

## MODELLING OF THE ELASTIC PROPERTIES OF NANOPARTICLE FILLED RESINS

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### Abstract

*The assessment of nanocomposite mechanical properties is a challenging task. Their hierarchical structure, spanning from nano to macro length-scales, urges to account for the characteristic phenomena of each length-scale and to bridge their effects from the smaller scale to the macroscale.*

*In the present work two different approaches for the estimation of the elastic modulus of a nanoparticle filled polymer are proposed and compared. Both the models account for the emergence of an interphase layer embedding the nanoparticle, with mechanical properties different from those of the matrix.*

### 1 Introduction

One of the most interesting features characterizing nanocomposite material is that they offer outstanding improvements of mechanical and physical properties at very low filler concentrations, thus assisting in the achievement of high-level performances across various engineering applications.

In nanomodified polymers, as the filler size is decreased to the nanoscale, intra- and supra-molecular interactions lead to the emergence of an interphase zone whose properties differ from those of both constituents and whose thickness may be comparable to the particle size. Sevostianov and Kachanov [1] showed that the effect of such interphase on the overall mechanical properties can be substantial, depending on the ratio of the interphase thickness to the particle size and the variability of the properties across the interface thickness.

Moreover other complexities which may arise in the material configuration, such as macromolecular chain entanglement or imperfect bonding, can be accounted for through the “apparent” elastic properties of the interphase.

In this work two different approaches for the estimation of the elastic modulus of a nanoparticle filled polymer are analyzed and compared. Both of them account for the emergence of an interphase layer embedding the nanoparticle, with mechanical properties different from those of the matrix.

The first method makes use of Hashin and Shtrikman’s micromechanical solution [2] within a two step-analysis and provides an analytical estimation of the elastic modulus of the nanocomposites, explicitly accounting for the size and properties of the interphase.

The second approach makes a combined use of the Voronoi cell concept and of the finite element method. This approach, initially proposed by Davy and Guild [3] for microparticle reinforced polymers, is based on the construction of a FE axisymmetrical cell of which the

size depends on the nanoparticle radius and on the filler volume fraction and provides a numerical estimation of the global stiffness of the studied system. Relevant results are discussed and compare with the aim to shown the influence of all the involved parameters.

## 2 A nanostructural model based on Hashin and Shtrikman's solution

By using variational principles in the linear theory of elasticity, Hashin and Shtrikman [2] provided the upper and lower bounds for the effective elastic moduli,  $K^*$  and  $G^*$ , of an isotropic composite material comprising a matrix (m) and a filler (p):

$$K_m + \frac{f_p (K_p - K_m)}{1 + (1 - f_p) R_m (K_p - K_m)} \leq K^* \leq K_p + \frac{(1 - f_p) (K_m - K_p)}{1 + f_p R_p (K_m - K_p)} \quad (1a)$$

$$G_m + \frac{f_p (G_p - G_m)}{1 + (1 - f_p) Q_m (G_p - G_m)} \leq G^* \leq G_p + \frac{(1 - f_p) (G_m - G_p)}{1 + f_p Q_p (G_m - G_p)} \quad (1b)$$

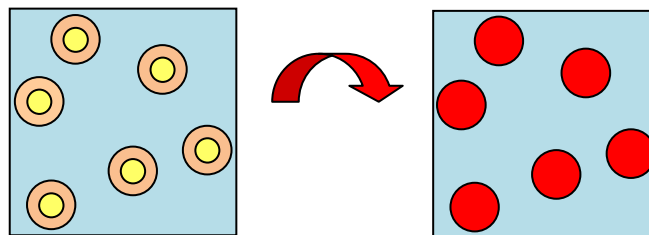
where:

$$R_k = \frac{3}{3K_k + 4G_k}, \quad Q_i = \frac{6(K_k + 2G_k)}{5G_k(3K_k + 4G_k)} \quad k = m, p \quad (2)$$

$f_p$  is the filler volume fraction and subscripts m and p refers to the matrix and the filler, respectively.

Eqs. (1) can be easily extended to account for the presence of a spherical interphase layer embedding the nanoparticle, with elastic properties different from those of the matrix, by using a two-step analysis.

Under the hypothesis of isolated particles, namely low volume fractions, and perfectly bonded surface (Figure 1a), each particle and the surrounding interphase material can be changed for an "equivalent homogeneous spherical particle (EHP)" of radius  $a=r_0+t$ , being  $r_0$  the radius of the original nanoparticles and  $t$  the interphase thickness (Figure 1b).



**Figure 1.** Conversion of the three-phase nanocomposite into an equivalent two-phase material.

Then, as a first step, the elastic properties of the *EHP*,  $K'$  and  $G'$ , can be thought of as the lower bound of the effective elastic moduli of a two phase material constituted by the interphase and the nanoparticle only, which can be estimated according to Eqs. (1):

$$K' = K_i \left\{ 1 + \frac{\left(\frac{r_0}{a}\right)^3 \left(\frac{K_p}{K_i} - 1\right)}{1 + \left[1 - \left(\frac{r_0}{a}\right)^3\right] \frac{1 + \nu_i}{3(1 - \nu_i)} \left(\frac{K_p}{K_i} - 1\right)} \right\} \quad G' = G_i \left\{ 1 + \frac{\left(\frac{r_0}{a}\right)^3 \left(\frac{G_p}{G_i} - 1\right)}{1 + \left[1 - \left(\frac{r_0}{a}\right)^3\right] \frac{8 - 10\nu_i}{15(1 - \nu_i)} \left(\frac{G_p}{G_i} - 1\right)} \right\} \quad (3)$$

As a second step, the elastic properties of the nanocomposite,  $K_C$  and  $G_C$ , can be assessed through the lower bound of the effective elastic moduli of the two phase material constituted by the matrix and the *EHP*:

$$K_C = K_m \left\{ 1 + \frac{f_p \left(\frac{a}{r_0}\right)^3 \left(\frac{K'}{K_m} - 1\right)}{1 + \left[1 - f_p \left(\frac{a}{r_0}\right)^3\right] \frac{1 + \nu_m}{3(1 - \nu_m)} \left(\frac{K'}{K_m} - 1\right)} \right\} \quad G_C = G_m \left\{ 1 + \frac{f_p \left(\frac{a}{r_0}\right)^3 \left(\frac{G'}{G_m} - 1\right)}{1 + \left[1 - f_p \left(\frac{a}{r_0}\right)^3\right] \frac{8 - 10\nu_m}{15(1 - \nu_m)} \left(\frac{G'}{G_m} - 1\right)} \right\} \quad (4a-b)$$

Finally the modulus of elasticity in tension of the nanocomposite,  $E_C$ , can be determined as:

$$E_C = \frac{9K_C G_C}{3K_C + G_C} \quad (5)$$

The validity of Eqs. (4a) and (4b) is hampered by the condition  $f_p \left(\frac{a}{r_0}\right)^3 < 1$ , providing the following limitation on the interphase thickness  $t$ :

$$t < r_0 \frac{1 - \sqrt[3]{f_p}}{\sqrt[3]{f_p}} \quad (6)$$

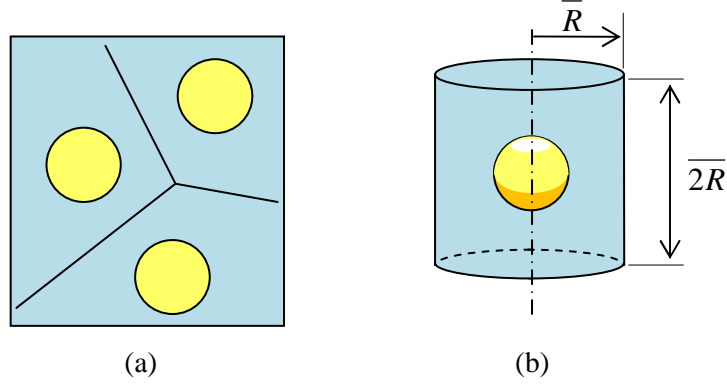
It is worth mentioning here that a “two-step” analysis using Hashin’s solution has also been proposed by Dorigato *et al.* [4] with the aim to take into account agglomeration effects arising in nanocomposites. However in the first step of their analysis, Dorigato *et al.* [4] suggested to use the upper bound Eq. (1) instead of the lower one, as proposed in the present work.

### 3 A FE approach based on the Voronoi cell

The Voronoi cell approximation was developed by Davy and Guild [3] with the aim to determine the stiffening effects due to spherical particles within a matrix using finite element analysis, under the hypothesis of homogeneous Poisson process of particles, with a further correction to account for the non-overlapping of particles. The Voronoi cell surrounding each particle is defined as the set of points belonging to the space which is regarded as the domain of the distribution, characterized by being closer to the center of the particle belonging to that cell than to every other center of particle in the material [3] (Figure 2a). Generally speaking, this cell can be much irregular; in order to overcome this Davy and Guild [3] proposed to reshape it into a cylinder with the same volume. This approximation is consistent with the nature of the stress state around a spherical particle under uniaxial loading [5, 6]. The size of the equivalent cylinder is defined by the following averaged radius (Figure 2b):

$$\bar{R} = \sqrt[3]{\frac{2}{3f_p}} r_0 \quad (7)$$

Where  $r_0$  is the radius of the spherical filler and  $f_p$  the volume fraction.



**Figure 2.** (a) Schematic representation of Voronoi's cells surrounding particles in a 2D space. (b) The equivalent Voronoi's cell proposed by Davy and Guild [5].

The method proposed by Davy and Guild is modified here to account for an interphase layer embedding the nanoparticle, with elastic properties different from those of the matrix (see Figure 3a). Such a region is assumed to be homogeneous, with uniform elastic properties. By doing so, the outer interphase radius,  $t+r_0$ , should always be lower than  $\bar{R}$ , so that the following condition on the on the interphase thickness holds :

$$t \leq r_0 \left( 1 - \sqrt[3]{\frac{2}{3f_p}} \right) \quad (8)$$

The equivalent Voronoi cell can be used within a finite element analysis with aim to determine the elastic modulus of the nanocomposite by simply evaluating the global stiffness of the cell. The polar symmetry of the analyzed system allows one to use axy-symmetric plane elements for the finite element analysis. With reference to Figure 3b, symmetric boundary conditions can be used, along  $AB$ , further reducing the complexity of the analysis. An example of the mesh used in the FE models is shown in Figure 3c.

The boundary conditions applied to the cell are shown in Figure 3 and can be summarized as follows:

- all nodes along  $BC$  are constrained to the same displacement  $u_x$ ;
- all nodes along  $DC$  are constrained to the same displacement  $u_y$ ;
- a constant stress  $\bar{\sigma}$  is finally applied along  $DC$ .

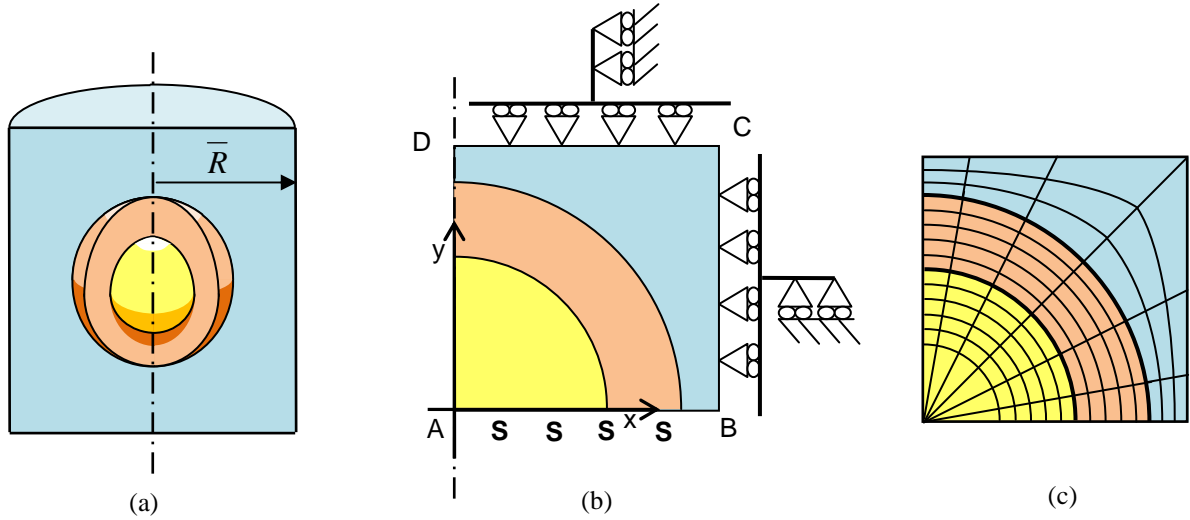
Accordingly, the averaged stiffness of the FE cell can be calculated as follows:

$$\bar{E} = \frac{\sigma}{\varepsilon} = \frac{\sigma}{\delta \bar{R}^{-1}} \quad (9)$$

where  $\delta$  is the  $u_y$  displacement of the nodes along  $DC$ .

In addition a statistical correction, ( $E_{corr}$ ) related to particle dispersion, can be introduced. The elastic modulus of the nanocomposite can be finally estimated according to the following expression:

$$\frac{1}{E_c} = \frac{1}{E} + \frac{1}{E_{corr}} \quad \frac{1}{E_{corr}} = \frac{1}{2} \left( \frac{\bar{R}^3}{r_0^3} \right) \left( \frac{R^3}{r_0^3 E} \right)^{II} CV(f_p) \quad (10 \text{ a-b})$$



**Figure 3.** (a) The equivalent Voronoi cell proposed to account for an interphase layer. (b) Geometry and boundary conditions of the axis-symmetric cell used in the FE calculations. (c) Example of the mesh used in the FE analyses.

The second order differential term in Eqs. (10 a-b),  $\left( \frac{R^3}{r_0^3 E} \right)^{II}$ , can be approximated, using the finite difference method, as:

$$\left( \frac{R^3}{r_0^3 E} \right)^{II} = \left( \frac{R_1^3}{r_0^3 E_1} + \frac{R_2^3}{r_0^3 E_2} - 2 \frac{\bar{R}^3}{r_0^3 E} \right) / \Delta^2 \quad (11)$$

where  $E_1$  and  $E_2$  are the averaged Young modulus associated to cells of radius  $R_1$  and  $R_2$ :

$$\frac{R_{1,2}^3}{r_0^3} = \frac{\bar{R}^3}{r_0^3} \pm \Delta \quad (12)$$

Being  $\Delta$  the step size (convenient values of  $\Delta$  are listed in Table 1).

The coefficient of variation,  $CV$ , accounting for particle statistical distribution can be calculated as follows:

$$CV(f_p) = \left[ \left( f_p^2 / 1.1108 \right) \left( 1 - 2 \int_0^1 u^{-3} e^{\left( -k \left( u^{-1} + 3u^{\frac{1}{3}} - 4 \right) \right)} du \right) \right] - 1 \quad (13)$$

where  $k$  can be obtained from the following equation:

$$\frac{1-f_p}{f_p} = \int_0^1 u^{-2} e^{\left(-k\left(u^{-1}+3u^{\frac{1}{3}}-4\right)\right)} du \quad (14)$$

$f_p$	$\Delta$	CV	$f_p$	$\Delta$	CV
0.02	8	0.705579	0.1	1	0.4652
0.04	6	0.632405	0.2	0.6	0.27647
0.06	4	0.569664	0.3	0.4	0.14935
0.08	2	0.514471	0.4	0.2	0.061194

Table 1. Values for CV and  $\Delta$ , as a function of  $f_p$ , to be used in Eq. (10) and Eq. (11).

### 5 Results and discussion

The aim of this section is to compare the results which can be obtained with the model proposed.

Figure 4 shows the values of the normalized elastic modulus,  $E_c/E_m$ , where  $E_m$  is the Young modulus of the polymer matrix, versus the nanoparticle radius. The effect of the interphase thickness and of the nanoparticle size is evident. For a given value of  $t$ , the smaller the particle size the higher the overall elastic modulus. Conversely, as the nanoparticle size increases, the overall elastic modulus asymptotically decreases. This effect is due to the reduced influence of the interphase for larger nanoparticles. It is also evident that beyond particle radii greater than about 70 nm, independently of the interphase thickness, the nanocomposite elastic modulus tends towards the same constant value.

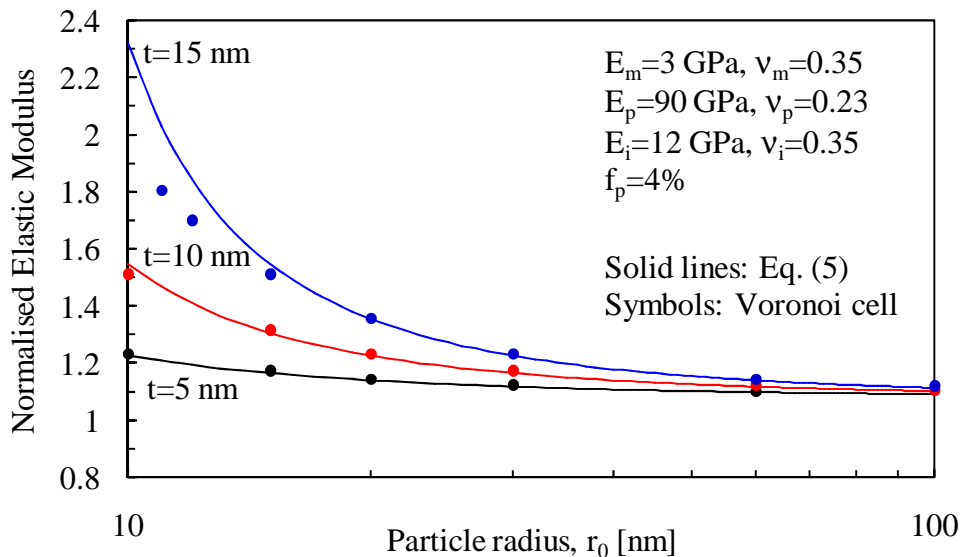
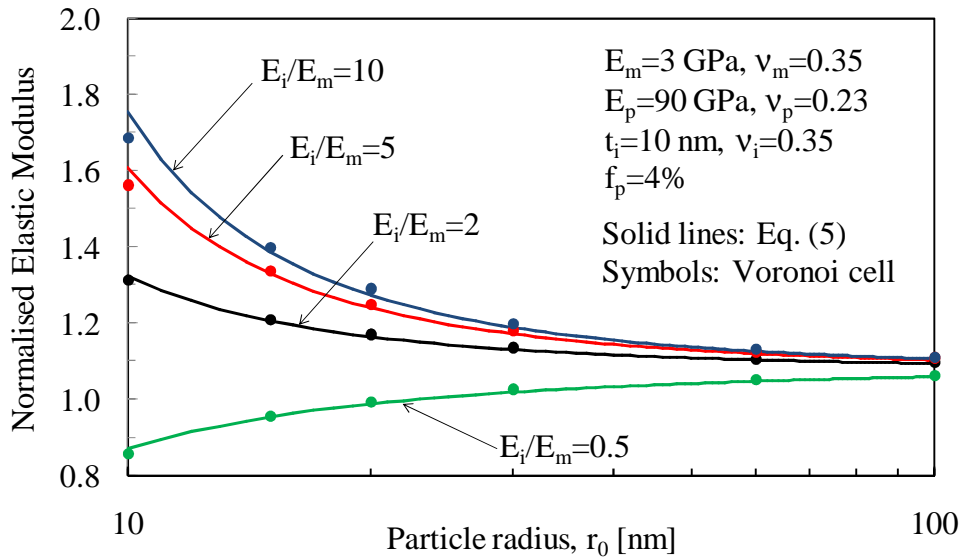


Figure 4. Effect of the particle radius and of the interphase thickness on the normalized nanocomposite elastic modulus. Comparison between Eq. (5) and Eq. (10a).

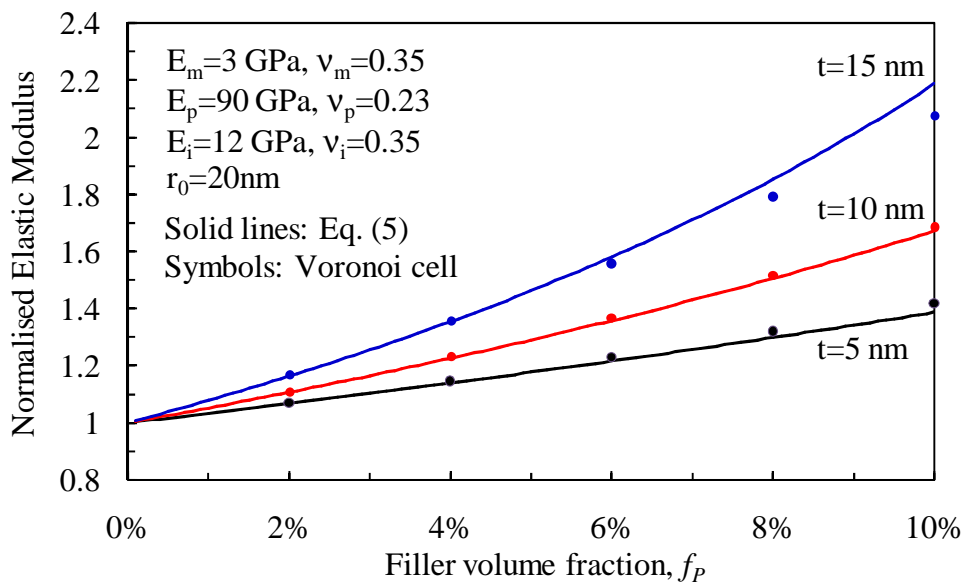
Differently, Figure 5 shows the effect of the elastic properties of the interphase on the normalised elastic modulus of the nanocomposite. It is evident that as the interphase elastic

stiffness increases the nanocomposite elastic modulus increases, while for softer interphases the nanocomposite stiffness is lower than that of the matrix.

Figures 4 and 5 also show that the results obtained by using the two analyzed method are in good agreement as far as conditions given by Eq. (6) and Eq. (8) are guaranteed.



**Figure 5.** Effect of the particle radius and of the  $E_i/E_m$  ratio on the normalized nanocomposite elastic modulus. Comparison between Eq. (5) and Eq. (10a).



**Figure 6.** Effect of the filler volume fraction and of the interphase thickness on the normalized nanocomposite elastic modulus. Comparison between Eq. (5) and Eq. (10a).

Finally Figure 6 shows the normalized elastic modulus of the nanocomposite versus the nanofiller volume fraction for different interphase thickness. It is evident that, for a given value of  $f_p$ , the thicker the interphase layer, the higher the overall elastic modulus. Moreover, it is evident that both methods predict an elastic modulus monotonically increasing as a function of the nanoparticle volume fraction. This trend disagrees with the behaviour of “stiffness leveling” exhibited by the experimental data which is universally acknowledged to

be due to aggregation effects arising at higher volume fractions and which are, by hypothesis, neglected by the models proposed in the previous sections.

## 6 Conclusions

In this work two different approaches for the estimation of the elastic modulus of a nanoparticle filled polymer are analyzed and compared. Both the proposed models account for the emergence of an interphase layer embedding the nanoparticle, with mechanical properties different from those of the matrix. It has been shown that both models are able to seize the effect of the interphase thickness and elastic properties. Moreover the models are able to account for the nanoparticle size, the smaller the particle radius the higher the overall elastic modulus.

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