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An approach to study the roles of percolation threshold and interphase in tensile modulus of polymer/clay nanocomposites

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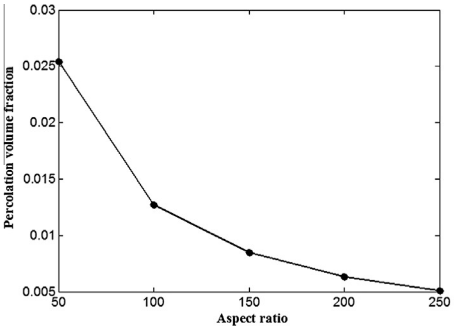
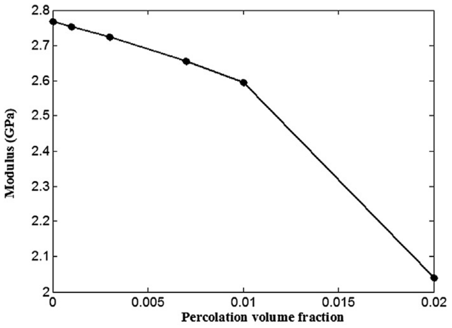
GRAPHICAL ABSTRACT





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ABSTRACT

The effect of percolation threshold on the mechanical properties of insulate polymer nanocomposites has been briefly investigated in literature. In this work, an approach is suggested to study the percolation threshold and interphase role in polymer/clay nanocomposites (PCN) by a model for tensile modulus. The percolation threshold is related to the aspect ratio of clay layers and the predictions of the suggested methodology are compared with the experimental data.

A low percolation threshold is obtained by high aspect ratio of clay layers which increases the modulus. Also, the developed model suggests the accurate results compared to experimental data assuming the interphase role. According to the calculations, the best modulus of PCN is achieved by the thinnest clay layers and the thickest interphase between polymer and clay.

1. Introduction

The clay layers are intercalated or exfoliated in the polymer matrices to fabricate the polymer/clay nanocomposites (PCN) [1–5]. In the intercalated state, the inter-layer spacing increases due to entrance of polymer chains into the stacks of clay, where the layers are wholly separated and the individual layers are well isolated in the polymer matrix in the exfoliated structure. The morphology of clay layers in polymer matrix depends to the surface chemistry of clay and matrix type as well as the processing condition [6,7]. Moreover, the reinforcing level of PCN significantly correlates to the morphology of clay and the interfacial bonding between polymer matrix and clay. The literature reports extensively indicated that the weak dispersion of clay layers and poor interface/interphase decreases the mechanical performance of PCN [8–10].

The considerable level of nanoparticles surface area and the strong interfacial interaction between polymer matrix and nanoparticles in nanocomposites produce a third phase around the nanoparticles as interphase. It was well reported that the interphase is formed in the polymer nanocomposites and the properties

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of interphase control the mechanical behavior of nanocomposites [11,12]. However, the interphase is difficultly characterized by the experimental methods due to the small size and complex nature. Additionally, the conventional theories for mechanical properties of composites do not regard the interphase character [13,14]. As a result, it is required to suggest new models or update the old models for nanocomposites. A number of authors have considered the interphase in the old models for mechanical behavior to improve their predictability [15–17]. These models facilitate the calculation of interphase properties by the experimental results of mechanical tests.

The percolation threshold in polymer nanocomposites is defined as the minimum volume fraction of filler, above which the nanoparticles form a continuous network according to the percolation theory [18,19]. This term is extensively applied for conductive nanocomposites in which the electrical conductivity is obtained above the percolation threshold [20]. With increasing in the content of conducting nanofiller in nanocomposites, a percolation transition is shown where the electrical conductivity of the nanocomposite significantly grows and it changes from an insulator to a conductor. This behavior is attributed to the formation of conducting network through the insulating matrix when the nanofiller content is at or above the percolation threshold. This phenomenon is studied in the literature by experimental and theoretical work to identify the critical factors that determine the percolation threshold. According to the previous studies, a strong correlation was proposed between the percolation threshold and the aspect ratio of fillers [20].

The percolation threshold was also studied in insulate nanocomposites containing cellulose whiskers and nanoclay [21,22]. Favier et al. [21] successfully explained the unusually high values of shear modulus in the reinforced films with cellulose whiskers by percolation effect. Also, the percolation threshold or overlap concentration was correlated to aspect ratio of nanoclay layers [22]. However, the percolation term has been less studied in the literature for mechanical behavior of insulate nanocomposites, while it determines the level of nanoparticles networking in polymer matrix which explains the unusually high values of mechanical properties.

In this study, a new approach is suggested to study the percolation threshold in PCN by Ouali model [23] for tensile modulus. This approach relates the percolation threshold to the aspect ratio of clay layers. The predictions are compared with the experimental data. Also, the role of interphase is considered in the Ouali model and the predictions are studied. Additionally, the influences of percolation threshold as well as interphase properties on the tensile modulus are well deliberate.

2. New approach

Ouali et al. [23] added the percolation concept to the Series model for tensile modulus of composites as:

$$E = \frac{(1-2\psi+\psi\phi_f)E_mE_f + (1-\phi_f)\psi E_f^2}{(1-\phi_f)E_f + (\phi_f-\psi)E_m} \tag{1}$$

where “E_m” is the matrix modulus. Also, “ϕ_f” and “E_f” show the volume fraction and tensile modulus of filler. The “ψ” parameter is related to the volume fraction of percolating phase (ϕ_{per}) as:

$$\psi = 0 \quad \phi_f \leqslant \phi_{per} \tag{2}$$

$$\psi = \phi_f\left(\frac{\phi_f-\phi_{per}}{1-\phi_{per}}\right)^b \quad \phi_f > \phi_{per} \tag{3}$$

where “b” is the percolation exponent. According to several studies on the percolation, “b” takes the value of 0.4 in a three-dimensional (3D) system [23].

When $\psi = 0$, the Ouali model reduces to Series model for tensile modulus of composites [24] as:

$$E = \frac{E_mE_f}{(1-\phi_f)E_f + \phi_fE_m} \tag{4}$$

Plummer et al. [22] suggested a relation between percolation threshold and aspect ratio of clay layers (α) by numerical simulations on randomly oriented ellipsoids with different aspect ratios by:

$$\phi_{per} \approx \frac{1.27}{\alpha} \tag{5}$$

where $\alpha = l/t$; “l” and “t” are the length/diameter and thickness of clay layers, respectively.

The clay layers commonly show very high “α”, due to the small thickness and large length. In this condition, $\phi_{per} \approx 0$ is obtained based on Eq. (5) which reduces Eq. (3) to:

$$\psi = \phi_f^{1.4} \quad \phi_f > \phi_{per} \tag{6}$$

By replacing of “ψ” from Eq. (6) into Eq. (1), the modulus can be approximately calculated in $\phi_f > \phi_{per}$ by:

$$E = \frac{(1-2\phi_f^{1.4}+\phi_f^{2.4})E_mE_f + (1-\phi_f)\phi_f^{1.4}E_f^2}{(1-\phi_f)E_f + (\phi_f-\phi_f^{1.4})E_m} \approx \frac{(1-2\phi_f^{1.4})E_mE_f + \phi_f^{1.4}E_f^2}{E_f} \tag{7}$$

which relates the modulus of PCN with different properties of nanocomposite components.

Moreover, the interphase may be formed in PCN which contain a high level of interfacial area between clay layers and polymer chains, i.e. very high “α”. Eq. (7) does not consider the role of interphase in PCN. Since the interphase is created around the nanoparticles, Eq. (7) can be developed by interphase properties as:

$$E = \frac{(1-2\phi_f^{1.4})E_mE_f + \phi_f^{1.4}E_f^2 + (1-2\phi_i^{1.4})E_mE_i + \phi_i^{1.4}E_i^2}{E_f+E_i} \tag{8}$$

where “ϕ_i” and “E_i” are the volume fraction and modulus of interphase, respectively. Also, “ϕ_i” is correlated to the thickness of clay layers and interphase in PCN [25] as:

$$\phi_i = \phi_f\left(\frac{2t_i}{t}\right) \tag{9}$$

where “t_i” is the thickness of interphase. By replacing of Eq. (9) into Eq. (8), the modulus can be calculated by the properties of polymer matrix, nanoparticles and interphase.

3. Results and discussion

3.1. Evaluation of models by experimental data

In this part, the original and the developed models are used to calculate the modulus in some reported samples from previous studies. Also, the effects of “α” and “ϕ_{per}” on the calculated modulus by the original model are studied. At the final step, the effects of interphase properties on the modulus of PCN are discussed according to the developed model.

Fig. 1 illustrates the predictions of the original model for polyamide 12 (PA12)/clay sample from [26] and poly (butylene terephthalate) (PBT)/clay example from [27]. This model can calculate the modulus by $\alpha = 1000$ and 300 for PA12/clay and PBT/clay samples,