A THREE-PHASE RULE OF MIXTURES MODEL FOR THE EFFECTIVE ELASTIC PROPERTIES OF THE COMBINATION OF DISPERSED AND AGGLOMERATED MULTI-WALL CARBON NANOTUBES IN A POLYMER MATRIX

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Abstract
Polymers are reinforced with nanosized particles to improve the mechanical properties of the polymer. To obtain a nanocomposite with better properties, a key condition is to have a good dispersion of the reinforcing particles. However, even at low concentrations the polymer-particle interface increases rapidly with better dispersion of the agglomerates. Processing challenges, such as dispersion stability and viscosity build-up, makes it difficult to obtain a high degree of dispersion, i.e. mainly freely suspended particles. Therefore, one typically ends up with a modified polymer system with both dispersed nanoparticles and agglomerates.

Mathematical models are established for calculating the effect of the nanoreinforcement on the macroscopic mechanical properties. In this paper, a three-phase rule of mixtures model is presented for the effective Young's modulus of a polymer reinforced with multi-wall carbon nanotubes (MWCNTs). The model takes into account both the dispersed MWCNTs and agglomerates of nanotubes, to quantify the influence on the effective Young's modulus for a varying degree of dispersion. Model parameters are estimated from a differential sedimentation particle size analysis.

1 Introduction
Since the landmark paper by Iijima [1] in 1991, a lot of research has been done on utilizing the exceptionally good mechanical properties of carbon nanotubes (CNTs), see e.g. [2;3] and the references therein. One area of research has been focused on improving the effective Young's modulus of neat polymer systems by adding CNTs. A neat thermoset polymer may typically have a Young's modulus on the order of 1 to 3GPa [3;4], whereas the Young's modulus of CNTs is in the order of 0.3 to 1TPa [3;5-9].

A good dispersion of the CNTs is one essential factor for improving the mechanical properties of a nanomodified polymer system, compared to a neat system. If the interparticle distance is too short, or the nanotubes are entangled or agglomerated, the nanotubes may instead of reinforcement in the polymer material, act as imperfections. From a chemical and processing point of view, several other factors will also affect the mechanical properties of the CNT reinforced polymer system, such as the nanotube production method, type (single-wall or multi-wall), aspect ratio, waviness, nanotube length and orientation distribution, surface treatment and functionalisation, adhesion between the matrix and the nanotubes, as well as the load transfer [3;10-12].

Several experimental techniques and instruments are available for analysing the properties of the nanocomposite, also techniques to evaluate the degree of dispersion or exfoliation. Typically, CNTs show a bimodal distribution with both fully dispersed and entangled agglomerates of nanotubes. The process of separating one single nanotube from an agglomerate can thus be seen as an exfoliation. Various examples and an overview of experimental results may be found in [3;9].

Experiments are often complex, time consuming and expensive. Future development will therefore benefit from a strong coupling with mathematical models, as an important and useful tool, and an aid for understanding the behaviour of nanocomposite materials in more detail. Establishing accurate and detailed models will hence be essential to get a precise description of the properties of the composites on a nano level.

Fisher and Brinson [3] refer to two main modelling approaches for nanocomposites, that is, the "bottom-up" and the "top-down" approaches. The "bottom-up" approach starts out with the atomistic structure of the nanoreinforcement and the matrix. Typical model techniques are quantum mechanics, molecular dynamics and Monte-Carlo simulations [3;5]. These modelling approaches end up in fairly large systems to be solved for only a small part of the composite material, e.g. one single nanotube and a relatively short polymer chain, as the number of atoms is large. This small part should then be representative for the entire nanocomposite. The "top-down" approach, on the other hand, is based on continuum mechanics, where the nanoparticles and nano- or microinclusions are treated as continuum elements. Care must, however, be taken when applying the continuum mechanics approach, since the structure and the interactions at the atomistic level is essential for a precise description of the mechanical properties [3;5].

In this paper, we will apply the "top down" approach, employing a rule of mixtures model with the purpose of describing the effective elastic modulus of multi-wall carbon nanotubes (MWCNTs) dispersed in a polymer system, taking both exfoliated nanotubes and agglomerates into account. The model includes separate submodels for the dispersed nanotubes and for the agglomerates. We therefore refer to the model as a *three-phase rule of mixtures model*. Since the model includes separate parts, this may also be considered as a framework for defining and including more sophisticated submodels. Some of the model parameters in the model presented can be estimated from the particle size distribution determined by differential sedimentation particle analysis.

2 Mathematical models

2.1 Models for dispersed carbon nanotubes in a polymer matrix

A relatively simple rule of mixtures model for the effective Young's modulus E_{DNT} of the nanocomposite with dispersed single-wall carbon nanotubes (SWCNTs) is given by Fidelus *et al.*[13],

$$E_{DNT} = \lambda E_{CNT} V_{NT} + E_m (1 - V_{NT}) , \tag{1}$$

where V_{NT} in their model refers to the volume fraction of the dispersed nanotubes, and E_{CNT} and E_m denote the elastic moduli of the nanotubes and the neat matrix, respectively. Moreover, λ is the so-called Krenchel's coefficient, which for 3D randomly oriented rods with high aspect ratio may be set to a constant value (i.e. $\lambda = 0.2$).

Assuming that models for short-fibre reinforced composites can be applied to carbon nanotube reinforced polymer composites, alternative rule of mixtures models, explicitly including the elastic properties of the constituent materials, fibre length and fibre orientation functions can be established, see e.g. [14]. The parameters then need to be fitted to be in accordance with experimental data for the nanocomposites.

The Mori-Tanaka model is another approach for modelling the elastic properties of CNTs embedded in a polymer system, see e.g. [15;16]. This method is referred to as a promising micromechanics method for accurate modelling of nanocomposites, see [3] and the references therein.

More sophisticated model approaches may also be applied, often referred to as hybrid models. These models are believed to be even more accurate, in that more of the effects listed above, which will influence on the effective Young's modulus, are taken into account. As an example, Fisher *et al.* [17;18] and Bradshaw *et al.* [19] developed a finite element method (FEM) model for calculating the Young's modulus of a curved nanotube, and then applied this reduced value for curved nanotubes as input to a macro-mechanical model requiring straight nanotubes. FEM models are also very suitable for including interphase effects between the nanotubes and the surrounding matrix.

2.2 Models for agglomerates of nanotubes in a polymer matrix

For the models mentioned above, describing exfoliated CNTs in a polymer matrix, it is typically assumed that the CNTs are homogenously and well distributed in the matrix. Due to challenges in obtaining a perfect dispersion of the CNTs, the models may give an inaccurate prediction of the mechanical properties of a nanocomposite. For that reason, an additional model should be included, that also accounts for the agglomerated CNTs.

To the authors' knowledge, few attempts are reported on modelling the properties of agglomerates of CNTs. Searching the literature, one finds a model by Hashin [20], which is applied by Dzenis [21], for describing the elastic properties of a spherical particle inclusion in a matrix. The same model has also been applied by Dorigato *et al.* [22] for modelling agglomerates of spherical silica nanoparticles and microparticles, where the elastic properties of the inclusions are based on the Hashin-Shtrikman model [23]. Other geometric shapes of the agglomerated inclusions will, however, not fit into this modelling framework. One solution is to use the Mori-Tanaka model. This model is applicable to agglomerates with a non-spherical shape, as applied by Luo and Daniel [24] in their development of a three-phase polymer/nanoclay model, including the epoxy matrix and a combination of exfoliated clay nanolayers and nanolayer clusters.

A micromechanics model for modelling straight and curved CNTs in combination with agglomerates of CNTs has been presented by Shi *et al*. [15;16]. In their work they considered "spherical inclusions" in the composite, with elastic properties different from the surrounding material. The non-agglomerated fraction of nanotubes is evenly dispersed in the matrix outside the inclusions. From the Voigt model found in [25], a value for the Young's modulus of the inclusions may be calculated from

$$E_{in} = \frac{3}{8\xi}\left[c_r \zeta E_{CNT} + (\xi - c_r \zeta) E_m\right] + \frac{5}{8} \frac{\xi E_m E_{CNT}}{(\xi - c_r \zeta) E_{CNT} + c_r \zeta E_m}, \tag{2}$$

where ξ and ζ are parameters introduced to describe the agglomeration of CNTs. The parameter ξ denotes the volume fraction of inclusions in the representative volume element (RVE) with respect to the total volume of the RVE, whereas the parameter ζ describes the fraction of the volume of the CNTs contained in the inclusions with respect to the total volume of nanotubes in the RVE. In the special case when $\zeta = 1$, all the nanotubes are located in the "spherical inclusions". Moreover, c_r denotes the average volume fraction of CNTs in the composites, and E_{CNT} and E_m are the Young's moduli of the CNTs and the matrix, respectively. In this model, it is assumed that both the nanotubes and the matrix may be regarded as isotropic materials. As seen, the key parameters involved are the volume fractions of the different constituents that are included in the composite.

As another approach, one may assume that a rule of mixtures model may be used for composites with agglomerates. For a neat matrix with homogenously distributed agglomerates (and no exfoliated carbon nanotubes), the effective Young's modulus yields,

$$E_C = \beta E_{INC} V_{INC} + E_m (1 - V_{INC}), \tag{3}$$

where β is a model parameter assumed to be estimated from empirical data, i.e. calculated the same way as the Krenchel's coefficient for the dispersed nanotube composite model presented by Fidelus *et al.* [13]. Moreover, E_{INC} is the Young's modulus of the inclusions, and V_{INC} is the volume fraction of the agglomerated CNTs *and* the matrix inside the inclusions with respect to the total volume of the RVE. That is, $V_{INC} = V_{ANT} + V_m^{INC}$, where V_{ANT} is the volume fraction of the agglomerates, and V_m^{INC} is the volume fraction of the matrix inside the inclusions. The volume fraction of the matrix inside the inclusions needs to be defined separately from the matrix volume fraction outside the inclusions to be consistent with the expression for the Young's modulus in (2). As before, E_m denotes the Young's modulus of the neat matrix, and $V_m = 1 - V_{INC}$ is the volume fraction of the neat matrix outside the inclusions.

Now, consider again the Shi *et al.* model above with all the nanotubes contained in the inclusions. In this case the expression for the Young's modulus in (2) can be applied for the inclusions part in (3), with ζ equal to unity. Denoting the effective modulus E_{INC}, we obtain the following expression:

$$E_{INC} = \frac{3}{8\xi}\left[c_r E_{CNT} + (\xi - c_r) E_m\right] + \frac{5}{8} \frac{\xi E_m E_{CNT}}{(\xi - c_r) E_{CNT} + c_r E_m}. \tag{4}$$

This latter expression may then again be inserted into (3), for calculating the overall effective properties of a composite where only agglomerates are present. Moreover, relating the parameter c_r to the parameters in (1) and (3), we can write $c_r = V_{ANT} + V_{NT}$.

3 A three-phase rule of mixtures model for CNTs

Now we can establish a three-phase model, where both dispersed carbon nanotubes and agglomerates are contained. In this case, the agglomerates are described as particles of micro size, and the matrix material is now the polymer matrix containing the dispersed nanotubes. Assuming a rule of mixtures model approach is appropriate, we have that

$$E_C = \psi E_{INC} V_{INC} + E_{DNT} (1 - V_{INC}) , \quad (5)$$

where ψ, generally, is a Krencel's coefficient estimated from experimental tests. Also remembering that $V_{NT} + V_{ANT} + V_m^{INC} + V_m = 1$, the general model in (5) can alternatively be written

$$E_C = \psi E_{INC} (V_{ANT} + V_m^{INC}) + E_{DNT} (V_{NT} + V_m) . \quad (6)$$

The final three-phase model is now given by inserting the model in (4) for the agglomerates, and the model in (1), or a similar model described in Section 2.1, for the dispersed nanotubes, into (5), or, alternatively, (6). The model parameters must be estimated from experimental results.

4 Estimation of model parameters

At the time of writing, no in-house test data are available to compare the Young's modulus obtained from tests with model calculations applying the above three-phase model. However, predictions can be made, using the differential sedimentation particle size analysis, applying an analytic disc centrifuge (DCF) to estimate the amount of dispersed and agglomerated CNTs [12]. From recent work by Frømyr *et al.* [26] for dispersion of MWCNTs in a curing agent for an epoxy system, the DCF technique seems to be promising for this purpose; we refer to the paper and the references therein for more details.

A typical result from a disc centrifuge analysis is depicted in Figure 1, showing the size distribution for a sample of MWCNTs dispersed in a solvent. In the DCF, the mass distribution of the hydrodynamic (Stokes) radius of the particles is registered, forming a bimodal shaped distribution. This distribution has a narrow peak at small diameters, i.e. for the dispersed MWCNTs. The agglomerates are much larger with a wide size distribution. Based on these data points, curve fitting techniques can be applied for establishing an expression for the dispersed nanotubes and for the agglomerates, respectively. Then, by integrating the two functions in their respective diameter interval, and relating these results to the total volume of MWCNTs in the test sample, one obtains values for the volume fraction of the agglomerates and for the exfoliated MWCNTs. These values are then applied as input to the model expression in (5) or (6).

The three remaining parameters – ξ for the packing density of the agglomerates, V_m^{INC} for the volume fraction of the matrix inside the inclusions, and the model parameter ψ – must be tuned based on test results, as well as additional available information about the properties of the agglomerates.

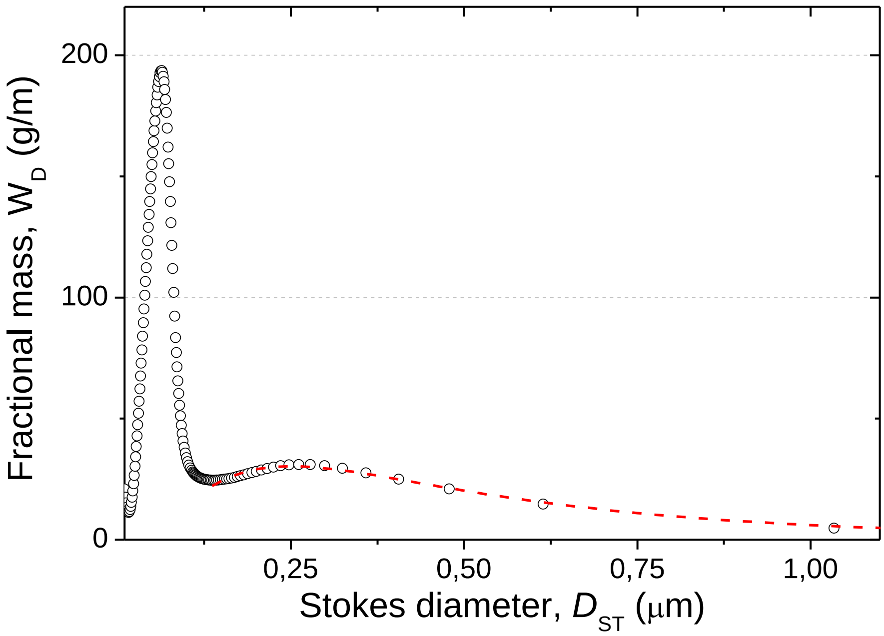

Figure 1. A typical DCF particle size distribution of MWCNTs in a curing agent dispersed by ultrasonication. The red line is a log-normal fit to the larger mode representing the agglomerated MWCNTs.

5 Summary

In this paper, a three-phase rule of mixtures model for the elastic properties of polymer matrix systems with dispersed nanotubes and agglomerates of nanotubes has been presented. The modelling is based on establishing submodels for each part, i.e. a model for the dispersed carbon nanotubes and a model for the agglomerates of the nanotubes. The type of submodel applied for the dispersed nanotubes and for the agglomerates, i.e. the level of detail in the modelling, can be evaluated in each case. In this way, one or more of the effects that influence the mechanical properties of the nanocomposites can be accounted for.

The material models include parameters that must be determined from experimental tests. The differential sedimentation particle size analysis, applying an analytic disk centrifuge to predict the amount of fully dispersed and agglomerated MWCNTs, has been considered to be a useful technique.

Future work will include parameter estimation for different weight fractions of MWCNT dispersed in a thermoset polymer system. Comparison between the suggested modelling approaches and experimental tests will then be performed.

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