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Research paper

Development of Hashin-Shtrikman model to determine the roles and properties of interphases in clay/$CaCO_3$/PP ternary nanocomposite

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ABSTRACT

The Hashin-Shtrikman model underpredicts the bulk, shear and Young's moduli of the prepared clay/$CaCO_3$/PP ternary polymer nanocomposite (TPN) by ignoring the interphase between polymer matrix and nanoparticles. In this study, the Hashin-Shtrikman model was developed assuming the thickness and strength of interphases. Also, the thickness and strength of interphases in the ternary samples could be calculated by the developed Hashin-Shtrikman and Pukanszky models, respectively using the experimental results of mechanical properties. The predictions of the developed model showed good agreement with the experimental data at different Mt and $CaCO_3$ contents assuming the interphase role which validate the current approach. According to the calculations, the strong and thick interphases were formed in the TPN at low nanofiller concentrations. This occurrence for the present samples was explained by the material and processing parameters. However, the thickness and strength of interphases weakened by increasing in clay content, probably due to the poor dispersion of nanoparticles and reduced interfacial area/adhesion at this condition.

1. Introduction

The development of polymer composites has continued in scientific and industrial areas, due to the significant properties achieved at low nanofiller contents such as high modulus, acceptable thermal stabilization, poor flammability and low permeability (Fasihi and Abolghasemi, 2012; Fernández et al., 2013; Huskić et al., 2013; Kalbasi et al., 2012; Mauroy et al., 2015; Monfared and Jalali-Arani, 2015; Salkhord and Sadeghi Ghari, 2015; Shabanian et al., 2015). The improvement of properties is mostly due to the excellent aspects of nanofillers such as very small size, high surface area and large modulus. For example, montmorillonite (Mt) as a known type of clay mineral shows a high modulus (about 180 GPa), and large specific surface area (750 $m^2\ g^{-1}$ at completely exfoliated state). Therefore, it can cause a large reinforcing effect in polymers (Mirabedini et al., 2012; Razavi-Nouri and Karami, 2014; Zare, 2016b, 2016e; Zare and Garmabi, 2015). However, the quality of filler dispersion and interfacial adhesion between polymer matrix and nanofiller play main roles in final properties of polymer composites.

Although the effects of many material and processing parameters on the properties of polymer composites have been investigated for two decades, there is still a considerable attention in different communities to achieve desirable properties. The high-tech products require a wide knowledge of all factors affecting the properties of polymer composites. Also, polymer composites have shown a problem of toughness-stiffness optimization. Researchers have reported that TPN containing two nanofillers or polymers can offer much improved properties such as tensile modulus and impact strength (Chen et al., 2007).

The mechanical properties of composites mostly depend on characteristics of components, composition, interfacial interaction between the constituents, etc. (Mauroy et al., 2015; Razavi et al., 2015; Zare, 2016c, 2016d). There are relatively few studies on the interphase properties of ternary samples in the literature. The modeling can be an acceptable technique to examine the interphase in polymer composites without any precise and practical method for evaluation of interfacial properties in composites. The theoretical analysis can provide valuable information which enables the achievement of anticipated properties (Pahlavanpour et al., 2013; Zare, 2016f, 2016g). Also, micromechanic models such as Halpin-Tsai, Guth, Paul, Cox, Kerner, etc. which consider two separate phases as matrix and filler cannot predict accurate values for mechanical properties (Zare and Garmabi, 2012, 2014). It seems that a strong interphase between polymer and nanofillers is formed which affects the properties of polymer composites. In other words, micromechanic models do not incorporate the role of interphase and thus, underpredict the mechanical properties of polymer composites.

In this paper, Hashin-Shtrikman model for bulk and shear moduli of isotropic and quasi-homogeneous composites is developed for a TPN containing clay mineral and $CaCO_3$ nanoparticles. Since experimental and theoretical results are spaced, the effects of interphase are assumed

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in this model and the obtained outputs are compared with experimental data. Additionally, the interphases properties are calculated by the developed Hashin-Shtrikman and Pukanszky models.

2. Materials and methods

PP homopolymer as matrix (ZH500, MFI = 10 g/10 min, 230 °C, 2.16 kg) was received from Navid Zar Shimi Company, Iran. The modified Mt with a quaternary ammonium salt (Cloisite 20A) was purchased from Southern Clay Products with average thickness of 2 nm for each layer. Maleic anhydride grafted PP (PPgMA) (PB3150) with 0.5 wt% of maleic anhydride was supplied from Crompton Corp. and used as a compatibilizer between PP and Mt. A same content of PPgMA and Mt was mixed in all samples. Also, precipitated $CaCO_3$ (Socal312) with average radius of 35 nm and a coated layer of stearic acid was provided from Solvay.

After a dry mixing, melt compounding of samples was performed by a co-rotating twin screw extruder, Brabender TSE 20/40D (D = 20 mm, L/D = 40). Screw speed and feeding rate were kept at 250 rpm and 3 kg/h, respectively. The temperature profile was set from hopper to die at 210 to 230 °C. Also, the injection molding of extruded samples was performed using a MonoMat 80 injection molding machine at melt and mold temperatures of 245 and 80 °C, respectively.

Tensile test was performed by Z050 (Zwick) according to ASTM D638 at crosshead speed of 50 mm/min. The reported values are the average measurement of at least 5 samples.

3. Results and discussion

A linear elastic deformation was suggested by Hashin and Shtrikman (1961) assuming the isotropy and quasi-homogeneity of materials without any dependency to geometry of components. The lower bounds for bulk "K" and shear "G" moduli of composites were expressed as:

$$K = K_m + \frac{\varphi_f (K_f - K_m)}{1 + (1-\varphi_f)\frac{3(K_f - K_m)}{3K_m + 4G_m}} \quad (1)$$

$$G = G_m + \frac{\varphi_f (G_f - G_m)}{1 + (1-\varphi_f)\frac{6(K_m + 2G_m)(G_f - G_m)}{5G_m(3K_m + 4G_m)}} \quad (2)$$

Also, the upper bounds of moduli were given by:

$$K = K_f + \frac{(1-\varphi_f)(K_m - K_f)}{1 + \varphi_f \frac{3(K_m - K_f)}{3K_f + 4G_f}} \quad (3)$$

$$G = G_f + \frac{(1-\varphi_f)(G_m - G_f)}{1 + \varphi_f \frac{6(K_f + 2G_f)(G_m - G_f)}{5G_f(3K_f + 4G_f)}} \quad (4)$$

where subscripts "m" and "f" indicate matrix and filler phases, respectively. "φ_f" is the volume fraction of nanofiller which for a TPN with two nanofillers is $\varphi_f = \varphi_{f1} + \varphi_{f2}$, in which "$\varphi_{f1}$" and "$\varphi_{f2}$" are volume fractions of Mt and $CaCO_3$, respectively. In this TPN, "K_f" and "G_f" at different nanofiller contents are expressed as:

$$K_f = \varphi_{f1} K_{f1} + \varphi_{f2} K_{f2} \quad (5)$$

$$G_f = \varphi_{f1} G_{f1} + \varphi_{f2} G_{f2} \quad (6)$$

Young's modulus (E) of an isotropic solid can be determined (Dorigato et al., 2013) as:

$$E = \frac{9KG}{3K + G} \quad (7)$$

Also, assuming matrix, filler and composite as isotropic elastic solids, "K" and "G" can be calculated (Dorigato et al., 2013) as:

$$K_j = \frac{E_j}{3-6\nu_j} \quad (8)$$

$$G_j = \frac{E_j}{2 + 2\nu_j} \quad (9)$$

where "j" index refers to matrix, filler or composite and "ν" is Poisson ratio. "ν" for a TPN is determined by:

$$\nu = \varphi_{f1}\nu_{f1} + \varphi_{f2}\nu_{f2} + \varphi_m \nu_m \quad (10)$$

"E", density (ρ) and "ν" for PP, Mt and $CaCO_3$ from data sheets (Zare and Garmabi, 2012) and the calculations of "K" and "G" by Eqs. (8) and (9) are shown in Table 1. In addition, experimental "E" and yield strength (σ) by tensile test as well as the calculations of "ν", "K" and "G" (Eqs. (8)–(10)) for all prepared TPN are reported in Table 2. These values of "E", "K" and "G" are considered as experimental data and compared with model predictions. All moduli of prepared samples improve by addition of both Mt and $CaCO_3$ nanofillers, but less moduli for sample reinforced with 6 wt% Mt and 20 wt% $CaCO_3$ is measured, possibly due to some undesirable phenomena such as the poor dispersion of nanoparticles at high nanofiller contents.

If only the weight percentages of nanofillers were important, the sample with 6 wt% Mt and 20 wt% $CaCO_3$ displayed the highest moduli. However, the reported findings clearly indicate the significant role of dispersion quality of nanoparticles, interfacial adhesion between polymer matrix and nanofiller, etc. beside the reinforcing effects of nanoparticles in properties of composites. As a result, many parameters affect the moduli of polymer composites, which should be well considered in modeling of properties. In addition, "σ" data show a small variation at different nanofiller compositions. However, they give the worst levels at high nanofiller concentrations. Moreover, the values of "ν" for all samples are less than "ν" for neat PP matrix as 0.38, but, the calculated "ν" results change in a narrow range of 0.37–0.38 in all samples.

Figs. 1–3 depict the experimental results of TPN and the lower and upper bounds of "K", "G" and "E" by Eqs. (1)–(7). The large modulus of nanofillers causes a close predictions by upper and lower bounds models for polymer composites. However, the increase rate of moduli is higher by upper bound model compared to lower one. Also, high differences between experimental data and predictions are illustrated for all moduli of prepared samples. These discrepancies are not peculiar for polymer composites, because many effective parameters such as nanoparticles dispersion and interphase properties are not supposed in Hashin-Shtrikman model.

The most improvement of mechanical properties in polymer composites is attributed to formation of strong interphases between polymer matrix and both nanofillers, which can properly transfer the load from matrix to nanoparticles. Likewise, the high dispersion and distribution of nanoparticles in polymer matrix result in a large interface

Table 1
The characteristics of neat PP, MMT and $CaCO_3$.

Materials	E (GPa)	d (g/cm^3)	ν	K (GPa)	G (GPa)
PP	2.17	0.91	0.38	3.01	0.79
MMT	178	1.77	0.27	129	70.1
$CaCO_3$	26	2.71	0.31	22.81	9.92