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Influence of waviness and curliness of fibres on mechanical properties of composites

Anna Y. Matveeva [a,*], Sergey V. Pyrlin [b], Marta M.D. Ramos [b], Helmut J. Böhm [c], Ferrie W.J. van Hattum [a]

[a] Institute for Polymers and Composites, Polymer Department, University of Minho, 4800-053 Guimaraes, Portugal
[b] Computational and Theoretical Physics Group, Center of Physics & Department of Physics, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal
[c] Institute of Lightweight Design and Structural Biomechanics (ILSB), TU Vienna, 1040 Vienna, Austria

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ABSTRACT

Polymeric composite materials reinforced by curved cylindrical inclusions of very high aspect ratio are studied for their elastic stiffness. The waviness and curliness of the fibres are described by sinusoidal and helical models with different amplitudes and spiral radii, respectively. Effects are investigated in detail by finite element-based homogenisation methods, analytical models and molecular dynamics simulations. Within the finite element models two types of discretisation are considered for the fibres, using continuum solid and beam elements, respectively. Periodic boundary conditions or a special set of mixed boundary conditions are applied for approximating the effective elastic properties. The analytical investigations use a mean-field approximation in which inhomogeneities are split into unconnected segments of appropriate orientation, the elasticity tensor being calculated with a Mori–Tanaka method. It is shown that both curved fibre geometries, sinusoidal and helical, significantly reduce the longitudinal elastic stiffness of the composite. Beam element-based fibre models and analytical solutions give low and high estimates, respectively, for the elastic constants. The continuum mechanical results are found to be in good agreement with the molecular dynamics predictions.

1. Introduction

The primary motivation for the investigation of two- and three-dimensionally curved fibres comes from polymeric composites reinforced with carbon nanotubes (CNT). In previous work, polycarbonate (PC) was mixed with CNT of weight fractions from 0.5% to 7% using twin a screw extruder and an injection moulding machine[1] [33]. The experimentally determined properties show a marked deviation from the values predicted theoretically for unidirectional reinforcements [16] and several attempts were made to understand and explain such behaviour. Since the dispersion of the nanotubes is known to be one of the key factors influencing the mechanical properties of such composites [7,22], in a first step the influence of agglomerations was studied by continuum micromechanics, classical mean-field methods being modified to take into account the level of dispersion. In these models inadequate dispersion of CNT as expected was found to give rise to degradation of the mechanical properties, but not to a degree sufficient for covering the gap between theoretical estimates and experimental data.

Additional investigations of the composites' structure at the nanoscale by Transmission Electron Microscopy (TEM) showed that the carbon nanotubes tend to have strongly curved shapes.[2] This may be due to high aspect ratios, the associated low bending stiffness, and to surface defects that are introduced during the synthesis of carbon nanotubes. The Multi-Walled Carbon Nanotubes (MWCNT), Nanocyl 7000, used in the injection moulded samples mentioned above were produced by the CVD method. This is a relatively cheap way for large-scale production of nanotubes, which, however, tends to lead to structural disorder and defects, and, as a result, the nanotubes show wavy and curly shapes [24,35], see Fig. 1.

To improve the understanding of the behaviour of such fibrous reinforcements, it is essential to develop models taking into account wavy and curly fibre geometries. Molecular dynamics and ab initio methods can give accurate results and describe phenomena at the nanoscale, but they are very expensive computationally. Mostly they focus on single-walled nanotubes and assume defect-free surfaces or a small number of point-like defects such as vacancies or Stone–Wales defects. In contrast, analytical micromechanical models can give low-cost but coarser approximations.

* Corresponding author. Tel.: +351 960388057.
E-mail address: anna@dep.uminho.pt (A.Y. Matveeva).

[1] Extrusion and compounding was done at the Promolding B.V., Den Haag by Jyri Tiusanen.

[2] Work was done at the Research Institute for Technical Physics and Materials Science, Hungarian Academy of Science, Budapest, by Bernadeth Kiss-Pataki.

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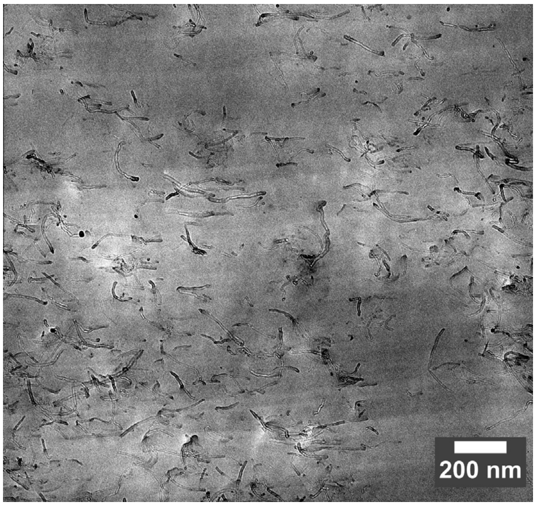

Fig. 1. TEM image of PC + 3 wt% CNT.

Based on mean field approximations they can be applied tosimulate the macroscopic behaviour of composite materials. When such analytical solutions cannot be obtained easily or more detailed information is required on the meso- or macroscales, then finite element-based homogenization can be applied. Due to the very high aspect ratios of nanotubes, approximating their geometry with continuum solid elements is rather expensive computationally. Alternatively, CNT can be modelled as beam elements that are linked to the solid elements describing the matrix via the embedded element technique [8], providing an attractive combination of accuracy and computational costs. Accordingly, detailed investigations of modelling nanocomposites with different finite element (FE) models (beam and continuum solid discretisations of the CNT) were carried out, the results being compared to analytical and molecular dynamics predictions.

2. Background

Carbon nanofibers (CNF) and carbon nanotubes (CNT) are considered to be among the most promising reinforcements for improving the physical properties of polymers [32,14]. They are known as multifunctional materials due to their combination of high strength and stiffness with good thermal and electrical conductivity, as well as unique optical and barrier properties [1]. Because of their exceptionally high aspect ratio and high surface area together with a low density, even a small volume fraction of CNT can potentially transfer their superior properties to the polymer matrix. However, when such nano-sized inhomogeneities are used as reinforcements of polymers for the production of composites on the macro-scale, phenomena occurring at the nano- and microscales, such as waviness, surface defects, as well as imperfect bonding between nanotubes and polymer can dramatically degrade the composite's properties. Thus special attention should be given to understanding how such micro-structural effects influence the overall behaviour of composites. Separate control of these factors requires computational tools for predicting the mechanical response of the processed material, on both the macro- and microstructural levels. In the present work special attention is given to the investigation of the effects of the waviness and curliness of nanotubes.

Several analytical and numerical schemes for studying fibre waviness and curliness can be found in the literature. Slepyan et al. [30] studied the effective elastic properties of composites consisting of helical inclusions in an elastic matrix using the superposition of fundamental solutions for a homogeneous elastic space (matrix without fibres) and the constitutive and equilibrium equations for the rods. This work is limited to inhomogeneities of regular shapes, and cannot be extended to arbitrary geometries. Hsiao and Daniel [13] introduced an analytical procedure for modelling the effect of wavy fibres, dividing them into infinitesimally thin slices. A similar model was suggested by Shi et al. [29], where CNTs are considered as helical fibres sliced into segments and the stresses are integrated along the length of the nanotube. Such simplified analytical procedures can be applied to inclusions of arbitrary shape, but due to the significant simplification the accuracy of the predicted properties is limited. For detailed study of the macroscopic mechanical properties of inhomogeneous materials with complex phase geometries FE-based homogenization models are among the most appropriate tools. Composites consisting of a polymeric matrix reinforced by carbon nanotubes can be considered as linear elastic materials with embedded isotropic or anisotropic inhomogeneities. Periodic arrangements of wavy or curly CNT in general will result in orthotropic macro-behaviour. Garnich and Karami [6] presented a model, where a unit cell containing a wavy fibre is used for determining the composite lamina elastic constants for a range of amplitude-to-wavelength ratios. Shao et al. [28] studied the effect of the waviness of CNTs and of interfacial debonding between them and the matrix on the effective moduli. Fisher and Bradshaw [3,5] proposed a semi-analytical model combining the finite element method and analytical micromechanics to examine the influence of CNT waviness on the reinforcing capabilities of CNT, the nanotubes being modelled as isotropic cylinders of sinusoidal shape. Spanos and Esteva [31] studied the influence of entangled and non-straight fibres on the effective elastic and thermal properties of polymer nanocomposites using an embedded finite element technique. Their approach is based on generating random microstructures by Monte Carlo simulation and computing the effective properties depending on the microstructural parameters.

The above analytical and FEM methods make use of strong assumptions, such as solid cylindrical shape, isotropic behaviour and perfect bonding with the matrix that can give rise to significant effects on the nanoscale. Schmidt and Tserpes modelled nanotubes as straight, hollow cylinders with transversely isotropic material properties in [25] and orthotropic ones in [34] in order to elucidate the influence of interface stiffness and thickness on the effective elastic properties. Additional parameters such as anisotropy, hollowness of nanotubes, effects of their interface with the matrix as well as dispersion, orientation and aspect ratio distributions can lead to more accurate results for the elastic properties of polymeric composites reinforced with curved carbon nanotubes.

The present work focuses on the effect of the nanotubes' curviness, but it can be extended to hollow nanotubes with anisotropic properties and with interphases or imperfect interfaces. For numerical simulations this can be achieved, e.g., by introducing extra layers with appropriate properties around the fibres, and in analytical models by substituting curved, hollow inclusions with solid cylindrical inhomogeneities having effective properties. Based on series of parametric studies related to different fibre geometries, the influence of CNT curviness is investigated in the framework of analytical and numerical continuum micromechanics. For validation of the proposed approaches, normalised predictions for the effective elastic modulus are compared with molecular dynamics simulations.

3. Analytical model

The relation between the average and local behaviour is a well-known problem in micromechanics of composites. Continuum