there will be a great deal of interest in the near future of nano-composites by achieving high intercalation ratio, high exfoliation ratio, perfect modelling, understanding all effective parameters.

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