G. V. Kozlov, K. S. Dibirova, G. M. Magomedov,
Bob A. Howell, G. E. Zaikov, O. V. Stoyanov, K. S. Abzaldinov

THE REINFORCEMENT MECHANISM OF NANOCOMPOSITES

POLYETHYLENE/ORGANOCLAY ON SUPRASEGMENTAL LEVEL

Ключевые слова: нанокомпозит, полиэтилен, органоглина, модуль упругости, нанокластеры, межфазные области.

Предложен структурный механизм наполненных органоглиной полимерных нанокомпозитов на супрасегмент-ном уровне. Согласно этого механизма модуль упругости нанокомпозитов определяется по размеру областей локальной упорядоченности (нанокластерам) по аналогии с натуральным нанокомпозитом (полимером). Образование плотноупакованных поверхностных областей в нанокомпозитах при введении нанонаполнителей является физической основой уменьшения размеров нанокластеров.

Keywords: Nanocomposite, polyethylene, organoclay, elasticity modulus, nanoclusters, interfacial regions.

The structural mechanism of polymer nanocomposites filled with organoclay on suprasegmental level was offered. Within the frameworks of this mechanism nanocomposites elasticity modulus is defined by local order domains (nanoclusters) sizes similarly to natural nanocomposites (polymers). Densely-packed interfacial regions formation in nanocomposites at nanofiller introduction is the physical basis of nanoclusters size decreasing.

Introduction

Very often a filler (nanofiller) is introduced in polymers with the purpose of the latter stiffnes increase. This effect is called polymer composites (nanocomposites) reinforcement and it is characterized by reinforcement degree E_c/E_m (E_n/E_m), where E_c, E_n and E_m are elasticity moduli of composite, nanocomposite and matrix polymer, accordingly. The indicated effect significance results to a large number of quantitative models development, describing reinforcement degree: micromechanical [1], percolation [2] and fractal [3] ones. The principal distinction of the indicated models is the circumstance, that the first ones take into consideration the filler (nanofiller) elasticity modulus and the last two – don't. The percolation [2] and fractal [3] models of reinforcement assume, that the filler (nanofiller) role comes to modification and fixation of matrix polymer structure. Such approach is obvious enough, if to account for the difference of elasticity modulus of filler (nanofiller) and matrix polymer. So, for the considered in the present paper nanocomposites low density polyethylene/Na⁺-montmorillonite the matrix polymer elasticity modulus makes up 0.2 GPa [4] and nanofiller – 400-420 GPa [5], i.e. the difference makes up more than three orders. It is obvious, that at such conditions organoclay strain is equal practically to zero and nanocomposites behavior in mechanical tests is defined by polymer matrix behavior.

Lately it was offered to consider polymers amorphous state structure as a natural nanocomposite [6]. Within the frameworks of cluster model of polymers amorphous state structure it is supposed, that the indicated structure consists of local order domains (clusters), immersed in loosely-packed matrix, in which the entire polymer free volume is concentrated [7, 8]. In its turn, clusters consist of several collinear densely-packed statistical segments of different macromolecules, i.e. they are an amorphous analog of crystallites with

stretched chains. It has been shown [9], that clusters are nanoworld objects (true nanoparticles-nanoclusters) and in case of polymers representation as natural nanocomposites they play nanofiller role and loosely-packed matrix-nanocomposite matrix role. It is significant that the nanoclusters dimensional effect is identical to the indicated effect for particulate filler in polymer nanocomposites – sizes decrease of both nanoclusters [10] and disperse particles [11] results to sharp enhancement of nanocomposite reinforcement degree (elasticity modulus). In connection with the indicated observations the question arises: how organoclay introduction in polymer matrix influences on nanoclusters size and how the variation of the latter influences on nanocomposite elasticity modulus value. The purpose of the present paper is these two problems solution on the example of nanocomposite linear low density polyethylene/Na⁺-montmorillonite [4].

Experimental

Linear low density polyethylene (LLDPE) of mark Dowlex-2032, having melt flow index 2.0g/10 min and density 926 kg/m³, that corresponds to crystallinity degree of 0.49, used as a matrix polymer. Modified Na⁺-montmorillonite (MMT), obtained by cation exchange reaction between MMT and quaternary ammonium ions, was used as nanofiller MMT contents makes up 1-7 mass % [4].

Nanocomposites linear low density polyethylene/Na⁺-montmorillonite (LLDPE/MMT) were prepared by components blending in melt using Haake twin-screw extruder at temperature 473 K [4].

Tensile specimens were prepared by injection molding on Arburg Allounder 305-210-700 molding machine at temperature 463 K and pressure 35 MPa. Tensile tests were performed by using tester Instron of the model 1137 with direct digital data acquisition at temperature 293 K and strain rate ~ 3.35×10^{-3} s⁻¹. The

average error of elasticity modulus determination makes up 7 %, yield stress – 2 % [4].

Results and Discussion

For the solution of the first from the indicated problems the statistical segments number in one nanocluster n_{cl} and its variation at nanofiller contents change should be estimated. The parameter n_{cl} calculation consistency includes the following stages. At first the nanocomposite structure fractal dimension d_f is calculated according to the equation [12]:

$$d_f = (d-1)(1+\nu), \qquad (1)$$

where d is dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case $d=3$), ν is Poisson's ratio, which is estimated according to mechanical tests results with the aid of the relationship [13]:

$$\frac{\sigma_Y}{E_n} = \frac{1-2\nu}{6(1+\nu)}, \qquad (2)$$

where σ_Y and E_n are yield stress and elasticity modulus of nanocomposite, accordingly.

Then nanoclusters relative fraction φ_{cl} can be calculated by using the following equation [8]:

$$d_f = 3 - 6\left(\frac{\varphi_{cl}}{C_\infty S}\right)^{1/2}, \qquad (3)$$

where C_∞ is characteristic ratio, which is a polymer chain statistical flexibility indicator [14], S is macromolecule cross-sectional area.

The value C_∞ is a function of d_f according to the relationship [8]:

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3}. \qquad (4)$$

The value S for low density polyethylenes is accepted equal to 14.9 Å^2 [15]. Macromolecular entanglements cluster network density ν_{cl} can be estimated as follows [8]:

$$\nu_{cl} = \frac{\varphi_{cl}}{C_\infty l_0 S}, \qquad (5)$$

where l_0 is the main chain skeletal bond length which for polyethylenes is equal to 0.154 nm [16].

Then the molecular weight of the chain part between nanoclusters M_{cl} was determined according to the equation [8]:

$$M_{cl} = \frac{\rho_p N_A}{\nu_{cl}}, \qquad (6)$$

where ρ_p is polymer density, which for the studied polyethylenes is equal to ~ 930 kg/m^3, N_A is Avogadro number.

And at last, the value n_{cl} is determined as follows [8]:

$$n_{cl} = \frac{2M_e}{M_{cl}}, \qquad (7)$$

where M_e is molecular weight of a chain part between entanglements traditional nodes ("binary hookings"), which is equal to 1390 g/mole for low density polyethylenes [17].

In Fig. 1 the dependence of nanocomposite elasticity modulus E_n on value n_{cl} is adduced, from which E_n enhancement at n_{cl} decreasing follows. Such behavior of nanocomposites LLDPE/MMT is completely identical to the behavior of both particulate-filled [11] and natural [10] nanocomposites.
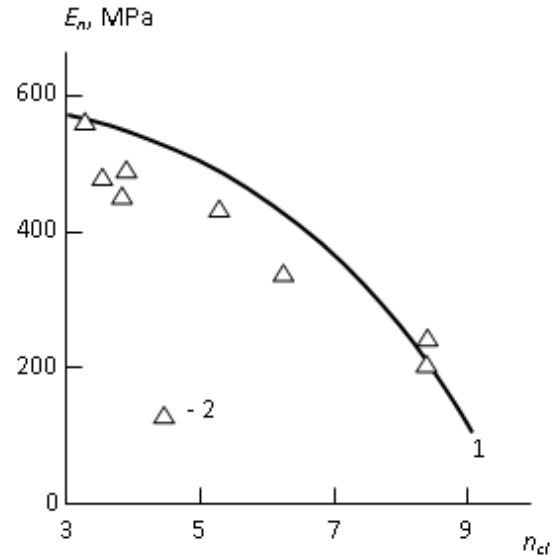

Fig. 1 - The dependences of elasticity modulus E$_n$ on Statistical segments number per one nanocluster n$_{cl}$ for nanocomposites LLDPE/MMT. 1 – calculation according to the equation (8), 2 – the experimental data

In paper [18] the theoretical dependences of E_n as a function of cluster model parameters for natural nanocomposites was obtained:

$$E_n = c\left(\frac{\varphi_{cl}\nu_{cl}}{n_{cl}}\right), \qquad (8)$$

where c is constant, accepted equal to 5.9×10^{-26} m^3 for LLDPE.

In Fig. 1 the theoretical dependence $E_n(n_{cl})$, calculated according to the equation (8), for the studied nanocomposites is adduced, which shows a good enough correspondence with the experiment (the average discrepancy of theory and experiment makes up 11.6 %, that is comparable with mechanical tests experimental error). Therefore, at organoclay mass contents W_n increasing within the range of 0-7 mass % n_{cl} value reduces from 8.40 up to 3.17, that is accompanied by nanocomposites LLDPE/MMT elasticity modulus growth from 206 up to 569 MPa.

Let us consider the physical foundations of n_{cl} reduction at W_n growth. The main equation of the reinforcement percolation model is the following one [9]:

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

where φ_n and φ_{if} are relative volume fractions of nanofiller and interfacial regions, accordingly.

The value φ_n can be determined according to the equation [5]:

$$\varphi_n = \frac{W_n}{\rho_n}, \qquad (10)$$

where ρ_n is nanofiller density, which is equal to ~ 1700 kg/m^3 for Na$^+$-montmorillonite [5].

Further the equation (9) allows to estimate the value φ_{if}. In Fig. 2 the dependence $n_{cl}(\varphi_{if})$ for nanocomposites LLDPE/MMT is adduced.
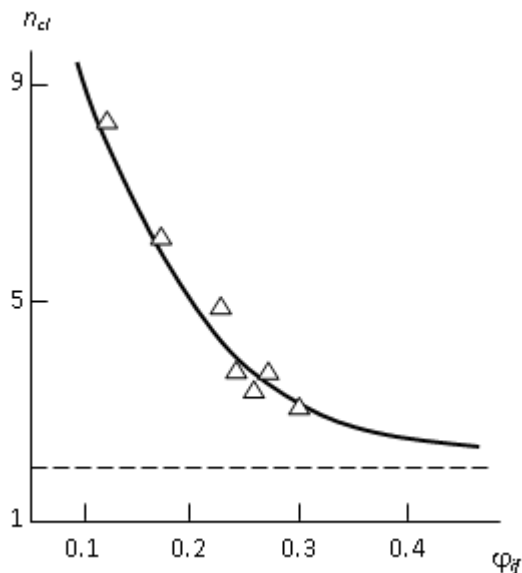

Fig. 2 - The dependence of statistical segments number per one nanocluster n_{cl} on interfacial regions relative fraction φ_{if} for nanocomposites LLDPE/MMT. Horizontal shaded line indicates the minimum value $n_{cl}=2$

As one can see, n_{cl} reduction at φ_{if} increasing is observed, i.e. formed on organoclay surface densely-packed (and, possibly, subjecting to epitaxial crystallization [9]) interfacial regions as if pull apart nanoclusters, reducing statistical segments number in them. As it follows from the equations (9) and (8), these processes have the same direction, namely, nanocomposite elasticity modulus increase.

Conclusions

Hence, the obtained in the present paper results demonstrated common reinforcement mechanism of natural and artificial (filled with inorganic nanofiller) polymer nanocomposites. The statistical segments number per one nanocluster reduction at nanofiller contents growth is such a mechanism on suprasegmental level. The indicated effect physical foundation is the densely-packed interfacial regions formation in artificial nanocomposites.

References

1. Ahmed S., Jones F.R. J. Mater. Sci., 1990, v. 25, № 12, p. 4933-4942.
2. Bobryshev A.N., Kozomazov V.N., Babin L.O., Solomatov V.I. Synergetics of Composite Materials. Lipetsk, NPO ORIUS, 1994, 154 p.
3. Kozlov G.V., Yanovskii Yu.G., Zaikov G.E. Structure and Properties of Particulate-Filled Polymer Composites: the Fractal Analysis. New York, Nova Science Publishers, Inc., 2010, 282 p.
4. Hotta S., Paul D.R. Polymer, 2004, v. 45, № 21, p. 7639-7654.
5. Sheng N., Boyce M.C., Parks D.M., Rutledge G.C., Abes J.I., Cohen R.E. Polymer, 2004, v. 45, № 2, p. 487-506.
6. Bashorov M.T., Kozlov G.V., Mikitaev A.K. Materialovedenie, 2009, № 9, p. 39-51.
7. Kozlov G.V., Novikov V.U. Uspekhi Fizicheskikh Nauk, 2001, v. 171, № 7, p. 717-764.
8. Kozlov G.V., Zaikov G.E. Structure of the Polymer Amorphous State. Utretch, Boston, Brill Academic Publishers, 2004, 465 p.
9. Mikitaev A.K., Kozlov G.V., Zaikov G.E. Polymer Nanocomposites: Variety of Structural Forms and Applications. New York, Nova Science Publishers, Inc., 2008, 319 p.
10. Kozlov G.V., Mikitaev A.K. Polymers as Natural Nanocomposites: Unrealized Potential. Saarbrücken, Lambert Academic Publishing, 2010, 323 p.
11. Edwards D.C. J. Mater. Sci., 1990, v. 25, № 12, p. 4175-4185.
12. Balankin A.S. Synergetics of Deformable Body. Moscow, Publishers of Ministry Defence SSSR, 1991, 404 p.
13. Kozlov G.V., Sanditov D.S. Anharmonic Effects and Physical-Mechanical Properties of Polymers. Novosibirsk, Nauka, 1994, 261 p.
14. Budtov V.P. Physical Chemistry of Polymer Solutions. Sankt-Peterburg, Khimiya, 1992, 384 p.
15. Aharoni S.M. Macromolecules, 1985, v. 18, № 12, p. 2624-2630.
16. Aharoni S.M. Macromolecules, 1983, v. 16, № 9, p. 1722-1728.
17. Wu S. J. Polymer Sci.: Part B: Polymer Phys., 1989, v. 27, № 4, p. 723-741.
18. Kozlov G.V. Recent Patents on Chemical Engineering, 2011, v. 4, № 1, p. 53-77.

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