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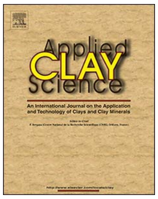

Research paper

A two-step technique for tensile strength of montmorillonite/polymer nanocomposites assuming filler morphology and interphase properties

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ABSTRACT

This paper presents a two-step methodology for prediction of tensile strength in montmorillonite/polymer nanocomposites (MPN) assuming the effects of montmorillonite morphology (intercalation/exfoliation) and interphase properties. The suggested technique is evaluated by the experimental data of tensile strength in some samples. A good agreement is shown between experimental measurements and predictions, which can determine the intercalation/exfoliation level and interphase properties. A high aspect ratio of Mt platelets increases the interfacial interaction and mechanical involvement between polymer chains and nanoparticles causing high strengthening effect. Moreover, high concentration of well-exfoliated Mt as well as thick and strong interphase produces desirable tensile strength in MPN.

1. Introduction

Montmorillonite (Mt) includes the stacks of silicate platelets with small crystalline structures (Manias et al., 2001). The nano-platelets of Mt have thin thickness (about 1 nm) and high length, which cause very large interfacial area and significant involvement with polymer chains in Mt/polymer nanocomposites (MPN) (Azhar and Olad, 2014; Ghari and Jalali-Arani, 2016; Monfared and Jalali-Arani, 2015; Shabanian et al., 2015; Tayefi et al., 2017; Zare et al., 2017a). So, Mt can improve the properties of polymers including stiffness, strength and crystallinity (Dehkordi et al., 2015; Zahedi et al., 2015; Zare and Rhee, 2017b). Mt is frequently modified with ammonium surfactants to raise its compatibility with hydrophobic polymers. The reinforcing efficiency of Mt in MPN depends on its dispersion quality and interfacial/interphase properties (Zare, 2016c, 2017). Mt is intercalated or exfoliated in the polymer matrix during the fabrication of nanocomposite. In the intercalated case, the polymer chains enter the Mt in a regular fashion and the inter-platelet spacing increases in the well-structured stacks (Durmuş et al., 2007; Zare, 2016h). However, the Mt platelets are entirely separated and the individual platelets are dispersed in the whole polymer matrix in the exfoliated state. The dispersion level of Mt in the nanocomposites is controlled by surface modification of platelets and processing parameters. The reports have designated that the poor dispersion of Mt deteriorates the mechanical properties of MPN (Fornes et al., 2004; Park et al., 2001). So, much attempt has been made by the researchers to promote the dispersion of Mt in polymer matrix. Also, an effective stress transfer from polymer matrix to Mt is essential to achieve the noteworthy mechanical properties. The large surface area of nano-platelets produces a high interfacial area between polymer chains and nanoparticles, which affects the mechanical behavior. Therefore, the influences of interphase properties are important which directly depend on the interfacial adhesion/interaction between polymer matrix and nanoparticles (Zare, 2016b, 2016d, 2016f). The previous investigators manipulated many processing and martial parameters to improve the interphase characteristics in nanocomposites (Chen et al., 2015; Durmuş et al., 2007; Zulfiqar et al., 2015).

The conventional models for mechanical properties of composites cannot answer the demands for polymer nanocomposites, due to disregarding the size effect and dispersion quality of nano-platelets in polymer matrix as well as the interphase level (Zare, 2015, 2016a). As a result, these parameters cause a significant difference between the experimental data and the predictions of conventional models. A number of investigators have considered these parameters, particularly interphase in polymer nanocomposites by new or developed models to improve the predictability of the models (Montazeri and Naghdabadi, 2010; Zare, 2016e, 2016j; Zare and Rhee, 2017a, 2017c). However, the prior studies have not considered the dispersion level of Mt and interphase properties by a simple model, while these factors mainly affect the mechanical behavior of MPN. Also, the previous work significantly investigated the tensile modulus, but the tensile strength was briefly examined. Thus, study on the effects of interphase and morphology on the tensile strength of MPN is useful. The main novelty of this paper is

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the estimation of tensile strength in MPN assuming the interphase level and filler morphology by a simple technique using a micromechanics model.

In the present work, a two-step methodology is suggested for tensile strength of MPN by the roles of intercalation/exfoliation of Mt and interphase properties. A modified model is applied to predict the strength of Mt-interphase particles at the first step. After that, Mt-interphase particles are assumed as filler phase in the polymer matrix and the tensile strength of MPN is calculated by the same model. The experimental data of several samples are used to evaluate the model and to determine the dispersion quality of Mt and interphase properties. Also, the impacts of main parameters involving Mt and interphase properties on the tensile strength of MPN are discussed.

2. Modeling approach

Lazzeri and Phuong (2014) suggested a model for tensile strength of MPN based on the Rule of mixtures model and Kelly-Tyson model as:

$$\sigma = \eta_0 \varphi_f \sigma_f \left(1 - \frac{\sigma_f}{4\tau\alpha}\right) + \sigma_m^{'}(1 - \varphi_f) \tag{1}$$

where "η_0" is the orientation factor which is equal to 1 for fully dispersed nano-platelets. "φ_f" and "σ_f" are the volume fraction and tensile strength of filler. "τ" is also the interfacial shear strength between polymer matrix and Mt. "α" is aspect ratio of Mt platelets as $\alpha = l / t$; "l" and "t" are the length and thickness of Mt platelets, respectively. Also, "$\sigma_m^{'}$" is the tensile strength of polymer matrix at the break strain of Mt which is approximately equal to the tensile strength of polymer matrix (σ_m).

To calculate the tensile strength in the MPN assuming the morphology of Mt and interphase properties, a two-step method is suggested. The intercalated/exfoliated platelets and their surrounding interphase are assumed as particles at the first step and their strength is calculated by Eq. (1). The volume fraction and strength of the polymer chains among the intercalated platelets are insignificant in comparison to interphase and Mt. So, their role is not assumed in the strength of Mt-interphase particles.

To predict the tensile strength of Mt-interphase particles by Eq. (1), the interphase is assumed as matrix and the Mt platelets as filler. So, the strength of Mt-interphase particles is expressed as:

$$\sigma_p = \eta_o \frac{\varphi_f}{\varphi_f + \varphi_i} \sigma_f \left(1 - \frac{\sigma_f}{0.5\sigma_i \frac{l}{Nt + s(N-1)}}\right) + \sigma_i \left(1 - \frac{\varphi_f}{\varphi_f + \varphi_i}\right) \tag{2}$$

where "φ_i" and "σ_i" are the volume fraction and tensile strength of interphase, respectively. In Eq. (2), "τ" as interfacial shear strength is assumed as $\tau = \sigma_i / 8$ according to the predictions of "τ" in the previous reports (Lazzeri and Phuong, 2014). Also, "α" as aspect ratio is expressed as $\alpha = l / [Nt + s\ (N - 1)]$ for intercalated Mt; where "N" is the number of Mt platelets in the stacks and "s" is the distance between the Mt platelets. Obviously, $\alpha = l / t$ is obtained in the case of exfoliated platelets ($N = 1$). The "φ_i" in MPN containing completely exfoliated platelets is calculated by:

$$\varphi_i = \varphi_f \left(\frac{2t_i}{t}\right) \tag{3}$$

where "t_i" is the thickness of interphase. The "φ_i" level decreases when the Mt platelets are well intercalated in the polymer matrix. So, the "φ_i" in MPN containing intercalated/exfoliated Mt platelets can be expressed as:

$$\varphi_i = \frac{\varphi_f \left(\frac{2t_i}{t}\right)}{N} \tag{4}$$

where $N = 1$ shows one platelet in the stacks indicating the completely exfoliated structure. In this condition, Eq. (3) is obtained for well-exfoliated platelets.

At the second step, the Mt-interphase particles are assumed as dispersed particles in the polymer matrix. In this condition, the aspect ratio of particles is expressed as:

$$\alpha_p = \frac{l}{Nt + (N - 1)s + 2t_i} \tag{5}$$

The tensile strength of MPN containing Mt-interphase particles can be calculated by development of Eq. (1) as:

$$\sigma = \eta_0 (\varphi_f + \varphi_i)\sigma_p \left(1 - \frac{\sigma_p}{0.5\sigma_i \left(\frac{l}{Nt + (N-1)s + 2t_i}\right)}\right) + \sigma_m (1 - \varphi_f - \varphi_i) \tag{6}$$

which correlates the tensile strength of MPN to the properties of polymer matrix, Mt and interphase as well as the intercalation/exfoliation of Mt in the polymer matrix.

3. Results and discussion

The two-step technique is used to predict the tensile strength in several samples at different levels of intercalated/exfoliated platelets and interphase properties. Moreover, the influences of Mt content and dimensions, interphase thickness and strength and the intercalated/exfoliated level on the tensile strength of MPN are discussed.

Fig. 1 illustrates the experimental data for organically modified Mt (OMt)/PP (Liu and Wu, 2001), OMt/PA6(Fornes et al., 2001), OMt/PS (Park et al., 2001) and sepiolite/PA6 (Bilotti et al., 2009) samples and the predictions of the suggested method considering the proper levels for interphase and intercalation/exfoliation of Mt. In all calculations, $\eta_o = 0.6$ and $\sigma_f = 2500$ MPa are assumed (Lazzeri and Phuong, 2014). As shown, the predictions appropriately follow the experimental data at all nanofiller concentrations, which validate the suggested method for estimation of strength. The level of Mt intercalation/exfoliation and the properties of interphase can be determined by using the two-step method to the experimental results. The values of "t_i" and "σ_i" depend on the levels of gyration radius of macromolecules (R_g) and the strength of polymer matrix and Mt. The "t_i" cannot be higher than "R_g". Also, "σ_i" should be expressed between the levels of "σ_m" and "σ_f". The acceptable levels of (N, t_i, σ_i) are calculated by applying the experimental data of tensile strength to the presented method.

The best values of (N, t_i, σ_i) are obtained for OMt/PP sample as (2, 5, 100) and (5, 10, 250). Also, the values of (2, 10, 280) and (5, 20, 480) are found for OMt/PA6 sample. The (N, t_i, σ_i) values of (2, 10, 85) and (5, 30, 195) are calculated for OMt/PS sample. Moreover, the best levels of (2, 3, 180) and (5, 40, 710) are achieved for sepiolite/PA6 specimen. As observed, all the values of (N, t_i, σ_i) are obtained in the allowable ranges which show the correctness of the suggested method. The dissimilar values of "t_i" and "σ_i" at a constant "N" (similar morphology) display the different properties of interphase depending on the miscibility/compatibility between polymer matrix and Mt (Durmuş et al., 2007; Hemmati et al., 2014). The morphological images can be used to estimate the level of average "N" and calculate the average levels for "t_i" and "σ_i" by the presented approach.

The TEM images for OMt/PA6 nanocomposites containing 1.5 wt% OMt and three types of PA6 with different molecular weights, low molecular weight (LMW), medium molecular weight (MMW) (studied here in Fig. 1b) and high molecular weight (HMW) (Fornes et al., 2001) are shown in Fig. 2. HMW (Fig. 2a) and MMW (Fig. 2b) nanocomposites show more exfoliation of OMt layers in the polymer matrices, but LMW sample (Fig. 2c) reveals less exfoliation and more intercalation of OMt by thicker and darker strips. So, the TEM images demonstrate the intercalation/exfoliation of OMt layers in the samples which confirm the predictions of the suggested methodology.

Fig. 3 illustrates the effects of "φ_f" and "N" on the tensile strength of MPN by the suggested method at $l = 1\ \mu m$, $t = 5$ nm, $t_i = 5$ nm,