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A new approach in modeling of mechanical properties of nanocomposites: effect of interface region and random orientation

**Esmail Sharifzadeh · Ismail Ghasemi ·
Mohammad Karrabi · Hamed Azizi**

Abstract The Young's modulus of polymer nanocomposites is predicted using a numerical approximation system (NAS) model based on fully exfoliated nanoparticles, random orientation (with platelet and cylindrical forms), and nanoparticles of specific shapes (e.g., square platelets, nanotubes, and spherical). The thickness of interface between the polymer matrix and nanoparticles which plays an important role in reinforcing mechanism of nanocomposites is also employed in NAS model as a crucial parameter. The modulus of interface region on the surface of nanoparticle is another significant parameter which is taken into account through mathematical modeling procedure of NAS model as it may indicate the manner by which the polymer matrix bonds to the surface of nanoparticles. NAS model proposes a general formulation through which the Young's modulus of a nanocomposite could be easily predicted, while the involving parameters change due to the shape of nanoparticle (e.g., platelet, cylindrical or spherical). The final predications of NAS model are validated by comparing them with the results of tensile tests for polyamide (PA)/Cloisite 30B nanocomposite system and the results reported in other similar studies on the mechanical properties of polymer nanocomposites.

Keywords Modeling · Polymer nanocomposite ·
Interface region · Random orientation · Mechanical
properties · Young's modulus

Introduction

Polymer nanocompsites have attracted a lot of attention due to their high performance which is attributed to the drastic enhanced effects of nanoparticles on mechanical properties. However, they excel other common counterpart-composites in lighter weight and less required reinforcements. Consequently, many investigations have been carried out to model the mechanical properties of this group of materials. Halpin presented a model for laminated systems assuming randomly oriented fibers in a matrix [1, 2]. Other researchers have intended to develop the theory of a rigid dispersed phase in a non-rigid matrix, based on Einstein's equation to calculate the viscosity of a suspension of rigid inclusions [3–5]. Assuming interactions between the dispersed particles, Deng et al. [6, 7] proposed a model termed as "interaction direct derivation" (IDD), in which Eshelby tensors were used to impose the influence of particle shape in the model. Takayanagi [8] introduced another model assuming the semi-crystalline polymers consisting of amorphous and crystalline phases used for polymer composites, blends, and also nanocomposites. Jianfeng et al. [9] proposed a straight forward analytical approach to estimate the mechanical properties of polymer nanocomposites. Their model could treat nanocomposites comprised of nanoparticles as isolated or aggregated dispersed phase.

Based on different assumptions, there are further models which describe the mechanical response mechanisms of polymer nanocomposites against applied stresses. However, a nanocomposite consists of three different phases (matrix, interface, and reinforcing phase). By enhancing the mechanical properties, interface plays a remarkable role in nanocomposite systems. Most of the introduced models suffer from lack of accuracy in the final results caused by ignoring the interface region which

E. Sharifzadeh · I. Ghasemi (✉) · M. Karrabi · H. Azizi
Department of Plastics, Iran Polymer and Petrochemical Institute,
P.O. Box 14965/115, Tehran, Iran
e-mail: i.ghasemi@ippi.ac.ir

has an irrefutable quota in nanocomposites' mechanical properties. By taking into account the interface region in Takayanig's model, Xiang et al. [10] found better agreement and more reliable results in mechanical properties of the nanocomposites. Deng et al. [11] considered effective particles, comprised of nanoparticles and interface factor, to simplify the calculation procedure. This was a new approach in which a nanocomposite can be considered as a convenient short- or long-fiber composite. In the case of platelet and cylindrical nanoparticles, the orientation should be considered as an important factor. Xing et al. have assumed two vertical and perpendicular orientations of particles to the direction of exerted stress which certainly improves the results. This parameter has a key role by which the accuracy of model can be affected. In this work, random orientation of nanoparticles in a nanocomposite is assumed to be comprised of interface region. It is essential to find out that how an exerted stress works on the interface region due to the orientation angle. Unlike the recently published works, a basically different model is presented here which describes the mechanical properties of all specific composites comprised of plate-like, cylindrical, or spherical nanoparticles. The thickness of interface and the modulus of the surface of nanoparticles are two important parameters which both directly affect the properties. In this study, a numerical approximation system (NAS) is proposed to predict the mechanical properties of nanocomposites including the influence of effective parameters. Furthermore, based on the error value, more than one possible answer could be found for the interface thickness and the modulus of the surface of nanoparticle. Therefore, the best answer could be reasonably chosen. Bonding between the functions on the surface of a nanoparticle and the corresponding groups on the polymer chain causes a variation of modulus in normal direction of nanoparticle surface. This effect continues towards the end of interface region where after the modulus does not change any more.

Samples of PA/Cloisite 30B were prepared to check the accuracy NAS model. Besides, other data from corresponding investigations were also used to prove the generality of our model.

Model background

NAS model can be proposed in three different sections:

1. Nanocomposites including platelet nanoparticles.
2. Nanocomposites including cylindrical nanoparticles.
3. Nanocomposites including spherical nanoparticles.

Equivalent box model (EBM) is used in order to simplify the assumed geometrical structure of NAS model [8,
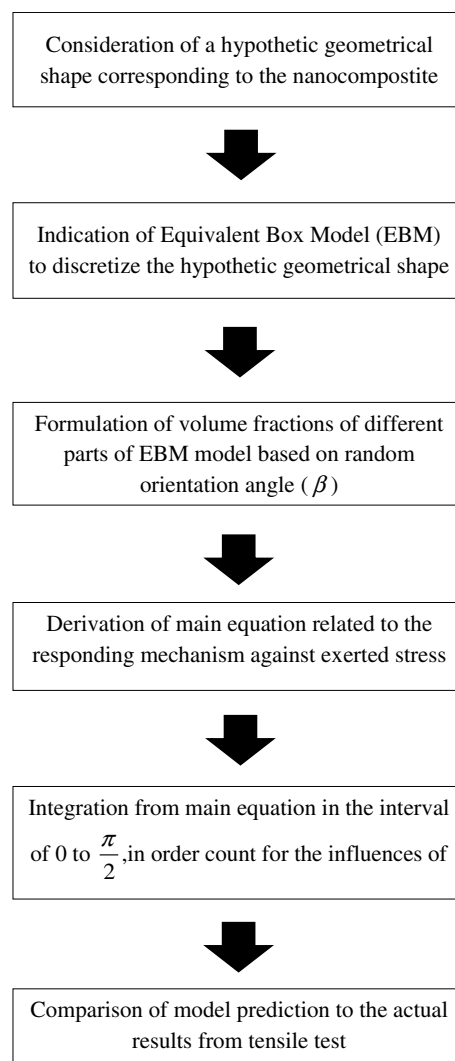
Scheme 1 Flow chart describing the whole analytical process under study

12]. The variation of modulus at the interface is assumed to be linear to simplify the calculation of modulus which characterizes the mechanical properties of this region. Here, the constituted particles in the polymeric matrix are considered to be fully exfoliated, which is a general presumption for the given sections which are totally reliable at low content of dispersed phase and good mixing. Interface, nanoparticle, and matrix region are assumed to be isotropic in nanoscale as well as nanocomposite in macroscale. In interface region, the bonding between nanoparticle and matrix is extremely stiff which loses its failure possibility during the exposure to any stress. Modeling algorithm is based on unidirectional exposed stress on the surface of nanocomposite, whereas the dispersed phase is assumed to be randomly oriented and the direction of exerted stress is ignorable. Scheme 1 illustrates a flowchart describing the whole analytical process.
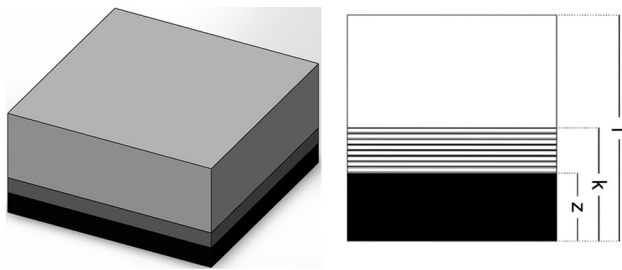
Fig. 1 The 3D geometrical structure of NAS model and its corresponding 2D structure for nanocomposites comprising platelet nanoparticles
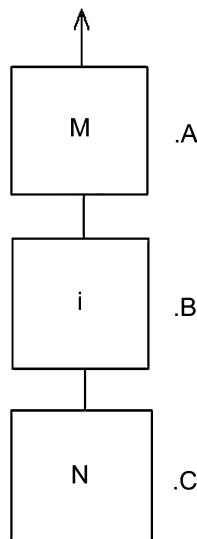

Fig. 2 Considered equivalent box model (EBM) corresponding to the 2-D assumed structure of nanocomposite comprised of platelet nanoreinforcing particles. Subscripts *M*, *i,* and *N* denote matrix phase, interface region, and nanoparticle, respectively

Nanocomposites comprised of platelet nanoparticles

Figure 1 illustrates the proposed model schematically, which consists of nanoparticle, interface, and matrix phases. Each region is considered as a discrete part which acts separately based on its volume fraction. The orientation angle of nanoparticles to the direction of exerted stress is indicated as β, which is in the range of 0°–90°.

EBM model is used to show how three different constituent parts are arranged in series (Fig. 2). For each *A*, *B,* and *C* sections in Fig. 2, the volume fractions are as follows:

$$\phi_A = 1 - k$$
$$\phi_B = k - z \qquad (1)$$
$$\phi_C = z,$$

where k and z are the model parameters.

As shown in Fig. 3, increasing β to the values higher than 0°, the exerted stress (σ) will be segregated into two
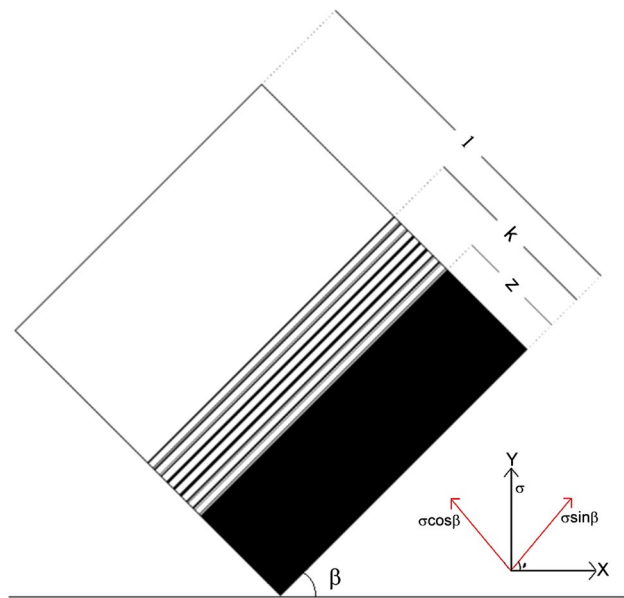

Fig. 3 Effects of nano-reinforcing particles orientation angle (β) on the considered structure of NAS model

different stress components which are, $\sigma \sin(\beta)$ and $\sigma \cos(\beta)$ (Fig. 3).

Subsequently the strain corresponding to each section of EBM model is

$$\varepsilon_A = \frac{\sigma \cos(\beta)}{E_A}$$
$$\varepsilon_B = \frac{\sigma \cos(\beta)}{E_B} \qquad (2)$$
$$\varepsilon_C = \frac{\sigma \cos(\beta),}{E_C}$$

where σ is the unidirectional exerted stress, E_M, E_i, and E_N are the modulus of polymeric matrix, interface region, and nanoparticle, respectively.

Final strain of the components in series arrangement:

$$(\varepsilon_c)_s = \varepsilon_A \phi_A + \varepsilon_B \phi_B + \varepsilon_C \phi_C \qquad (3)$$

While there are two perpendicular stress components, it can be helpful to use Poisson's ratio to correlate two induced strains on different directions. However, the stress component $\sigma \sin(\beta)$ can be considered as shear stress exerted on the geometrical structure and the corresponding EBM model which results as

$$G_c = \frac{1}{\frac{\phi_C}{G_C} + \frac{\phi_B}{G_B} + \frac{\phi_A}{G_A}}$$
$$G = \frac{E}{2(1+\vartheta)} \text{ and } E = \frac{\sigma \sin(\beta)}{\varepsilon} \qquad (4)$$
$$(\varepsilon_c)_P = \left[\frac{\phi_C}{E_N}\frac{(1+\vartheta_C)}{(1+\vartheta_{Cc})} + \frac{\phi_B}{E_i}\frac{(1+\vartheta_B)}{(1+\vartheta_{Cc})} + \frac{\phi_A}{E_M}\frac{(1+\vartheta_A)}{(1+\vartheta_{Cc})}\right]\sigma \sin(\beta)$$

where ϑ_A, ϑ_B, and ϑ_C are the Poisson's ratio for matrix, interface, and nanoparticle, respectively and G is the shear modulus of different parts. Generally the Poisson's ratio for polymers is in the range of 0.3–0.5 [13]. In this case, the Poisson's ratio for composite obeys the rule of mixtures:

$$\vartheta_{Cc} = \phi_A \vartheta_A + \phi_B \vartheta_B + \phi_C \vartheta_C, \tag{5}$$

where ϕ indicates the volume fraction and subscripts M, i, and N denote matrix phase, interface region, and nanoparticle, respectively.

The modulus of interface is a linear function of distance from the surface of nanoparticles [10]:

$$E_i(a) = E_i(0) + \frac{E_M - E_i(0)}{k - z}(a - z), \tag{6}$$

where $E_i(0)$ is the modulus of interface region on the surface of nanoparticle and a is the variable thickness of interface in the normal direction.

Using reverse mixtures rule, the modulus of interface region can be calculated:

$$\frac{1}{E_B} = \frac{1}{(k - z)} \int_z^k \frac{da}{E_i(a)}, \tag{7}$$

whereas both shear and tensile components of exerted stress are functions of β, the modulus of nanocomposite should be indicated as a function of the orientation angle as follows:

$$
\begin{aligned}
E_C(\beta) &= [\sqrt{N + \cos^2(\beta)(M - N)}]^{-1} \\
M &= \left[\frac{\phi_C}{E_C} + \frac{\phi_B}{E_B} + \frac{\phi_A}{E_A}\right]^2 \\
N &= \left[\frac{\phi_C}{E_C}\frac{(1 + \vartheta_C)}{(1 + \vartheta_{Cc})} + \frac{\phi_B}{E_B}\frac{(1 + \vartheta_B)}{(1 + \vartheta_{Cc})} + \frac{\phi_A}{E_A}\frac{(1 + \vartheta_A)}{(1 + \vartheta_{Cc})}\right]^2
\end{aligned}
\tag{8}
$$

The parameters k and z are functions of interface thickness (τ).

Parameters k and z are calculated based on the analogy of considered geometrical model and the characteristics of nanoparticle in real sample, e.g. analogy of interface area (between nanoparticle and interface region) in actual sample and hypothetical geometry of a nanocomposite structure:

$$
\begin{aligned}
z &= \frac{\phi_d}{w} \\
k &= \frac{\phi_d}{w}\left(1 + \frac{2\tau}{wt}\right),
\end{aligned}
\tag{9}
$$

where τ and t are thicknesses of interface and platelet particle, respectively, w indicates the numerical correlation between the proposed model and real sample, and ϕ_d is the volume fraction of nanoparticles in real samples.

Considering an isotropic nanocomposite system in macroscale, the total modulus is given by

$$E_C = \frac{\int_0^{\frac{\pi}{2}} E_C(\beta) \cdot d\beta}{\frac{\pi}{2}} \tag{10}$$

Nanocomposites comprised of cylindrical nanoparticles

The calculation procedure for this model is generally the same as pervious section. Figure 4 illustrates a general approach for cylindrical model consisting of three co-axial cylindrical structures in which the core is considered to be the nanoparticle, the internal shell is the interface region, and the external one is the polymeric matrix. EBM model is used to describe three different indicated parts in series of the main model which constitute different elements (Fig. 5). The volume fraction corresponding to each section of EBM model is as follows:

$$
\begin{aligned}
\phi_{mA} &= \frac{\frac{\lambda}{2} - \frac{1}{2}k\sqrt{1 - k^2}}{\frac{\pi}{4}} \\[4pt]
\phi_{i1} &= \frac{\frac{\theta k^2}{2} - \left(\frac{1}{2}z\sqrt{k^2 - z^2}\right)}{\frac{1}{2}(\varphi - \lambda) + \frac{1}{2}\left(k\sqrt{1 - k^2} - z\sqrt{1 - z^2}\right)} \\[4pt]
\phi_{mB} &= \frac{\frac{1}{2}(\varphi - \lambda) + \frac{1}{2}\left(k\sqrt{1 - k^2} - z\sqrt{1 - z^2}\right) - \left[\frac{\theta k^2}{2} - \left(\frac{1}{2}z\sqrt{k^2 - z^2}\right)\right]}{\frac{1}{2}(\varphi - \lambda) + \frac{1}{2}\left(k\sqrt{1 - k^2} - z\sqrt{1 - z^2}\right)} \\[4pt]
\phi_n &= \frac{\frac{\pi z^2}{4}}{\frac{\pi}{4} - \left[\frac{\varphi}{2} - \frac{1}{2}z\sqrt{1 - z^2}\right]} \\[4pt]
\phi_{i2} &= \frac{\frac{1}{4}\pi(k^2 - z^2) - \left(\frac{\theta k^2}{2} - \frac{1}{2}z\sqrt{k^2 - z^2}\right)}{\frac{\pi}{4} - \left(\frac{\varphi}{2} - \frac{1}{2}z\sqrt{1 - z^2}\right)} \\[4pt]
\phi_{mC} &= \frac{\frac{\pi}{4}(1 - k^2) - \frac{1}{2}\left[\varphi - \theta k^2 - z(\sqrt{1 - z^2} - \sqrt{k^2 - z^2})\right]}{\frac{\pi}{4} - \left(\frac{\varphi}{2} - \frac{1}{2}z\sqrt{1 - z^2}\right)},
\end{aligned}
\tag{11}
$$

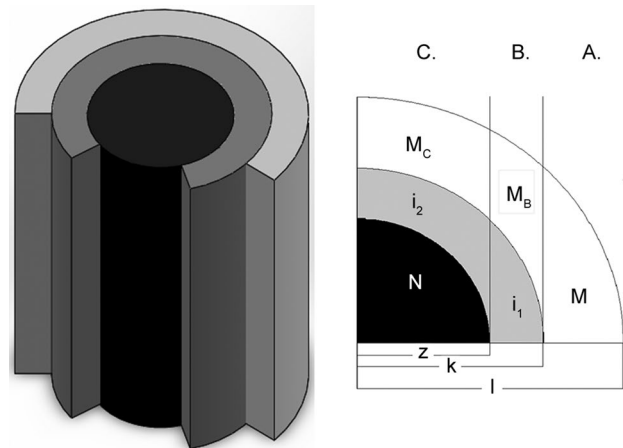where parameters θ, λ and φ can be calculated as follows:

Fig. 4 The 3-dimensional geometrical structure of NAS model and its corresponding 2-dimensional structure for nanocomposites comprised of cylindrical nano-reinforcing particles
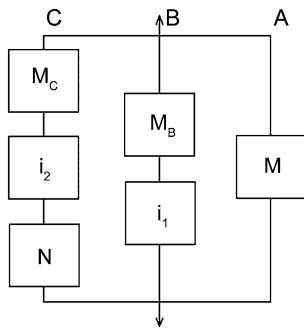
Fig. 5 Considered equivalent box model (EBM) corresponding to the 2-D assumed structure of nanocomposite comprised of cylindrical nano-reinforcing particles. Subscripts *M, i,* and *N* denote matrix phase, interface region and nanoparticle, respectively

$$\theta = \arcsin\left(\frac{\sqrt{k^2 - z^2}}{k}\right)$$
$$\lambda = \arcsin\left(\sqrt{1 - k^2}\right) \tag{12}$$
$$\varphi = \arcsin\left(\sqrt{1 - z^2}\right),$$

where *k* and *z* are the model parameters.

Similar to "Nanocomposites comprised of cylindrical nanoparticles", both components of exerted stress [σ sin(β) and σ cos(β)] should be taken into consideration as β reaches values higher than 0°. In the case of each stress component, the model response should be characterized. The shear component has significant influence on the final properties of the composite which is a function of modulus and Poisson's ratio. Based on assumed cylindrical structure in Fig. 3 the volume fraction of sections *A, B,* and *C* are required to calculate the total strain of composite due to the tensile component of the exerted stress:

$$\phi_A = \frac{\frac{\lambda}{2} - \frac{1}{2}k\sqrt{1 - k^2}}{\frac{\pi}{4}}$$

$$\phi_B = \frac{\frac{1}{2}(\varphi - \lambda) + \frac{1}{2}\left(k\sqrt{1 - k^2} - z\sqrt{1 - z^2}\right)}{\frac{\pi}{4}} \tag{13}$$

$$\phi_C = \frac{\frac{\pi}{4} - \left(\frac{\varphi}{2} - \frac{1}{2}z\sqrt{1 - z^2}\right)}{\frac{\pi}{4}}$$

Subsequently, the strain of each section of model according to tensile component is as follows:

$$\varepsilon_A = \frac{\sigma \cos(\beta)}{E_M}$$
$$\varepsilon_B = \frac{\sigma \cos(\beta)}{\phi_{i1}E_i + \phi_{mB}E_M} \tag{14}$$
$$\varepsilon_C = \frac{\sigma . \cos(\beta)}{\phi_n E_N + \phi_{i2}E_i + \phi_{mC}E_M},$$

where ϕ_x indicates the volume fraction of different parts of EBM model and subscripts *M, i,* and *N* denote matrix phase, interface region, and nanoparticle, respectively.

The total strain of nanocomposite according to tensile component is

$$(\varepsilon_C) = \phi_A\varepsilon_A + \phi_B\varepsilon_B + \phi_C\varepsilon_C \tag{15}$$

where ϕ and ε indicate the volume fraction and strain of different parts of EBM model.

In series arrangement of EBM model against stress component $\sigma \cos(\beta)$, the Young's modulus can be proposed as follows:

$$G_s = \frac{1}{\frac{\phi_A}{G_A} + \frac{\phi_B}{G_B} + \frac{\phi_C}{G_C}}$$
$$G_{i,\,i=A,B,C} = \frac{E_i}{2(1 + \vartheta_i)} \tag{16}$$

G_A, G_B, and G_C are given as

$$G_A = \frac{E_M}{2(1 + \vartheta_M)}$$

$$G_B = \frac{E_B}{2(1 + \vartheta_B)} \rightarrow \begin{cases} \dfrac{1}{E_B} = \dfrac{\phi_{mB}}{E_M} + \dfrac{\phi_{i1}}{E_i}, \quad E_B' = \phi_{mB}E_M + \phi_{i1}E_i \\ \vartheta_B' = \phi_{i1}\vartheta_i + \phi_{mB}\vartheta_M, \quad \vartheta_B = \vartheta_B'\dfrac{E_B}{E_B'} \end{cases}$$

$$G_C = \frac{E_C}{2(1 + \vartheta_C)} \rightarrow \begin{cases} \dfrac{1}{E_C} = \dfrac{\phi_{mC}}{E_M} + \dfrac{\phi_{i2}}{E_i} + \dfrac{\phi_N}{E_N}, \quad E_C' = \phi_{mC}E_M + \phi_{i2}E_i + \phi_N E_N \\ \vartheta_C' = \phi_{i2}\vartheta_i + \phi_{mC}\vartheta_M + \phi_N\vartheta_N, \quad \vartheta_C = \vartheta_C'\dfrac{E_C}{E_{C'}} \end{cases} \tag{17}$$

$$E_S = \left(\frac{\phi_A}{E_M}\frac{(1 + \vartheta_M)}{(1 + \vartheta_S)} + \frac{\phi_B}{E_B}\frac{(1 + \vartheta_B)}{(1 + \vartheta_S)} + \frac{\phi_C}{E_C}\frac{(1 + \vartheta_C)}{(1 + \vartheta_S)}\right)^{-1} \text{ where } \begin{cases} E_S = 2G_S(1 + \vartheta_S) \\ \vartheta_s = \varphi_A\vartheta_M + \varphi_B\vartheta_B + \varphi_C\vartheta_C, \end{cases}$$

where ϑ is Poisson's ratio and E is Young's modulus. Subscripts M, N, and i denote matrix, nanoparticle, and interface, respectively.

In parallel arrangement of EBM model against stress component $\sigma \sin(\beta)$ the Young's modulus can be proposed as follows:

$$G_P = \frac{1}{\frac{\phi_{ip}}{G_i} + \frac{\phi_{Mp}}{G_M} + \frac{\phi_N}{G_N}} \rightarrow \begin{cases} \phi_{ip} = k^2 - z^2 \\ \phi_{Mp} = 1 - k^2 \\ \phi_N = z^2 \end{cases}$$

$$E_p = \left(\frac{\phi_{ip}}{E_i} \frac{(1+\vartheta_i)}{(1+\vartheta_C)} + \frac{\phi_{Mp}}{E_B} \frac{(1+\vartheta_M)}{(1+\vartheta_C)} + \frac{\phi_N}{E_N} \frac{(1+\vartheta_N)}{(1+\vartheta_C)} \right)^{-1}$$

$$\rightarrow \begin{cases} E_p = 2G_p(1+\vartheta_C) \\ \vartheta_C = \phi_{ip}\vartheta_i + \phi_{Mp}\vartheta_M + \phi_N E_N \end{cases} \quad (18)$$

The variation of modulus at the interface region is considered to be linear through $\vec{r}$ direction [10]; therefore, the modulus of this phase is

$$E_i(a) = E_i(0) + \frac{E_M - E_i(0)}{k - z}(a - z)$$

$$\frac{1}{E_i} = \frac{2}{(k^2 - z^2)} \int_z^k \frac{a \cdot da}{E_i(a)} \quad (19)$$

E_c could be found as a function of β using Eqs. 11–19:

$$\varepsilon_C(\beta) = \left(\sqrt{(\varepsilon_C)_P^2 + (\varepsilon_C)_S^2} \right) \rightarrow \begin{cases} (\varepsilon_C)_S = \frac{\sigma \cos(\beta)}{E_S} \\ (\varepsilon_C)_P = \frac{\sigma \sin(\beta)}{E_P} \end{cases} \quad (20)$$

$$\frac{1}{E_C(\beta)} = \frac{\varepsilon_C(\beta)}{\sigma}$$

Rearranging Eq. 20 results in

$$E_C(\beta) = \left(\sqrt{N + \cos^2(\beta)(M - N)} \right)^{-1}$$

$$M = \left(\frac{\phi_A}{E_M} \frac{(1+\vartheta_M)}{(1+\vartheta_s)} + \frac{\phi_B}{E_B} \frac{(1+\vartheta_B)}{(1+\vartheta_s)} + \frac{\phi_C}{E_C} \frac{(1+\vartheta_C)}{(1+\vartheta_s)} \right)^2$$

$$N = \left(\frac{\phi_{iP}}{E_i} \frac{(1+\vartheta_i)}{(1+\vartheta_C)} + \frac{\phi_{mP}}{E_M} \frac{(1+\vartheta_M)}{(1+\vartheta_C)} + \frac{\phi_N}{E_N} \frac{(1+\vartheta_N)}{(1+\vartheta_C)} \right)^2 \quad (21)$$

In the case of nanocomposites comprised of cylindrical nanoparticles, k and z are calculated as follows:

$$z = \sqrt{\frac{\phi_d}{w}}$$

$$k = \sqrt{\frac{\phi_d}{w}\left(1 + \frac{\tau}{4rw}\left(2 + \frac{\tau}{r}\right)\right)}, \quad (22)$$

where r is the radius of an individual nano-cylindrical particle, τ is thickness of interface, w indicates the numerical
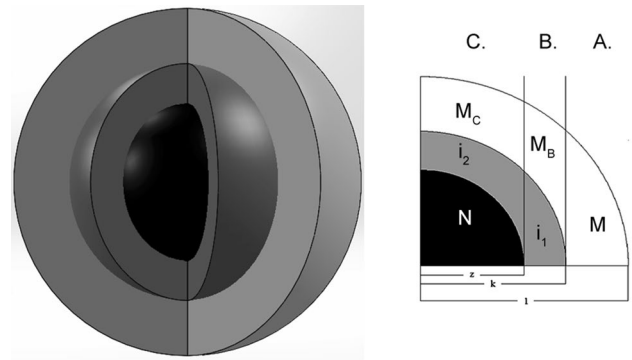

Fig. 6 The 3-dimensional geometrical structure of NAS model and its corresponding 2-dimensional structure for nanocomposites comprised of spherical nano-reinforcing particles
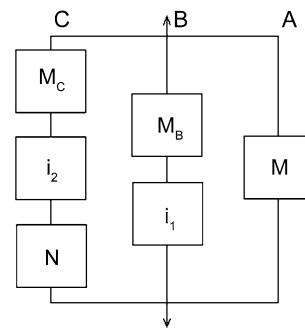

Fig. 7 Considered equivalent box model (EBM) corresponding to the 2-D assumed structure of nanocomposite comprised of spherical nano-reinforcing particles. Subscripts M, i, and N denote matrix phase, interface region and nanoparticle, respectively

correlation between the proposed model and real sample, and ϕ_d is the volume fraction of nanoparticles in real samples.

Since the nanocomposite is considered isotropic in macroscale, Eq. (20) should be averaged to obtain an exclusive value for E_c. The following equation shows the total modulus of composite as a function of dispersed phase volume fraction:

$$E_C = \frac{\int_0^{\frac{\pi}{2}} E_C(\beta) \cdot d\beta}{\frac{\pi}{2}} \quad (23)$$

Nanocomposite comprised of nano-spherical dispersed phase

In nanocomposites comprised of nano-spherical dispersed phase, model components are just considered in series (because of spherical coordination). Figure 6 illustrates the spherical structure which consists of nanoparticle (the core), interface (internal shell), and the matrix phases

(external shell). The EBM model is also used to show the sequence of constituent sectors of the assumed spherical model (Fig. 7). Based on the same assumptions as in the latter sections, the volume fraction of each sector is

$$\varphi_{mA} = \frac{(1-k)\left[3(1-k^2)+(1-k)^2\right]}{4}$$

$$\varphi_{iB} = \frac{(k-z)\left[3(k^2-z^2)+(k-z)^2\right]}{(1-z)\{3.(1-z^2)+(1-z)^2-(1-k)[3(1-k^2)+(1-k)^2]\}}$$

$$\varphi_{mB} = 1 - \varphi_{iB}$$

$$\varphi_n = \frac{4-z^3}{4-(1-4)\left[3(1-z^2)+(1-z)^2\right]} \tag{24}$$

$$\varphi_{iC} = \frac{4(k^3-z^3)-(k-z)\left[3(k^2-z^2)+(k-z)^2\right]}{4-(1-z)\left[3(1-z^2)+(1-z)^2\right]}$$

$$\varphi_{mc} = 1 - (\varphi_N + \varphi_{iC})$$

The shear modulus of nanocomposite system is proposed as follows:

where ϑ is Poisson's ratio and E is Young's modulus. Subscripts M, N, and i denote matrix, nanoparticle, and interface, respectively.

The volume fractions of sections A, B, and C (Fig. 6) are as follows:

$$\varphi_A = \frac{(1-k)\left[3(1-k^2)+(1-k)^2\right]}{4}$$

$$\varphi_B = \frac{(1-z)\left[3(1-z^2)+(1-z)^2\right]-(1-k)\left[3(1-k^2)+(1-k)^2\right]}{4} \tag{26}$$

$$\varphi_C = 1 - (\varphi_A + \varphi_B)$$

The model characteristic parameters (z and k) are calculated through following equations:

$$z = \sqrt[3]{\frac{\phi_d}{w}}$$

$$k = \sqrt[3]{\frac{\phi_d}{w}\left(1+\frac{1}{8w}\left(\frac{(r+\tau)^3}{r^3}-1\right)\right)}, \tag{27}$$

$$G_T = \frac{1}{\frac{\phi_A}{G_A}+\frac{\phi_B}{G_B}+\frac{\phi_C}{G_C}}$$

$$G_A = \frac{E_M}{2(1+\vartheta_M)}$$

$$G_B = \frac{E_B}{2(1+\vartheta_B)} \rightarrow \begin{cases} \dfrac{1}{E_B}=\dfrac{\phi_{mB}}{E_M}+\dfrac{\phi_{i1}}{E_i}, E'_B=\phi_{mB}E_M+\phi_{i1}E_i \\[2mm] \vartheta'_B=\phi_{i1}\vartheta_i+\phi_{mB}\vartheta_M, \vartheta_B=\vartheta'_B\dfrac{E_B}{E'_B} \end{cases} \tag{25}$$

$$G_C = \frac{E_C}{2(1+\vartheta_C)} \rightarrow \begin{cases} \dfrac{1}{E_C}=\dfrac{\phi_{mC}}{E_M}+\dfrac{\phi_{i2}}{E_i}+\dfrac{\phi_N}{E_N}, E'_C=\phi_{mC}E_M+\phi_{i2}E_i+\phi_N E_N \\[2mm] \vartheta'_C=\phi_{i2}\vartheta_i+\phi_{mC}\vartheta_M+\phi_N\vartheta_N, \vartheta_C=\vartheta'_C\dfrac{E_C}{E_{C'}} \end{cases},$$

Table 1 Comprehensive equation of NAS model for different geometries of nano-reinforcing particles

$$E_C = \frac{2}{\pi}\int_0^{\frac{\pi}{2}}E_C(\beta)\cdot d\beta \qquad E_C(\beta) = \left(\sqrt{N+\cos^2(\beta)(M-N)}\right)^{-1}$$

Geometrical structure of nano-particle	M	N	β
Platelet	$\left(\frac{\phi_A}{E_M}+\frac{\phi_B}{E_i}+\frac{\phi_C}{E_N}\right)^2$	$\left(\frac{\phi_A}{E_M}\frac{(1+\vartheta_A)}{(1+\vartheta_{Cc})}+\frac{\phi_B}{E_i}\frac{(1+\vartheta_B)}{(1+\vartheta_{Cc})}+\frac{\phi_C}{E_N}\frac{(1+\vartheta_C)}{(1+\vartheta_{Cc})}\right)^2$	$0-\frac{\pi}{2}$
Cylindrical	$\left(\frac{\phi_A}{E_M}\frac{(1+\vartheta_M)}{(1+\vartheta_s)}+\frac{\phi_B}{E_B}\frac{(1+\vartheta_B)}{(1+\vartheta_s)}+\frac{\phi_C}{E_C}\frac{(1+\vartheta_C)}{(1+\vartheta_s)}\right)^2$	$\left(\frac{\phi_{iP}}{E_i}\frac{(1+\vartheta_i)}{(1+\vartheta_C)}+\frac{\phi_{mP}}{E_M}\frac{(1+\vartheta_M)}{(1+\vartheta_C)}+\frac{\phi_N}{E_N}\frac{(1+\vartheta_N)}{(1+\vartheta_C)}\right)^2$	$0-\frac{\pi}{2}$
Spherical	$\left(\frac{\phi_A}{E_M}\frac{(1+\vartheta_M)}{(1+\vartheta_{Co.})}+\frac{\phi_B}{E_B}\frac{(1+\vartheta_B)}{(1+\vartheta_{Co.})}+\frac{\phi_C}{E_C}\frac{(1+\vartheta_C)}{(1+\vartheta_{Co.})}\right)^2$	–	$\frac{\pi}{2}$

where r is the radius of an individual nano-cylindrical particle, τ is thickness of the interface, w indicates the numerical correlation between the proposed model and real sample, and ϕ_d is the volume fraction of nanoparticles in real samples.

Similar to the last two sections, the variation of modulus in the interface region is considered to be linear in $\bar{r}$ direction [10]. Therefore, the modulus for this region is calculated as follows:

$$\frac{1}{E_i} = \frac{3}{(k^2 - z^2)} \int_z^k \frac{a^2 da}{E_i(a)} \qquad (28)$$

Consequently the total modulus of nanocomposite is

$$E_T = \left(\frac{\phi_A}{E_M} \frac{(1 + \vartheta_M)}{(1 + \vartheta_T)} + \frac{\phi_B}{E_B} \frac{(1 + \vartheta_B)}{(1 + \vartheta_T)} + \frac{\phi_C}{E_C} \frac{(1 + \vartheta_C)}{(1 + \vartheta_T)} \right)^{-1}$$

$$\text{where} \begin{cases} E_T = 2G_T(1 + \vartheta_T) \\ \vartheta_T = \varphi_A \vartheta_M + \varphi_B \vartheta_B + \varphi_C \vartheta_C \end{cases} \qquad (29)$$

As a result, the final equation of NAS model can be represented as follows:

$$E_C(\beta) = \left(\sqrt{N + \cos^2(\beta)(M - N)} \right)^{-1} \text{ and}$$

$$E_C = \frac{\int_0^{\frac{\pi}{2}} E_C(\beta) \cdot d\beta}{\frac{\pi}{2}} \qquad (30)$$

Table 1 shows the parameters M and N for different categories of NAS model.

Experimental

Materials and sample preparation

The polyamide 6 (Akulon F223D) was purchased from DSM company with density of 1.13 (g/cm^3), and layer-shaped montmorillonite modified with a quaternary ammonium salt (cloisite 30B) was provided from Southern Clay Products with specific gravity of 1.98 (g/cm^3). Both materials were dried in a vacuum oven for 24 h at 80 °C. The samples were prepared via melt mixing in an internal mixer (Brabender 55 WTH) with mixing temperature of 235 °C and rotor speed of 60 rpm for 10 min. Thereafter, the dumb-bell form samples were molded by a compression molding machine with temperature of 240 °C. The samples were dried at 80 °C for 24 h before tensile test.

Tensile test

Using SANTAM STM-20 tensile tester with crosshead speed of 45 mm/min, tensile measurements were taken in accordance with ASTM D-638 at room temperature. The Young moduli of the samples were determined by the initial slope of stress–strain curves, and the results are reported as the average of five runs.

Results and discussion

The experimental and predicted moduli are demonstrated in Fig. 8. Clearly, the predicted modulus from NAS model shows a high degree of agreement with experimental data. Furthermore, some other reported results of different studies on modulus of nanocomposites (containing various shapes of nano-reinforcing phase) were also used to investigate the validity of the proposed models (Figs. 9, 10, 11, 12). Table 2 lists the data of tensile modulus and Poisson's ratio of polymer matrix and nanoparticles of each figure. However, the Poisson's ratio of interface region is considered to be 5 % less than the Poisson's ratio of polymer matrix as a good approximation which leads to good results. As a result, the modulus of nanocomposite system increases by increasing the thickness of interface; however, the modulus on the surface of nanocomposite also plays an important role. For the reason

Fig. 8 Comparison of experimental result with the predictions of NAS model (PA/Cloisite 30B). $w = 1$, error (%) = 0.1, $\tau = 1.64 \times 10^{-8}$, $E(0)/E_M = 1.84$
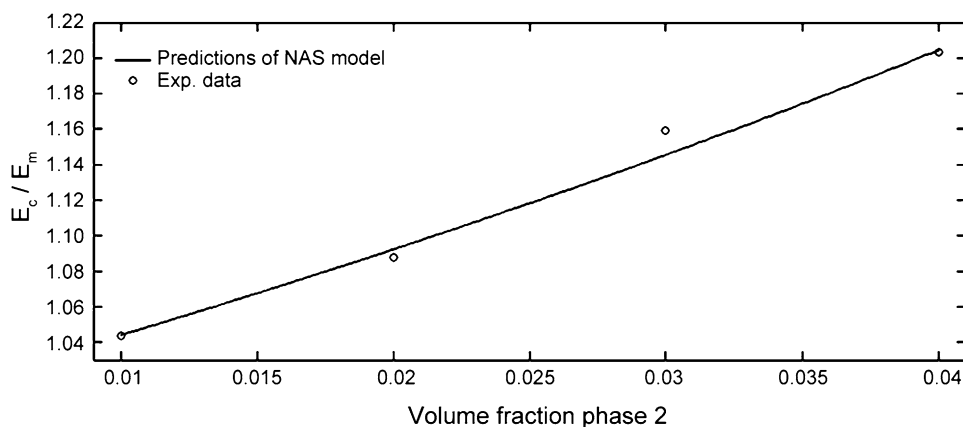
that the geometrical differences of nano-reinforcing particle directly affect the calculation procedure, it has been shown that the proposed model can perfectly cover all possible differences. Considering the random orientation of nano-reinforcing particle placed in the polymeric matrix, the direction of exerted stress on the sample is negligible although the orientation is meaningless for spherical shape nanoparticles. By ignoring those terms by which the interface is involved in modeling procedure, the proposed models could be also used for untreated nano-reinforcing particles because there is no interface region in such systems.

Conclusion

Considering region and random orientation of nano-reinforcing particles in nanocomposite systems, a model including three different parts was proposed. All parts were based on the same presumptions which reveal the similarity of modeling fundamentals. Dispersion of particles was assumed to be fully exfoliated, which means there was no agglomeration in the final nanocomposite sample. Three different shapes of nanoparticles (platelet, cylindrical, and spherical) were considered in each model. Acceptable and remarkable coincidence of NAS predictions of

Fig. 9 Comparison of experimental results with the predictions of NAS model (PA/montmorillonite); $w = 1$, error (%) = 0.2, $\tau = 9 \times 10^{-9}$, $E(0)/E_M = 15.65$ [10]
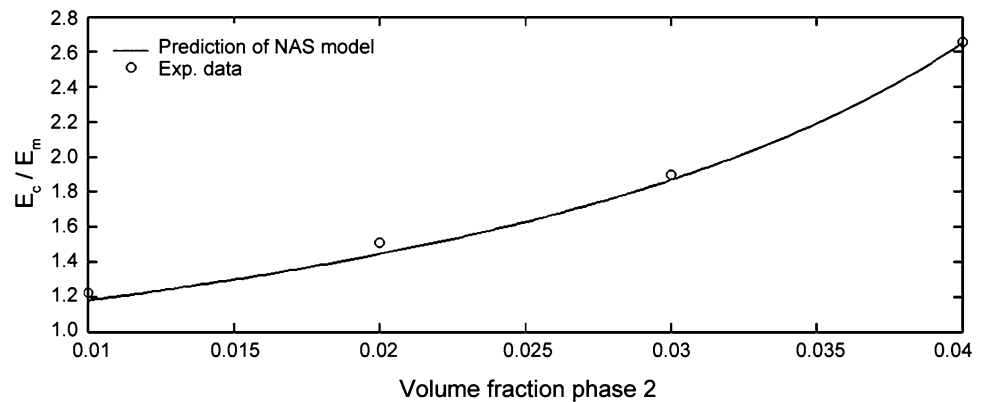

Fig. 10 Comparison of experimental results with the predictions of NAS model (SBR/CNT); $w = 2$, error (%) = 3.7, $\tau = 9.6 \times 10^{-8}$, $E(0)/E_M = 485152.04$ [14]
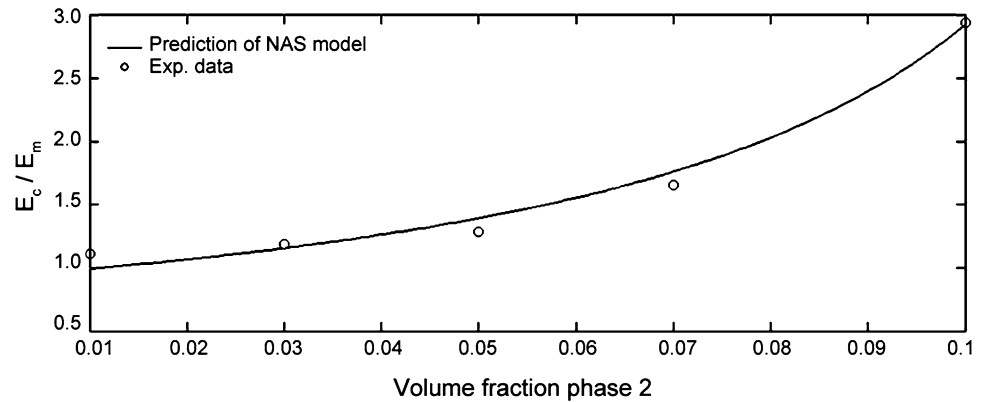

Fig. 11 Comparison of experimental results with the predictions of NAS model (iPP/CNT); $w = 1$, error (%) = 0.4, $\tau = 1.76 \times 10^{-8}$, $E(0)/E_M = 857.62$ [15]
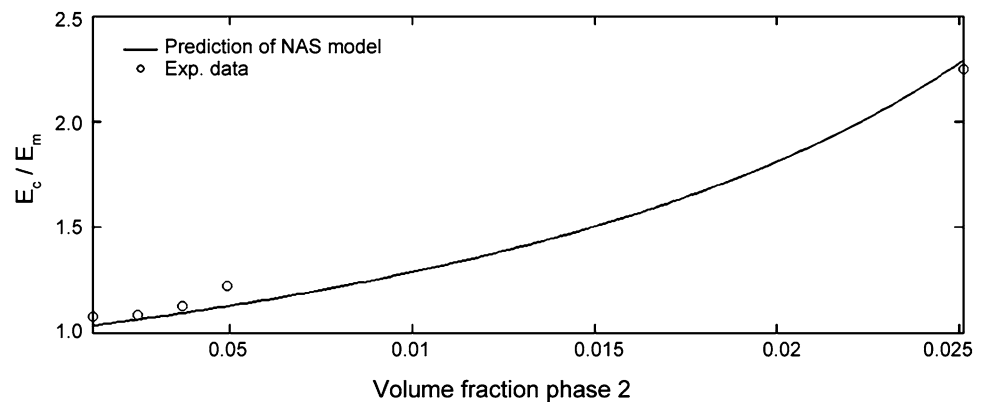
Fig. 12 Comparison of experimental results with the predictions of NAS model (epoxy/TiO$_2$); $w = 4$, error (%) = 0.1, $\tau = 1.15 \times 10^{-8}$, $E(0)/E_M = 31.89$ [16]
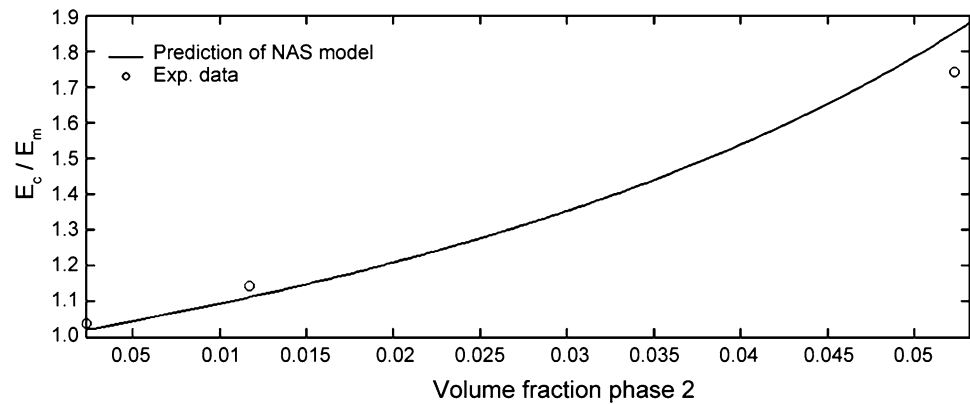

Table 2 Data applied in NAS model to predict Young's modulus of nanocomposite systems

Figure number	polymer matrix			Nano particles			
	Matrix	Young's modulus (Mpa)	Poisson's ratio	Nano particle	Type	Young's modulus (Gpa)	Poisson's ratio
8	Polyamide (nylone 6, Akulun)	3,200	0.39	Montmorillonite (Cloisite 30B)	Platelet	5–16 [20]	0.144 [20]
9	Polyamide 6	509 [10]	0.39	Montmorillonite	Platelet	20.36 [10]	0.144 [20]
10	SBR	2	0.48	Multi wall carbon nano tube (MWCNT)	Cylindrical	900 [18]	0.04–0.11 [19]
11	iPP	≃1,600 [15]	0.35–0.37 [21]	Carbon nano tube (CNT)	Cylindrical	1,236 [17]	0.261 [17]
12	Epoxy	2,462 [16, 23]	0.4925 [22]	TiO$_2$	Spherical	230	0.27

experimental data proves that the whole presumptions and mathematical procedures are sufficiently accurate. It should also be mentioned that because of complications arising from complex mathematical calculations, MATLAB software is generally used as programing software.

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