

## STRUCTURE-PROPERTY RELATIONSHIP IN POLYMER NANOCOMPOSITES

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### Abstract

*The elastic properties of polymer reinforced with nanoparticles were predicted based on the modified Eshelby's equivalent inclusion methods and Mori-Tanaka's concept of 'average stress' in the matrix. These composite properties have been averaged over all directions and weighted by the orientation distribution function. The influence of the orientation ordering and the distribution of the distances between nanofillers on the mechanical reinforcement have been investigated and have been related to the dispersion quality of the system. Experimental validation was done on samples made in a mini-calendar through high shear mixing of carbon nanofibers with Epoxy resin. It was shown experimentally that above a critical concentration of nanoparticles in the composite, the mechanical properties will decrease due to agglomeration effects. A method is proposed to introduce this effect into existing micromechanical models.*

### 1 Introduction

Carbon nanofibers/ carbon nanotubes are considered to be one of the most highly potential fillers to improve the material properties of polymers. They are known as multifunctional materials due to their exceptionally high aspect ratio and high surface area in combination with a low density, high strength and stiffness. To exploit these superior properties in a macroscopic composite the close relations between the local structure at micro-and/or nano-level and the effective properties of polymer nanocomposites are investigated.

Based on the methods of statistical mechanics and homogenization theory, the microstructure is mathematically described and effective elastic properties are determined. The aim of this work is to find balance between orientation state, dispersion effect, aspect ratio and volume fraction of CNT/CNF in order to achieve maximum macroscopic mechanical response.

### 2 Analytical micromechanics

Any continuum model for mechanical properties replaces the multi-phase composite material with a homogeneous continuum. Estimation of properties of that continuum involves averaging the properties of the phases. The current discussion is restricted to cases when the 2-phase material is presented by polymer with embedded rigid prolate spheroidal inclusions of constant aspect ratio. Therefore reinforced phase introduces anisotropy and agglomeration effect, which means that the averaging process must account for the orientation of that phase and for the effective surface area between inclusions and polymer.

Existing micromechanical models based on Eshelby's equivalent inclusion methods, [3], and Mori-Tanaka's average internal stresses in the matrix, [7], were utilized to predict the elastic mechanical properties of considered nanocomposites [2,5,6].

For bulk mechanical properties, the stiffness tensor for dilute composites can be written as, [8]:

$$C = C_m + V_f A^{Eshelby} (C_f - C_m) \quad (1)$$

$$A^{Eshelby} = (I + ES_m (C_s - C_m))^{-1} \quad (2)$$

where  $A^{Eshelby}$  — strain concentrator tensor,  $E$  — Eshelby tensor related to the geometry of the inclusion,  $S$  — elastic compliance tensor.

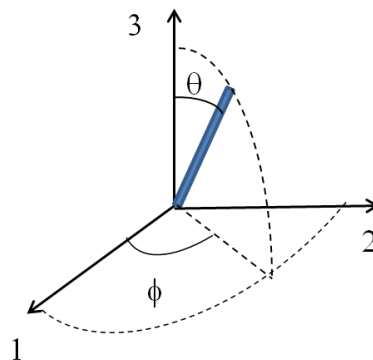
For concentrated composites, the Eshelby model was modified by introducing interactions between particles; in this case the strain concentrator will be changed to [9]:

$$A^{MT} = A^{Eshelby} ((1 - V_f)I + V_f A^{Eshelby})^{-1} \quad (3)$$

### 2.1 Orientation effect

Now consider a unit volume with inclusions that are differently oriented. Therefore all inclusions behave differently to the average matrix stress  $\sigma_m$  and average matrix strain  $\epsilon_m$ . The properties of the composite are calculated as an average of the unidirectional properties over all directions, weighted by the orientation distribution function. It is assumed that all inclusions have the same prolate spheroidal shape. Therefore the rotation around the axis of symmetry  $x'_3$  along the inclusion doesn't change the orientation of the spheroid and rotation angle around this axis becomes 0. In this case is a complete description of the fibre orientation state and is calculated from Monte Carlo simulations as a function of two variables  $\theta$  and  $\phi$  as is indicated in Figure 1, [9]. In this case the orientation function  $\rho(\theta, \phi)$  is used with normalization condition:

$$\int_0^{2\pi} \int_0^\pi \rho(\theta, \phi) \sin \theta d\theta d\phi \quad (4)$$



**Figure 1** Coordinate system and definitions of  $\theta$ ,  $\phi$

According to [9], the average stress and strain inside the inclusion can be written as:

$$\langle \epsilon_f(\theta, \phi) \rangle = \langle A^{MT}(\theta, \phi) \rangle \epsilon_m \quad (5)$$

$$\langle \sigma_f(\theta, \phi) \rangle = \langle C_f A^{MT} C_m^{-1}(\theta, \phi) \rangle \sigma_m \quad (6)$$

Where the angle brackets denote the orientation average. Similarly to Equations (5) and (6) from Equation (1) the effective modulus of the composite can now be written as:

$$C = (V_m C_m + V_f \langle C_f A^{MT} \rangle) (V_m I + V_f \langle A^{MT} \rangle)^{-1} \quad (7)$$

The orientation average of the mechanical strain concentration tensor is:

$$\langle A^{MT}(\theta, \phi) \rangle = \int_0^{2\pi} \int_0^\pi \overline{A}^{MT}(\theta, \phi) \rho(\theta, \phi) \sin(\theta) d\theta d\phi \quad (8)$$

The transformed Mori-Tanaka strain concentrator is known in local coordinates  $\{x'_1, x'_2, x'_3\}$ . In order to calculate the effective modulus  $C$  the volume averages  $\langle A^{MT} \rangle$  need to be transformed to  $\overline{A}^{MT}$  with respect to the global  $\{x_1, x_2, x_3\}$  coordinates:

$$\overline{A}^{MT} = [T^*] A^{MT} [T]^T \quad (9)$$

$[T]$  — is a matrix to rotate the components of tensor strain, and  $[T^*] = [W] [T] [W]^{-1}$  — to rotate the components of engineering strain, where  $[W]$  is transformation matrix between engineering strain and tensor strain.

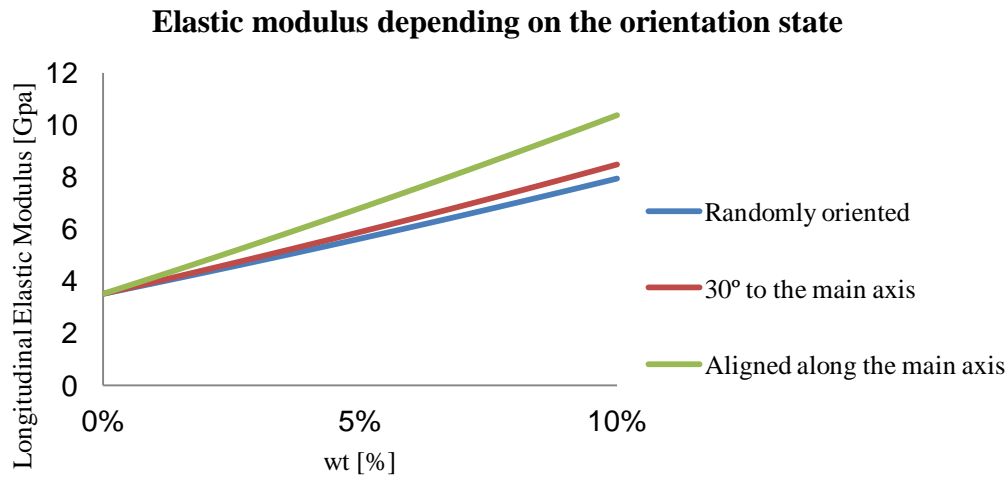


Figure 2 Theoretical calculations of Young modulus for Epoxy + CNF

### 3 Experimental results

In order to verify the validity of the above models, ‘model’ composites were prepared, containing varying amounts of nanofillers, but prepared under constant conditions. The composites used in this study were all manufactured using a 3 Roll-Machine (Exact 80E, Exakt Vertriebs GmbH/ Hamburg, Germany) which is known for its high shear mixing, leading to high levels of dispersion. Samples were prepared using an identical approach as used in the work of Gojny [4] where mixtures containing 0-3 wt% of CNF (The VGCNF

Pyrograph III<sup>TM</sup>, PR-19-LHT-XT, Applied Sciences, Inc) in a Epon epoxy matrix (Epon Resin 862, Hexion Specialty Chemicals) were submitted to a series of passes through the rollers with different gap settings (30, 20, 10 and 5 microns) to enable good dispersion.

Tensile tests have been carried out on the prepared model composites at room temperature using universal INSTRON testing machine fitted with a 50 kN load cell. Results are presented in Figure 3 for varying fractions of polymer nanocomposites and compared with theoretical estimation of Young modulus for Epoxy resin with randomly oriented carbon nanofibers (Epoxy + CNF:  $E_{CNF} = 300Gpa$ ,  $E_{Epoxy} = 2.7Gpa$ ,  $length = 5\mu$ ,  $diam = 150 nm$ ).

The experimental results show that the Young's modulus for composite filled with 3 wt% CNF is lower than for those samples with nanofibers concentration of 1.5 wt%. This effect can be explained by the differences in dispersion quality of the sample: at high concentrations of nanofillers a higher level of agglomerations is found that increases inefficient surface area as was discussed previously. As a result it can be concluded that samples with lower volume fraction up to 2% Vf of CNF/CNT, that can be well- dispersed by introducing high shear forces, result in mechanical properties identical to those of composites with higher volume fraction.

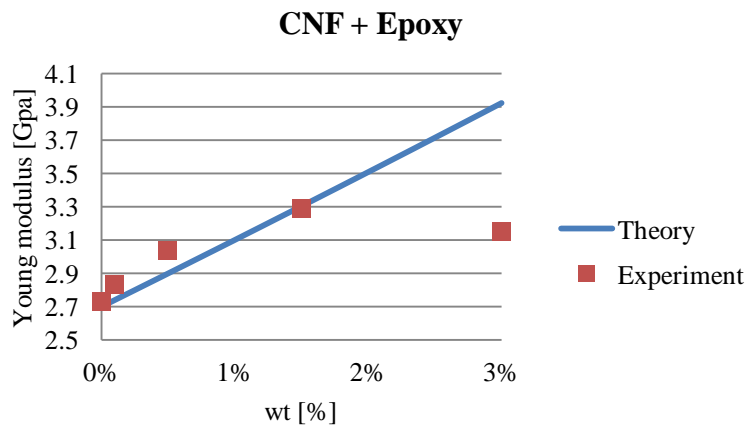


Figure 3 Results of tensile tests on neat and nano-modified epoxy resin

To estimate the quality of dispersion of prepared composites direct visualization of CNF based on light optical microscopy technique was utilized [1,10]. Thin slices with thickness of 10 microns from each sample were cut by Microtome Leiza with glass knives. Approximately 100 optical micrographs from each sample (1280 x 1024 pixels, total resolution 1 pixel=0.132 microns) were taken by using a Optical Microscope Olympus BH2 in combination with a digital camera Leica DFC 280. Typical optical micrographs are shown on the Figure 4.

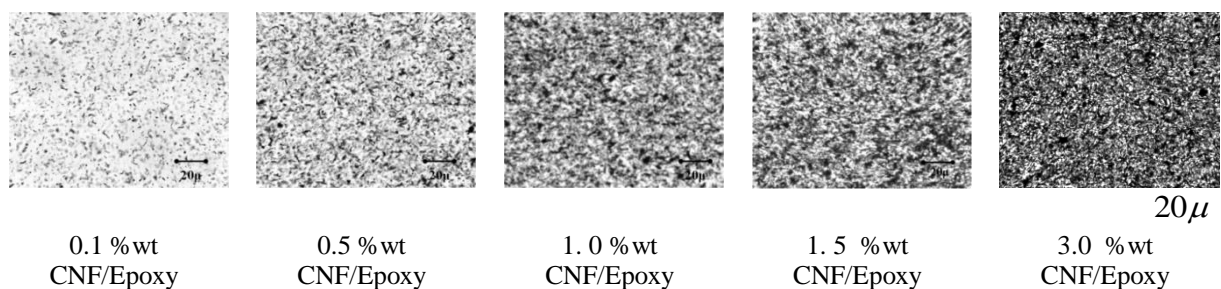


Figure 4 Optical micrographs of CNF/ Epoxy

Although the obtained optical micrographs presented in Figure 4 only approximately show the dispersion quality of prepared composites, the full quantitative treatment of the data, according to the methodology described in [11,12], can give a more thorough description of the relationship between dispersion level and resulting mechanical response of the system. To offer a complete and reliable way of prediction desired composite properties, further analysis and understanding of the nanocomposites' behaviour are still essential, especially focused on processing-morphology relationships [13]. In addition, the current study proposes a method for the calculation of inefficient surface area in the polymer system filled with rod-like nanofillers to be incorporated in existing micromechanical models.

#### 4 Model development

As a result of the high surface area of nanotubes/nanofibers, the magnitude of their body forces is less than the magnitude of the attracting forces acting between the surfaces, such as Van der Waals forces, inducing agglomeration. The primary issue that distinguishes well dispersed CNT/ CNF from composite with agglomerations is the “effective” surface area which for perfectly dispersed nanotubes is much higher than for agglomerated. This directly affects the transfer of the superior properties of nanotubes/nanofibers to the matrix: the presence of agglomerated nanotubes/nanofibers negatively influences the nanocomposite properties.

Thus in order to effectively predict nanocomposite properties, it is required to introduce this effect into the micromechanical models. The current research has focused on the influence of the orientation and the distance from centre to centre distributions between nanotubes/nanofibers on the effective surface area. It is assumed that due to the interaction between polymer and nanofillers, the effective surface area resulting of two neighbouring nanotubes will be decreased relatively to the sum of the surface areas of the individual nanotubes (Figure 5):

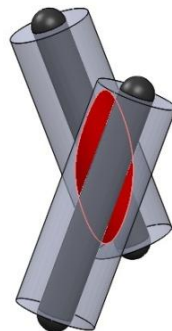


Figure 5 Inefficient surface area

Thus, if the shortest distance between 2 nanoparticles is too small, due to the influence of Van der Waals forces, the properties cannot be transferred from nanoparticle to the polymer in that area. The calculation of inefficient surface area is expressed through shortest distance from centre to centre between nanoparticles based on orientation distribution function and the angle between them, based on analytical geometrical equations.

The influence of the orientation state on the efficiency of the surface area for 2 nanoparticles is exemplarily shown in Figure 6. It can be seen that if the angle between 2 nanoparticles is too small, the effective surface area can be reduced upto 50%.

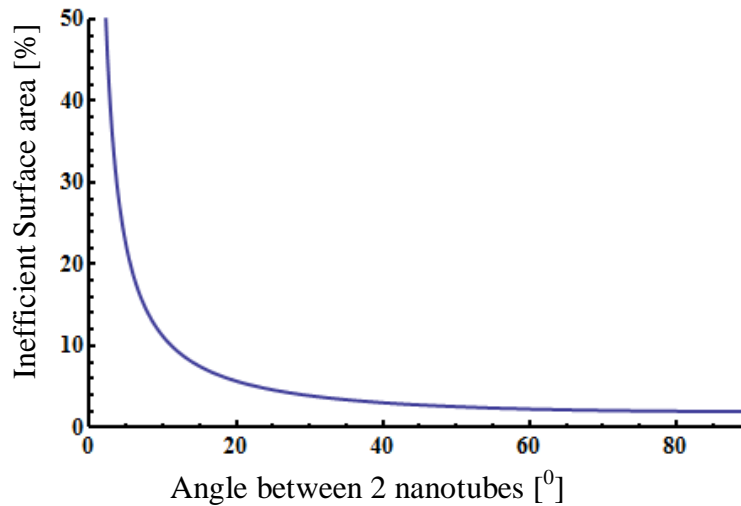


Figure 6 Inefficient surface area

As the surface area has a direct relation with volume fraction of composite material it can be integrated into the micromechanical model for determination the elastic modulus of material as in (10)

(10)

$$C = \frac{\int_0^{\pi/2} \int_0^{\sigma} C_m + S_{ef}(\gamma, a) A^{MT} (C_r - C_m) \Phi(\gamma, a) d\gamma da}{\int_0^{\pi/2} \int_0^{\sigma} \Phi(\gamma, a) d\gamma da} \quad (10)$$

where  $C_r, C_m$  — elastic tensors of nanotube and matrix respectively,  $A_{MT}$  — Mori-Tanaka stress tensor,  $S_{ef}$  — ineffective surface area,  $\Phi(\gamma, a)$  — distribution function of shortest distances between nanotubes together with their orientation state and  $\sigma$  — maximum distance between nanoparticles, when Van der Waals forces are significant.

Equation (10) is implemented in a commercial software package (Wolfram Mathematica 8) to calculate the stiffness matrix of nanocomposite taking into account the agglomeration effects. Required input data for the software are material properties of polymer and reinforcement phase, volume fraction of the inclusion and its aspect ratio. Additionally it requires orientation distribution function and distribution of distances from centre to centre, which can be indirectly derived from the quantified grey scale analysis on the composites. The complete characterization of the material data required for the modelling, its implementation into the software and comparison with experimental data and is the subject of current ongoing research.

## 5 Conclusions

Existing micromechanical models were used to predict the elastic properties of polymer nanocomposites. The predictions were subsequently compared with experimental data that showed a decrease of properties with increasing fibre content, due to limited dispersion. The large discrepancy observed between theory and experiment, was attributed to the limits of existing models to incorporate dispersion effects. A method was proposed to introduce this effect, through a description of ineffective surface area that can be incorporated into the existing models. Its practical implementation and complete experimental evaluation is currently under way.

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