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Research paper

Effects of imperfect interfacial adhesion between polymer and nanoparticles on the tensile modulus of clay/polymer nanocomposites

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ABSTRACT

This work investigates the effects of incomplete interfacial adhesion between polymer and nanoparticles on the predicted tensile modulus of clay/polymer nanocomposites (CPNs). The Halpin-Tsai and Hui-Shia models which assume the perfect interfacial adhesion commonly overpredict the modulus in CPN. Accordingly, the samples include imperfect interfacial bonding at polymer-filler interface. In this condition, the effective aspect ratio and volume fraction of nanoclay are defined using "L_c" as the essential distance for the normal stress to reach the clay strength and "τ" as the interfacial shear strength. The values of "L_c" and "τ" are calculated for several samples and also, their roles in the predicted modulus are determined. It is shown that low "L_c" and high "τ" result in a significant modulus, because they indicate the great levels of interfacial properties in CPN. Also, the large and thin platelets can produce a high modulus depending to the level of Interfacial parameters.

1. Introduction

The growing interest in polymer nanocomposites initiates from the improvement of fundamental properties and also, the development of new materials to meet different applications. The significant changes in properties of polymer nanocomposites are occurred by very low content of nanofillers (about 5 wt.%) such as nanoclay, graphene and carbon nanotubes (Mauroy et al., 2015; Norouzi et al., 2015; Shabanian et al., 2015; Zare et al., 2015; Zare, 2015c). Montmorillonite (Mt) is a mica-type silicate clay which consists of small crystalline particles shaped by stacks of platelets (Wang et al., 2008). Mt is frequently organically modified with ammonium surfactants to make it compatible with most hydrophobic polymers (Mallakpour and Dinari, 2013; Zulfiqar et al., 2015).

The great interfacial area at very low volume fraction of well-dispersed nanoparticles can affect the behavior of polymer matrix such as stiffness, thermal stability, transparency and crystallinity. Generally, a homogeneous dispersion of nanoparticles in polymer matrix as well as strong interfacial interaction is required to achieve significant mechanical reinforcement such as strength and modulus (Hajibeygi et al., 2015; Kalbasi et al., 2012). The researchers have tried to manipulate the material and processing parameters to achieve the best properties in recent years. The literature is full of more examples of these studies in different nanocomposites (Huskić et al., 2013; Kalbasi et al., 2012; Ke et al., 1999; Yeganeh et al., 2015). Furthermore, the behavior of nanocomposites has received much attention from both experimental and theoretical approaches. All attempts aim to reach a material with optimized conditions such as significant properties, light weight, low cost and easy fabrication.

The mechanical properties especially modulus and strength correlate to many factors such as type, concentration, aspect ratio and dispersion feature of nanoparticles as well as the properties of interface/interphase around the nanoparticles (Fernández et al., 2013; Huskić et al., 2013). The interface/interphase determines the nanoscale interaction and the efficiency of stress transfer from matrix to nanoparticles. As known, a poor interface/interphase causes the debonding of particles from polymer matrix during the stress loading. As a result, a poor interface/interphase may remove the advantages of nanoparticles in nanocomposites. Some authors have studied the interface/interphase properties by modeling of mechanical behavior. In this regard, the Young's modulus and tensile strength of nanocomposites were applied to measure the thickness, modulus and strength of interphase (Zare, 2015d; Zare and Garmabi, 2015a, 2015b). They clearly reported that the interphase properties substantially change the mechanical properties of polymer nanocomposites.

The experimental and theoretical studies have reported that an incomplete interfacial adhesion is formed in many nanocomposites which results in imperfect stress transfer between polymer and nanoparticles. This work investigates the effects of incomplete interfacial adhesion on the predicted modulus of clay/polymer nanocomposites (CPN) by Halpin-Tsai and Hui-Shia models. These models are expressed by "L_c" as the essential distance for normal stress to reach the clay strength and "τ" as interfacial shear strength. The "L_c" and "τ" are calculated and evaluated for some samples using the experimental modulus. Likewise, the effects of "L_c" and "τ" as well as some material properties on the predicted modulus are determined based on the expressed equations.

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2. Background

Halpin-Tsai and Hui-Shia models have assumed the unidirectional aligned platelets and perfect interfacial adhesion between polymer and nanoparticles in polymer nanocomposites. They are used in this study to demonstrate the effect of incomplete interfacial adhesion in CPN.

The semi-empirical Halpin-Tsai model (Halpin, 1969) which has been used for different types of nanocomposites is expressed as:

$$E_{11} = E_m\left(\frac{1+\eta\xi\phi_f}{1-\eta\phi_f}\right) \quad (1)$$

$$E_{22} = E_m\left(\frac{1+2\eta\phi_f}{1-\eta\phi_f}\right) \quad (2)$$

$$\eta = (E_f/E_m-1)/(E_f/E_m+\xi) \quad (3)$$

$$\xi = 2/\alpha \quad (4)$$

where "E_{11}" and "E_{22}" are the tensile moduli of composite in longitudinal and transverse directions, respectively. "E_m" and "E_f" are also the tensile moduli of matrix and filler, respectively. "ϕ_f" is volume fraction of filler and "α" is inverse aspect ratio of platelets as t/l, "t" and "l" are the thickness and length of platelets.

The Hui-Shia model (Hui and Shia, 1998) was also suggested for tensile modulus of composites with similar assumptions of Halpin-Tsai model as:

$$E_{11} = \frac{E_m}{1-\frac{\phi_f}{A}} \quad (5)$$

$$E_{22} = \frac{E_m}{1-\frac{\phi_f}{4}\left(\frac{1}{A}+\frac{3}{A+B}\right)} \quad (6)$$

$$A = \phi_f + \frac{E_m}{E_f-E_m} + 3\left(1-\phi_f\right)\left[\frac{(1-g)\alpha^2-\frac{g}{2}}{\alpha^2-1}\right] \quad (7)$$

$$B = \left(1-\phi_f\right)\left[\frac{3(\alpha^2+0.25)g-2\alpha^2}{\alpha^2-1}\right] \quad (8)$$

$$g = \frac{\pi}{2}\alpha. \quad (9)$$

These models commonly over-predicted the tensile modulus in different polymer nanocomposites (Fornes and Paul, 2003; Wang et al., 2008; Zare and Garmabi, 2014).

The tensile modulus for CPN containing randomly 3 dimensional (3D) platelets (Fornes and Paul, 2003) is calculated by:

$$E = 0.49E_{11} + 0.51E_{22}. \quad (10)$$

A poor interface/interphase cannot bear the high interfacial shear stress during the applied stress which typically leads to yielding or debonding at or near the interface. In this condition, the interfacial shear stress causes a slower build-up of normal stress in platelets (Shia et al., 1998). So, a larger distance is crucial for normal stress to reach the tensile strength of clay platelets (σ_f). As a result, a high portion of platelet area is not wholly loaded which reduces the reinforcement effect of platelets in CPN.

The profiles of normal stress (σ) in a platelet at two possible states are shown in Fig. 1a. According to the Kelly-Tyson model (Zare, 2015a), the strength of composites depends to the critical length as "L_c" which is the minimum length necessary for efficiently transferred stress from matrix to platelets. When $L_c \le x \le d/2$ (the first case), "σ" reaches "σ_f" before the debonding of whole length of platelet. However, when $0 \le x \le L_c$ (the second case), the entire length of platelet is taken up before "σ" reaches to "σ_f". "L_c" is defined as the essential distance for the normal stress to reach "σ_f" as:

$$L_c = \frac{\sigma_f t}{2\tau} = \frac{\sigma_f \alpha l}{2\tau}. \quad (11)$$

By rearranging the above equation, "τ" (Fig. 1b) can be linked with "L_c" as:

$$\tau = \frac{\sigma_f t}{2L_c} = \frac{\sigma_f \alpha l}{2L_c}. \quad (12)$$

When a platelet is completely bonded to matrix, the average normal stress ($\overline{\sigma}$) is equal to "σ_f", but "$\overline{\sigma}$" is less than "σ_f" at poor interface/interphase resulting in a smaller effective length of platelet (Shia et al., 1998) (Fig. 1c) as:

$$\overline{\sigma} l = \sigma_f l_{eff}. \quad (13)$$

Using the last equation, the effective aspect ratio (α_{eff}) and volume fraction (φ_{eff}) of platelets reduce which finally decreases the reinforcing efficiency of nanoparticles. "α_{eff}" and "φ_{eff}" at $x < 2L_c$ were defined (Shia et al., 1998) as:

$$\alpha_{eff} = \alpha\frac{4L_c}{l} \quad (14)$$

$$\phi_{eff} = \phi_f\left(\frac{l}{4L_c}\right). \quad (15)$$

Also, they were expressed at $x > 2L_c$ (Shia et al., 1998) as:

$$\alpha_{eff} = \alpha\left(\frac{1}{1-\frac{L_c}{l}}\right) \quad (16)$$

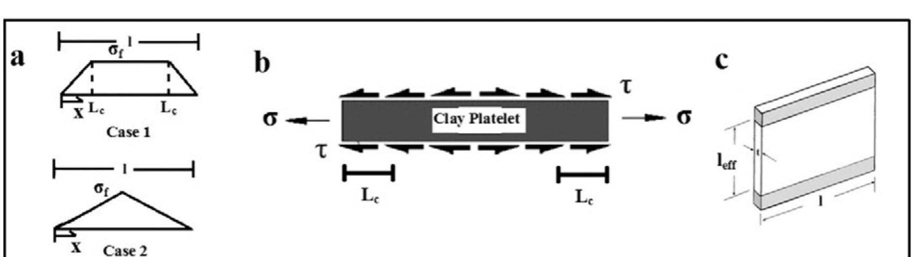

Fig. 1. a) The profiles of normal stress at two different cases: $x > 2L_c$ and $x < 2L_c$, b) "τ" and "L_c" in platelets and c) "l_{eff}" assuming incomplete interfacial adhesion by "l_{eff}".