THEORETICAL MODELLING OF THE ELASTIC MODULUS OF POLYMER NANOCOMPOSITES

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Abstract
In this paper, mathematical models are investigated and suggested for the calculation of the elastic modulus of polymer nanocomposites, with particular emphasis on the effect from agglomerates and the particle interphase properties. The multi-phase Mori-Tanaka model and an interphase model are considered as two relevant models, as these models only require the designation of a few system independent parameters. The model calculations are compared to results from other models, as well as experimental data for nanocomposites with silica particles, multi-walled carbon nanotubes (MWCNTs) and different variants of graphene. The suggested theoretical models are found to be applicable for analysis of nanocomposites with various nanoparticles, and are considered to be relevant tools in a general multi-scale 'model toolbox'.

1. Introduction

Polymers are widely used in engineering applications, e.g. as adhesive and in fibre-reinforced composites where it constitutes the continuous phase. Model analysis of lightweight materials, such as composites, is becoming more important in the design, development and analysis of novel and complex structures. There is often a desire or need to improve the mechanical properties of the polymers, especially for advanced high-performance applications. In recent years, a lot of effort has therefore gone into investigating the effect of adding nano-sized inclusions, such as e.g. nanoclay, nanosilica, carbon nanotubes (CNTs) and carbon nanofibres (CNFs) [1-3], and lately also different variants of graphene, see e.g. [4] and the references therein.

The macroscopic nanocomposite material parameters are required in finite element (FE) modelling, for analysis of the nanocomposite itself, or of a composite material where the nano-modified polymer constitutes the matrix of a continuous fibre-reinforced material. One important mechanical property is the Young's modulus of the nanocomposite. Most of the commonly used inclusions have a higher elastic modulus than the polymer itself, and may therefore contribute to an increased value.

For the models to be able to handle inclusions of various geometries, they must be flexible, while at the same time giving accurate predictions. In practice, the nanocomposite structure on the micro-level may be difficult to understand in detail. A detailed microstructural understanding may, however, not be required on a macroscopic level. Therefore, the mathematical models should have model parameters with physical meaning, without being directly system dependent, but they should still be sophisticated enough to give an accurate estimate and be able to predict the behaviour observed in experimental testing.

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The main aim of this work is to identify and establish flexible and system-independent mathematical model tools for the prediction of the elastic modulus of multi-phase nanocomposites. The elastic modulus of the nanocomposite will depend on different factors, see e.g. [5]. In this paper, the influence on the modulus from the interphase around the nanoparticles and from agglomerates or a percolation network will be considered. A continuum mechanics approach is assumed to be applicable [4-6].

2. Mathematical modelling

Different models have been presented and applied for calculation of the Young's modulus of nanocomposites. Most of these models are based on short-fibre composites models, assuming perfect dispersion (i.e. no agglomerates or particle percolation) and a "no-slip" boundary condition at the particle-matrix interface. Some modelling approaches include the possibility for altering between "no-slip" and "slippage" at the interphase. The Halpin-Tsai equations, in different versions, are also often applied. A brief model overview can be found in [5].

In this paper, a set of more flexible models for nanocomposites are considered; the Mori-Tanaka approach and an interphase model. For spherical particles the interphase seems to be an important factor, where the interphase model can be applied. Particle agglomeration, or the formation of percolation networks, is more likely for non-spherical particles, which can be handled by the multi-phase Mori-Tanaka model.

2.1. Models

The multi-phase Mori-Tanaka method makes it possible to include more than one inclusion phase, for example the combination of dispersed nanoparticles and voids/agglomerates, or a second type of particle with other elastic properties and/or a different geometric shape [7-9]. This method has been reported to agree well with experimental results, e.g. [6] and the references therein. Different model variants based on the Mori-Tanaka approach can be found in the literature, see e.g. [10] for a review, but in this paper we apply the variant described by Thorvaldsen *et al.* [5], where the Young's modulus of the nanocomposite is given by

$$C_C = \left(V_0 C_0 + \sum_{r=1}^{N-1} V_r C_r A_r^{dil} \right) A_0 \tag{1}$$

Here, the first term in the parenthesis is the contribution to the Young's modulus from the matrix phase, and the sum contains the contribution from the particle phases. More details are found in [5]. The current model does not include any particle interphase properties.

As an alternative approach to models with a slippage condition, it can be assumed that the binding characteristics can be expressed by the elastic properties of an interphase surrounding the particles, i.e. a "second matrix phase". The elastic properties will typically vary (radially) through the interphase, with a smooth transition from the particle surface to the surrounding bulk polymer. A high interphase elastic modulus indicates good binding and less flexibility to deform when loaded, whereas a low interphase elastic modulus indicates a weaker binding with more flexibility to deform when loaded. An effective interphase model has been presented by Odegard *et al.* [11;12]. In this case, a "no-slip" condition at the interface between the particle and the interphase, and between the interphase and the bulk matrix has been assumed. However, the interphase itself introduces the wanted flexibility. In this case, the Young's modulus of the composite is expressed by (restricted to one type of particles),

$$C_C = C_m + \left[\left(V_p + V_i \right) \left(C_i - C_m \right) A_{pi} + V_p \left(C_p - C_i \right) A_p \right] \left[V_m I + \left(V_p + V_i \right) A_{pi} \right]^{-1} \tag{2}$$

where the elastic properties and volume fractions of the matrix (m), interphase (i) and free particles (p) are included. A more detailed description can, again, be found in [5].

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2.2. Model parameters

As already described, the interphase is defined as the region surrounding the particles, with different elastic properties compared to the bulk matrix. We assume that the interphase has a constant thickness t_i, and that the radius of the interphase r_i is expressed as $r_i = nr_p$. The dimensionless parameter n is here denoted the *interphase thickness factor*. The elastic properties are assumed constant through the interphase, and the thickness of the interphase is included in the calculations through the expressions for the volume fractions. It can be shown, see e.g. [5], that the volume fraction of the interphase is $(n^3 - 1)$ times the volume fraction of the particles, that is, $V_i = (n^3 - 1)V_p$, which puts some limitations in the maximum amount of free particles.

For nanocomposites with non-spherical particle inclusions, it is likely that the particles are not fully dispersed, and that a second inclusion phase is present in the form of particle agglomerates or a percolation network. The elastic properties of agglomerates of initially entangled particles will generally be quite different from the properties of the percolated networks of initially free particles. Different approaches may thus be needed.

The volume fractions of the dispersed (i.e. free) particles and agglomerates can be estimated using the degree of exfoliation (DOE) φ_{DOE}, which can be expressed as $\varphi_{DOE} = V_{p,f} / V_p$, where $V_{p,f}$ is the volume fraction of free particles, and V_p is the total volume fraction of particles in the composite. The DOE for a given nanocomposite can be estimated from a particle size analysis, see e.g. [13], and the DOE will vary as a function of volume fraction of V_p.

For some nanocomposites with non-spherical particles, the Young's modulus of the nanocomposite increases up to a certain volume fraction of nanoparticles, before the modulus is reduced and approaches a constant level independent of the volume fraction of the nanoparticles. The amount of particles where the Young's modulus is at its maximum, is referred to as the *percolation limit* [14], defined as the fraction of particles in the composite where the particles starts percolating into a network. Chatterjee [15] has presented a "switching function", $f_s(V_p)$, to model the amount of non-free particles in nanocomposites. Below the percolation limit, all particles are assumed to be free and well-dispersed, and $f_s(V_p) = 0$. Above the percolation limit, the volume fraction of the particles belonging to the percolation network is given by $V_a = V_p f_s(V_p) = V_p(1 - e^{-A((V_p/V_c)-1)^{0.474}})$. The remaining part of the particles is uniformly dispersed in the composite. In the above expressions, V_p is the total number of particles, whereas V_c is the volume fraction of particles defining the percolation limit, and A is an adjustable factor which modulates the width of the transition.

3. Results

Experimental data for different nanocomposites are compared with the results obtained using the above described models. Additional models are also included for comparison. More results than included here can be found in [5].

3.1. Spherical particles

Experimental tests for two nanosilica/epoxy composites are reported in [5]. For these systems, a perfect dispersion of the spherical silica particles is assumed, and, hence, a two-phase nanocomposite is considered. The Young's modulus can in this case be estimated from both the two-phase Mori-Tanaka model and the interphase model.

For the amine-cured composite, the two different models, together with the Halpin-Tsai equation (see e.g. [5] and the references therein for more details), are plotted together with the experimental data in

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Fig. 1(a). The interphase thickness factor as a function of silica volume fraction is selected in the range from 1.05 to 1.1, and the elastic modulus of the interphase is in this case set to a constant value of 4.0 GPa. As can be observed, the Halpin-Tsai equation overestimates the elastic modulus of the composite. However, both the Mori-Tanaka two-phase model and the interphase model estimate the elastic modulus very well for all volume fractions of silica (provided the selected interphase characteristics are employed for the interphase model).

The modelling and experimental results for the anhydride-cured composite are given in Fig. 1(b). In this case, the interphase thickness factor is set much higher, and varied between 1.7 and 1.4 as a function of the silica volume fraction. The elastic modulus of the interphase is also in this case set to a constant value of 4.0 GPa. As can be seen in the figure, the Halpin-Tsai equation and the interphase model estimate the elastic modulus of the composite very well. The two-phase Mori-Tanaka model, on the other hand, underestimates the elastic modulus of the composite. As has been shown in [5], selecting a lower and constant interphase thickness factor of 1.3, and instead varying the interphase elastic modulus of the anhydride-cured composite may be relevant. It was found that an interphase modulus between 5.0 and 6.0 GPa agrees well with the experimental data, whereas an elastic modulus of 4.0 GPa underestimates the composite modulus.

A more thorough discussion of the model parameter values for each system, as well as a discussion of the different properties of the two nanocomposite systems, can be found in [5].

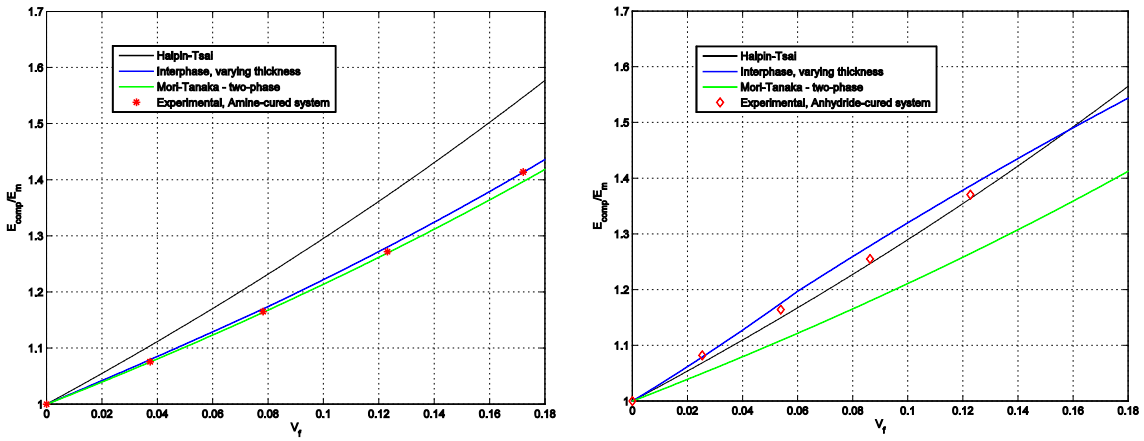

Figure 1. Normalized Young's modulus for two nanosilica/epoxy composites. a) Amine-cured and b) anhydride-cured composite. In this case, V_f denotes the volume fraction of well-dispersed particles.

3.2. Non-spherical particles

The three-phase Mori-Tanaka model is applied for three different nanoparticle/polymer systems, as non-free particles are expected for higher volume fractions of nanocomposites with non-spherical particles. Also, agglomerates or a percolated network of particles are expected to influence more on the elastic modulus of the nanocomposite than will the particle interphase properties. The "switch function" and the DOE function are employed for estimation of the amount of non-free particles. For comparison, a three-phase parallel model and a variant of the Takayanagi model [16], which both have been presented by Loos and Manas-Zloczower [14], are also included. The two latter models (only) apply the "switch function" for estimating the amount of non-free particles.

First, experimental data for base-washed graphene oxide (bwGO) and graphene oxide (GO) in a poly(methyl methacrylate) (PMMA) matrix [17] are compared with the model calculations. From the experimental results, the Young's modulus increases up to a particle volume fraction of 0.0052 before

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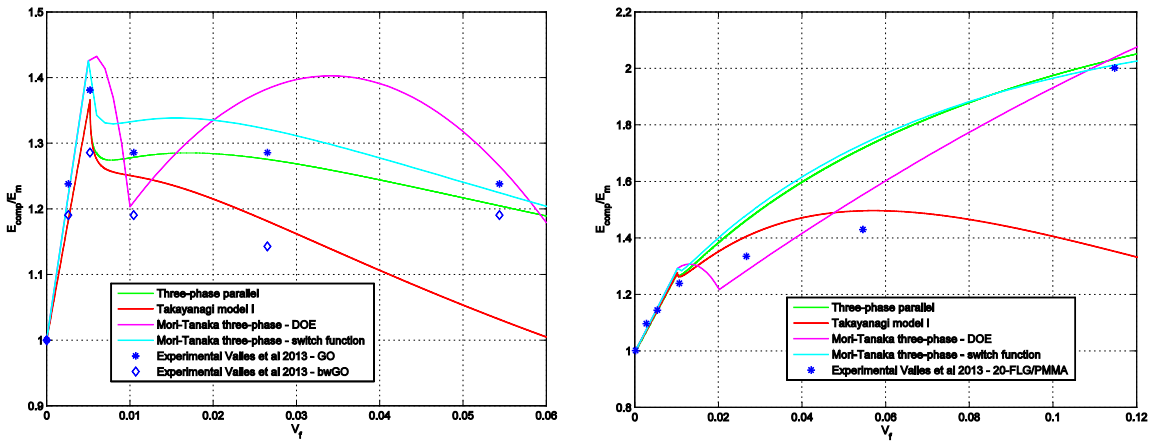
dropping to a lower level. This volume fraction may be considered as the percolation limit in this case, i.e. the fraction where the non-free particles will start influencing the elastic properties. For all models $E_m = 2.1$ GPa and $E_a = 0.5$ GPa. To best fit the model calculations to the experimental data, E_p is set to 350 GPa in Mori-Tanaka model, whereas for the two other models E_p is set to 150 GPa. The applied values are in the range reported in the literature, see e.g. [4] and the references therein. Furthermore, for the Mori-Tanaka model the aspect ratio for the disc-shaped inclusions is assumed to be $\alpha = l/d = 1/20000$. Moreover, $\varphi_{DOE} = 1.0$ from zero to $V_p = 0.005$, and then decreases linearly to $\varphi_{DOE} = 0.25$ at $V_p = 0.01$, before it decreases linearly to $\varphi_{DOE} = 0.05$ at $V_p = 0.06$. The "switch function" parameter $A = 0.95$ for all models. As can been seen from the plots in Fig. 2(a), all the involved models are capturing the peak elastic modulus for volume fraction of 0.0052. The Mori-Tanaka model using the DOE function, results in a drop in modulus at $V_p = 0.01$, but then gives a too high increase before starting to decrease again. A more sophisticated DOE function may be required to obtain a good match for higher volume fractions in this case. Using the Mori-Tanaka model with the "switch function" is found to agree very well with the experimental data – also for higher volume fractions. This is also the case for the three-phase parallel model. The Takayanagi model underestimates the composite modulus for higher volume fractions. Note that a higher Young's modulus is applied for the particles in the Mori-Tanaka model compared to the other two models. The three-phase parallel model and the Takayanagi model thus both indicate a much lower elastic modulus for the bwGO/GO, which is close to the minimum elastic modulus value that has been reported. Moreover, only the Mori-Tanaka model explicitly applies a representative aspect ratio for the bwGO/GO particles.



(a) (b)

Figure 2. Nanocomposites with a PMMA matrix and a) bwGO/GO particles, and b) 20-FLGs.

Second, experimental data for PMMA reinforced by few-layer graphene (FLG) nanoparticles are considered [18]. For the FLGs with an average diameter of 20 μm (20-FLG), the elastic modulus of the nanocomposite is found to increase as a function of the particle volume fraction, as the size of the FLGs are above a critical size for load transfer. From the experimental results in this case, the Young's modulus increases linearly up to a particle volume fraction of around 0.01. This volume fraction may in this case be considered as the percolation limit. For all models $E_m = 2.1$ GPa and $E_a = 0.5$ GPa. Again, to best fit the model calculations to the experimental data, for the Mori-Tanaka model $E_p = 120$ GPa, whereas for the two other models $E_p = 60$ GPa. The FLGs are said to have a thickness of maximum 5 nm, and thus for the Mori-Tanaka model the aspect ratio for the disc-shaped

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inclusions $\alpha = 5/20000$. Moreover, $\varphi_{DOE} = 1.0$ from zero to $V_p = 0.01$, and then decreases linearly to $\varphi_{DOE} = 0.4$ at $V_p = 0.02$, before it decreases linearly to $\varphi_{DOE} = 0.35$ at $V_p = 0.12$. The "switch function" parameter $A = 0.35$ for all models. As displayed in Fig. 2(b), with the current parameter values all the models capture the increase in modulus for low FLG volume fractions. Moreover, the Mori-Tanaka and the three-phase parallel models are also able to estimate the elastic modulus for higher volume fractions where non-free particles are expected. The Takayanagi model again underestimates the composite modulus for higher volume fractions. Again, one should notice the higher Young's modulus employed for the Mori-Tanaka model compared to the other two models. Also, the Mori-Tanaka model is the only model which explicitly applies the reported aspect ratio for the 20-FLG particles.

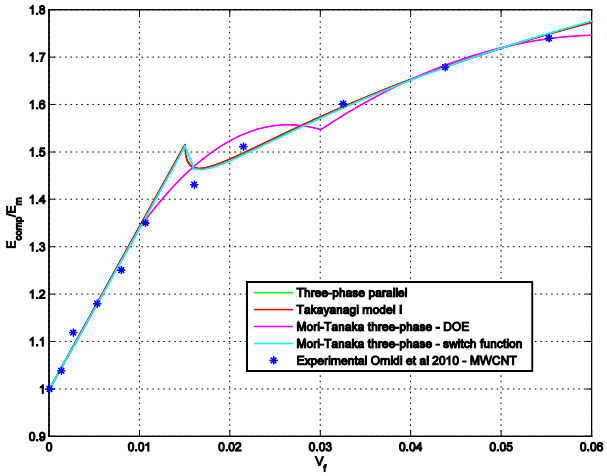

Figure 3. Normalized Young's modulus for a MWCNT/polymer nanocomposite.

In this third case, experimental data for a MWCNT/polymer nanocomposite reported by Omidi *et al.* [19] (also reported in [14]) have been compared with the model calculations. The density of the matrix is in our models set to 1200 kg/m^3, which is close to the density of the main component of the matrix (LY-5052; $\rho = 1170$ kg/m^3). This matrix density results in a lower volume fraction compared to what has been reported in [14]. In this case, the volume fraction for which the agglomerates are assumed to influence on the elastic properties is set to 0.015. For all models $E_m = 3.11$ GPa and $E_a = 5$ GPa. For the Mori-Tanaka model $E_p = 1000$ GPa, whereas for the two other models $E_p = 110$ GPa. For the Mori-Tanaka model the aspect ratio for the fibre-like inclusions $\alpha = 1000/15$. Moreover, $\varphi_{DOE} = 1.0$ from zero to $V_p = 0.01$, and then decreases linearly to $\varphi_{DOE} = 0.525$ at $V_p = 0.03$, before it decreases linearly to $\varphi_{DOE} = 0.35$ at $V_p = 0.06$. The "switch function" parameter $A = 0.6$ for all models. As can be seen from the plots in Fig. 3, with the current set of parameter values the calculated elastic modulus agree well with the experimental data for all the models. The percolation limit is not significant in this case, and hence using the "switch function" for estimating the volume fraction of agglomerated particles gives a non-physical modulus peak. This peak is avoided in the Mori-Tanaka model when using the DOE function. It should be noted that the three-phase parallel model and the Takayangi model both indicate a too low Young's modulus for the MWCNTs, whereas the Mori-Tanaka model indicates a value in the order of 1TPa; as an example Lu [20] reported a Young's modulus of 975 GPa. As the Mori-Tanaka also explicitly applies the reported aspect ratio of the MWCNTs, this model is considered as the most representative model in this case.

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4. Summary and conclusions

In this paper, different mathematical models are described for the elastic modulus of nanoparticle/ polymer systems as a function of volume fraction of the particles. Agglomerates/percolation networks and particle interphase properties are two relevant factors for the elastic modulus of nanocomposites. A set of flexible models for nanocomposites, which are relevant in multi-scale modelling of advanced high-performance composite structures (including finite element method analyses), has been described. The suggested models for modelling of the nanocomposites, i.e. the multi-phase Mori-Tanaka model and the Odegard *et al.* interphase model, are composite system-independent models containing a few general model parameters with a clear physical meaning. For describing the interphase properties in the interphase model, only two parameters are included; the interphase thickness factor and the interphase elastic modulus. For the Mori-Tanaka model, the elastic properties of all phases, as well as the particle aspect ratio, are explicitly applied in the calculations of the composite elastic properties.

The two suggested models are found to be applicable to nanocomposites with spherical particles, where the interphase properties seems to be important for the Young's modulus of the composite as a function of volume fraction of particles. For comparison, the often applied Halpin-Tsai equation is found to overestimate the nanocomposite modulus. Moreover, the three-phase Mori-Tanaka model is compared with experimental data found in the literature, and demonstrated to be applicable to polymer composites with different non-spherical particles, that is, composites with base-washed and non-washed graphene oxide particles, few-layer graphene particles and MWCNTs. For all three cases using this model, representative parameter values have been applied for the different materials. For comparison, calculations using a three-phase parallel model and a modified version of the Takayanagi model have been demonstrated to also agree well with experimental results – especially for low volume fractions. However, for these two latter models a Young's modulus of the particles that is much lower than the values reported in the literature had to be chosen; the most significant deviation from reported values is seen in the case of the MWCNT/polymer nanocomposite. In addition, for the two latter models, the aspect ratio of the particles is not explicitly applied in the calculations.

As a final and overall conclusion, the multi-phase Mori-Tanaka model and the Odegard *et al.* interphase model are found to be flexible, system-independent and applicable for calculating the elastic properties of the various nanocomposites, including both low and high volume fractions. For these two models representative parameter values with a physical meaning are employed.

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