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Considering the filler network as a third phase in polymer/CNT nanocomposites to predict the tensile modulus using Hashin-Hansen model

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ABSTRACT

In this paper, a conventional Hashin-Hansen model is developed to analyze the tensile modulus of polymer/CNT nanocomposites above the percolation threshold. This model for composites containing dispersed particles utilizes the aspect ratio of the nanofiller (α), the number of nanotubes per unit area (N), the percolation threshold (φ_p) and the modulus of the filler network (E_N), assuming that the filler network constitutes a third phase in the nanocomposites. The experimental results and the predictions agree well, verifying the proposed relations between the modulus and the other parameters in the Hashin-Hansen model. Moreover, large values of “α”, “N” and “E_N” result in an improved modulus of the polymer/CNT nanocomposites, while a low percolation threshold results in a high modulus.

1. Introduction

Much research has focused on the development of high-performance materials for advanced applications by the addition of nanoparticles into polymer matrices. Among the various types of nanoparticles, carbon nanotubes (CNTs) have attracted extensive attention as a novel reinforcement for polymer nanocomposites since 1991 [1–11]. CNTs consist of a single or several graphite layers with small diameters (1–100 nm) and large lengths (1–10 μm). Additionally, CNTs exhibit a Young's modulus of 1 TPa, a tensile strength in the range of 10–50 GPa, and an exceptional electrical conductivity [12–14]. These properties, along with their remarkable physical dimensions such as their high aspect ratio, large surface area, outstanding mechanical behavior and good conductivity properties, suggest that CNTs may be used as a promising reinforcement in advanced nanocomposites. However, the van der Waals attraction between CNTs causes agglomerates to form during the synthesis procedure [15,16].

Polymer/CNT nanocomposites exhibit a high electrical conductivity when the volume fraction of CNTs is higher than the percolation threshold [17–19]. That is, the percolation threshold is the minimum concentration of nanofiller of the filler network that results in an acceptable conductivity. Many authors have studied the percolation threshold as an important parameter in polymer nanocomposites [20–22]. One main concern is determining whether a similar percolation effect also exists regarding the mechanical properties of nanocomposites. This has been confirmed in the positive, where a similar abrupt change was reported for the tensile modulus of polymer nanocomposites by the addition of filler concentration [23–26]. Researchers have identified the percolation threshold for mechanical properties through experimental and theoretical approaches. Although such an abrupt change in the mechanical behavior cannot be entirely attributed to the electrical percolation threshold, mechanical percolation is found to be similar to electrical percolation in polymer/CNT nanocomposites [27].

From the theoretical point of view, several models have been suggested that express the electrical conductivity above the percolation threshold, including power-law functions of various parameters [28,29]. Ouali et al. [30] considered both the percolation effect and an inverse rule for the mixtures to model the tensile modulus of conventional composites. Various researchers have estimated the tensile modulus of polymer nanocomposites above the percolation threshold using the Ouali model [31,32]. However, these conventional models cannot accurately predict the percolation threshold using only the tensile modulus because they do not consider the more unusual properties of nanofillers, such as their high aspect ratio, big surface area and networking above a certain concentration. As a result, the percolation

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phenomenon for the mechanical properties of polymer nanocomposites has been studied relatively little in the literature. In addition, the percolation threshold, which is related to formation of the filler network, is inversely related to the aspect ratio of the nanoparticles [33,34]. Thus, the high aspect ratio of CNTs results in a nanoparticle network at low filler concentrations.

In this paper, the Hashin-Hansen model for the tensile modulus of composites containing dispersed particles is developed, considering the filler network above the percolation threshold as a third phase. The proposed model is expressed as a function of several parameters, including the aspect ratio and Young's modulus of the nanofiller, the number of nanotubes per unit area, and the modulus of the CNT network. In the proposed equations, the values of these parameters are determined using experimental measurements of the modulus for several different samples. Furthermore, the Hashin-Hansen model is analyzed by plotting the modulus as a function of the main parameters and investigating the relationships between the modulus and the other parameters.

2. Development of model

The Hashin-Hansen model [35] for the Young's modulus of polymer composites containing dispersed particles is expressed as:

$$E_R = \frac{E_m + E_f + (E_f - E_m)\varphi_f}{E_m + E_f - (E_f - E_m)\varphi_f} \tag{1}$$

where "E_m" and "E_f" are the Young's moduli of matrix and filler, respectively. Also, "φ_f" is filler volume fraction. The "E_R" as relative modulus is expressed as the tensile modulus of composite divided to the matrix modulus.

This model cannot accurately predict the modulus of polymer nanocomposites because it does not consider certain aspects of nanoparticles, such as their high surface area, large aspect ratio, and exceptional Young's modulus. Moreover, the high aspect ratio of CNTs causes the low percolation threshold that forms the nanoparticle network at low filler concentrations. However, the filler network is not considered in conventional models, including the Hashin-Hansen model. If the nanoparticle network is considered as a third phase in the nanocomposites, the Hashin-Hansen model is modified to:

$$E_R = \frac{E_m + E_f + (E_f - E_m)\varphi_f + E_N + (E_N - E_m)\varphi_N}{E_m + E_f - (E_f - E_m)\varphi_f + E_N - (E_N - E_m)\varphi_N} \tag{2}$$

where "E_N" and "φ_N" are the modulus and volume fraction of network, respectively. Clearly, in absence of network ($E_N = \varphi_N = 0$), this model reduces to the original one (Eq. (1)).

The "φ_N" parameter generally depends to the filler volume fraction (φ_f) as:

$$\varphi_N = A\varphi_f \tag{3}$$

The "A" parameter is also a function of the main properties of nanoparticles and network as:

$$A = \sqrt{\frac{NlE_N}{L^2 dE_f}} \tag{4}$$

where "N/L^2" is the number of nanotubes per unit area and "l" and "d" are the length and diameter of nanotubes, respectively. Assuming the aspect ratio of nanofiller ($\alpha = l/d$) and $L = 10$, the "A" parameter is expressed by:

$$A = \sqrt{\frac{N\alpha E_N}{100E_f}} \tag{5}$$

As a result, the "φ_N" parameter depends to "φ_f" as:

$$\varphi_N = \sqrt{\frac{N\alpha E_N}{100E_f}}\varphi_f \tag{6}$$

Using the expression of "φ_N" from above equation into Eq. (2) results in:

$$E_R = \frac{E_m + E_f + (E_f - E_m)\varphi_f + E_N + (E_N - E_m)\sqrt{\frac{N\alpha E_N}{100E_f}}\varphi_f}{E_m + E_f - (E_f - E_m)\varphi_f + E_N - (E_N - E_m)\sqrt{\frac{N\alpha E_N}{100E_f}}\varphi_f} \tag{7}$$

The above equation is the modified Hashin-Hansen model for the tensile modulus of polymer nanocomposites above the percolation threshold. This model is evaluated experimentally using the modulus of various reported samples, approximating the values of the main parameters via the parameter "A".

The percolation threshold for modulus of CNT networks was given [27] by:

$$\varphi_p = \frac{2.2}{\alpha} \tag{8}$$

which correlates the percolation with aspect ratio of CNT nanoparticles. By applying of Eq. (8) into Eq. (5), the "A" parameter can be expressed by percolation threshold as:

$$A = \sqrt{\frac{2.2NE_N}{100\varphi_p E_f}} \tag{9}$$

Also, the developed model can be given by the percolation threshold as:

$$E_R = \frac{E_m + E_f + (E_f - E_m)\varphi_f + E_N + (E_N - E_m)\sqrt{\frac{2.2NE_N}{100\varphi_p E_f}}\varphi_f}{E_m + E_f - (E_f - E_m)\varphi_f + E_N - (E_N - E_m)\sqrt{\frac{2.2NE_N}{100\varphi_p E_f}}\varphi_f} \tag{10}$$

indicating the relationship between the modulus of the polymer/CNT nanocomposites and "φ_p", i.e., the percolation threshold.

3. Results and discussion

The predictability of the proposed model is presented for several samples taken from the existing literature. Moreover, the modulus is plotted as a function of the different parameters to confirm the validity of the proposed model.

Fig. 1 shows the experimental results and predictions of the proposed model for poly (ether ether ketone) (PEEK)/multi-walled carbon nanotube (MWCNT) [36], poly (ethylene terephthalate) (PET)/MWCNT [37], polyurethane (PU)/MWCNT [38] and phenolic/MWCNT [39] samples. Equation (10) calculates the modulus, and the methods for estimating the considered parameters are shown in Table 1. Some parameters were reported in previous studies, some are constant, while others are obtained by using the proposed model based on the experimental results. It is observed in Fig. 1 that the calculations of the proposed model show good agreement with the experimental results at all filler concentrations. Accordingly, the acceptable predictability of the proposed model is verified for polymer/CNT nanocomposites. The proposed model assumes the existence of a filler network in the samples, allowing it to accurately predict the improved modulus of the nanocomposites due to network formation. The best values for the parameter "A" are calculated as 2.83, 15.5, 26.46 and 44.72 for the PEEK/MWCNT, PET/MWCNT, PU/MWCNT and phenolic/MWCNT samples, respectively. Assuming the average value of "α" is 200 and $E_N = E_f = 1000$ GPa, the values of "N" are obtained as 4, 120, 350 and 1000 for the PEEK/MWCNT, PET/MWCNT, PU/MWCNT and phenolic/MWCNT samples, respectively. Accordingly, the best and the worst numbers of CNTs per unit area are observed in the PEEK/MWCNT and phenolic/MWCNT nanocomposites, respectively. The calculated values of "N" are reasonable in the sense that the sample with the highest "N"