

Micromechanical modeling-based self-consistent scheme of polymer-layered silicate nanocomposites

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Résumé :

Dans cette communication, nous présentons une approche micromécanique utilisant un schéma autocohérent basé sur le modèle de la double inclusion pour prédire les constantes élastiques macroscopiques des nanocomposites polymère-argile. Le modèle micromécanique incorpore la nanostructure des piles d'argile, modélisées comme des sphéroïdes isotropes transverses, et la région contrainte, modélisée comme une interphase autour des renforts. Pour prendre en compte les effets de taille, l'épaisseur de l'interphase et les dimensions des particules sont prises comme des paramètres explicites du modèle. Au lieu d'une résolution itérative de l'équation implicite du schéma autocohérent, notre formulation aboutit à un système d'équations qui peut être résolu simultanément pour déterminer les constantes élastiques macroscopiques. Les capacités du modèle sont discutées par des comparaisons avec des données expérimentales et l'approche de Mori-Tanaka largement utilisée dans la littérature récente pour cette classe de matériaux.

Abstract :

In this communication, we present a micromechanical approach for the prediction of the overall moduli of polymer-clay nanocomposites using a self-consistent scheme based on the double-inclusion model. The micromechanical model incorporates the nanostructure of clay stacks, modeled as transversely isotropic spheroids, and the so-called constrained region, modeled as an interphase around reinforcements. To account for length scale effects, the interphase thickness and the particle dimensions are taken as explicit model parameters. Instead of solving iteratively the basic implicit homogenization equation of the self-consistent scheme, our formulation yields to a pair of equations that can be solved simultaneously for the overall elastic moduli. The model capabilities are critically discussed by comparisons with both experiments and the Mori-Tanaka approach widely used in recent literature for this class of materials.

Keywords: Nanocomposites, nanoclay, interactions, interphase, micromechanics-based model

1 Introduction

In the past few years, a considerable amount of research has been conducted to provide a better understanding of the mechanical behavior of polymer composites with nanoscale reinforcements such as nanotube-reinforced, silica nanoparticle-reinforced and nanoclay-reinforced composites. These materials are termed nanocomposites because one or more of the dimensions of the reinforcing particle is about a few nanometers of magnitude. Among them, the most promising composite materials could be polymer-clay nanocomposites based on organic polymers and inorganic clay minerals consisting of silicate layers, see for instance Refs [1-2]. Polymer-clay nanocomposites have attracted during recent years great consideration from researchers and industrials since they exhibit enhanced mechanical properties. This improvement is observed for a very low weight fraction of nanofillers (nanometric fillers) compared to conventional

microcomposite materials containing larger particles. Their lightweight and the high availability of the reinforcing phase make this new class of materials as a perfect candidate in several structural and functional applications. It is also shown that polymer-clay nanocomposites, compared to pure polymer, present remarkable physical and chemical properties such as high thermal stability and excellent barrier properties against gases and water [2]. The stiffening effect of the nanoclay particles is generally explained in terms of its intense interactions with the polymer matrix (leading to a reduced chain segment mobility in the vicinity of clay nanoplatelets), aspect ratio, nanoscopic size, spatial distribution and arrangements of intercalating polymer chains in the intersilicate layers. Depending on the state of clay dispersion, the nanocomposites can be sorted into three typical structures:

- Conventional microcomposites, when the clay is in its originally aggregated state with no intercalation of polymer chains into the silicate interlayer space.
- Intercalated nanocomposites, when polymer chains fill the silicate interlayer space forming a well-ordered multilayer with alternating organic/inorganic slices.
- Exfoliated nanocomposites, when silicate platelets are individually delaminated and fully dispersed in a continuous polymer matrix.

The morphology of the nanocomposites, i.e. intercalation or exfoliation, mainly depends on the achievement process (e.g. polymerization, compounding and solution methods), the type of the clay (and/or the corresponding surface treatment), the type of the polymer matrix, the thermodynamic interaction between the polymer matrix and the clay but also the clay concentration into the matrix material. The best performances in the mechanical properties are commonly observed with the fully exfoliated structures [1-9], resulting in very thin particles with large aspect ratios. The major difference between nanocomposites and composites with microscopic size particles is the surface area per unit volume and the number of particles embedded in the matrix material for a given volume fraction. Most investigations were focused on nanoclay-reinforced composite materials processing and on their microstructural and mechanical characterizations [2]. In the meantime, there is still a need to establish predictive mechanical tools for an accurate optimization of this recent class of materials. Whereas continuum mechanics models are successfully applied to microcomposite materials, the modeling of the overall elastic properties of polymer-clay nanocomposites has been less addressed to date. The used models include the rule of mixtures, the Halpin-Tsai equation and the Eshelby-type micromechanical models [3-7]. Although these models were found to be able to reproduce the elastic response of nanocomposites, several crucial physical issues, such as length scale effects and active interaction between the nanofillers, remain to be solved to definitely confirm the micromechanical based modeling as a pertinent approach for such materials. Indeed, inherent to their structure, these models are not able to account for the inter-inclusion interaction in the composite materials. Although there is generally a low dilution of clay particles in the nanocomposites, the interaction between particles cannot be overlooked because of the nanoscale of one dimension resulting in a large surface area per unit volume. In the present paper, we propose a formulation of the overall moduli of composite materials reinforced with transversely isotropic spheroids using a self-consistent approach based on the double-inclusion model proposed by Hori and Nemat-Nasser [10]. This approach is used in order to take into account not only the particle-matrix interaction, but also the interaction between particles.

2 Model formulation

In this section, we give the prediction of the elastic constants of composite materials reinforced with randomly oriented transversely isotropic spheroids with arbitrary aspect ratio. This prediction is based on the double-inclusion model proposed by Hori and Nemat-Nasser [10] using the consistency condition, in which the infinite reference medium is replaced by the overall composite material. As shown schematically in figure 1 each inclusion I with stiffness tensor \mathbf{C}_I is surrounded by a coating of matrix material named coated-inclusion (CI) with stiffness tensor \mathbf{C}_M to form a double-inclusion (DI), which is in turn embedded in an infinite reference medium having a stiffness tensor \mathbf{C}_0 and subjected to the same boundary conditions than those of the material. For general basis of the double-inclusion model, the reader may also refer to the book of Nemat-Nasser and Hori [10]. In the case of multiphase composites, considering the double-inclusion model using consistency condition, the basic formula giving the stiffness tensor \mathbf{C} of the composite can be written as:

$$\mathbf{C} = \mathbf{C}_M + \sum_{I=1}^n f_I (\mathbf{C}_I - \mathbf{C}_M) : \mathbf{A}_I \quad (1)$$

where f_I ($I=1,2,\dots,n$) is the volume fraction of each inclusion I .

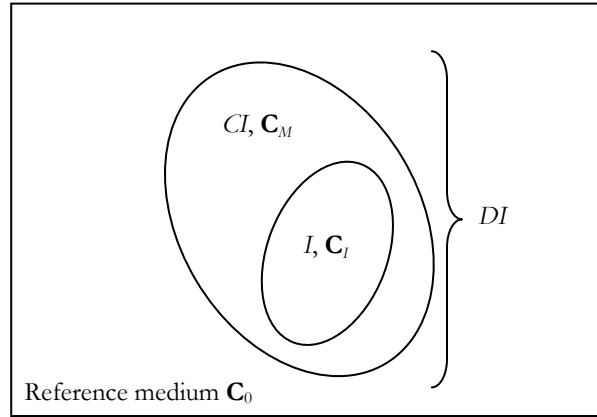


FIG. 1 – Topology of the double-inclusion model.

When each inclusion I ($I=1,2,\dots,n$) and its double-inclusion DI are coaxial and have similar spheroidal shapes, the strain concentration tensor \mathbf{A}_I is defined as:

$$\mathbf{A}_I = \mathbf{I} + \mathbf{S}_I : [(\mathbf{C} - \mathbf{C}_I)^{-1} : \mathbf{C} - \mathbf{S}_I]^{-1} \quad (2)$$

in which \mathbf{S}_I is the Eshelby tensor corresponding to the inclusion I . Details for expressions of \mathbf{S}_I for the inclusions of various shapes can be found in the book of Nemat-Nasser and Hori [10]. We assume that all the inclusions I in the multiphase composite have the same shape and the same elasticity. Consequently, the material becomes a two-phase composite composed with the matrix material to which we confer the subscript 1 and the inclusions to which we confer the subscript 2. This notation will be implemented in the whole paper. For a two-phase composite material reinforced with randomly oriented transversely isotropic spheroid particles, the formula (1) can be re-written as:

$$\mathbf{C} = \mathbf{C}_1 + f_2 \{(\mathbf{C}_2 - \mathbf{C}_1) : \mathbf{A}_2\} \quad (3)$$

Curly brackets $\{\bullet\}$ represent an average over all possible orientations of term (\bullet) . The volume fraction of the spheroid particles is given by:

$$f_2 = \frac{4}{3} \frac{\pi a^2 b}{V} \quad (4)$$

where a and b are the half-lengths of the major and minor axis of the spheroids, respectively, and V is the volume of the double-inclusion DI . To greatly facilitate the tensorial computations in the equation (3), the Walpole [11] symbolic notation for transversely isotropic tensors is employed. The reader is referred to Refs. [5, 8] for more details. In the case of a randomly orientation of the reinforcements in the matrix material, the overall stiffness tensor \mathbf{C} in the equation (3) becomes a fourth-rank isotropic tensor:

$$\mathbf{C} = 3\kappa \mathbf{J} + 2\mu \mathbf{K} \equiv (3\kappa, 2\mu) \quad (5)$$

in which κ and μ are the overall bulk and shear moduli and, \mathbf{J} and \mathbf{K} are two fourth-rank tensors related, respectively, to the spherical part and the deviatoric part.

The matrix material being isotropic, the relation (3) can be re-written as:

$$(3\kappa, 2\mu) = (3\kappa_1, 2\mu_1) + f_2 \{\mathbf{T}\} \quad (6)$$

After a series of lengthy but straightforward derivations, the overall bulk and shear moduli κ and μ can be

evaluated:

$$\begin{aligned}\kappa &= \kappa_1 + \frac{f_2}{3} \Phi \\ \mu &= \mu_1 + \frac{f_2}{2} \Psi\end{aligned}\quad (7)$$

where $\{\mathbf{T}\} = \{(\mathbf{C}_2 - \mathbf{C}_1) : \mathbf{A}_2\} = (\Phi, \Psi)$.

The explicit expressions of Φ and Ψ can be found elsewhere [8]. The pair of implicit equations (7) can be simultaneously solved via any mathematical software (e.g., Mathematica or Matlab), thus we avoid the cumbersome iterative resolution required by the self-consistent scheme. Using the self-consistent scheme, a closed formulation was given by Walpole [11] for the overall moduli of composite materials reinforced by disc-like particles, i.e. transversely isotropic spheroids with zero aspect ratio. Note that the developments drawn in this paper give a general formulation, function of an arbitrary aspect ratio, which lead to the Walpole solution [11] if the aspect ratio is zero.

3 Results and discussion

As noted above, there are in general three types of nanocomposite materials reinforced by silicate layers. In the case of the intercalated nanocomposite structure, a hierarchical morphology of the silicate stacks was explicitly introduced in the theoretical formulation from an equivalent stiffness method in which the silicate stacks are replaced by homogeneous equivalent particles containing several silicate layers and interlayer matrix [8]. It relies on clay structural parameters, including the average silicate interlayer spacing d_{001} and the average number N of silicate layers per clay stack. This hierarchical structure was also suggested for individual silicate layer surrounded by a constrained region in the case of the exfoliated nanocomposite structure [8]. The inputs for the developed micromechanical model are given elsewhere [8-9].

The effect of the aspect ratio on the overall stiffness of composite material reinforced with randomly oriented spheroids is investigated without the consideration of the constrained region. Figure 2 shows the evolution of the overall bulk and shear moduli as functions of the particle volume fraction and for various aspect ratios. It is seen from this figure that the smaller the aspect ratio, the stronger its impact on the overall moduli of the composite material. Our predictions are contained within the Hashin-Shtrikman (H-S) and Voigt-Reuss bounds.

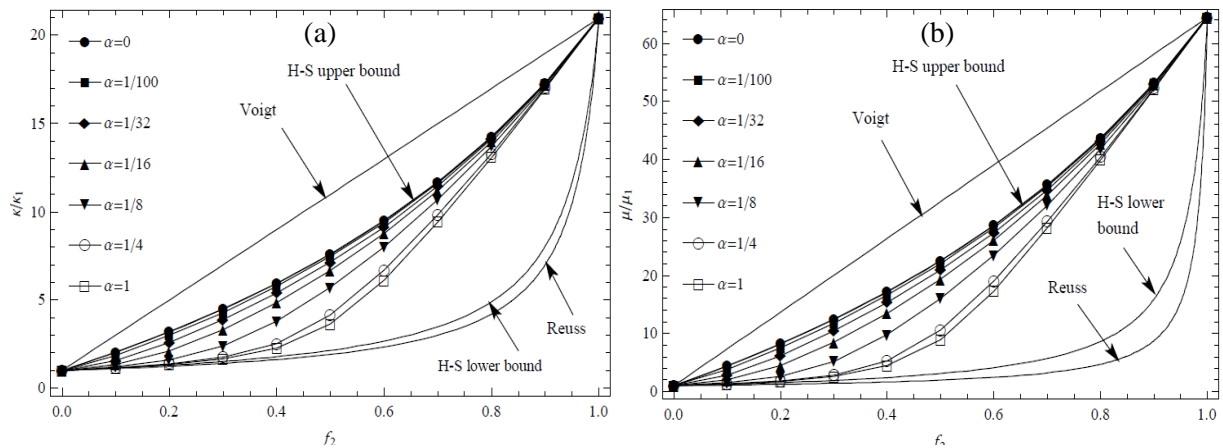


FIG. 2 – Effect of the aspect ratio on the overall (a) bulk and (b) shear moduli of composite materials reinforced with randomly oriented isotropic spheroid particles.

The effect of the particle size is investigated by varying its length from 200 to 1000 nm while keeping its aspect ratio constant and equal to 1/200. We consider the exfoliated nanocomposite with 0.02 volume fraction of silicate, surrounded by the constrained region. For a given interphase thickness, the effect of particle length on the overall elastic modulus of the exfoliated nanocomposite can be clearly seen in figure 3. When the interphase is stiffer than the bulk matrix material (figure 3a), it can be seen that the smaller the particle length, the higher the composite stiffness enhancement. At the micrometer scale, i.e. for high particle length, the

particle size effect is less predominant. When we assign to the interphase a weaker stiffness than that of the bulk matrix material (figure 3b), decreasing the particle size leads to a softening of the nanocomposite.

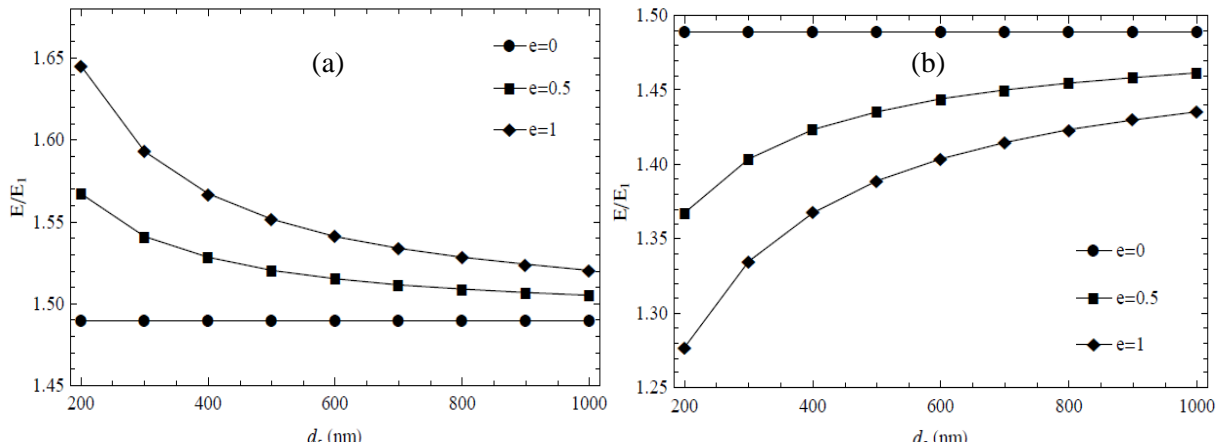


FIG. 3 – Effect of particle length d_s and the interphase thickness e (in nm) on the overall Young's modulus of composite materials reinforced with randomly oriented isotropic spheroid particles: (a) $E_i = 10 \times E_1$, (b) $E_i = 0.1 \times E_1$.

In figure 4a are shown our theoretical predictions, the Mori-Tanaka predictions according to Wang and Pyrz [5] and the experimental overall Young's modulus of polyimide-MMT clay nanocomposite materials characterized by Tyan et al. [12]. For both models, two values of the particle aspect ratio are considered: 1/200 and 1/100. Based upon X-ray diffraction curves, Tyan et al. [12] indicate that exfoliated silicate platelets are homogeneously dispersed in the polyimide matrix. The Mori-Tanaka predictions of Wang and Pyrz [5] underestimate the experimental data for the two aspect ratios. Wang and Pyrz [5] explained this result simply by the alignment of the silicate platelets even if they are homogeneously dispersed in the matrix material. However, there is no real indication in the paper of Tyan et al. [12] of any preferential orientation of silicate platelets. While the Mori-Tanaka model underestimates the experimental points, it can be clearly observed that our theoretical predictions with a platelet aspect ratio of 1/200 are very close to the experimental data. While, according to our theoretical predictions, it is very hard to see any contribution of the constrained region, this latter is required in the Mori-Tanaka model in order to get more stiff predicted values and therefore to correct the underestimation.

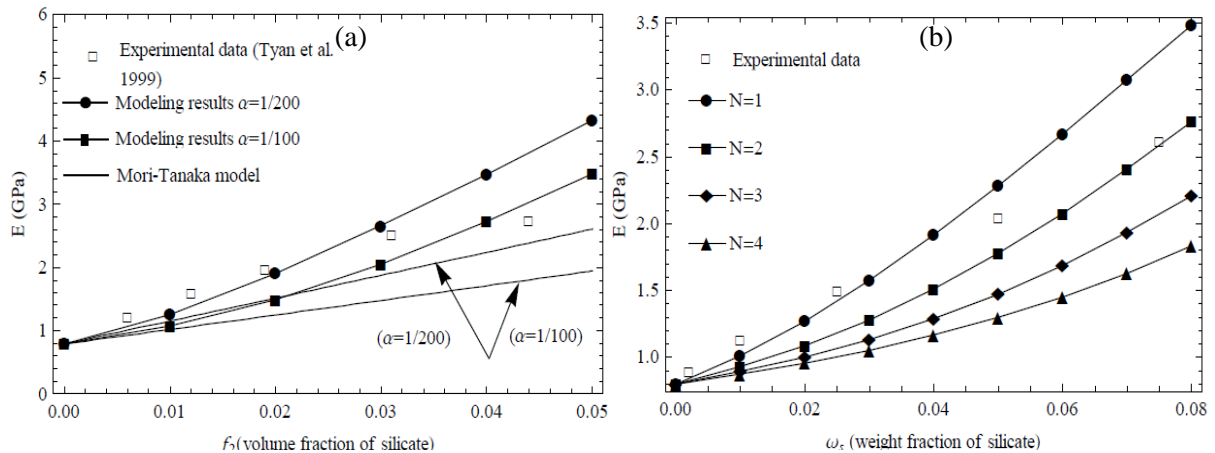


FIG. 4 – Theoretical predictions of the overall Young's modulus compared to experimental data of (a) polyimide-MMT clay nanocomposites characterized by Tyan et al. [12] and (b) polyamide-6-MMT clay nanocomposites characterized by Anoukou et al. [9].

In figure 4b are shown our theoretical predictions and the experimental overall Young's modulus of polyamide-6-MMT clay nanocomposite materials characterized by Anoukou et al. [9]. The effect of the average number N of silicate layers in the equivalent particles on the overall Young's modulus is shown in the figure, with N ranging from 1 to 4, from completely exfoliated ($N = 1$) to well intercalated ($N \geq 2$)

nanocomposite. The theoretical predictions are represented as functions of the weight fraction of silicate to take into account the intercalated structure [9]. Note that the average silicate interlayer spacing d_{001} was taken equal to 4 nm. Increasing N results in a drastic diminution in modulus. The theoretical predictions taking into account the clay stacks structure seem to give credence to the idea that the nanocomposite tends to be intercalated when clay content increases. Obviously, the structural parameter values found for the clay must be seen as average values incorporating the fact that aggregates and exfoliated platelets are coexisting in the material.

4 Conclusion

In this work, dealing with polymer composites reinforced with nanoclay, we have presented a micromechanical approach using a self-consistent approach based on the double-inclusion model. Our development accounts both for the randomly orientation of reinforcements and for the contribution of the constrained region. The resulting formulation yielded to a pair of equations solved simultaneously for the overall elastic moduli of nanocomposite materials. The proposed model falls within the H-S bounds and reduces to that proposed by Walpole [11] when the constrained region is disregarded and the inclusion aspect ratio tends to zero. The proposed model relates the overall elastic stiffness of nanostructured material with its structural parameters. Using the general proposed formulation, a parametric study was achieved to evaluate the respective effects of clay structural parameters, nanoscopic size of particles and interphase characteristics on the overall nanocomposite stiffness. The efficiency of the proposed model to predict the experimental elastic response of polymer-clay nanocomposites was shown.

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