Predicting the properties of micro- and nanocomposites: from the microwhiskers to the bristled nano-centipedes

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The paper draws on the similarities between the well-known process of whiskerization of microfibres and the recent idea of bristled nanowires. The new method for evaluation of the effective elastic properties of such materials is suggested based on the model of four-component composition. This model assumes the transverse isotropy of continuum and predicts five elastic moduli and density as independent effective constants. An example of calculation of the constants for the particular materials is given. It shows the significant increase in the shear strength of composites with whiskerized or bristled fibres.

Keywords: composite materials; fibres; whiskers; effective properties; nanoscale; microscale

1. Introduction: microwhiskers and bristled nanowires

Nanotechnologies and nanomaterials are arguably the most actively and extensively developing research areas at the end of the last/beginning of this century. The number of publications in scientific periodicals and conference proceedings, fully or partially devoted to nanotechnologies and nanomaterials, rapidly increases. However, the development of nanomechanical models and their application to investigation of mechanical behaviour of nanomaterials in a systematic way is not happening yet. Present studies of the mechanical behaviour of nanoparticles, nanoformations and nanomaterials are still in their infancy. Only external manifestations of mechanical phenomena are detected, but their mechanisms have not been studied yet.

An attempt to formulate basic problems of nanomechanics and to suggest possible ways how to solve them using the knowledge accumulated within the solid mechanics and, more generally, continuum mechanics was undertaken by Guz et al. (2005, 2007a,b). This paper considers a particular problem of modelling properties of two classes of fibrous composite materials (figure 1) that are additionally reinforced either by whiskerizing the microfibres or by bristling the nanowires.

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One contribution of 20 to a Theme Issue ‘James Clerk Maxwell 150 years on’.
Several decades ago, whiskers were looked at as a new class of materials: very promising and very expensive—much the same as we look at nanofibres now. According to Katz & Milewski (1978), whiskers are a generic class of fibres that have been grown under controlled conditions that lead to the formation of a single crystal. This crystal has a fibre or elongated form. Whiskers possess mechanical strength equivalent to the binding forces of adjacent atoms. They are strong because they are essentially perfect crystals and their extremely small diameters allow little room for the defects that weaken larger crystals. More than 100 materials, including metals, oxides, carbides, halides, nitrides, graphite and organic compounds, can be prepared as whiskers. Whiskerization was suggested as a special form of supplementary reinforcement, particular to carbon fibres. Since carbon fibres were frequently used with resin matrices, such composites exhibited low shear strength due to poor bonding. The technique of whiskerization consists in the addition of whiskers to the composites by growing them directly on the surfaces of the carbon fibres (figure 1a). Whiskerizing introduces an integral bond between the whiskers and the carbon fibres. Katz & Milewski (1978) reported a three to five times increase in the interfacial shear bond for different combinations of carbon fibres and epoxy matrices.

After almost four decades since the introduction of whiskerized microfibres, they found a new incarnation in the emerging world of nanomaterials. The paper by Wang et al. (2004) describes the CdTe nanowires coated with SiO2 nanowires. The resulting composition is wittily named by the authors as ‘the bristled nanocentipedes’. Two types of CdTe nanowires are reported: MSA and TGA stabilized. The former has a diameter of 4.5–6.5 nm, and the latter 3 nm. Figure 1b shows the MSA-stabilized ‘wire coating’ with numerous nearly parallel bristles growing perpendicular to the surface, also known as the brush-like composition (Wang et al. 2004). Evidently, the structure ‘CdTe nanowire–SiO2 nanowires’ consists of three components: CdTe wire forms the solid core, which is jointed continuously with coating from SiO2 nanowires in the form of some solid shell, and then the shell is coated periodically by bristled and smooth zones. Particularly, for the case shown in figure 1b, we can loosely assume that the core radius is 3 nm, the shell thickness 15 nm, the bristled/smooth zone length 6 nm and the length of bristles 32 nm.

There are striking similarities between the well-known process of whiskerization of microfibres and the recent idea of bristled nanowires. Both whiskerized microfibres and bristled nanowires exhibit similar geometrical structure and can
be used for the same ultimate purpose of fabricating composite materials with improved fibre–matrix adhesion and hence the increased shear strength. If we consider the structure ‘CdTe nanowire–SiO₂ nanowires’ placed in the matrix, the total number of components in the composition would be as high as four—the matrix being the fourth component in addition to the three components mentioned above. Therefore, in order to study the effective properties of the entire composite and the effect of reinforcement with whiskerized microfibres or bristled nanowires on the overall performance of the material, we need a four-component model, the development of which is the main subject of this paper.

2. The four-component structural model

The proposed structural model for composites reinforced by whiskerized microfibres or bristled nanowires is based on the assumption that fibres are arranged in the matrix periodically as a quadratic or hexagonal lattice. Then the representative volume element (unit cell) consists of the matrix and a coated fibre (figure 2a). Here the coating itself has several sub-components (figure 2b,c), which is a new feature of the model. The coated fibre is assumed to consist of three different parts: solid core; solid coating (homogeneous shell); and ‘bristled coating’ (composite shell). The fourth component in the model is the matrix. Subsequently, the following notations are used to distinguish the four components of composite: (fc) for the fibre core; (fs) for the fibre solid coating; (fb) for the fibre bristled coating; and (m) for the matrix.

Three out of four components are homogeneous materials, e.g. Epon 828 epoxy matrix, SiO₂ solid coating and CdTe solid fibre core, with known properties (Young’s modulus, shear modulus, Poisson ratio, density, etc.). However, the bristled coating is itself a composite consisting of, for example, the Epon 828 matrix reinforced by SiO₂ nanowires (figure 2c). The effective properties of this component were evaluated separately beforehand. The simplest way to do this...
is by using the classical Voigt and Reuss bounds (see Kelly & Zweben 2000). For this purpose, we would need to know the diameter and the length of bristles and their number per unit surface area of microfibres or nanowires.

Then we can proceed with the proposed four-component model. The model is a generalization of the existing three-component model (Van Fo Fy 1971; Guz & Rushchitsky 2004a, b, 2007). Instead of the thin shell model for the fibre coating, two different components are distinguished: the solid coating surrounding the fibre and the bristled coating surrounding the solid coating. Here, both coatings are not supposed to be thin.

The mathematical formulation of the model is based on considering the four simple states of plane elastic equilibrium of the unit cell (a square with the side $l_{\text{unit}}$, figure 3a), i.e. longitudinal tension, transverse tension, longitudinal shear and transverse shear, and using the Muskhelishvili complex potentials (Muskhelishvili 1953) for each domain occupied by a separate component. The model yields the explicit formulae for five effective elastic constants of the transversally isotropic medium, which represent the macroscopic properties of the considered composite.

The procedure for deriving the explicit expressions of effective constants for the suggested four-component structural model is by no means a trivial mathematical exercise. Owing to lack of space, here it can be given only in outline for one of the constants, namely the shear modulus $G$. During the first stage, two shear stress components and one displacement component are expressed in each domain occupied by a separate component (figure 3a) using the Muskhelishvili complex potentials. The three boundary conditions on the domain interfaces are the conditions of perfect bonding between the components. Here, the possible case of imperfect adhesion between the fibre core and the matrix can be taken into account by considering one of the four components, i.e. the coating layer, with the appropriately reduced properties. The cornerstone of the analytical procedure is the representation of the Muskhelishvili potentials by a harmonic complex function, which is regular in the domain of fibre core (circle $A^{(fc)}$ in figure 3a)

$$
\varphi_{(fc)}(z) = \sum_{k=0}^{\infty} a_{2k}^{(fc)} \frac{z^{2k+1}}{2k+1},
$$

(a)

(b)

Figure 3. (a) The representative area of a four-component composite. (b) Contours for evaluation of integrals.

a function in the form of Laurent series, which is regular in the domain of fibre solid coating (ring $A^{(fs)}$ in figure 3a)

$$
\varphi_{(fs)}(z) = \sum_{k=-\infty}^{\infty} a_{2k}^{(fs)} \frac{z^{2k+1}}{2k+1},
$$

Phil. Trans. R. Soc. A (2008)
a function in the form of Laurent series, which is regular in the domain of fibre bristle coating (ring $A^{(fb)}$ in figure 3a)

$$\varphi^{(fb)}(z) = \sum_{k=-\infty}^{\infty} a_{2k}^{(fb)} z^{2k+1},$$

(2.3)

a doubly periodic function constructed using the Weierstrass functions in the domain of the matrix $(A^{(m)})$ in figure 3a

$$\varphi^{(m)}(z) = a_0^{(m)} z - \lambda^2 a_2^{(m)} \left( \frac{1}{z} - \sum_{n=1}^{\infty} \alpha_{n,0} \frac{z^{2n+1}}{2n + 1} \right)$$

$$+ \sum_{k=1}^{\infty} \sum_{n=1}^{\infty} a_{2k+2}^{(m)} \lambda^{2k+2} \alpha_{n,k} \frac{z^{2n+1}}{2n + 1} - \sum_{k=1}^{\infty} a_{2k+2}^{(m)} \lambda^{2k+2} \alpha_{n,k} \frac{z^{2n+1}}{2n + 1},$$

(2.4)

where $\alpha_{n,k}$ are the constants used in the theory of Weierstrass functions (Gradshteyn & Ryzhik 2000), $\lambda = 2r_{(fb)}/l_{init}$.

Then the averaged stresses and strains for each of the domains are calculated using the contour integrals (figure 3b). This procedure results in the following expression for the effective longitudinal shear modulus of the entire four-component composition

$$G = G^{(m)} \frac{c^{(m)} + 2c^{(fb)} + c^{(m)} G^{(fb)} G_{(fb)}^{-1} + 4c^{(fb)} \left(1 + G^{(fb)} G_{(fb)}^{-1}\right)^{-1} + 8c^{(fb)} \left(1 + G^{(fb)} G_{(fb)}^{-1}\right)^{-1} \left(1 + G_{(fb)} G_{(fb)}^{-1}\right)^{-1}}{c^{(m)} + (2 - c^{(m)}) G^{(fb)} G_{(fb)}^{-1}}.$$

(2.5)

Equation (2.5) yields the well-known formulae for two- and three-component models (Van Fo Fy 1971; Guz & Rushchitsky 2004a, b, 2007) as the particular cases. The former will follow from equation (2.5) if the volume fraction of solid coating $c^{(ss)} = 0$ and the shear moduli of solid coating, $G^{(ss)}$, and fibre core, $G^{(fc)}$, are the same; the latter will follow from equation (2.5) if the volume fraction of bristled coating $c^{(fb)} = 0$ and the shear moduli of bristled, $G^{(fb)}$, and solid, $G^{(ss)}$, coatings are the same.

Similarly, the explicit expressions for the other four effective constants for the entire four-component composition are deduced.

3. Results for the particular compositions

As an example of calculation of the effective constants, let us consider the unidirectional fibre-reinforced composite consisting of the epoxy matrix Epon 828 and Thornel 300 fibres bristled by the graphite whiskers—a structure similar to that presented in figure 1a, which is modelled here as shown in figure 2. The typical properties of graphite whiskers are mean diameter 1 μm, length 40 μm, Young’s modulus 1 TPa, shear modulus 0.385 TPa, Poisson ratio 0.3 and density 2250 kg m$^{-3}$ (Katz & Milewski 1978). The geometrical dimensions used for computing are $r_{(fc)} = 4$ μm, $r_{(fs)} = 6$ μm and $r_{(fb)} = 50$ μm. Three different densities of whiskerization are examined: dense, with 120 whiskers over the fibre diameter and 50 whiskers over 100 μm of the fibre length; medium, with,
respectively, 60 and 50 whiskers; and sparse, with, respectively, 30 and 50 whiskers. The medium density is a limiting case for single bristles growing from the fibre surface. The dense density (two times higher than the medium density) corresponds to two bristles growing from the same nest on the fibre surface. At a distance from the fibre surface, the bristles separate with some space between them still remaining for the matrix material to fill in. The three cases give the volume fractions of whiskers, $c_w = 0.25, 0.125$ and 0.063, respectively.

The values of all five effective constants for the entire composite were computed by the method outlined in §2. The results show that the properties in the direction of fibres are the most sensitive to the density of bristles. The increase in the number of bristles per unit surface of the fibres gives a very strong rise to the value of Young’s modulus. However, the shear modulus, being the driving parameter for the strength estimation of the entire composition, is significantly less sensitive to this factor. The values of shear modulus for the considered cases of sparse, $G_{\text{sparse}}$, medium, $G_{\text{medium}}$, and dense, $G_{\text{dense}}$, whiskerization are given in table 1, together with the values of shear modulus for the same composition without whiskers, $G_0$.

### 4. Discussion and conclusions

This paper presented the new four-component structural model for predicting the mechanical properties of whiskerized microfibres and bristled nanowires. The considered example for the calculation of the effective constants for the particular materials shows the significant increase (from 1.7 times in the case of sparse reinforcement up to three times in the case of dense reinforcement) in the shear modulus in composites with whiskerized or bristled fibres.

Undoubtedly, even after verification of predicted properties for bristled nanowires by comparing them with the results of specially designed experiments, the suggested approach can be considered as merely the first step towards modelling bristled nanowires and their application. Even a four-component model is an idealization of the complex internal structure of the considered materials. However, it can provide us with important insight into some basic relationships between the properties of constituents and the overall performance of such materials: following Maxwell (1876), ‘in a scientific experiment the circumstances are so arranged that the relation between a particular set of phenomena may be studied to the best advantage’.

Ultimately, any mechanics of materials, including mechanics of nanomaterials, envisages analysis of materials for structural applications, be it on macro-, micro- or nanoscale (Guz & Guz 2006). It is therefore a logical conclusion that

<table>
<thead>
<tr>
<th>$G$ (GPa)</th>
<th>$c^{(m)}=0.7$</th>
<th>$c^{(m)}=0.6$</th>
<th>$c^{(m)}=0.5$</th>
<th>$c^{(m)}=0.4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{\text{dense}}$</td>
<td>1.355</td>
<td>1.505</td>
<td>1.674</td>
<td>1.872</td>
</tr>
<tr>
<td>$G_{\text{medium}}$</td>
<td>1.374</td>
<td>1.528</td>
<td>1.701</td>
<td>1.905</td>
</tr>
<tr>
<td>$G_{\text{sparse}}$</td>
<td>1.391</td>
<td>1.544</td>
<td>1.715</td>
<td>1.913</td>
</tr>
<tr>
<td>$G_0$</td>
<td>0.9636</td>
<td>0.9649</td>
<td>0.9660</td>
<td>0.9671</td>
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any research on nanomaterials should be followed by the analysis of nanomaterials working in various structures and devices. Micro- and nano-structural applications seem to be the most natural and promising areas of the nanomaterials usage. They do not require large industrial production of nanoparticles that are currently rather expensive. It seems pertinent to recall a discussion on mechanical properties of new materials that took place more than 40 years ago. In the concluding remarks, Bernal (1964) said: ‘Here we must reconsider our objectives. We are talking about new materials but ultimately we are interested, not so much in materials themselves, but in the structures in which they have to function.’ The authors believe that nanomechanics faces the same challenges that micromechanics did 40 years ago, which Prof. Bernal described so eloquently.

References


