Models of Nanofibrous Composite Fracture Toughness[1]

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Keywords: composite, nanofillers, adhesion, fracture toughness.

Abstract. In this paper the modeling of strength and fracture toughness of nanofibrous composites is based on the consideration: 1) the shear strength between nanofibres and polymeric/ceramic matrix and 2) the crack bridging mechanism due to nanofibers which connect the crack surfaces. The special fracture criterion for a problem of quasi-static growth of a nanocrack/microcrack with the bridged zone of a large scale is proposed and considered. In frames of the considered model the macroscopic parameters of nanofibrous composites are modeled on the base of the nano/micro parameters of material structure.

Introduction

Composites based on polymers or ceramics matrix and filled by nanosized particles or nanotubes are materials with strong and tough mechanical properties. The mechanisms of toughening these materials by nanoparticles have investigated experimentally [1-3]. From the experimental observations it has been found:1) the main parameter which defines the nanocomposite strength is the adhesion between matrix and nanofiller; 2) the crack bridging mechanism 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 and the two-parametric fracture criterion for a problem of quasi-static growth of a crack with large scale bridged zone are considered.

Shear-lag model for nanotube-polymer matrix interaction

The model of nanotube-polymer adhesion based on the shear-lag approach was proposed previously in [4] and discussed in the frames of nanomechanics in [5]. In our approach, it is supposed that a nanotube is a straight cylindrical fiber of length L_c embedded in an infinite polymer matrix. A nanotube under an external normal loading has only displacements along its axis and a thin layer of the polymer matrix adjacent to a nanotube is bearing only shear stresses (interface layer). 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) as follows

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

where G_1 is the shear modulus of the interface layer under an elastic strain.

We will also suppose, if the shear stresses τ_i exceed a 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

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

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 displacement of the nanotube axis attains 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 stress at the detachment state (τ_{cr}) may be nonzero. After combining of equations (1) and (2) we can write the interface deformation law as follows

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

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. 1).

The deformation with the softening ($\tau_{cr} < \tau_m$, the bottom sign in (3-4)), or with the hardening ($\tau_{cr} \ge \tau_m$, the upper sign in (3-4)), can be considered in dependence on the values τ_m and τ_{cr}, see Fig.1.

The equation of equilibrium for an infinitely small part of the nanotube embedded in the polymer matrix has the following form

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

where D, d are the outer and inner tube diameters, σ - is the normal load at the arbitrary nanotube fiber section.

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

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

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 axis and the possibility of the nanotube detachment, we obtain the following system of the differential equations for the axial displacements of the nanofiber:

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

where

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

The point x_m in (7) is the position along the axis of the nanotube where the deformation law changes 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 $u = u_m$

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

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

$$u_{cr} = u_2(x_{cr}) = u_3(x_{cr}), \quad \left.\frac{\partial u_2}{\partial x}\right|_{x=x_{cr}} = \left.\frac{\partial u_3}{\partial x}\right|_{x=x_{cr}} \qquad (9b)$$

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.

The simple case of the constant thickness of the interface layer thickness (H) was initially considered. The equations (7) in this case have the known analytical solution. The different types of the boundary conditions for the embedded nanotube, the shear stresses distributions along of a nanotube axis and normal stresses in the nanotube section were considered based on the solution of the equations (7).

The relation between the crack opening displacement and the bonds tractions (the bond deformation law) depends on the model of nanotube-matrix interaction. The general form of spring-like bonds deformation law which can be obtain from the equations (7) and the boundary conditions at the nanotube ends can be written as follows, [6]

$$u_i(x) = c_0(x, \sigma)q_i(x), \qquad (10)$$

where the function c_0 can be considered as the effective bond compliance, $\sigma = \sqrt{q_x^2 + q_y^2}$ is the modulus of the traction vector, $i = x, y$, q_i are normal and shear tractions on the cracks surfaces.

The stresses and displacements at the crack end zone are determined from numerical solution of the singular integral-differential equations system or the boundary element solution for general case of the bond deformation law.

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

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

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 $x = L_c$ are adopted the following boundary conditions

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

the dependence of the shear stresses over the nanotube axis can be obtained as follows

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

By using formula (13) we can write for the average shear stresses

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

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 [5].

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

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

Dimensionless shear stresses for the linear deformation law can be obtained by incorporating eqs. (13) and (14)

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

Within the framework of the linear deformation law the maximal value of the shear stresses is observed on loaded end of the nanotube ($x = L_c$).

The following parameters of nanotubes and matrix were used for the computation: 1) the nanotube external diameter - $D = 5\,nm$; 2) the nanotube internal diameter - $d = 4.32\ nm$; the wall thickness of single-wall nanotube - $h = 0.34\ nm$; the critical length of the nanofiber - $L_c = 100\ nm$; the elastic modulus of the nanotubes - $E_f = 1\,TPa$; the Poisson ratio - $\nu = 0.25$; the critical external stress - $\sigma_f = 50\,GPa$; the thickness of the intermediate layer - $H = D$. The parameter (G_2) of the hardening part of the deformation law was chosen supposing that $0 \le G_2 \le G_1$. The case $G_2 = 0$ corresponds to the ideal plastic flow. The values of the relative stiffness of the interface layer for the given values of D, H, E_f and $\varepsilon = 0.0005,\ 0.00025,\ 0.000125$ are determined as follows

$$\mu_1 = \frac{G_1}{E_f}\frac{D}{H} = 2.0\cdot10^{-4}; 1.0\cdot10^{-4}; 0.5\cdot10^{-4} \tag{17}$$

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

The dependencies of the shear stress over the nanotube length for different values of the relative stiffness of the layer, are given in Fig. 2. Note, that the results in Fig. 2 are close to the experimental results [7,8] where the shear stresses for nanotube based composites were investigated: 138 MPa (epoxy matrix) and 186 MPa (polystyrene matrix).

One can also see in Fig. 2 that if 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 it can write $\lambda_1 = \dfrac{2\delta L_c\sqrt{\mu_1}}{D} \approx 1$

and, therefore, we obtain

$$\tau_i(t) \to \sigma_f \left[\frac{D}{4L_c} \left(1 - \frac{d^2}{D^2} \right) \right], \quad \tau_R = \frac{\tau_i}{\tau_a} \to 1 \tag{18}$$

that is similar to ideally-plastic case [5].
The approaches considered in [9] can be used in the general case of nanotubes with non-straight axis.

Two-parametric fracture criterion

Supposing that the bonds stresses and the crack opening along the crack end zone are known, the total potential energy of a body containing a crack with bridged zone (in the absence of body forces) is

$$\Pi = \int_v w(\varepsilon_{ij})dv - \int_{s_e} t_i u_i ds + \int_{s_i} \Phi(u)ds, \tag{19}$$

where $w(\varepsilon_{ij})$ is the density of the deformation energy in the body volume v, ε_{ij} are the components of the strain tensor; t_i, u_i are the tractions and displacements at the body boundary and (or) crack surfaces s_e; $\Phi(u)$ is the density of the strain energy of the bonds in the crack end zones, u is the crack opening in the end zones of area s_i.

The crack limit equilibrium corresponds to the following condition

$$-\frac{\partial \Pi}{\partial \ell} = \underbrace{-\frac{\partial}{\partial \ell} \left[\int_v w(\varepsilon_{ij})dv - \int_{s_e} t_i u_i ds \right]}_{G_{tip}(d,\ell)} - \underbrace{\frac{\partial}{\partial \ell} \int_{s_i} \Phi(u)ds}_{G_{bond}(d,\ell)} = 0 \tag{20}$$

The terms in the brackets represent the strain energy release rate at creation of a new crack surface and the last term is the rate of the energy absorption in the crack end zone and is associated with the energy necessary to create a unit of its new surface. Note, that within the framework of the model the rate of the energy absorption depends on the end zone size and bond characteristics. The equilibrium end zone size is not assumed to be constant. It can be determined from condition (20) while searching for the critical load needs additional conditions of the bond rupture.
In the general case the strain energy release rate can be defined through the stress intensity factors.
The stress intensity factors (SIF) $K_{I,II}$ for the interface bridged crack are determined in [6].

Let us calculate the rate of the energy absorption for the interface crack with bonding. Denote by $U_{bond}(d,\ell)$ the work of the deformation of bonds and by $G_{bond}(d,\ell)$ the rate of the energy absorption per unit thickness of the body. Then

$$U_{bond}(d,\ell) = b \int_{\ell-d}^{\ell} \Phi(u)dx, \quad G_{bond}(d,\ell) = \frac{\partial U_{bond}(d,\ell)}{b \, \partial \ell} \tag{21}$$

where b is the body thickness.
The density of the strain energy of the bonds is equal to

$$\Phi(u) = \int_0^{u(x)} \sigma(u)du, \quad u(x) = \sqrt{u_x^2(x) + u_y^2(x)}, \quad \sigma = \sqrt{q_x^2 + q_y^2} \tag{22}$$

After differentiation in formula (21) with respect to the upper and the bottom limits of the integral Finally, we obtain the following expression for the rate of the energy absorption [10]

$$G_{bond}(d,\ell) = \int_{\ell-d}^{\ell} \left(\frac{\partial u_y(x)}{\partial \ell} q_y(u) + \frac{\partial u_x(x)}{\partial \ell} q_x(u) \right)dx - \int_0^{u_{cr}} \sigma(u)du + G_c \tag{23}$$

where the second term is the density of deformation energy allocated at break of the bond at the trailing edge of the crack end zone and G_c is the matrix toughness (constant value).

Taking into account the notation from (23) the condition of the crack tip limit equilibrium (20) can be rewritten as follows (see the details in [10])

$$G_{tip}(d,\ell) = G_{bond}(d,\ell) \qquad (24)$$

Condition (24) is necessary but insufficient for searching for a limit equilibrium state of the crack tip and the end zone. This condition enables us to determine the end zone size, d_{cr}, such that the crack tip is in an equilibrium at the given level of the external loads. To search for the limit state of both the crack tip and end zone within the framework of the model one should introduce an additional condition, e.g., the condition of bond limit stretching at the trailing edge of the end zone $x_0 = \ell - d_{cr}$

$$u(x_0) = ([u_x(x_0)]^2 + [u_y(x_0)]^2)^{1/2} = \delta_{cr} \qquad (25)$$

where δ_{cr} is the bond rupture length.

If

$$G_{tip}(d,\ell) \geq G_{bond}(d,\ell) \qquad (26)$$

at a certain end zone size, d, and

$$u(\ell - d) < \delta_{cr} \qquad (27)$$

then the crack length increases with the end zone growth up to the size d_{cr} without bond rupture. This stage of the crack growth can be treated as the system shakedown to the given level of the external loads (sub-critical crack growth).

The crack tip advance with simultaneous bond rupture at the trailing edge of the end zone occurs if both conditions

$$u(\ell - d) \geq \delta_{cr} \qquad (28)$$

and (26) are fulfilled.

The regime of bond rupture at the trailing edge of the end zone without the crack tip advance is observed then conditions

$$G_{tip}(d,\ell) < G_{bond}(d,\ell) \qquad (29)$$

and (28) are fulfilled. In this case the size of the end zone decreases and tends to the limit value d_{cr} at the given load.

The end zone size and crack length are reserved within the framework of the model if the inequalities (29) and (27) hold. Thus, the bond rupture characteristics and load level determine the fracture regimes: 1) the crack tip advance with the end zone growth; 2) end zone shortening without the crack tip advance; 3) the crack tip advance and bond rupture at the trailing edge of the end zone.

Solving jointly eqs. (24-25) we can determine the critical external loads σ_0, the end zone size d_{cr} and the adhesion fracture resistance at the crack limit equilibrium state for the given crack length and bond characteristics.

The dependencies of the adhesion fracture resistance (it is obtained from the solution of the system of equations (24) and (25)) for the case of an uniform bonds stresses, P_0, are shown in Fig 3, where

$$G_b = P_0 u_{cr}, \quad \eta = G_c \big/ G_b$$

and the case $(\eta = 0, G_c = 0)$ is the case of zero matrix toughness $((G_c \ll G_b)$. As the crack length increases the adhesion fracture resistance tends to the constant value.

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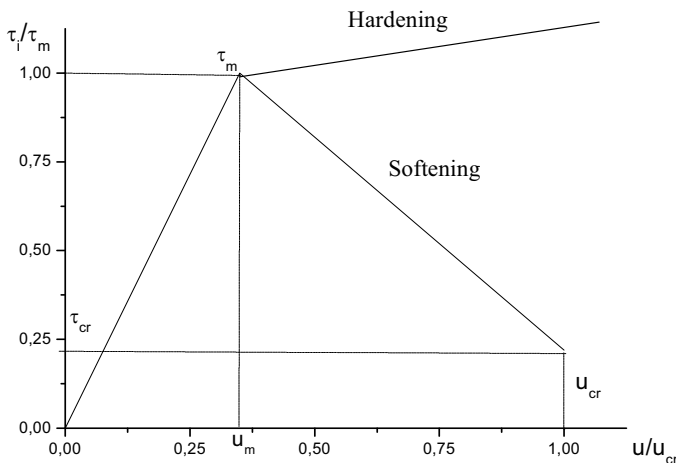
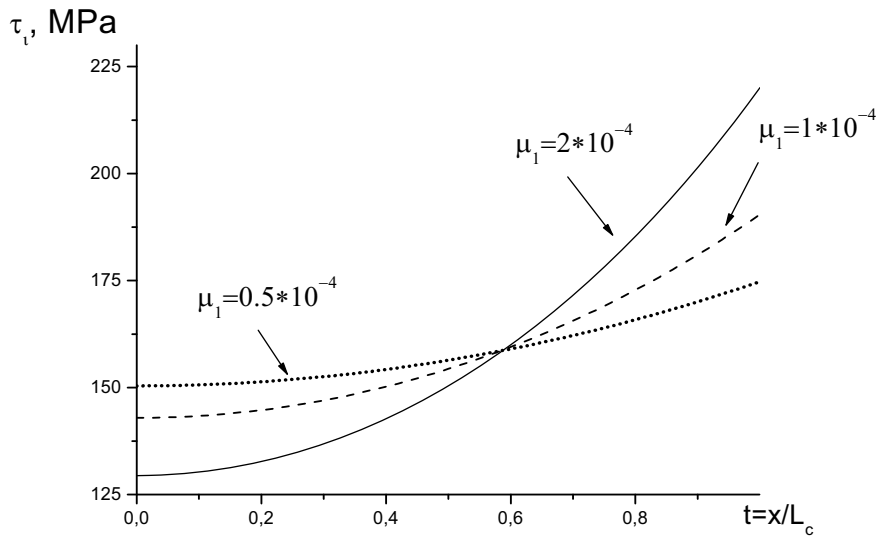Fig. 1 Bilinear shear stress-displacement law for the interface layer, u/u_{cr} is relative displacements

Fig. 2 Distribution of the shear stresses over the nanotube length for different values of the relative stiffness of the interface layer, μ_1
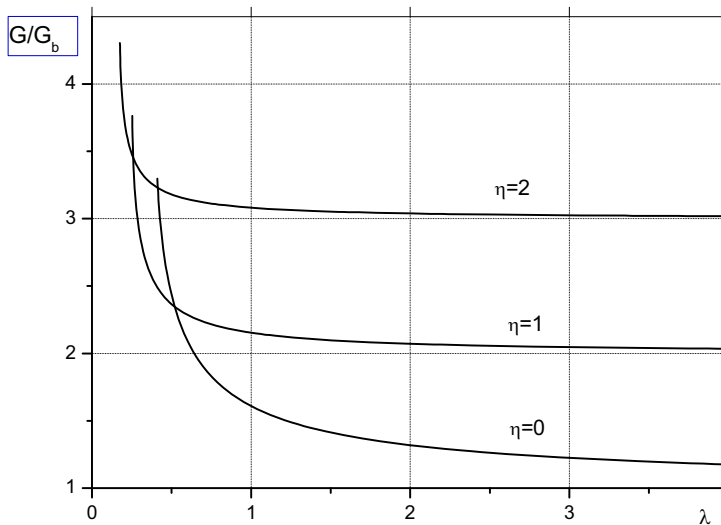

Fig 3. The adhesion fracture energy vs the crack length