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MECHANICAL MODELLING OF NANOTUBE-POLYMER ADHESION

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The modelling of the shear strength of nanotubes based nanocomposites is considered. To model the shear strength of nanocomposites it is assumed that the zone of the adhesive interaction between nanotubes and a polymeric matrix is a thin interface layer which has resistance only in the relation to action of shear stresses and has the given curve of deformation. The stress state of nanotubes and a polymeric matrix is determined in the assumption, that the nanotube is a cylindrical fibril with the straight axis, embedded in a infinite polymeric matrix and the displacement along the axis of the nanotube under the action of the external loading along this direction are much more than others components of the nanotube and matrix displacements. The analytical solutions for the axial displacement and normal stress in the nanotubes and the shear stresses in the interface layer for a case of the bilinear deformation curve of an intermediate layer with elastic and hardening or softening branches are obtained.

Keywords: modelling, nanotube-polymer adhesion.

1. Introduction

Composites based on polymers or ceramics matrix and filled by nanosized particles or nanotubes are materials with very strong and tough mechanical properties. The mechanisms of toughening these materials by nanoparticles investigated experimentally and theoretically [1–4]. From the experimental observations (see [1, 2, 5]) it has been found: 1) the main parameter which defines the nanocomposite strength is the adhesion between matrix and nanofiller; 2) the crack bridging mechanisms is very important during nanocracks formations and fracture of nanocomposites. Noted also that in the most observed cases the size of the nanocrack bridged zones were comparable with the whole crack size. These cases need special consideration during the bridged zone and crack tip growth. Below the mechanical model to describe the nanotubes-polymer matrix adhesion (which is the basis for formulation of the bridged crack problem for nanocomposites) is considered.

2. Model of nanotube-polymer adhesion

The model of nanotube-polymer adhesion based on the shear-lag approach was proposed previously in [6] and discussed in the frame of nanomechanics in [7]. In the frames of our approach, it is assumed that the nanotube is a straight cylindrical fiber of length L_c embedded in an infinite polymer matrix (Fig. 1). The nanotube under the external normal loading has only the displacements along its axis and the thin layer of the polymer matrix adjacent to the nanotube is bearing only shear stresses. It is also supposed that the interfacial shear stresses between the polymer matrix and the nanotube depend on the interface layer thickness (H) and the fiber (nanotube) axis displacement (u)

$$\tau_i = \kappa_1 u, \quad \kappa_1 = \frac{G_1}{H}, \tag{1}$$

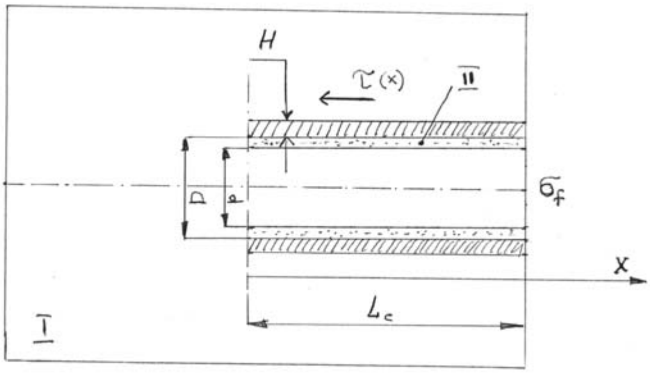

Fig. 1. Nanotube (II) embedded in a polymer matrix (I) under the action of the external normal stresses, H is the interface layer thickness

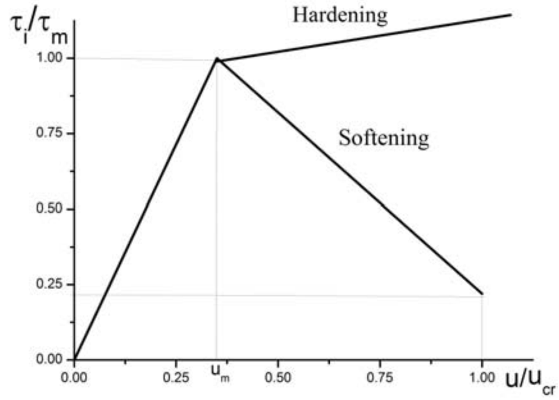

Fig. 2. Bilinear shear stress-displacement law for the interface layer

We will also suppose, if the shear stresses τ_i exceed the given value $\tau_m = \kappa_1 u_m$ then shear stresses in the interface layer between the fiber and the matrix are described by the equation

$$\tau_i = \tau_2 \pm \kappa_2 u, \quad \kappa_2 = \frac{G_2}{H} \tag{2}$$

where G_2 is the shear modulus of the interface layer on the hardening/softening parts of the deformation law curve, $u > u_m$.

If the displacements of the nanotube axis attain the critical value u_{cr} then the detachment of the nanotube from the matrix occurs.

Note, that the interface layer thickness (H) may depend, in general, on the position along the nanofiber (coordinate x) and the shear stresses at the detachment state (τ_{cr}) may be nonzero.

Combining equations (1) and (2) we can write the interface deformation law as follows

$$\tau_i(x) = \begin{cases} \kappa_1 u(x), & 0 < u(x) \leqslant u_m \\ \tau_2 \pm \kappa_2 u(x), & u_m < u(x) \leqslant u_{cr} \\ 0 & u(x) > u_{cr} \end{cases} \tag{3}$$

where $\kappa_{1,2}$ are the stiffness on the hardening/softening parts of the shear-displacement law

$$\kappa_1(x) = \frac{G_1}{H} = \frac{\tau_m}{u_m}, \quad \kappa_2 = \frac{G_2}{H} = \frac{|\tau_{cr} - \tau_m|}{u_{cr} - u_m}, \quad \tau_2 = u_m(\kappa_1 \mp \kappa_2) \tag{4}$$

and the value u_{cr} is the critical elongation of the nanofiber (see Fig. 2).

In dependence on the values τ_m and τ_{cr} the deformation with the softening ($\tau_{cr} < \tau_m$), the bottom sign in (3-4), or with the hardening ($\tau_{cr} \geqslant \tau_m$), the upper sign in (3-4), can be considered, see Fig.2.

Next, we will write the equilibrium equation for an infinitely small part of the nanotube embedded in the polymer matrix. This equation has the following form

$$0.25\pi\left(D^2 - d^2\right)\frac{d\sigma(x)}{dx} = \pi D \tau_i(x) \tag{5}$$

Suppose that the axial deformation of the nanotube fiber is elastic, then, taking into account the temperature difference during the cure, ΔT, we can write

$$\sigma(x) = E_f\left(\frac{du(x)}{dx} - \alpha_f \Delta T\right) \tag{6}$$

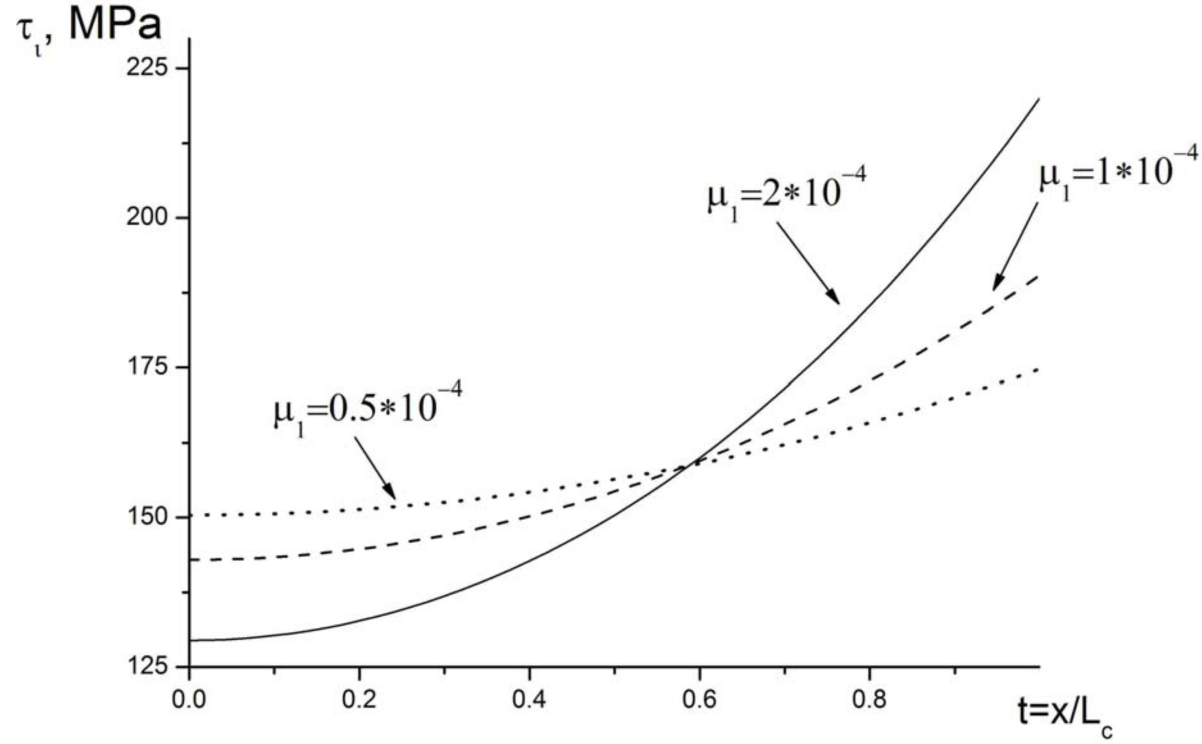

Fig. 3. Distributions of the shear stresses over the nanotube length for different values of the relative stiffness of the interface layer, μ_1

where E_f and α_f are the elastic modulus and the thermal expansion coefficient of the nanotube, respectively.

Finally, substituting equations (3) and (6) into the equilibrium equation (5), taking into attention the changing of the shear stress law along the nanotube and the possibility of the nanotube detachment, we obtain the following system of the differential equations for the axial displacements of the nanofiber:

$$\begin{cases} \dfrac{d^2u_1}{dx^2} - \beta_1^2 u_1 = 0, & 0 < x \leqslant x_m \\ \dfrac{d^2u_2}{dx^2} + \beta_2^2 u_2 = R_2, & x_m < x \leqslant x_{cr} \\ \dfrac{d^2u_3}{dx^2} = 0, & x_{cr} < x \leqslant L_c \end{cases} \tag{7}$$

where

$$\mu_{1,2} = \frac{G_{1,2}}{E_f}\frac{D}{H}, \quad \beta_{1,2} = \frac{2\delta\sqrt{\mu_{1,2}}}{D} \quad R_2 = \frac{4\tau_2\delta^2}{E_f D}, \quad \delta = \frac{D}{\sqrt{D^2 - d^2}} \tag{8}$$

The point x_m in (7) is the position along the axis of the nanotube where the deformation law is changed according to Eq. (2) and the point x_{cr} is the detachment point position. This system of the differential equations solves together with the appropriate boundary conditions and the additional conditions of continuity and compatibility at the point of changing the deformation law x_m where $u = u_m$

$$u_m = u_1(x_m) = u_2(x_m), \quad \left.\frac{\partial u_1}{\partial x}\right|_{x=x_m} = \left.\frac{\partial u_2}{\partial x}\right|_{x=x_m} \tag{9}$$

and the conditions at the detachment point x_{cr} where $u = u_{cr}$

$$u_{cr} = u_2(x_{cr}) = u_3(x_{cr}), \qquad \left.\frac{\partial u_2}{\partial x}\right|_{x=x_{cr}} = \left.\frac{\partial u_3}{\partial x}\right|_{x=x_{cr}} \tag{10}$$

Note, that if the interface layer thickness (H) depends on the coordinate then equations (7) can only be solved numerically, for instance, by finite difference method.

We initially have considered the simple case of the constant thickness of the interface layer thickness (H). The equations (8) in this case have the analytical solution. Based on the analytical solution of the equations (8) we considered different types of the boundary conditions for the embedded nanotube model and have got the shear stresses distributions along of a nanotube axis.

3. Estimation of nanocomposites shear strength

Let's define the average shear stress τ_a along of a nanotube part of the length L_c as follows

$$\tau_a = \frac{1}{L_c}\int_0^{L_c} \tau_i(x)dx \tag{11}$$

For a case when the shear stresses $\tau_i(x)$ are dependent on the axis displacements u linearly in the whole range of the external loading and at the nanotube sections $x = 0$ and $x = L_c$ (see Fig. 1) are adopted the following boundary conditions

$$\sigma(L_c) = E_f \left.\frac{\partial u_1}{\partial x}\right|_{x=L_c} = \sigma_f, \quad \sigma(0) = E_f \left.\frac{\partial u_1}{\partial x}\right|_{x=0} = 0 \tag{12}$$

we can obtain the dependence of the shear stresses over the nanotube axis:

$$\tau_i(t) = \frac{\sigma_f}{2\delta}\sqrt{\mu_1}\frac{\cosh\left(\frac{2\delta L_c\sqrt{\mu_1}}{D}t\right)}{\sinh(\lambda_1)}, \quad \lambda_1 = \beta_1 L_c, \quad t = x/L_c; \tag{13}$$

By using formula (13) we can write

$$\tau_a = \frac{\sigma_f\sqrt{\mu_1}}{2\delta L_c \sinh(\lambda_1)}\int_0^{L_c} \cosh(\beta_1 x)\, dx = \frac{\sigma_f D}{4L_c\delta^2} = \sigma_f\left[\frac{D}{4L_c}\left(1 - \frac{d^2}{D^2}\right)\right] \tag{14}$$

Let's note, that the average value of the shear stresses (14) coincides with the value of the shear stress for an ideally-plastic matrix [6, 7].

The dimensionless shear stresses (the shear stress concentration factor, SCCF) can be defined as follow

$$\tau_R(t) = \frac{\tau_i}{\tau_a} \tag{15}$$

By incorporating Eqs. (13) and (14) we obtain for the linear deformation law

$$\tau_R(t) = \frac{\tau_i}{\tau_a} = \lambda_1\frac{\cosh(\lambda_1 t)}{\sinh(\lambda_1)} = \frac{2\delta L_c}{D}\sqrt{\mu_1}\frac{\cosh\left(\frac{2\delta L_c\sqrt{\mu_1}}{D}t\right)}{\sinh(\lambda_1)} \tag{16}$$

Within the framework of the linear deformation law the maximal value of the shear stresses is observed on loaded end of the nanotube ($x = L_c$). Let's evaluate the physical-mechanical parameters in (8)–(16). According to the data presented in [7] the wall thickness

($h = 0.5(D - d)$) of single-wall nanotubes is $h = 0.34nm$ and the external diameter is about $D = 2 - 5\,nm$. Supposing that $D = 5\,nm$ then the internal diameter is $d = 4.32\,nm$ and

$$\delta = \frac{D}{\sqrt{D^2 - d^2}} \approx 1.986 \qquad (17)$$

According to [7] the critical length of a nanofiber is about $L_c \approx 100 - 500\,nm$ and the critical external stress σ_f vary between 20 and $150\,GPa$. The elastic modulus of the nanotubes is in the range $E_f = 0.8 - 1,8\,TPa$ [6, 8].

Information regarding other parameters of the model is rather undetermined. The thickness of the interface layer H strongly depends on the types of adhesion. There are several methods to improve interaction between nanotubes and polymeric matrix. For example, chemical attachment or cross linking of nanotube walls and polymeric matrix (functionalization) has been proposed as one of the techniques to improve the interfacial bonding. Based on molecular dynamics simulation it was shown [9–11] that the shear strength of nanotubes-matrix interface and the critical length for load transfer are essentially improved by chemical cross-linking the nanotubes and matrix. The length of a functionalization group is about $0.1 - 0.2\,nm$ [9]. Therefore, the lower bound of the thickness of the interface layer is $H = (0.04 - 0.1)\,D$ and the upper reasonable bound of this parameter is not more than the nanotube diameter $H \approx D$. Let's proceed to the determination of other parameters of the deformation law.

We can evaluate the bounds for the shear modulus G_1 supposing that the distance between the functionalize attached groups is not more then the nanotube diameter as in the numerical simulation [9-11] and the thickness of the functionalize group is less than the nanotube wall thickness $h = 0.34nm$. In this case the upper bound for the elastic modulus of the interface layer is

$$E_1 < \frac{h}{D + h} E_f \qquad (18)$$

If Poisson's ratio for the interface layer equals $\nu = 0.25$ and $D = 2 - 5\,nm$ we obtain

$$G_1 < \frac{0.5h}{(D + h)} \frac{E_f}{(1 + v)} \approx 0.05 E_f \qquad (19)$$

The elastic modulus of the polymer matrix is about $E_m = 2 \div 3.5\ GPa$, therefore the bounds for the shear modulus of the interface layer are

$$\psi G_m \leqslant G_1 \leqslant \frac{\varepsilon E_f}{2(1 + \nu)}, \quad \varepsilon < \frac{h}{D + h} \qquad (20)$$

where the parameter $\psi < 1$ is determined by the equality of the adhesion without the functionalization and is the shear modulus of the matrix.

We also can choose the parameter (G_2) of the hardening part of the deformation law supposing that $0 \leqslant G_2 \leqslant G_1$. The case $G_2 = 0$ corresponds to the ideal plastic flow. Finally, we will use the following parameters for the computation: 1) the nanotube external di ameter - $D = 5\,nm$; 2) the nanotube internal diameter $d = 4.32\,nm$; 3) the wall thickness of single-wall nanotube $h = 0.34\,nm$; 4) the critical length of the nanofiber $L_c = 100\,nm$; 5) the elastic modulus of the nanotubes $E_f = 1\ TPa$; 6) the Poisson ratio - $\nu = 0.25$; 7) the critical external stress is $\sigma_f = 50\,MPa$ [9–11]; 8) the thickness of the intermediate layer $H = D$.

The values of the parameter ε in (20) are chosen as $\varepsilon = 0.0005,\ 0.00025,\ 0.000125$ and the shear modulus of the interface layer is calculated according to

$$G_1 = \frac{\varepsilon E_f}{2(1 + \nu)} \qquad (21)$$

The values of the relative stiffness of the interface layer for the given values of D, H, E_f and ε are determined as follows

$$\mu_1 = \frac{G_1}{E_f}\frac{D}{H} = 2.0 \cdot 10^{-4}; 1.0 \cdot 10^{-4}; 0.5 \cdot 10^{-4} \tag{22}$$

The average shear stresses for linear deformation law and given above values of parameters σ_f, L_c, D, d is equal to $\tau_a \approx 158.44\, MPa$.

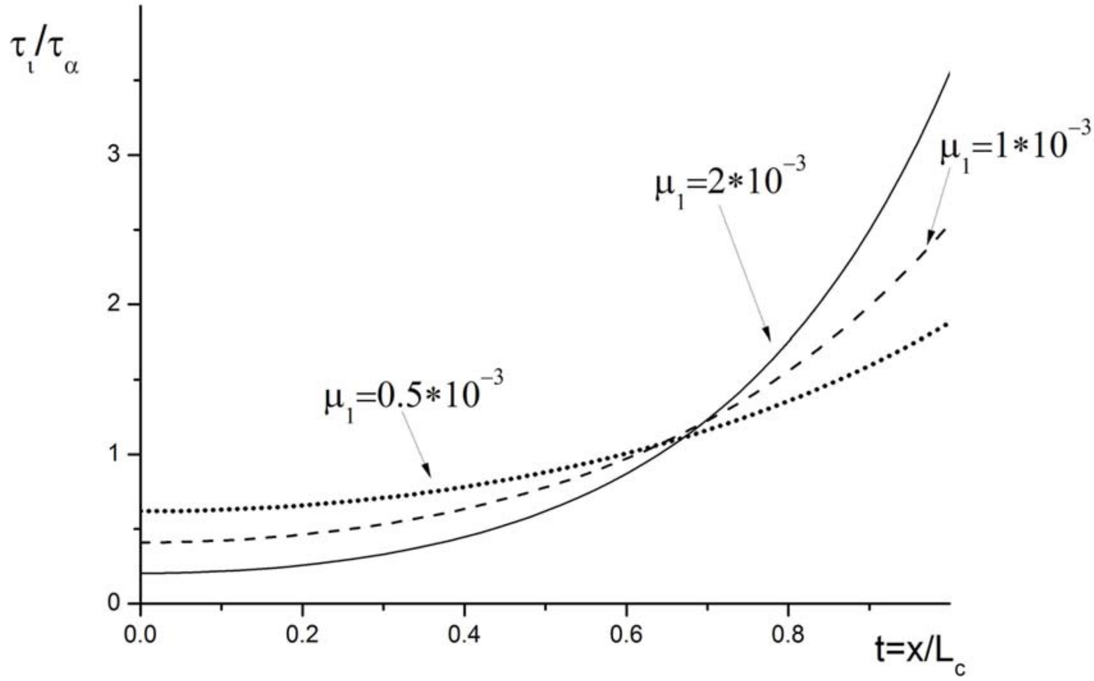

Fig. 4. Distributions of the relative shear stresses along nanotube axis for different values of the relative stiffness of the interface law, $\mu_{1\alpha} = 10\mu_1$

The dependencies of the shear stresses over the nanotube length for different values of the relative stiffness of the layer, are given in Fig. 3. Note, that the results in Fig. 3 are close to the experimental results [9–10] where the shear stresses for nanotube based composites were investigated: $138 MPs$ (epoxy matrix) and $186 MPa$ (polystyrene matrix). One can also see in Fig. 3 that when the relative stiffness of the interface layer is decreasing then the distribution of the shear stresses tends toward the uniform state.

For a small parameter μ_1 we can write

$$\lambda_1 = \frac{2\delta L_c \sqrt{\mu_1}}{D} \approx 1$$

and therefore we obtain

$$\tau_i(t) \to \sigma_f \left[\frac{D}{4L_c}\left(1 - \frac{d^2}{D^2}\right)\right], \quad \tau_R = \frac{\tau_i}{\tau_a} \to 1 \tag{23}$$

this is similar to ideally-plastic case [6,7].

The distributions of the dimensionless shear stress (SCCF) along the nanotube axis for the values of relative stiffness $\mu_{1\alpha} = 10\mu_1$ (μ_1 from (22)) are shown in Fig. 4. Noted, when the relative stiffness of the interface layer is increasing by 10 times then the distribution of the shear stresses tend toward more non-uniform state. For example, if $\mu_1 = 0.5 \cdot 10^{-4}$ then $\tau_R(1)/\tau_R(0) \approx 1.085$ and for $\mu_{1\alpha} = 2 \cdot 10^{-3} = 40\mu_1$ (see Fig. 4) we obtain $\tau_R(1)/\tau_R(0) \approx 17.75$. Noted, that if the stiffness of polymer matrix is decreasing then the shear stresses are tending to uniform state.

Above results can be use for the formulation of the bond deformation law in the frame of the crack bridging model, [11].

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