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Dependence of the functional characteristics of polymer composites on the diameter of reinforcing carbon nanotubes

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A model is proposed that explains the dependence of the functional characteristics of polymer composites reinforced with carbon nanotubes on their radius. It is shown that the functional characteristics of the composite decrease inversely proportional to the radius of the tubes.

Keywords: Polymer nanocomposites, carbon nanotubes, elastic-strength properties.

It has been established that high physical and chemical performance characteristics of carbon nanotubes (CNTs) may be transferred to a polymer matrix when CNTs are used as fillers [1,2]. Specifically, CNTs have the capacity to improve stress-strain properties (elastic limit, strength, impact toughness, and hardness [2–6]). It was demonstrated in our earlier studies that the impact resistance increases significantly at certain concentrations of reinforcing CNTs [7,8]. CNTs are capable of interacting effectively with a polymer matrix and prevent the development of cracks [9–12]. A significant enhancement of mechanical characteristics of a polymer composite (PC) may be achieved even with small amounts of added CNTs. Specifically, the tensile strength of a polymer composite was increased by 35% (from 66 ± 3 MPa in an unmodified polymer to 84 ± 2 MPa) in [13] by increasing the concentration of multi-walled CNTs (MWCNTs) from 0.1 to 0.5 mass%. The tensile strength reached its maximum value of 90 ± 4 MPa in an epoxy composition with added fluorinated CNTs. The composite with 0.1 mass% of fluorinated CNTs also had the maximum Young's modulus (1644 ± 8 MPa, which is 30% higher than the value for a composite without additives) among all the studied composites. The authors of [13] have concluded that the optimum degree of filling, which provides a simultaneous improvement of several stress-strain properties (compressive and tensile moduli, compressive strength, and impact toughness), is close to 0.1 mass%. In a number of other studies, a considerable enhancement of mechanical characteristics was observed at significantly higher CNT concentrations [14,15]. The highest resistance to pendulum impact (impact toughness) recorded in [7] corresponded to the range of CNT concentrations of $2.5-3.9$ mass% in PC−CNT, and an increase in absorption of the kinetic energy of an indenter in PC−CNT impacted at a velocity of $100-115$ m/s was observed in [8] within the range of CNT concentrations from 0 to 10 mass% (with the maximum absorption reached approximately at 7 mass%).

Note the spread of optimum values of CNT concentration in polymer nanocomposites (PNCs) that is revealed when the results of different studies are compared [16]. For example, the strength characteristics, such as tensile strength (TS), of CNT-reinforced PNCs reach their maxima either at CNT concentrations of several mass percent [5,17,18] or at concentrations below one percent [4,19,20].

The reasons for this discrepancy, which was attributed to the variation of properties of the polymer matrix and to the difference in CNT-polymer composite synthesis techniques, have not been discussed.

In the present study, we attempt to find an explanation for the spread of mechanical parameters of polymer CNT nanocomposites by attributing it to the properties of nanotubes themselves. We analyze how the multi-walled nature of ideal MWCNTs may affect their functional activity, which is understood in the broad sense of the term. In the present case, functional activity is, first and foremost, the intensity of interaction of MWCNTs with the polymer matrix in PNC−CNT media.

Let us denote the activity of a single n-walled MWCNT as A_n and assume that this activity is proportional to area S_n of the peripheral MWCNT wall, while the inner tube layers do not interact with the external environment; i. e.,

$$A_n = f_n S_n, \tag{1}$$

where f_n is the activity coefficient, which factors in, among other things, the concentration of various structural defects on the MWCNT surface. The lateral surface area depends on number of layers n:

$$S_n = 2\pi r_n l = 2\pi \big(r_1 + d(n-1) \big) l, \tag{2}$$

where r_1, r_n are the inner and outer MWCNT radii, respectively (r_1 may vary from 0.3 to 10 nm), d (0.355 nm) is the interlayer distance, and l is the tube length.

The functionality of CNT-enriched composites depends not only on the properties of the polymer matrix and process technologies, but also on the concentration and properties of the CNT filler.

Activity $A_{n@PNC}$ of MWCNTs in the polymer matrix may be expressed as the product of activity A_n and number $P_{n@PNC}$ of individual MWCNTs in the composite:

$$A_{n@PNC} = A_n P_{n@PNC}. \qquad (3)$$

$P_{n@PNC}$ may be calculated based on the concentration of n-MWCNTs in the PNC (C_n):

$$P_{n@PNC} = C_n \frac{M_{PNC}}{M_n}, \qquad (4)$$

where M_{PNC} is the PNC mass, and the mass of an individual MWCNT (M_n) may be estimated as the mass of all carbon ions that make up this MWCNT. The number of carbon atoms in the ith MWCNT layer (N_{Ci}) is specified by the surface area of this layer and the density of carbon atoms in it (N_{Cg}):

$$N_{Ci} = 2\pi r_i l N_{Cg} = 2\pi (r_1 + (i-1)d) l N_{Cg}. \qquad (5)$$

It is fair to assume that the density of C atoms in a MWCNT layer corresponds to the density in the basal graphite (graphene) plane (two atoms per hexagon area $(3\sqrt{3}/2)S^2 = 0.0523 \, nm^2$, where $S = 0.142$ nm is the C−C bond length in the hexagon):

$$N_{Cg} = \frac{2}{0.0523} = 38.24 \, at. \, C/nm^2. \qquad (6)$$

The mass of an individual n-walled MWCNT is derived from (5), (6):

$$M_n = 2\pi \left(r_1 + (n-1)\frac{d}{2} \right) n l N_{Cg} M_C, \qquad (7)$$

where $M_C \approx 1.99 \cdot 10^{-23}$ g is the mass of a carbon atom. The following estimate of MWCNT activity in the polymer matrix is derived from Eqs. (1)−(7):

$$A_{n@PNC} = f_n \left[2\pi (r_1 + (n-1)d) l N_{Cg} \right] \left[C_n \frac{M_{PNC}}{M_n} \right]$$

$$= f_n \left[2\pi (r_1 + (n-1)d) l N_{Cg} \right]$$

$$\times \left[C_n \frac{M_{PNC}}{\left[2\pi (r_1 + (n-1)\frac{d}{2}) n l N_{Cg} M_C \right]} \right]$$

$$= f_n \left[(r_1 + (n-1)d) \right] \left[C_n \frac{M_{PNC}}{(r_1 + (n-1)\frac{d}{2}) n M_C} \right] \quad (8)$$

or

$$A_{n@PNC} \left[\frac{n M_C}{f_n C_n M_{PNC}} \right] = 1 + (n-1) \frac{d}{2r_1 + (n-1)d}. \quad (9)$$

If $n \gg 1$ and $nd \gg r_1$,

$$A_{n@PNC} \approx f_n C_n \frac{M_{PNC}}{n M_C}. \qquad (10)$$

It is clear that the activity of MWCNTs in composites decreases in inverse proportion to the number of layers. Alongside with the variation of PNC synthesis regimes, this factor may influence the discrepancy in the observed properties of PNCs (e.g., impact resistance) reported in different studies.

Equation (9) yields the following for single-walled CNTs (SWCNTs) ($n = 1$):

$$A_{1@PNC} = f_1 C_1 \frac{M_{PNC}}{M_C}, \qquad (11)$$

while double-walled CNTs (DWCNTs) ($n = 2$) have

$$A_{2@PNC} = f_2 C_2 \left(1 + \frac{d}{2r_1 + d} \right) \left(M_{PNC}/2M_C \right). \qquad (12)$$

To a fairly good approximation, we may assume that the activity coefficient of CNTs does not change with an increase in the number of layers; i.e., $f_1 = f_2 = \ldots f_n$. With the CNT concentration being constant ($C_1 = C_2 = \ldots C_n$), we then find

$$A_{2@PNC} = A_{1@PNC} \left(1 + \frac{d}{2r_1 + d} \right) \Big/ 2 \qquad (13)$$

and

$$A_{n@PNC} = A_{1@PNC} \left(1 + \frac{(n-1)d}{2r_1 + (n-1)d} \right) \Big/ n. \qquad (14)$$

The influence of concentration and type of added nanoparticles on the mechanical properties of nanocomposites was investigated in [19]. Specifically, the influence of SWCNTs, DWCNTs, and MWCNTs with concentrations of 0.1, 0.3, and 0.5 mass% on TS was examined. It was found that the TS value increases by 44 % for SWCNTs, by 37.4 % for DWCNTs, and by 35.9 % for MWCNTs (relative to the polymer material without CNTs) at a CNT concentration of 0.3 mass%. These TS enhancement magnitudes correspond to activities $A_{1@PNC}$, $A_{2@PNC}$, and $A_{n@PNC}$.

Analyzing the $A_{2@PNC}/A_{1@PNC}$ ratio with the use of (11) and (13), we then obtain

$$\frac{A_{2@PNC}}{A_{1@PNC}} = \frac{1 + \frac{d}{2r_1 + d}}{2} = 0.85, \qquad (15)$$

which matches the experimental ratio of TS enhancements for DWCNTs and SWCNTs: 37.4/44 = 0.85.

Using interlayer distance $d = 0.355$ nm from (15), we obtain an estimate of inner DWCNT radius $r_1 \approx 0.43$ nm, which is a fairly reasonable value [1,2].

In a similar fashion, equating the ratio

$$\frac{A_{n@PNC}}{A_{1@PNC}} = \left(\frac{1 + (n-1)d}{2r_1 + (n-1)d} \right) \Big/ n$$

to the ratio of TS enhancements for MWCNTs and SWCNTs (35.9/44 = 0.816), we estimate the number of MWCNT layers at $n \approx 4$. It was assumed here that the inner radii

of MWCNTs and SWCNTs are the same; strictly speaking, they are not necessarily equal. It is clear that the presented estimates are based on a model of the ideal composite structure in which the presence of defects in CNTs is neglected. Therefore, the obtained numerical estimates of the inner radius of DWCNTs and the number of MWCNT layers are rather approximate.

The introduction of CNTs into an epoxy resin-based polymer matrix is an efficient method for enhancing the functional properties of composite materials. Small amounts of added CNTs make it possible to improve the properties of composites without increasing the sample mass and thickness, which is extremely important for practical application of these materials. However, the parameters obtained at the same concentration of CNTs in the composite are characterized by a certain spread. It was demonstrated in the present study that, alongside with differences in the properties of the polymer matrix and technological differences in the composite synthesis process, the CNT diameter plays a significant part in shaping the properties of the final composite. One particular conclusion from the above analysis is that the functionality of multi-walled tubes and, consequently, the functional characteristics of the composite degrade in inverse proportion to the MWCNT radius.

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Conflict of interest

The authors declare that they have no conflict of interest.

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