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Dependence of mechanical performances of polymer/carbon nanotubes nanocomposites on percolation threshold

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ABSTRACT

In this study, several models for the tensile modulus and strength of polymer/carbon nanotubes (CNT) nanocomposites (PCNT) are expressed as a function of percolation threshold. The roles of the CNT aspect ratio α and percolation threshold φ_p in the mechanical properties of PCNT are plotted according to the original and developed models. Furthermore, the effects of φ_p and various interfacial/interphase parameters on the PCNT tensile strength are presented through contour plots. The tensile modulus and strength of PCNT show a threshold at low φ_p values, indicating the important effect of the percolation behavior on the mechanical properties. Poor mechanical performances are seen at high φ_p values and different ranges of interfacial/interphase parameters. However, the lowest φ_p values and the highest ranges of interfacial/interphase parameters result in the most desirable PCNT strength.

1. Introduction

Nanocomposites show considerable reinforcement with only a small nanofiller content, and they can be fabricated easily and inexpensively [1–7]. Experimental and theoretical studies have extensively investigated the properties of polymer/carbon nanotubes (CNT) nanocomposites (PCNT) [8–11]. The substantial enhancement of the modulus and impact toughness of PCNT is attributed to the formation of a connected network of nanotubes above the percolation threshold [12,13]. The percolation threshold is the minimum nanoparticle volume fraction that forms a continuous network in the nanocomposites [14,15]. This term is generally applied to polymer nanocomposites containing conducting nanoparticles such as CNT and graphene in which electrical conductivity is obtained above the percolation threshold [16]. In other words, the percolation threshold is found when the electrical conductivity of a nanocomposite increases significantly and the nanocomposite changes from an insulator to a conductor owing to the formation of a conducting network in the insulating matrix.

The percolation threshold was also observed for the mechanical properties of polymer nanocomposites [17,18]. Favier et al. [17] discussed the remarkable shear modulus values seen in reinforced films with cellulose whiskers owing to the percolation effect. Mechanical percolation in polymer nanocomposites containing CNT or clay was inversely correlated to the aspect ratio or excluded volume of nanoparticles [19–21]. Studies have noted that the high aspect ratio of nanofillers (thin and large nanoparticles) significantly reduces the percolation threshold. However, few studies have focused on the percolation threshold for the mechanical properties of polymer nanocomposites although it can explain the high ranges of mechanical properties and the level of nanoparticle networks in polymer nanocomposites. Additionally, many parameters such as the interphase between the polymer matrix and nanoparticles and the agglomeration of nanoparticles affect the mechanical properties of nanocomposites [22–25]. The excellent surface area of nanoparticles usually creates interphase regions in polymer nanocomposites; these directly govern the mechanical properties of the nanocomposite [22,23]. Similarly, it was found that the interphase between the polymer matrix and nanoparticles can reduce the percolation threshold in nanocomposites due to the contribution of interphase zones to networks [19,21]. Moreover, agglomeration increases the size of nanoparticles; however, this negatively affects the mechanical properties of nanocomposites, because agglomeration reduces the surface area and efficiency of nanoparticles [24,25].

The properties of three-dimensional (3D) networks of nanoparticles in polymer nanocomposites were studied from fundamental and

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application viewpoints. Effective medium models were used to investigate the elastic properties of nanocomposites based on the continuum elasticity theory by the effects of matrix and filler phases [26]. Additionally, Chatterjee [27] assumed a random network of elastic fibers and generalized a proposed 2D model to 3D for the tensile and shear moduli of fiber networks. He combined the Halpin–Tsai model with the results of the percolation theory and presented a model for the modulus of nanocomposites containing dispersed and networked nanofillers over a wide range of volume fractions. However, this model is complex and needs some adjustable parameters for modeling.

In this study, the mechanical percolation threshold (φ_p) in PCNT is linked to the aspect ratio of CNT (α). By this assumption, several models such as Halpin–Tsai, Norris, Pukanszky and Callister for tensile, shear, and bulk moduli as well as tensile strength of polymer nanocomposites are expressed using φ_p. The effects of α and φ_p on the mechanical properties of PCNT are well discussed. Furthermore, the significances of interfacial/interphase parameters such as interphase thickness, interphase strength, quality of interfacial adhesion, and interfacial shear strength on the tensile strength of PCNT are presented. This paper reports the significant roles of the percolation threshold and interfacial/interphase properties in the mechanical performances of PCNT.

2. Expression of models as a function of percolation threshold

Chatterjee [27] suggested an inverse connection between percolation threshold and aspect ratio of CNT (α) as:

$$\varphi_p \approx \frac{1}{\alpha} \tag{1}$$

where α = l/d; l and d are the length and diameter of CNT, respectively.

The Halpin-Tsai model for 2D in-plane random arrangement of CNT (H-T2D) [28] is widely used for calculation of tensile modulus in PCNT which is presented as:

$$E = \frac{3}{8}E_L + \frac{5}{8}E_T \tag{2}$$

$$E_L = E_m\left(\frac{1+2\alpha\eta_L\varphi_f}{1-\eta_L\varphi_f}\right) \tag{3}$$

$$E_T = E_m\left(\frac{1+2\eta_T\varphi_f}{1-\eta_T\varphi_f}\right) \tag{4}$$

$$\eta_L = \left(E_f/E_m - 1\right)/\left(E_f/E_m + 2\alpha\right) \tag{5}$$

$$\eta_T = \left(E_f/E_m - 1\right)/\left(E_f/E_m + 2\right) \tag{6}$$

where E_L and E_T are the longitudinal and transverse moduli, respectively. E_m and E_f are the moduli of polymer matrix and nanoparticles, respectively. Also, φ_f shows the volume fraction of nanofiller.

Assuming the percolation threshold in PCNT, E_L and η_L are expressed as a function of φ_p by substituting of α from Eq. (1) into Eqs. (3) and (5) as:

$$E_L = E_m\left(\frac{1+2\frac{\eta_L\varphi_f}{\varphi_p}}{1-\eta_L\varphi_f}\right) \tag{7}$$

$$\eta_L = \left(E_f/E_m - 1\right)/\left(E_f/E_m + 2/\varphi_p\right) \tag{8}$$

The H-T2D can consider the percolation threshold by applying E_L and η_L from Eqs. (7) and (8).

Also, Norris [29] proposed a model for shear (G) and bulk (K) moduli of composites reinforced with thin oblate spheroids as:

$$G = G_m + \frac{1}{15}\varphi_f\left[\frac{\pi}{8\alpha}\frac{3-4\nu_m}{G_m(1-\nu_m)} + \frac{1-\nu_f}{G_f(1+\nu_f)}\right]^{-1} + \frac{2}{5}\varphi_f\left[\frac{\pi}{16\alpha}\frac{7-8\nu_m}{G_m(1-\nu_m)} + \frac{1}{G_f}\right]^{-1} \tag{9}$$

$$K = K_m + \frac{4}{9}\varphi_f\left[\frac{\pi}{8\alpha}\frac{3-4\nu_m}{G_m(1-\nu_m)} + \frac{1-\nu_f}{G_f(1+\nu_f)}\right]^{-1} \tag{10}$$

where subscripts m and f show the matrix and filler phases, respectively. Also, ν is the Poisson ratio. Assuming the percolation threshold, the Norris model is expressed as:

$$G = G_m + \frac{1}{15}\varphi_f\left[\frac{\varphi_p\pi}{8}\frac{3-4\nu_m}{G_m(1-\nu_m)} + \frac{1-\nu_f}{G_f(1+\nu_f)}\right]^{-1} + \frac{2}{5}\varphi_f\left[\frac{\varphi_p\pi}{16}\frac{7-8\nu_m}{G_m(1-\nu_m)} + \frac{1}{G_f}\right]^{-1} \tag{11}$$

$$K = K_m + \frac{4}{9}\varphi_f\left[\frac{\varphi_p\pi}{8}\frac{3-4\nu_m}{G_m(1-\nu_m)} + \frac{1-\nu_f}{G_f(1+\nu_f)}\right]^{-1} \tag{12}$$

which correlate the bulk and shear moduli to the percolation threshold.

Pukanszky [30] proposed a model for the tensile strength of composites by assuming the reinforcing of filler and the interfacial adhesion/interaction as:

$$\sigma_R = \frac{1-\varphi_f}{1+2.5\varphi_f}\exp\left(B\varphi_f\right) \tag{13}$$

where $\sigma_R = \sigma_c/\sigma_m$ is the relative strength, and σ_c and σ_m are the tensile strength of the composite and matrix, respectively. The term $(1-\varphi_f)/(1+2.5\varphi_f)$ shows the reduction of the effective load-bearing cross-section owing to the introduction of the filler. Furthermore, exp $(B\varphi_f)$ describes the filler-matrix interactions, and the interaction parameter B indicates the capacity of stress transfer between the polymer and filler components as a function of the thickness and strength of the interphase as well as the interfacial area between the polymer and filler as:

$$B = \left(1 + A_c\rho_f t\right)\ln\left(\frac{\sigma_i}{\sigma_m}\right) \tag{14}$$

where A_c and ρ_f are the specific surface area (the surface area of 1 g nanoparticles) and density of filler, respectively. Also, t and σ_i are the thickness and strength of interphase. Pukanszky's model has been used for various nanocomposites containing spherical, cylindrical, and layered nanoparticles [24,31]. The successful agreement between the experimental data and the calculations confirm the predictability of this model. B changed from negative values to below 100 in previous studies [32,33], because poor or strong interfacial interaction/adhesion between the polymer and nanoparticles mainly controls the tensile strength of nanocomposites.

A_c for cylindrical nanoparticles such as CNT is expressed by:

$$A_c = \frac{A}{m} = \frac{A}{\rho_f v} = \frac{2\pi Rl}{\rho_f \pi R^2 l} = \frac{2}{\rho_f R} = \frac{4\alpha}{\rho_f l} \tag{15}$$

where A, m, v and R are the surface area, mass, volume and radius of nanotubes, respectively. Assuming the percolation threshold by Eq. (1) into Eq. (15), A_c can be calculated by:

$$A_c = \frac{4}{\rho_f l\varphi_p} \tag{16}$$

By substituting of A_c from Eq. (16) into Eq. (14), B is expressed by percolation threshold as: