MODELING OF EFFECTIVE ELASTIC PROPERTIES OF COMPOSITE CONTAINING NANOPARTICLES WITH AN INHOMOGENEOUS INTERPHASE

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ABSTRACT

In the current study the effect of filler and interphase on elastic properties of epoxy/clay nanocomposite is estimated at nano- and macrolevels.

The interphase was introduced as a region with gradient of properties nearby the interface of matrix and filler particles. At nanolevel the elastic properties of one single particle containing interphase were considered. The effect of adhesion efficiency was taken into account in the region of the interphase. At macrolevel elastic properties of nanocomposite were described analytically considering the structural components of the nanocomposite: previously calculated effective elastic properties of filler particle containing interphase and elastic properties of the matrix. The results of calculated elastic properties of nanocomposite at macrolevel were compared with results of quasistatic tensile tests and good correlation was found.

It was shown that the thickness of the interphase and the adhesion efficiency should be considered due to their high influence on overall behavior of the nanocomposite. This analysis at nano- and microlevels provides possibility to estimate the effect of filler and interphase properties and content on effective elastic properties of nanocomposite in whole.

1. INTRODUCTION

Due to unique platelet-like layered structure, relatively high elastic modulus and surface of clay nanoparticles it's possible to enhance mechanical and barrier properties of polymers at low filler content (less than 6% by mass) comparing with conventional composites filled with micro-sized inclusions [1-7]. Generally layered silicate-filled composites could be divided into three groups: conventional composites filled with silicate aggregates and no matrix intercalated inside the aggregate stacks; intercalated nanocomposites where matrix material is located in the galleries between the clay platelets but layered structure remains and exfoliated nanocomposites where the filler platelets are divided and separated within the polymer matrix. It should be mentioned that these three cases are just idealization of possible state in composite. Real NC can contain all the structures mentioned above. The predominance of a particular type of structure mainly depends on the manufacturing method of a composite and the degree of dispersion of the filler in it.

Although there have been numerous material syntheses, tests and characterizations of layered silicate-filled nanocomposites in the literature, the fundamental mechanisms are not fully clear and are rarely discussed [2]. Therefore a better understanding and prediction ability is significant in accelerating development and application of nanocomposites.

It should be emphasized that effective properties of two-phase composites have been extensively studied and various micromechanical models have been developed [8-12]. It is well known that the basis of these micromechanics models is elastic solution of an infinite matrix containing one inclusion. Nevertheless many authors proposed that apart from two

base phases there is an interphase layer between particle and matrix and its properties should be taken into account [13-16].
Another point is that anisotropy of the layered silicate should be considered. A single layer of montmorillonite clay is a monoclinic crystal composed of two silica tetrahedral sheets and a central octahedral sheet [17]. Such a monoclinic sheet has 13 independent elastic constants. Taking into account the hexagonal configuration of the tetrahedrons in the two tetrahedral sheets and layered structure of montmorillonite clay it could be assumed that a stack of the silicate layers is a transversely isotropic medium. For the case of intercalated silicate in composite, the layered structure remains while the galleries between layers are filled with polymer. This case also could be represented as transversally isotropic medium from an overall point of view.
In current work the formulas for the composite filled with transversally isotropic spheroidal inhomogeneities with a zero aspect ratio (platelets) will be used. The interphase will be introduced as a region with gradient of properties nearby the interface of filler particle and matrix. At nanolevel the elastic properties of one single particle containing interphase are considered. The effect of adhesion efficiency is taken into account in the region of interphase. At macrolevel elastic properties of nanocomposite are described analytically considering the structural components of the nanocomposite: previously calculated effective properties of filler particle containing interphase and elastic properties of matrix.

2. EXPERIMENTAL

Bisphenol A epoxy resin was used as a matrix of the composite. The filler was intercalated octadecylamine modified montmorillonite-based organoclay. The filler content was varied from 0 till 6% by mass.
The dimensions of these orthogonal plates were in all our tests 2.0 × 8.0 × 130.0 (± 0.1) mm. Specimens were dried in an oven at 80ºC to remove internal stresses which appeared during their production before starting the tests.
Quasi static tensile tests were performed on the specimens with different clay content using Zwick testing machine with a crosshead speed of 5 mm/min at room temperature. Four filler mass concentrations c = 0, 2, 4 and 6% were used in order to study the effect of filler mass fraction on the mechanical behavior of NC under investigation. Four specimens per each filler mass fraction were tested and the values given correspond to their arithmetic mean value.
Thus the effective elastic properties of epoxy/montmorillonite NC were determined.

3. MODELING

Since special attention is given to the evaluation of interphase problem and efficiency of adhesion in nanocomposite appropriate formulas for the elastic properties of nanocomposite filled with randomly oriented transversally isotropic spheroids with zero small aspect ratio will be applied. Wang [2] showed that for the small filler volume fractions Norris approximate expressions [12] for bulk and shear moduli of composite material reinforced with isotropic oblate spheroids with small aspect ratio agree well with explicit Mori-Tanaka expressions which are widely applied for the prediction of nanocomposite properties. These approximate expressions can be written as

$$K = K_1 + \frac{4}{9} \cdot c_f \cdot \left(\chi \frac{\pi}{8} \frac{3 - 4 \cdot \nu_1}{\mu_1 \cdot (1 - \nu_1)} + \frac{1}{\mu_2} \frac{1 - \nu_2}{1 + \nu_2} \right)^{-1}, \tag{1}$$

$$\mu = \mu_1 + \frac{1}{15} \cdot c_f \cdot \left(\chi \frac{\pi}{8} \frac{3 - 4 \cdot \nu_1}{\mu_1 \cdot (1 - \nu_1)} + \frac{1}{\mu_2} \frac{1 - \nu_2}{1 + \nu_2} \right)^{-1} + \frac{2}{5} \cdot c_f \cdot \left(\chi \frac{\pi}{16} \frac{7 - 8\nu_1}{\mu_1 \cdot (1 - \nu_1)} + \frac{1}{\mu_2} \right)^{-1}, \tag{2}$$

where c_f is filler volume fraction, χ is aspect ratio of filler, K, μ and ν are the bulk, shear moduli and Poisson ratio of composite, respectively. Indices 1 and 2 represent matrix and filler properties. The aspect ratio χ is defined as filler particle's thickness related to its length and is for the case of nanocomposite filled with clay platelets much smaller than 1.

In the numerical calculations, the bulk and shear moduli of the matrix and filler are chosen in such way that they reflect the typical properties of epoxy resin and montmorillonite silicate, respectively. Therefore, the Young's modulus and Poisson ratio of the matrix are considered to be E_1 = 3.45 GPa and ν_1 = 0.35. The elastic modulus is also experimentally determined value. Unfortunately there is lack of the complete elastic constants of montmorillonite silicate. In the literature it is usually assumed that elastic modulus in the longitudinal direction is ranging from 140 GPa [2] to 175 GPa [18]. In this work it is assumed that E_2 = 168 GPa and ν_2 = 0.2. The aspect ratio is chosen to be about 0.015.

Then the calculated values of formulas (1) and (2) are used to evaluate the elastic modulus by the equation

$$E = \frac{9 \cdot K \cdot \mu}{3 \cdot K + \mu}. \tag{3}$$

The interphase was introduced as a region with gradient of properties nearby the interface of matrix and filler particles. At nanolevel the elastic properties of one single particle containing interphase were considered. The effect of adhesion efficiency was taken into account in the region of the interphase. In our previous investigation [1] it was shown that existence of interphase results in increase of equilibrium moisture content during sorption experiments and as a result a significant decrease of elastic moduli was observed. Since the analytical evaluation for both elastic and sorption properties was higher than that for experimental results it was concluded that interphase has elastic properties lower than the matrix and this conclusion will be used in current work.

The expression of the bulk modulus for the system of filler particle-interphase-matrix is assumed to follow the formula

$$K(x,k,R_f) = \begin{vmatrix} K_2 \text{ if } 0 \le x \le R_f \\ K_1 \cdot \left(1 - \frac{(K_2 - K_1)}{K_2} \cdot \exp\left(\frac{-(x - R_f)}{k \cdot R_f} \right) \right) \text{if } R_f \le x \le R_i(k, R_f), \\ K_1 \text{ otherwise} \end{vmatrix} \tag{4}$$

where x is the coordinate in one-dimensional approach, k is the efficiency of adhesion, R_f is the thickness of the filler particle. The adhesion efficiency is varying from 0 to 1 and expresses the strength of interaction between filler and matrix. The thickness of interphase R_i is denoted as the distance from filler particle to the matrix material with the deviation from matrix properties $\delta = 0.1$ % and is evaluated by formula

$$R_i(k,R_f) = R_f - R_f \cdot k \cdot \ln\left(\delta \frac{\delta \cdot K_2}{(K_2 - K_1)} \right).$$

The similar formulas could be written for the shear modulus.

Figure 1 shows the change of bulk modulus within the system of filler-interphase-matrix material. Four different filler contents corresponding to experimental ones are used in the analysis. It is evident from the figure that increasing filler radius the thickness of the interphase increases. This leads to decrease of effective bulk modulus for the system in whole.

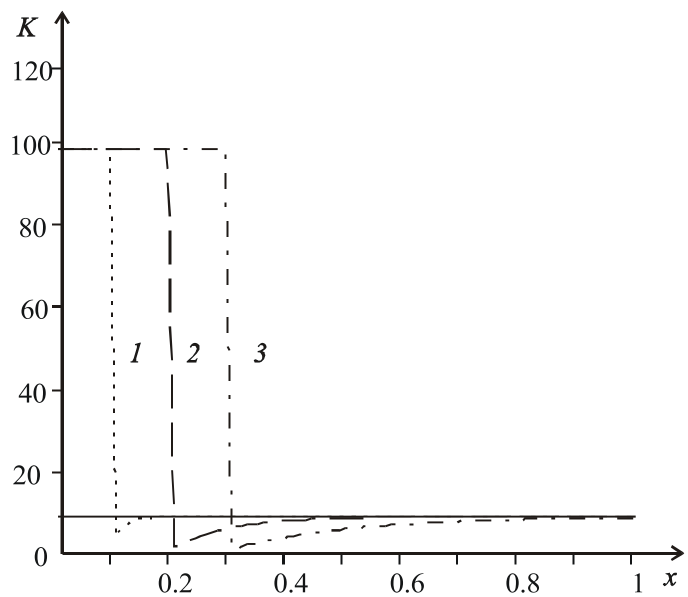

Figure 1: Bulk modulus of the 3-phase system for different filler contents R_f = 1, 2 and 3 % (numbers on the curves) and constant line – pure resin, $k = 0.3$.

Moreover the adhesion efficiency strongly influences the thickness of the interphase and in this way lowers the value of the elastic moduli with the increase of R_i. The dependence of interphase thickness on the filler thickness and adhesion efficiency is shown in Figure 2. It is clearly seen that with the increase of filler content or thickness of filler particle the thickness of interphase layer increases reaching maximal value for the highest adhesion efficiency ($k = 1$).

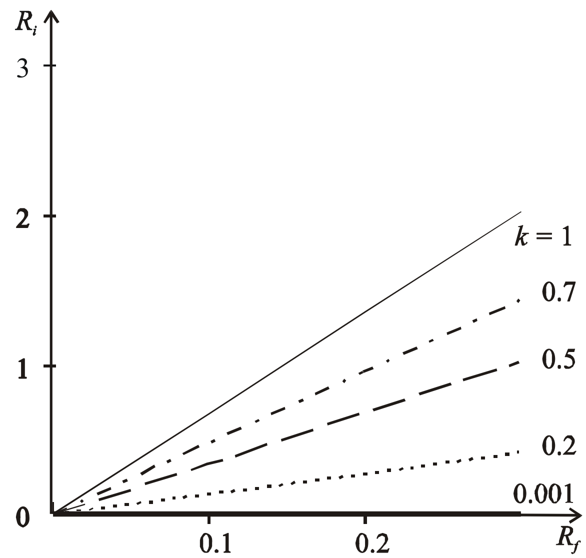

Figure 2: Thickness of the interphase vs. thickness of filler particle for different values of adhesion efficiency.

Then the derived variations of moduli were averaged for system of filler particle-interphase in order to get quasi-particle with constant properties using formulas

$$\overline{K}(k,R_f)=\frac{1}{x_{\max}}\cdot\int_0^{R_i(k,R_f)}K(x,k,R_f)dx\,, \tag{5}$$

$$\overline{\mu}(k,R_f)=\frac{1}{x_{\max}}\cdot\int_0^{R_i(k,R_f)}\mu(x,k,R_f)dx\,. \tag{6}$$

These elastic characteristics were used to evaluate the elastic modulus of nanocomposite taking into account degree of adhesion and presence of quasi-particles with averaged properties. The elastic modulus is determined by well known relation between elastic characteristics

$$\overline{E}(k,R_f)=\frac{9\cdot\overline{K}(k,R_f)\cdot\overline{\mu}(k,R_f)}{3\cdot\overline{K}(k,R_f)+\overline{\mu}(k,R_f)}\,. \tag{7}$$

The final result for the elastic modulus of the composite is showed in Figure 3. As it was mentioned before the elastic moduli in the interphase were assumed to be lower than that of the matrix. As seen from the figure adhesion efficiency greatly influences elastic properties of the composite and lowers the effective elastic modulus. It is interesting to notice that with the increase of adhesion efficiency the thickness of the interphase increases and so the content of the quasi-filler particles grows as well. Nevertheless the averaging by the diameter of the particle gives results which are monotonically growing functions in dependence of filler content.

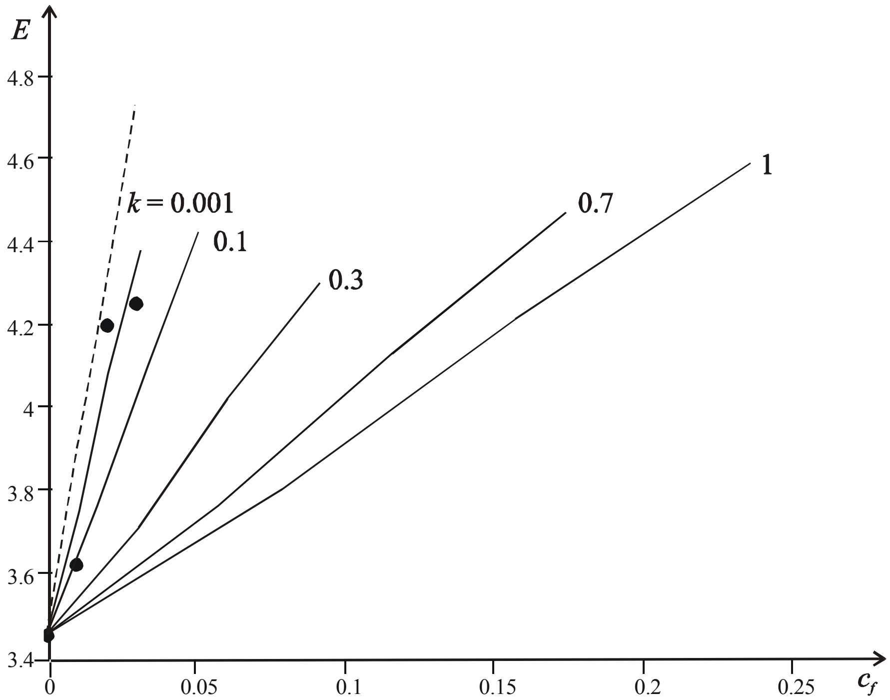

Figure 3. Effective elastic modulus vs. filler volume content (dots – experimental data, dotted line - evaluation by formula (3), solid lines – evaluation by formula (7).

4. COMPARISON BETWEEN MODEL PREDICTION AND EXPERIMENTS AND CONCLUSIONS

As pointed out before the silicate platelets could be dispersed in the polymer in three ways: in aggregates, as in intercalated layered nanocomposite and in exfoliated platelets. In the current work only the last case was considered due to primary emphasis on the interphase problem. The exfoliated platelets were represented as transversally isotropic spheroids with low aspect ratio (0.015). The expressions for the bulk and shear moduli of the composite were presented using expressions of Norris for randomly oriented platelets which are suitable for low filler contents. First the properties of quasi-particle were estimated at nanolevel considering efficiency of adhesion at different filler contents. It should be noted that the stiffness of filler particles in the direction of major axis is the dominating parameter in these calculations. Since the literature data for the elastic constants of montmorillonite is incomplete it could be concluded that these values could be varied in order to get better agreement with the experimental data.

According to the results obtained in the work the theoretical prediction using expressions of Norris agree quite well with the results of quasistatic tensile test. Nevertheless the results of this prediction are higher which can be described by the lack of precise values of parameters like elastic constants and aspect ratio of montmorillonite clay. Another possibility to describe this deviation is to introduce interphase layer. It is clear that taking into account adhesion efficiency and high surface of filler particles quite high content of quasi-particles is obtained in the case of nanocomposite. That’s why the thickness of the interphase and adhesion efficiency can greatly influence the mechanical behavior of the nanocomposite and should be considered. This analysis at nano- and microlevels provides possibility to estimate the effect of filler and interphase properties and content on effective properties of nanocomposite in whole.

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