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Percolation model of reinforcement efficiency for carbon nanotubes dispersed in thermoplastics

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ABSTRACT

Considerable experimental work on carbon nanotube-reinforced composites has shown that the reinforcement efficiency of carbon nanotubes (CNTs) becomes lower than the theoretical expectation when CNT content reaches a critical value. This critical volume fraction (percolation threshold) is considered related to the formation of percolating network. In this work, a percolation model is proposed to describe the observed sharp decrease in the reinforcement efficiency of multiwalled CNTs (MWCNTs) dispersed in thermoplastics when the CNT content exceeds the percolation threshold. The percolation threshold is estimated via a numerical simulation of randomly curved CNTs according to the statistics on geometrical features of real CNTs. The percolation model, integrated into the Halpin–Tsai equations, is verified using the experimental data of various thermoplastic composites reinforced with MWCNTs. The developed mechanical model achieves a good agreement with the measured moduli of nanocomposites, and demonstrates an excellent prediction capability over a wide range of CNT content.

1. Introduction

Carbon nanotubes (CNTs) have stimulated tremendous interest since their discovery in 1991 [1]. This kind of nano-material is regarded as a superior filler to make advanced composites with significantly improved mechanical performance at very low contents, due to their extraordinary mechanical properties and huge aspect ratio. In the past two decades, intensive research effort [2–4], experimental and theoretical, has been devoted to understanding the reinforcement mechanisms of CNTs within polymer-matrix composites in order to achieve full exploitation of their potential.

CNT-reinforced composites are widely considered similar to short fiber-reinforced composites. The modeling of mechanical properties for CNT-reinforced composites has borrowed substantial ideas from the continuum micromechanics theory well developed for short fiber-reinforced composites. Among those micromechanical models, the Halpin–Tsai equations [5] are one of the most popular models heretofore, which serves as a quick and simple way to predict the mechanical properties of CNT-reinforced composites. The Halpin–Tsai equations are regarded as an approximate form of the generalized self-consistent model [6]. This model can fit experimental results of short fiber-reinforced composites very well at low fiber volume fraction, which makes it extremely suitable for CNT-reinforced composites. The Halpin–Tsai equations were first introduced by Qian et al. [7] to predict the modulus of polystyrene reinforced with multiwalled carbon nanotubes (MWCNTs) and reached a good agreement with the measured results. Thostenson and Chou [8] modified the Halpin–Tsai equations toward its applicability to nanocomposites reinforced with unidirectional oriented MWCNTs, which has become a widely adopted method [9–12]. In their method, an MWCNT within the polymer matrix acts like a singlewalled carbon nanotube (SWCNT), and its outmost layer carries nearly the entire load transferred from the matrix, due to the weak inter-layer interaction in MWCNT. The equivalent SWCNT can be further simplified as an effective solid fiber with the same length and diameter. The modulus of the effective solid fiber (E_f) is calculated supposing that the load-bearing capability of the equivalent SWCNT is applied to its whole cross-section:

$$E_f = \frac{4t}{d} E_{CNT} \tag{1}$$

where E_{CNT} is the elastic modulus of the equivalent SWCNT. d is the diameter of the equivalent SWCNT, and t is the thickness of the outmost layer.

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By incorporating E_f into the Halpin–Tsai equations for non-aligned short fiber-reinforced composites [13], the elastic modulus of the nanocomposites containing randomly oriented CNTs (E_c) can be estimated through

$$\begin{aligned} \frac{E_c}{E_m} &= \frac{3}{8}\left(\frac{1+\zeta\eta_L v_f}{1-\eta_L v_f}\right)+\frac{5}{8}\left(\frac{1+2\eta_T v_f}{1-\eta_T v_f}\right) \\ \zeta &= \frac{2l}{d}, \quad \eta_L = \frac{E_f/E_m - 1}{E_f/E_m + \zeta}, \quad \eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2} \end{aligned} \tag{2}$$

where E_m is the modulus of the polymer matrix. l denotes the length of the equivalent SWCNT. ζ is a parameter depending on the geometry and boundary conditions of reinforcements. CNT volume fraction v_f can be converted from weight percentage w_f through

$$v_f = \left[1+\frac{\rho_{CNT}}{\rho_m}\left(\frac{1}{w_f}-1\right)\right]^{-1} \tag{3}$$

where ρ_{CNT} and ρ_m are the densities of CNT and polymer matrix, respectively.

In recent years, the Halpin–Tsai equations were modified by introducing an orientation factor and an empirical exponential shape factor to investigate the effects of tangled and aggregated CNTs on the nonlinear increase in modulus and strength of MWCNT-reinforced phenolic composites [14]. Waviness correction factors were incorporated to reflect the reduced reinforcement efficiency of curved CNTs [11,15]. In these modifications, curved CNTs are resolved into the components along and perpendicular to the direction that composites are stretched. The latter may carry small load transferred from the matrix. Thus it can be assumed that the curved CNTs lose part of their load-bearing ability, or they are equivalent to the straight CNTs of less volume faction. The phenomenological correction factors were used to adjust the CNT volume [11] or constant η in the Halpin–Tsai equations.

Although a great amount of work has demonstrated the significantly improved mechanical properties of CNT-reinforced composites over the pure polymers, the reinforcement efficiency of CNTs was often found to be lower than the theoretical expectation. Especially when the CNT content is relatively high, the measured moduli of the prepared nanocomposites are clearly below the predicted values [9,10,12,16,17]. Fig. 1 gives two typical examples of the polypropylene reinforced with SWCNTs [16] and MWCNTs [17]. It can be observed that the reinforcement efficiency of CNTs at high weight percentages (indicated by the slope of the dash line) is lower than the theoretical prediction (the slope of the solid line). The divergence between the predicted and the measured moduli in both cases becomes discernible at the CNT content around 1.5 wt% (about 0.8–1.0 vol%).

This discrepancy is usually attributed to two factors: (i) the inhomogeneous dispersion of CNTs within the matrix, which results in agglomerates acting as defects; and (ii) the imperfect bonding between CNTs and matrix, which leads to insufficient load transfer. However, the two factors, regarded as the key issues to make high-performance CNT-reinforced composites, are suspicious according to the published research. Despite the nature of CNTs that they are prone to entangle with one another, the current mixing techniques, if properly combined and applied, are capable of achieving a fairly uniform dispersion at low CNT contents around 1 wt% [18,19]. The reported observations of interfacial bonding remain conflicting. A few researchers found that the load-transfer from matrix to CNTs is poor [20,21], and a number of models assuming the imperfect CNT/polymer bonding were proposed [22,23]. On the other side, some experimental work indicates a sufficiently strong load-transfer ability of CNT/polymer interfaces [24,25], which also gets support from modeling [25,26]. In particular, the prediction obtained by the Halpin–Tsai equations based on the assumption of a perfect bonding between CNTs and polymer matrix can highly agree with the measured moduli at low CNT contents [7,9,12,16,17,27,28]. Furthermore, it is interesting that in these papers even though the measured moduli of CNT-reinforced composites become lower than the predicted values at relatively high CNT contents, a quasi-linear relation between the composite modulus and the CNT content is still clear but with reduced slope, as shown in Fig. 1. The finding suggests that the reinforcing effect of CNTs can be well modeled by the Halpin–Tsai equations at low CNT contents, but the reinforcement efficiency jumps suddenly to a lower level when the CNT content exceeds a critical value. Such a discrete reduction of reinforcement efficiency is hard to be simply ascribed to the aggravated agglomeration or the decrease in load transfer with the progressively increased CNT content.

Inspired by the electrical percolation of CNT-doped polymers, which describes a sharp drop in electrical resistivity of nanocomposites when the CNT content reaches a critical level (i.e. percolation threshold), the observed "turning point" of CNT reinforcement efficiency [29] was considered to be associated with the formation of a percolating network within the polymer matrix [29–32]. Martone et al. [30,31] introduced the percolation threshold into the modified rule of mixtures and investigated the effects of the CNT aspect ratio on its reinforcement efficiency. They think that agglomerated CNTs are prone to form micro-structures above the percolation threshold, which act as defects in the matrix and reduce the reinforcement efficiency of CNTs. Loos and Manas-Zloczower [29,32] divided the composites into three phases when the CNT content is above the percolation threshold: the matrix, the well-dispersed CNTs and the agglomerated CNTs. The three phases were connected using the mixed parallel and series models. The agglomerated CNTs build the percolating network, in which the CNTs are linked by weak bonds. Thus these CNTs have poor load-bearing capacity compared with their well-dispersed counterparts. The decrease in CNT reinforcement efficiency can be observed

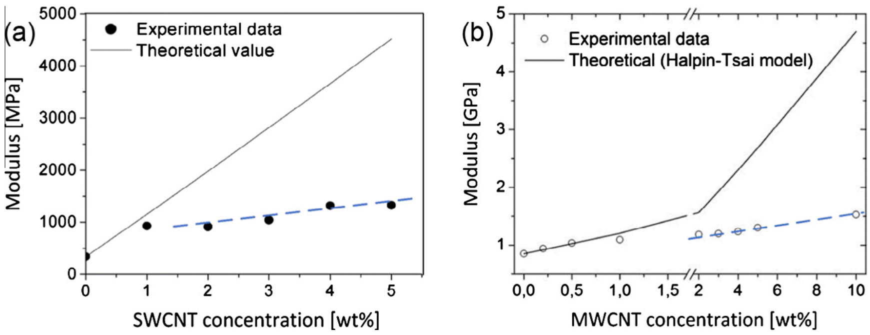

Fig. 1. Measured moduli and predicted moduli (using the Halpin–Tsai equations) of the polypropylene reinforced with (a) SWCNTs and (b) MWCNTs, reproduced from Refs. [16,17]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)