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## POLYMERS AS NATURAL NANOCOMPOSITES. 2. THE COMPARATIVE ANALYSIS OF REINFORCEMENT MECHANISMS

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**Abstract.** The complete similarity of reinforcement degree behaviour has been shown for nanocomposite epoxy polymer/Na<sup>+</sup>-montmorillonite and polyarylate, which is considered as the natural nanocomposite. The polyarylate structure description is given within the framework of cluster model of polymers amorphous state structure. The interfacial adhesion level influences strongly the reinforcement degree of indicated materials.

**Keywords:** polyarylate, nanocomposite, structure, reinforcement, adhesion.

### 1. Introduction

At present it becomes obvious that polymeric systems due to their structure features are always nanostructural systems [1]. However, such structure treatment can be various. So, A. Malamatov *et al.* [2] have used for this purpose the cluster model of polymers amorphous state structure, which assumes that the mentioned structure consists of local order domains (clusters) immersed in a loosely-packed matrix. In this case the latter is considered as the natural nanocomposite matrix and clusters are considered as the nanofiller. The cluster represents a set of several densely-packed collinear segments of different macromolecules with the size up to several nanometers [3]. It has been shown that such clusters are true nanoparticles – the nanoworld objects (nanoclusters) [2].

In this connection there arises a question about reinforcement (matrix polymer elasticity modulus enhancement) by nanoclusters and comparison of this important effect action with the similar effect for artificial nanocomposites, *i.e.* polymers, filled with one or another inorganic filler type. As it is known [4], nanoclusters relative fraction increase results into polymers elasticity modulus enhancement by analogy with nanofiller contents in artificial nanocomposites. Therefore there appears the

necessity of quantitative description and subsequent comparison of the reinforcement degree for two above-mentioned nanocomposite classes. The purpose of the present paper is a comparative analysis of the reinforcement degree by nanoclusters and layered silicate (organoclay) for polyarylate and nanocomposite epoxy polymer/Na<sup>+</sup>-montmorillonite, respectively.

### 2. Experimental

The polyarylate on the basis of iso- and terephthalic acids (PAr) with the molecular weight  $\sim 5 \cdot 10^4$  was used. PAr films of  $\sim 0.1$  mm thickness were prepared by the method of 5 % polymer solution in a methylene chloride pouring on cellophane substrate and by subsequent drying them in vacuum at temperature  $\sim 453$  K during 2 days for the complete removal of moisture and solvent. From these films the samples for mechanical testing in the form of “dogbone” having basic length of 40 mm and working width of 5 mm were cut out with the templet aid. The tests on uniaxial tension were made on an Instron testing machine at the strain rate  $\sim 10^{-3}$  s<sup>-1</sup> within the temperature limits of 293–413 K. Before testing the samples were maintained in a thermal chamber of the testing machine during 15 min for thermal equilibrium achievement. Each data point was obtained according to 5 samples tests results.

The data of nanocomposites epoxy polymer/Na<sup>+</sup>-montmorillonite (EP/MMT) mechanical tests are accepted according to the results of the paper [5].

### 3. Results and Discussion

The authors [6] considered the theoretical dependences of the reinforcement degree  $E_c/E_m$  (where  $E_c$  and  $E_m$  are elasticity moduli of composite and matrix polymer, respectively) on the filling degree  $\phi_f$  for three main cases.

1. The ideal adhesion between the filler and polymer matrix described by Kerner equation, which can be approximated by the following relationship:

$$\frac{E_c}{E_m} = 1 + 11.6j_f - 44.4j_f^2 + 96.3j_f^3 \quad (1)$$

2. Zero adhesional strength at the large friction coefficient between the filler and polymer matrix, which is described by the equation:

$$\frac{E_c}{E_m} = 1 + j_f \quad (2)$$

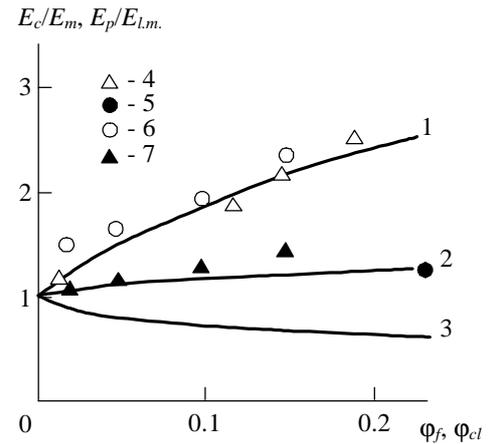
3. The interaction complete absence and an ideal slip between the filler and polymer matrix, when the composite elasticity modulus is practically defined by polymer cross-section and connected with the filling degree by the equation:

$$\frac{E_c}{E_m} = 1 - j_f^{2/3} \quad (3)$$

In Fig. 1 theoretical dependences of reinforcement degree ( $E_c/E_m$ ) for three above indicated cases are shown. Besides, in this Figure the experimental values  $E_c/E_m$  for nanocomposites EP/MMT at  $T < T_g$  and  $T > T_g$  (where  $T_g$  and  $T$  are glass transition and testing temperatures, respectively) are indicated by the points. As one can see, for glassy epoxy matrix the experimental data correspond to the Eq. (2), i.e. zero adhesional strength at the large friction coefficient, and for rubbery epoxy matrix – to the Eq. (1), i.e. the ideal adhesion between a nanofiller and polymeric matrix, described by Kerner equation. It should be noted that authors [2] explained the indicated above distinction by much larger length of epoxy polymer statistical segment in the second case.

To obtain similar comparison for natural nanocomposite (polymer) is impossible, since at  $TT_g$  nanoclusters are disintegrated and the polymer ceases to be quasi-two-phase system [7]. However, within the frameworks of two-step vitrification conception it has been shown [8, 9] that at temperature  $T_g'$ , which is equal to about  $(T_g - 50 \text{ K})$ , nonstable (smaller) clusters disintegration occurs, resulting in loosely-packed matrix devitrification at the indicated temperature [3]. Therefore, within the temperature range  $T_g' - T_g$  natural nanocomposite (polymer) is the analog of EP/MMT<sup>g</sup> nanocomposite with devitrificated matrix and at  $T < T_g'$  – the analog of this nanocomposite with glassy matrix. Calculations of PAR parameters, which are necessary for subsequent estimations, can be done as follows. The nanoclusters relative fraction  $\phi_{cl}$  (the contents of MMT  $\phi_f$  analog) can be estimated with the aid of the following percolation relationship [10]:

$$j_{cl} = 0.03(T_g - T)^{0.55} \quad (4)$$



**Fig. 1.** Dependences of reinforcement degree  $E_c/E_m$  and  $E_p/E_{l.m.}$  upon nanofiller  $j_f$  and nanoclusters  $j_{cl}$  contents, respectively: 1-3 – the theoretical dependences  $(E_c/E_m)(j_f)$  corresponding to the equations (1)-(3); 4, 5 – the experimental data  $(E_p/E_{l.m.})(j_{cl})$  for PAR at  $T = T_g' - T$  (4) and  $T < T_g'$  (5); 6, 7 – the experimental data  $(E_c/E_m)(j_f)$  for EP/MMT at  $T > T_g$  (6) and  $T < T_g$  (7)

Determination of loosely-packed matrix elasticity modulus  $E_{l.m.}$  (EP/MMT nanocomposites polymeric matrix elasticity modulus analog) can be done by means of graphic method. In Fig. 2 the dependence of  $E_p(\phi_{cl})$  upon PAR is shown, which is separated into two linear parts. The transition from one part to another occurs at  $\phi_{cl} \approx 0.28$ , that according to the equation (4) corresponds to  $T \approx 400 \text{ K}$  at  $T_g = 458 \text{ K}$  for PAR [11]. It is easy to see that the above indicated temperature of linear dependence  $E_p(\phi_{cl})$  slope change corresponds to the above mentioned definition  $T_g'$  criterion, namely,  $T_g' = (T_g - 50 \text{ K})$ . As it has been expected, the devitrification of loosely-packed matrix at  $T_g'$  results into a more strong change of polymer properties, that was also observed earlier [12]. The graphs  $E_p(\phi_{cl})$  extrapolation to  $\phi_{cl} = 0$  gives  $E_{l.m.} \approx 0.85 \text{ GPa}$  for the glassy loosely-packed matrix and  $E_{l.m.} \approx 0.38 \text{ GPa}$  – for the rubbery one. In Fig. 1 the comparison of the obtained by the indicated method reinforcement degree of natural nanocomposite (PAR) is adduced at the condition  $E_p = E_c$  and  $E_{l.m.} = E_m$  with theoretical calculation according to the Eqs. (1-3) at the condition  $\phi_{cl} = \phi_f$ . As one can see, at temperatures within the range  $T = T_g' - T_g$  ( $\phi_{cl} = 0.06 - 0.19$ ) the value  $E_p/E_{l.m.}$  corresponds to the Eq. (1), i.e. the ideal adhesion nanoclusters-loosely-packed matrix, and at  $T < T_g'$  ( $\phi_{cl} > 0.24$ ) – the Eq. (2), i.e. zero adhesional strength at a large friction coefficient. Hence, Fig. 1 data demonstrate clearly the complete analogy, both qualitative and quantitative, of reinforcement degree behaviour of natural (PAR) and artificial (EP/MMT) nanocomposites. The application of another microcomposite model (for example, accounting for strong anisotropy of layered silicate particles) can change the picture only quantitatively. Fig. 1 data give qualitative reinforcement degree correspondence at identical initial conditions of the indicated nanocomposites classes.

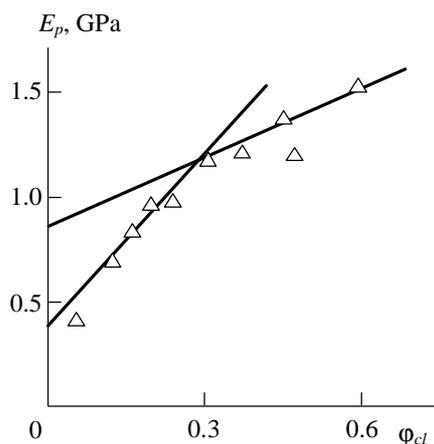


Fig. 2. The dependence of elasticity modulus  $E_p$  on nanoclusters relative fraction  $\phi_{cl}$  for PAR

#### 4. Conclusions

Therefore, the reinforcement degree behaviour analogy of polyarylate by nanoclusters and nanocomposite epoxy polymer/ $\text{Na}^+$ -montmorillonite by layered silicate gives one more reason to consider polymer as the natural nanocomposite. The interfacial adhesion level influences essentially the reinforcement degree. It is obvious that the following stage of this problem elaboration is clarification of physical significance of interfacial adhesion nanocluster-loosely-packed matrix and factors, which define it.

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#### ПОЛІМЕРИ ЯК ПРИРОДНІ НАНОКОМПЗИТИ. 2. ПОРІВНЯЛЬНИЙ АНАЛІЗ МЕХАНІЗМУ ЗМІЦНЕННЯ

**Анотація.** Показана повна подібність у підсиленні властивостей для нанокompозиту епоксидний полімер/ $\text{Na}^+$ -монтморилоніт і поліарилату, який вважається природним нанокompозитом. Опис поліарилатної будови поданий в межах каркасу кластерної моделі полімерів аморфної структури. Встановлено, що ступінь міжфазної адгезії значно впливає на підсилення властивостей вказаних матеріалів.

**Ключові слова:** поліарилат, нанокompозит, структура, зміцнення, адгезія.