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Property Modelling

Development of Halpin-Tsai model for polymer nanocomposites assuming interphase properties and nanofiller size

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ABSTRACT

The Halpin-Tsai model for Young's modulus of composites is developed for polymer nanocomposites reinforced with spherical nanoparticles assuming interphase properties (volume fraction, thickness and modulus) and nanofiller size. The accuracy of the developed model was evaluated by experimental data on various samples. Moreover, the interphase properties can be calculated by comparing the experimental data with model predictions. The main effects of nanoparticle and interphase sizes, as well as interphase modulus, on Young's modulus of nanocomposites are also described. The results show that the developed model can accurately predict the Young's modulus of polymer particulate nanocomposites assuming the role of the interphase. It is revealed that, disregarding the interphase or using unsuitable values for interphase properties, leads to inappropriate estimation of Young's modulus in nanocomposites.

1. Introduction

The significant properties of polymer nanocomposites as well as the wide range of their applications in various technologies have attracted much interest in scientific and industrial circles [1–6]. The nanocomposites show considerable enhancement of properties with only a small accessible nanofiller content, by using an easy fabrication method and at low cost. The theoretical and experimental studies on different types of polymer nanocomposites containing layered silicate (nanoclay), carbon nanotubes (CNT), silica (SiO_2), titanium dioxide (TiO_2), etc. have developed high-quality products for new applications or replacement of conventional products [7,8].

The improvement of mechanical properties in polymer nanocomposites is attributed to strong interfacial adhesion/interaction between polymer matrix and nanoparticles, which suitably transfers stress from the continuous matrix to the nanofiller. Also, small nanoparticles and their good dispersion play positive roles in behavior of polymer nanocomposites [9,10]. From a theoretical point of view, conventional models such as Halpin-Tsai and Guth cannot properly consider these parameters, and thus cannot give correct calculations for mechanical properties of polymer nanocomposites [11,12]. It was shown that an interphase forms in polymer nanocomposites due to high interfacial area and strong interfacial interactions between polymer and nanoparticles. The interphase as a third phase has different properties from polymer matrix and nanoparticles phases, which significantly affects the properties of polymer nanocomposites.

In recent years, several theoretical investigations on interphase properties have presented much information to attain desirable properties in polymer nanocomposites. The interphase properties have been studied using mechanical properties such as Young's modulus and yield strength [13,14]. In these works, some simple and useful models were developed, providing a practical technique for determination of interphase properties in polymer nanocomposites. Also, the role of interfacial adhesion in behavior of various nanocomposite systems such as shape memory polymer nanocomposites has been discussed in previous studies [15–17], where It was shown that interfacial/interphase characteristics play an important role in different behaviour of polymer nanocomposites.

The effects of volume fraction, aspect ratio and modulus of nanoparticles on Young's modulus of polymer nanocomposites can be evaluated by the best known Halpin-Tsai model [18]. However, the influence of nanoparticle size as well as interphase properties such as thickness and modulus cannot be examined by this model, while disregarding these parameters leads to incorrect estimation of modulus in polymer nanocomposites.

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In this paper, the Halpin-Tsai model for Young's modulus of polymer nanocomposites is developed assuming the interphase properties such as volume fraction, thickness and modulus of interphase and nanoparticle size. The accuracy of the developed model is evaluated using experimental modulus values of some reported samples from literature. Also, the interphase properties are calculated for reported samples and the effects of material and interphase properties on the prediction of Young's modulus are discussed.

2. Development of Halpin-Tsai model

Halpin and Tsai [18] introduced a mathematical model for polymer composites which has been successfully applied for different composites in the literature. This model is represented as:

$$E_R = \frac{1+\eta\xi\varphi_f}{1-\eta\varphi_f} \tag{1}$$

$$\eta = \left(E_f \big/ E_m - 1\right) \big/ \left(E_f \big/ E_m + \xi\right) \tag{2}$$

$$\xi = 2(\mathrm{l}/\mathrm{d}) \tag{3}$$

where "E_R" is relative modulus as E_c/E_m, "E_c" and "E_m" are the Young's modulus of composite and matrix, respectively. Also, "φ_f", "E_f", "l" and "d" are volume fraction, modulus, length and diameter of nanoparticles, respectively. $\xi = 2$ is considered for spherical nanoparticles in this article.

However, this model under predicts the modulus of polymer nanocomposites in most cases, as mentioned before. The volume fraction of interphase (φ_i) for nanocomposites containing spherical nanoparticles can be calculated by:

$$\varphi_i = \left[\left(\frac{R+R_i}{R}\right)^3 - 1\right]\varphi_f \tag{4}$$

where "R" and "R_i" are radius of nanoparticles and interphase thickness, respectively. If $R_i = 0$, $\varphi_i = 0$, which indicates the absence of interphase in polymer nanocomposites.

By addition of interphase effects to Halpin-Tsai model, it is developed for spherical nanoparticles contained nanocomposites to:

$$E_R = \frac{1+2\eta_f\varphi_f+2\eta_i\left[\left(\frac{R+R_i}{R}\right)^3-1\right]\varphi_f}{1-\eta_f\varphi_f-\eta_i\left[\left(\frac{R+R_i}{R}\right)^3-1\right]\varphi_f} \tag{5}$$

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

$$\eta_i = (E_i/E_m - 1)/(E_i/E_m + 2) \tag{7}$$

where "E_i" is Young's modulus of interphase.

3. Results and discussion

In this section, the correctness of the developed model is examined using experimental data of samples in reported valid literature. Also, the developed model is applied to calculate the interphase properties by experimental modulus. Subsequently, the effects of interphase properties on predicted modulus are explained.

Table 1 shows some reported samples chosen from literature and their characteristics. The experimental moduli of reported samples are fitted to the developed model to calculate the thickness and modulus of interphase. The modulus of interphase (E_i) varies from the modulus of polymer matrix (E_m) to modulus of nanofiller (E_f), i.e. $E_m < E_i < E_f$. Several "E_i" are chosen from this range and various "R_i" are obtained by comparing the developed model to experimental data. Finally, an average "R_i" is applied to the developed model and an exact "E_i" is calculated for any sample. The calculations of interphase properties are shown in Table 1. The highest "R_i" is obtained for No. 2 sample as 40 nm, and the smallest one is calculated as 1 nm for No. 5 sample. The "R_i" data are higher than "R" values in some samples, but also $R_i < R$ in others.

In addition, the highest and the smallest "E_i" are obtained as 6 and 1.7 GPa for No. 1 and No. 6 samples, respectively. The range of "E_i" is smaller than those of "E_f" in the present samples. However, the values of "R_i" and "E_i" are logically expressed in the correct ranges for polymer nanocomposites. Accordingly, the developed model can accurately predict interphase properties by Young's modulus of polymer nanocomposites.

Fig. 1 shows the experimental data and the predicted results by the model for No. 2 and 6 samples. As shown, good agreement is achieved between experimental and theoretical data by suitable interphase properties, which confirms the prediction capability of the developed model for Young's modulus of polymer particulate nanocomposites. However, disregarding the interphase ($R_i = 0$) or improper values for interphase properties, undoubtedly results in incorrect estimation of modulus for the reported samples, demonstrating the main effects of interphase characteristics for prediction of nanocomposite behavior.

Fig. 2 displays the calculated "φ_i" at different mass concentrations of nanoparticles (Eq. (4)) for No. 3 and 4 samples using "R" and "R_i" values reported in Table 1. It is found that "φ_i" is larger than "φ_f" in these samples at different nanofiller contents. Accordingly, interphase as a third phase between polymer matrix and nanoparticles occupies a significant volume fraction in polymer nanocomposites and plays a main role in their properties.

Fig. 3 shows the effects of "R" and "R_i" on "φ_i" according to Eq. (4) ($\varphi_f = 0.02$). It is observed that the smallest "φ_i" data are found by low "R_i" and high "R". However, "φ_i" has a higher level at smaller "R" and higher "R_i". The highest "φ_i", which results in the best Young's modulus, is achieved by the smallest nanoparticles and the thickest interphase. Accordingly, small nanoparticles and large interphase thickness have positive effects on Young's modulus of polymer particulate nanocomposites. The developed model also shows the detrimental effect of aggregated/agglomerated nanoparticles (high R) on "φ_i", which finally reduces the Young's modulus of polymer nanocomposites, independent of the significance of "R_i". Therefore, preventing some undesirable occurrences, such as the aggregation/agglomeration of nanoparticles and the poor interfacial adhesion/interactions, should be carefully considered in the fabrication process of polymer nanocomposites [25,26].

Fig. 4 illustrates the influences of "R_i" and "E_i" on Young's modulus of polymer nanocomposites by developed the model at $\varphi_f = 0.02$, R = 20 nm, E_m = 2 GPa and E_f = 60 GPa. The Young's modulus depends to both "R_i" and "E_i" levels at small "E_i", but it only relates to "R_i" level at higher "E_i". The smallest "E_R" is found at the lowest "R_i", while the largest "E_R" is obtained at the greatest levels of both "R_i" and "E_i". In fact, the high ranges of "R_i" and "E_i" have positive effects on the final "E_R" of polymer nanocomposites, but a small "R_i" is enough to get a poor "E_R". Therefore, the properties of interphase significantly affect the modulus of polymer nanocomposites. According to the developed model, providing a thick and strong interphase in polymer nanocomposites produces a largely improved modulus. Some techniques, such as the