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Development of Nicolais–Narkis model for yield strength of polymer nanocomposites reinforced with spherical nanoparticles

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ABSTRACT

In this paper, the Nicolais–Narkis model for yield strength of polymer nanocomposites containing spherical nanoparticles is developed assuming the role of interphase between polymer and nanofiller phases. The predictions of the developed model are compared with the experimental results and also, the effects of interphase properties on the yield strength are expressed.

The calculated results show that the developed model can give much accurate predictions for yield strength of nanocomposites by proper thickness and strength of interphase, while the yield strength is under-predicted by disregarding of interphase. The developed model demonstrates that the yield strength improves by reduction in nanoparticle size and increment in interphase thickness. Also, the detrimental effect of weak interfacial adhesion between polymer matrix and nanoparticles is revealed.

1. Introduction

Polymer nanocomposites display significant properties by only small nanofiller content [1–6]. The excellent properties of polymer nanocomposites cause different applications in various technologies such as automobile, household goods, agriculture, new energies, sensors and biotechnology. The previous studies aimed to achieve a high-quality product by an easy fabrication and low cost by experimental and theoretical views [5,7,8]. They provided much information in the literature which can guide the researchers in academia and industries.

One of the attractive properties of polymer nanocomposites is their mechanical properties such as modulus, strength and hardness. The mechanical properties of polymer nanocomposites have been analyzed by many suggested models for polymer composites [9–13]. However, the conventional models cannot properly calculate the properties of polymer nanocomposites due to the new characteristics of polymer nanocomposites compared to conventional composites. For example, many known models such as Halpin–Tsai and Guth under-predicted the Young's modulus of polymer nanocomposites attributed to disregarding of various important parameters such as the interfacial interactions, particles size and dispersion of nanoparticles [7].

The significant properties of polymer nanocomposites are qualified to the strong interfacial adhesion between polymer matrix and nanoparticles which properly transfers the applied stress from continuous matrix to nanofiller [14]. The strong adhesion between polymer and nanoparticles form the interphase around the nanoparticles which is different from both matrix and nanoparticles. Our group has investigated the interphase properties in polymer nanocomposites by the mechanical properties such as tensile modulus and yield strength [15–18]. In this regard, some beneficial models were proposed which give a practical and simple way for determination of interfacial/interphase properties in polymer nanocomposites. Also, the influences of the interfacial adhesion on the behavior of various nanocomposite systems such as shape memory polymer nanocomposites have been evaluated in previous studies [19]. These work clearly indicated the main role of interfacial/interphase properties in the final behavior of polymer nanocomposites.

The yield strength of polymer nanocomposites depends to various parameters such as the content of nanoparticles, the dispersion feature and the interfacial/interphase properties [16,17]. The yield strength has been evaluated in different nanocomposites from experimental and theoretical views [14,20,21]. In these studies, the effects of filler volume fraction and interfacial parameter on the yield strength were discussed. However, the influences of nanoparticles size as well as the interphase properties have not been studied in the previous efforts, while these parameters demonstrate important roles in the yield strength of polymer nanocomposites.

In this paper, the Nicolais–Narkis model for yield strength of polymer nanocomposites reinforced with spherical nanoparticles is developed assuming the interphase formation. Moreover, the predictions of the developed model are related to the

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experimental results. Also, the effects of nanoparticle size and interphase properties (thickness and strength) on the yield strength are evaluated by the proposed model.

2. Theoretical analysis

Nicolais and Narkis [20] suggested a model for yield strength of composites containing spherical particles by an interfacial parameter. In this study, this model is properly developed for this class of polymer nanocomposites based on the interphase properties.

According to Nicolais–Narkis model, when polymer and nanofiller have no interfacial adhesion, the nanoparticles cannot bear the stress and the stress is carried only by the matrix. Assuming a unit cube filled with n^3 uniformly dispersed spherical nanoparticles with "R" radius, yielding is happened in the minimum cross section of matrix (A) which is perpendicular to the stress direction as:

$$A = 1 - A_f \tag{1}$$

where "A_f" is the surface area of nanoparticles at the cross-section of cube perpendicular to the loading direction. In the case of no interfacial adhesion, the strength of nanocomposite depends on the effective area of load-bearing matrix as:

$$\sigma_c = \sigma_m(1 - A_f) \tag{2}$$

where "σ_c" and "σ_m" are the yield strength of composite and matrix, respectively. This equation can be modified as:

$$\sigma_R = 1 - A_f \tag{3}$$

where "σ_R" is the relative strength as σ_c/σ_m. "A_f" is given by:

$$A_f = \pi(nR)^2 \tag{4}$$

where "R" shows the radius of nanoparticles. The volume fraction of n^3 nanoparticles (ϕ_f) is also suggested by:

$$\phi_f = \frac{4}{3}\pi(nR)^3 \tag{5}$$

Substitution of "nR" from Eq. (5) into Eq. (4) leads to:

$$A_f = \pi\left(\frac{3}{4\pi}\right)^{2/3} \phi_f^{2/3} = 1.21\phi_f^{2/3} \tag{6}$$

Considering Eq. (6) into Eq. (3), the original Nicolais–Narkis model for yield strength of composites is expressed as:

$$\sigma_R = 1 - a\phi_f^{2/3} \tag{7}$$

where "a" value of 1.21 demonstrates no interfacial adhesion between polymer matrix and nanoparticles. Nevertheless, when a good interfacial adhesion is provided between matrix and nanofiller, the interfacial layer can transfer a fraction of stress from matrix to nanofiller. In this status, the yield strength includes the contribution of both matrix and nanofiller. Therefore, the value of "a" becomes smaller than 1.21, which displays a stronger adhesion at interface. So, "a" is an interfacial parameter which exhibits the properties of interphase/interface.

When a strong interfacial interaction/adhesion exists between polymer matrix and nanoparticles, an interphase is formed as a zone of polymer surrounding the nanoparticle with different physical and mechanical properties from both polymer and nanoparticles. If the effects of interphase were assumed, the stress can be transferred from matrix to nanoparticles via interphase. In this condition, some stress can be carried by the interphase and nanoparticles which results in:

$$\sigma_c = \sigma_m A_m + \sigma_i A \tag{8}$$

where "A_m" is the surface area of matrix and "A" includes the surface area of both interphase and nanoparticles at the cross-section of sample. Also, "σ_i" is the interphase strength. Here, the effect of nanofiller strength is considered by "σ_i", because the stress transferred by interphase plays the main role in nanocomposite strength. As a result, the "σ_i" determines the strengthening effects of both interphase and nanoparticles.

The "A_m" and "A" parameters in a unit cube are defined by:

$$A_m = 1 - n^2\pi(R+t)^2 \tag{9}$$

$$A = n^2\pi(R+t)^2 \tag{10}$$

where "t" is interphase thickness. Replacing of "A_m" and "A" from Eqs. (9) and (10) into Eq. (8), "σ_c" can be suggested as:

$$\sigma_c = \sigma_m - \sigma_m n^2\pi(R+t)^2 + \sigma_i n^2\pi(R+t)^2 \tag{11}$$

By rearranging of Eq. (5), "n^2" is given by:

$$n^2 = \left(\frac{\phi_f}{\frac{4}{3}\pi R^3}\right)^{2/3} \tag{12}$$

Substitution of "n^2" from above equation into Eq. (11) gives the "σ_R" as:

$$\sigma_R = 1 - 1.2\phi_f^{2/3}\left[\frac{(R+t)^2}{R^2} - \frac{\sigma_i}{\sigma_m}\frac{(R+t)^2}{R^2}\right] \tag{13}$$

The latter equation can be assumed as the developed Nicolais–Narkis model in which "a" is defined as:

$$a = 1.2\left[\frac{(R+t)^2}{R^2} - \frac{\sigma_i}{\sigma_m}\left(\frac{(R+t)^2}{R^2}\right)\right] \tag{14}$$

By this equation, the thickness and strength of interphase can be simply calculated using the yield strength data. If the interphase was neglected ($t=0$ and $\sigma_i=0$), $a=1.2$ is obtained which is consistent with the Nicolais–Narkis model in the case of no interfacial adhesion.

3. Results and discussion

The comparison between the experimental data for linear low density polyethylene (LLDPE)/SiO_2 from [17] as well as polypropylene (PP)/$CaCO_3$ from [22] and the theoretical predictions by Eq. (7) in absence of interphase ($a=1.21$) are observed in Fig. 1. In this condition, all predictions are below the experimental results at all nanofiller contents, which show the incorrect prediction of yield strength for nanocomposites in absence of interphase. It indicates that the interphase layer can transfer a portion of stress from polymer matrix to nanofiller and so, the yield strength of samples is affected by the properties of polymer matrix, nanoparticles and interphase such as the matrix strength, the dispersion quality of nanoparticles and the interphase properties [14].

Also, Eq. (7) predicts a decrement trend for yield strength of nanocomposites in absence of interphase which demonstrates that the yield strength worsens by nanofiller content when the interphase is disregarded. As a result, the nanoparticles cause a detrimental effect in nanocomposites ignoring the interphase. In addition, many reports in the literature show the little change of yield strength in polymer nanocomposites. However, the improvement of yield strength by addition of nanoparticles was also reported in some polymer nanocomposites [14,23]. The yield strength improves by nanofiller concentration in some samples such as LLDPE/SiO_2 (Fig. 1a) which is attributed to the effect of interphase based on the present models.

Fig. 2 displays the experimental data of yield strength for the reported samples and the predictions of Eq. (7) assuming the proper values for "a". The theoretical results acceptably agree with the experimental data at "a" values of -5 and 0.85 for LLDPE/SiO_2 and PP/$CaCO_3$ samples, respectively. According to the Nicolais–Narkis