THE AGGREGATION PROCESS AS A CAUSE OF LARGE-SCALE DISORDER IN NANOCOMPOSITES OF POLYMER/ORGANOCLAY

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Abstract. It has been shown that organoclay platelets aggregation in "packets" (tactoids) results in large-scale disorder intensification. It reduces the nanofiller anisotropy degree. In its turn, this factor decreases essentially the nanocomposites reinforcement degree. The interfacial adhesion role in anisotropy level definition has been shown.

Key words: nanocomposite, aggregations, reinforcement, anisotropy degree reinforcement, interphase adhesion.

Introduction

Organoclay belongs to anisotropic nanofillers, for which their anisotropy degree, i.e. ratio α of organoclay platelets (aggregates of platelets) length to thickness, has large significance [4]. The reinforcement degree E_n/E_m of nanocomposites polymer/organoclay can be estimated according to the equation [4]:

$$\frac{E_n}{E_m} = 1 + 2\alpha C_a \varphi_n, \qquad (1)$$

where E_n and E_m are elasticity moduli of nanocomposite and matrix polymer, respectively, C_a is an orientation factor, which is equal for organoclay to about 0.5 [4], φ_n is organoclay volume content.

In case of organoclay platelets aggregation, i.e. their "packets" (tactoids) formation [3], the

increase of such "packets" thickness takes place in comparison with a separate platelet, that results in the reduction of length/thickness ratio α at platelet constant length and, as consequence, the decrease of nanocomposites reinforcement degree is realized according to the equation (1). The present work purpose is the analytical study of organoclay aggregation, i. e. large-scale disorder, influence on reinforcement degree on the example of nanocomposites plasticate of poly(vinyl chloride) – organomodified montmorillonite.

Experimental

The plasticate of poly(vinyl chloride) (PVC) of mark U30-13A, prescription 8/2 GOST 5960-72 was used as a matrix polymer. The modification product of montmorillonite (MMT) of deposit Gerpegezh (KBR, Russian Federation), modified by urea with content of 10 mass % with cation-changing capacity of 95 mg-eq/100 g of clay was applied as a nanofiller. Organoclay content was varied within the limits of 1–10 mass %.

The nanocomposites PVC-MMT preparation was performed as follows. The components were mixed in a two-speed Diosna blender R 600/HC 2500, the design of which ensures intensive intermixing in turbulent regime with blends high homogenization and hot air blowing. After components intensive intermixing the composition was cooled up to temperature 313 K and processed on a twin screw extruder Thermo Haake, model Reomex RTW 25/42, production of German Federal Republic, at temperature 418–438 K and screw rotation speed of 48 rpm.

Sheet nanocomposite was obtained by a hot rolling method at temperature (433±10) K during 5-15 min. The samples in the shape of a two-sided spade with sizes according to GOST 112 62-80 were cut out by punch. Uniaxial tension mechanical tests have been performed on the universal testing apparatus Gotech Testing Machine CT-TCS 2000, production of German Federal Republic, at temperature 293 K and strain rate of ~ 2×10^{-3} s^{-1}.

Results and discussion

The nanofiller initial particles aggregation is the main process, enhancing large-scale disorder level in polymer nanocomposites. For each nanofiller type this process has its specific character, but in case of anisotropic nanofillers (organoclay, carbon nanotubes) application this process always decreases their anisotropy degree, i. e. aspect ratio α, that reduces nanocomposites reinforcement degree according to the equation (1). Let us consider the physical bases of the value α reduction at organoclay content increasing in the considered nanocomposites. As it is known [2], organoclay platelets number N_{pl} in "packet" (tactoid) can be determined as follows:

$$N_{pl} = 24 - 5.7 b_{\alpha}, \qquad (2)$$

where b_{α} is the dimensionless parameter, characterizing the level of interfacial adhesion polymeric matrix-nanofiller, which is determined with the aid of the following percolation relationship [3]:

$$\frac{E_n}{E_m} = 1 + 11 \left(c \varphi_n b_{\alpha} \right)^{1.7}, \qquad (3)$$

where c is constant coefficient, which is equal to 1.955 for intercalated organoclay and 2.90 – for exfoliated one.

In its turn, the value φ_n can be determined according to the well-known formula [3]:

$$\varphi_n = \frac{W_n}{\rho_n}, \qquad (4)$$

where W_n is nanofiller mass content; ρ_n is its density, which for nanoparticles is determined as follows [3]:

$$\rho_n = 188 \left(D_p \right)^{1/3}, \text{ kg/m}^3, \qquad (5)$$

where D_p is the initial nanoparticle diameter, which is given in nm.

In case of organoclay parameter D_p is determined as arithmetical means of its three basic sizes: length, width and thickness, which are equal to 100, 35 and 0.65 nm, respectively [5].

An alternative method of the value N_{pl} estimation gives the following equation [5]:

$$\chi = \frac{N_{pl} d_{pl}}{\left(N_{pl} - 1 \right) d_{001} + d_{pl}}, \qquad (6)$$

where χ is relative volume content of montmorillonite in tactoid («effective particle» [5]); d_{pl} is thickness of

organoclay separate platelet; d_{001} is interlayer spacing, i.e. the distance between organoclay platelets in tactoid, which can be estimated according to the following formula [2]:

$$d_{001} = 1.27 b_\alpha \text{, nm.} \qquad (7)$$

In its turn, parameter c is determined as follows [2]:

$$\chi = \frac{\varphi_n}{\varphi_n + \varphi_{if}}, \qquad (8)$$

where φ_{if} is a relative fraction of interfacial regions in nanocomposite, estimated with the aid of the following percolation relationship [3]:

$$\frac{E_n}{E_m} = 1 + 11\left(\varphi_n + \varphi_{if}\right)^{1.7}. \qquad (9)$$

The comparison of N_{pl} value calculations according to the equations (2) and (6) showed their close correspondence.

In Fig. 1 the dependence of $N_{pl}(\varphi_n)$ for nanocomposites PVC/MMT is adduced. As one can see, at quite enough small values $\varphi_n \leq 0.05$ fast growth of N_{pl} occurs, i.e. strong aggregation of organoclay initial platelets, and at $\varphi_n > 0.05$ the value N_{pl} achieves the asymptotic branch: $N_{pl} \approx 22$. As it was noted above, the reduction of nanofiller anisotropy degree, characterized by parameter α, was defined by its aggregation, the level of which could be characterized by parameter N_{pl}. In Fig. 2
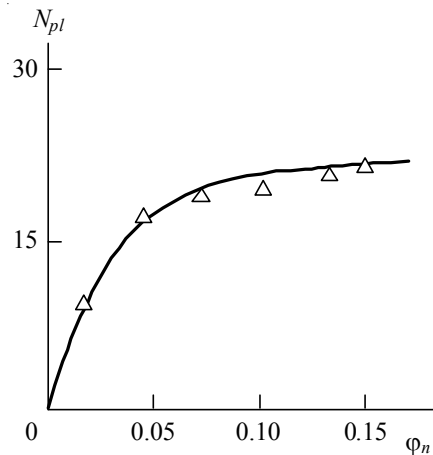

Fig. 1. The dependence of organoclay platelets number per one tactoid N_{pl} on nanofiller volume content φ_n for nanocomposites PVC-MMT
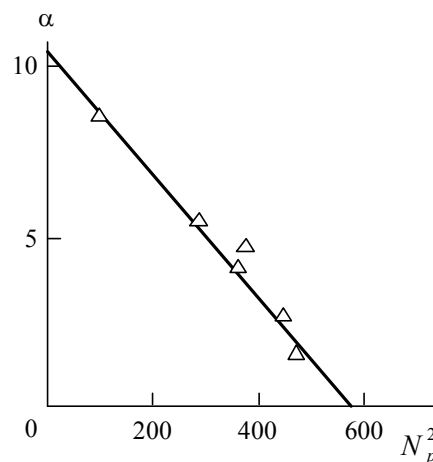

Fig. 2. The dependence of organoclay anisotropy degree α on its platelets number per one tactoid N_{pl} for nanocomposites PVC-MMT

the dependence $\alpha(N_{pl}^2)$ for the considered nanocomposites, where quadratic shape of dependence was chosen with the purpose of its linearization. As it was expected, the reduction of organoclay anisotropy degree, characterized by the parameter a, is observed at its platelets aggregation, characterized by the value N_{pl}, enhancement, which is expressed analytically by the following equation:

$$\alpha = 10.5 - 0.018N_{pl}^2, \qquad (10)$$

where the value a was estimated according to the equation (1).

Theoretical method of parameter α (α^T) estimation can be obtained as follows. Organoclay aggregates (tactoids) anisotropy degree can be determined according to the equation:

$$\alpha^T = \frac{L_{pl}}{t_{org}}, \qquad (11)$$

where L_{pl} is organoclay platelet length, which is equal to ~ 100 nm [3], t_{org} is its tactoid thickness.

In its turn, the value t_{org} is determined as follows:

$$t_{org} = d_{001}N_{pl} + 1. \qquad (12)$$

Besides, it should be born in mind, that experimental value α in the equation (1) is determined on the basis of reinforcement degree E_n/E_m, i. e. on the basis of mechanical tests results. This means that value α depends on conditions of stress transfer on interfacial boundary polymeric matrix-organoclay, i.e. on the parameter b_α value. Then parameter α^T can be determined finally as follows:

$$\alpha^T = \frac{L_{pl}b_\alpha}{1.27b_\alpha N_{pl} + 1}. \qquad (13)$$

In Fig. 3 the comparison of experimental a and calculated according to the equation (13) α^T values of organoclay tactoids aspect ratio, characterizing large-scale disorder level for the considered nanocomposites, is adduced. As one can see, good enough correspondence of experiment and theory is obtained (average discrepancy of α and α^T makes up ~ 9 %).

The equations (10) and (13) allow to predict reinforcement degree E_n/E_m on organoclay with known structural characteristics. In Fig. 4 the comparison of theoretical curves $E_n/E_m(\varphi_n)$, calculated according to the equation (1), where parameter α^T was determined according to the formulas (10) and (13), and the corresponding experimental data is adduced. As one can see, a good both qualitative (the theoretical curves are reflected experimental dependence maximum without existence of maximums for parameters N_{pl} and d_{001}) and quantitative correspondence of theory and experiment (their average discrepancy makes up less 2.5 %).

Let us consider in conclusion the influence of organoclay platelets aggregation or large-scale
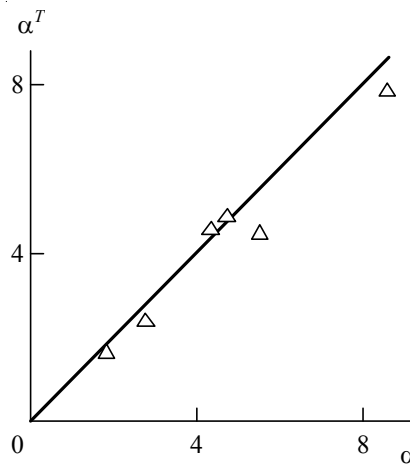

Fig. 3. The comparison of experimental α and calculated according to the equation (13) α^T organoclay anisotropy degree for nanocomposites PVC-MMT

disorder on the considered nanocomposites reinforcement degree. In Fig. 5 the experimental and calculated according to the equation (1) at organoclay aggregation minimum level (N_{pl}=9.70, b_α=2.51, α=8.6), corresponding to organoclay content W_n=1 mass %, dependences $E_n/E_m(\varphi_n)$ for nanocomposites PVC/MMT are adduced. As it follows from this comparison, both lower values of reinforcement degree and its decay at W_n >7 mass % are due precisely to organoclay platelets aggregation in "packets" (tactoids).

Conclusions

Thus, the present work results have demonstrated that organoclay platelets aggregation in "packets" (tactoids) causes large-scale disorder enhancement, that reduces nanofiller anisotropy degree. In its turn, this factor decreases essentially reinforcement degree (or elasticity modulus) of nanocomposites polymer-organoclay. Moreover, in case of large organoclay content (>7 mass %), reinforcement degree reduction at nanofiller content growth is observed. The important role of interfacial adhesion in anisotropy level determination has been shown.

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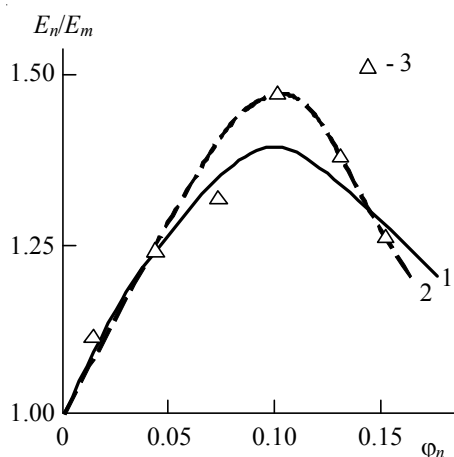2. Mikitaev A.K., Kozlov G.V., Zaikov G.E. *Polymer Nanocomposites: Variety of Structural*

Fig. 4. The comparison of calculated according to the equation (1) with the use of the formulas (10) (1) and (13) (2) for parameter α^T determination and experimental (3) dependences of reinforcement degree E_n/E_m on nanofiller volume content φ_n for nanocomposites PVC-MMT
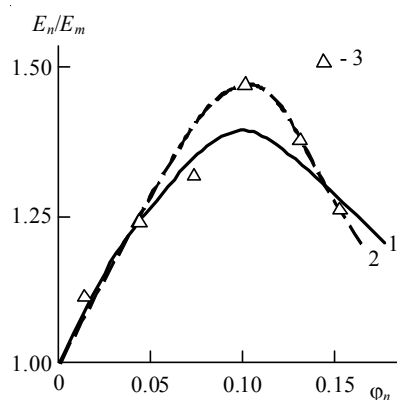

Fig. 5. The comparison of calculated according to the equation (1) at the condition of organoclay minimum aggregation (1) and experimental (2) dependences of reinforcement degree E_n/E_m on nanofiller volume content φ_n for nanocomposites PVC-MMT

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АНАЛИТИЧЕСКОЕ ИССЛЕДОВАНИЕ АГРЕГАЦИИ ПРИ ПРОИЗВОДСТВЕ НАНОКОМПОЗИТОВ

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Аннотация. Целью настоящей работы является аналитическое исследование агрегации при производстве нанокомпозитов поливинилхлорида. Показано, что агрегации влияют на снижение доли нанонаполнителя и степень анизотропии. В свою очередь, этот фактор существенно снижает степень армирования нанокомпозитов. Показана роль межфазной адгезии в анизотропии определенного уровня.

Ключевые слова: нанокомпозит, агрегации, армирование, усиление степени анизотропии, межфазная адгезия.