Musa Bashorov[1], Georgiy Kozlov[1], Gennady Zaikov[2] and Abdulakh Mikitaev[1]

POLYMERS AS NATURAL NANOCOMPOSITES.
1. THE REINFORCEMENT STRUCTURAL MODEL

[1] Kabardino-Balkarian State University, 173 Chernyshevskiy str., 360004 Nal'chik, Russia
*[2] N.M. Emanuel Institute of Biochemical Physics of Russian Academy of Sciences,
4 Kosygin str., 119334 Moscow, Russia*

Abstract. The structural treatment of amorphous glassy polycarbonate as natural nanocomposite was proposed. It has been shown that the polycarbonate stiffness is defined completely by the state of its structure, which is described within the frameworks of a local order model. The large reserves of stiffness raising for amorphous glassy polymers are demonstrated.

Keywords: polycarbonate, nanocomposite, solid-state structure, EPR, reinforcement.

1. Introduction

At present it becomes obvious that polymeric systems in virtue of their structure features are always nanostructural systems [1]. However, such structure treatment can be various. So, the authors [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 loosely-packed matrix. In this case the latter is considered as natural nanocomposite matrix and clusters – as nanofiller. A cluster represents itself 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 such treatment of a polymer structure the question of its stiffness a quires an important role, and this property is characterized by elasticity modulus E_p [4]. As it is known [4], the main task, solved at the introduction in polymers fillers of various kinds, is often namely stiffness raising, that results to the creation of a large number of microcomposite models, describing this effect [5]. As a rule, the indicated effect is characterized by the reinforcement degree E_c/E_m (where E_c and E_m are elasticity moduli of composite and polymer matrix, respectively), which for natural nanocomposites is given by the ratio $E_p/E_{l.m.}$ (where $E_{l.m.}$ is loosely-packed matrix elasticity modulus). The purpose of the present paper is the definition of structural factors, influencing on the elasticity modulus of natural nanocomposites (and exactly on their reinforcement degree) on the example of typical amorphous glassy polymer – polycarbonate.

2. Experimental

The industrial polycarbonate (PC) of the mark Makrolon (manufacture of firm Baier, German Federal Republic) with molecular weight not lower than $3 \cdot 10^4$.

As spin probe the nitroxil radical 2,2,6,6-tetramethyl-4-oxo-pyperidine-1-oxyl (TEMPON) of molecular weight 169 and volume 150 $Å^3$ was used:

Samples for research were prepared by polymer and probes combined solution in methylene chloride with the following solvent removal. The spin probes concentration makes up $\sim 10^{22}$–10^{23} spin/m^3. After the films have been obtained they were loaded in a thermostat and were maintained at temperature 313 K.
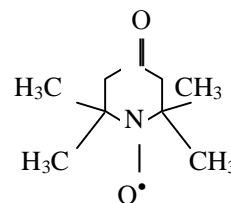
EPR spectra were obtained on a spectrometer of model 2543 of firm "Radiopan" (Poland) within the temperatures range 293–423 K.

For mechanical tests PC films of thickness ~ 0.1 mm were prepared by method of 5 % polymer solution in methylene chloride pouring with their subsequent drying in vacuum at temperature 393 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 the testing machine Instron at strain rate $\sim 10^{-3}$ s^{-1} within the temperatures range 293–413 K. Before testing these 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 five test results of the samples.

3. Results and Discussion

As it is known [6], the average distance r between two paramagnetic probes can be estimated according to the formula:

$$r = 38\left(\Delta H_{dd}\right)^{-1/3}, \text{Å} \tag{1}$$

where ΔH_{dd} is dipole-dipole interaction energy, expressed in Ersteds.

In its turn, the cluster size $2R_{cl}$ within the frameworks of cluster model is given as follows [3]:

$$2R_{cl} = 36\left(\frac{n_{cl}}{n_{cl}}\right)^{-1/3}, \text{Å} \tag{2}$$

where ν_{cl} is physical entanglements cluster network density, n_{cl} is segments number in one cluster. The values ν_{cl} and n_{cl} for PC are quoted in paper [2].

The comparison of the equations (1) and (2) shows that the value ΔH_{dd} has structural origin, namely:

$$\Delta H_{dd} \approx \left(\frac{n_{cl}}{n_{cl}}\right) \tag{3}$$

As the estimations according to the equation (3) have shown, in the temperatures range T=293-413 K ΔH_{dd} increase from 0.118 up to 0.328 Ersteds is observed.

Let us consider the interconnection of dipole-dipole interaction energy ΔH_{dd} with nanofiller (nanoclusters) particles geometry. A nanocluster is simulated as a cylinder with diameter D_{cl} and length l_{st}, where l_{st} is polymer chain statistical segment length. Consequently two cases of nanocluster-loosely-packed matrix contact can be considered: over butt-end surface with area S_b and over cylindrical surface with area S_c. The value D_{cl} is determined according to the following formula [7]:

$$D_{cl} = 2\left(\frac{n_{cl}S}{ph}\right)^{1/2} \tag{4}$$

where S is macromolecule cross-section area, which is equal to 30.7 Å^2 of PC [8], h is the packing coefficient, accepted equal to 0.868 in case of dense packing [7].

The value l_{st} can be determined according to the equation [9]:

$$l_{st} = l_0 C_\infty \tag{5}$$

where l_0 is the main chain skeletal bond length, which is equal to 1.25 Å for PC [10], C_∞ is characteristic ratio, which is the indicator of polymer chain statistical flexibility [11] and is determined according to the following relationship [12]:

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3} \tag{6}$$

where d is the dimension of Euclidean space, in which a fractal is considered (it is obvious, that in our case d=3), d_f is polymer structure fractal dimension, which is calculated according to the equation [13]:

$$d_f = (d-1)(1+n) \tag{7}$$

where ν is Poisson's ratio, estimated according to the mechanical tests results with the aid of the relationship [14]:

$$\frac{\sigma_Y}{E_p} = \frac{1-2n}{6(1+n)} \tag{8}$$

where σ_Y is yield stress, E_p is elasticity modulus.

Further the values S_b and S_c can be calculated with the aid of well-known geometrical formulas. In Fig. 1 the dependence ΔH_{dd} on the indicated areas ratio S_c/S_b for PC is shown. As one can see, ΔH_{dd} linear growth at the ratio S_c/S_b increase is observed, *i.e.* either at S_c enhancement or at S_b reduction. Such character of the dependence shown in Fig. 1 indicates unequivocally that nanocluster-loosely-packed matrix contact is realized just over nanocluster cylindrical surface. This effect should be expected since emerging from butt-end surface statistically distributed polymer chains complicate the indicated contact realization unlike relatively smooth cylindrical surfaces. It is natural to suppose that dipole-dipole interaction intensification or ΔH_{dd} increase results to natural nanocomposites elasticity modulus raising. The second so natural an assumption as nanocomposite at PC consideration is the influence on E_p value of nanocluster (nanofiller) relative fraction φ_{cl}, which is determined according to the following percolation relationship [15]:

$$j_{cl} = 0.03\left(T_g - T\right)^{0.55}, \tag{9}$$

where T_g and T are glass transition and testing temperatures, respectively. For PC T_g=423 K [6].

In Fig. 2 the dependence of the elasticity modulus E_p on complex argument $(\Delta H_{dd}\varphi_{cl})$ for PC is presented. As one can see, this dependence is linear, pass through coordinates origin and is described analytically by the following empirical equation:

$$E_p = 21\left(\Delta H_{dd} j_{cl}\right), \text{GPa} \qquad (10)$$

which accounting for the equation (3) can be rewritten as follows:

$$E_p = 21\left(\frac{n_{cl} j_{cl}}{n_{cl}}\right), \text{GPa} \qquad (11)$$

The Eq. (11) demonstrates clearly that E_p value and, hence, polymer reinforcement degree is a function of its structural characteristics describing within the frameworks of the cluster model [3]. Let's note, that since the parameters ν_{cl} and φ_{cl} are a function of testing temperature (see the Eq. (9)), then the parameter n_{cl} is the most suitable factor for the value E_p adjustment in practical purposes. In Fig. 3 the dependence $E_p(n_{cl})$ for $T = 293$ K in PC case, calculated according to the Eq. (11), is adduced, where the value φ_{cl} was determined according to the equation (9) and ν_{cl} magnitude is given by the following formula [3]:

$$n_{cl} = \frac{j_{cl}}{l_0 C_\infty S} \qquad (12)$$

As one can see, at small n_{cl} (<10) the sharp E_p growth is observed and at the smallest possible value $n_{cl} = 2$ the value $E_p \approx 13.5$ GPa. Since for PC $E_{l.m.} = 0.85$ GPa, then this gives the greatest reinforcement degree $E_p/E_{l.m.} \approx 15.9$. The similar effect was observed for epoxy polymer samples, subjected to solid-state extrusion and subsequent annealing [16]. Let's note, that the greatest attainable reinforcement degree for artificial nanocomposites (polymers filled with inorganic nanofiller) can not exceed 12 [2].
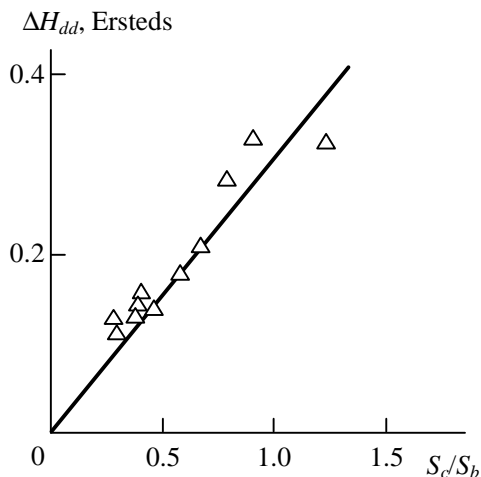

Fig. 1. The dependence of dipole-dipole interaction energy ΔH_{dd} on nanocluster cylindrical S_c and butt-end S_b surfaces areas ratio for PC
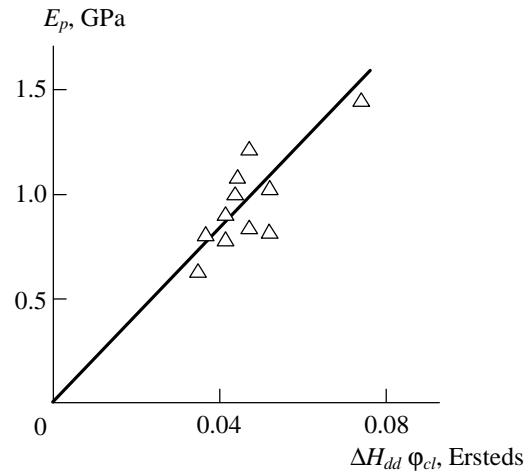

Fig. 2. The dependence of elasticity modulus E_p on complex argument $(\Delta H_{dd} \varphi_{cl})$ for PC
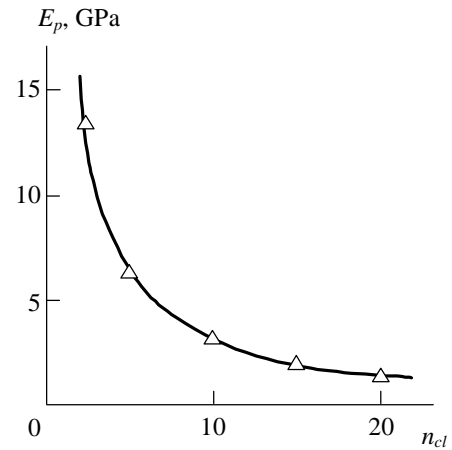

Fig. 3. The dependences of elasticity modulus E_p on segments number n_{cl} in one nanocluster, calculated according to the Eq. (11) for PC at $T = 293$ K

4. Conclusions

Therefore, the present paper results have shown that the elasticity modulus of amorphous glassy polycarbonate, considering as natural nanocomposite, is defined completely by its suprasegmental structure state. This state can be described quantitatively within the frameworks of the cluster model of polymer amorphous state structure and was characterized by the local order level. The reinforcement degree of natural nanocomposites can essentially exceed a similar parameter for artificial nanocomposites.

References

[1] Ivanchev S. and Ozerin A.: Vysokomol. Soed. B, 2006, **48**, 1531.

[2] Malamatov A., Kozlov G. and Mikitaev M.: Mekhanismy uprochneniya polimernych nanokompozitov. Izd-vo RKhTU Mendeleeva, Moskwa 2006.

[3] Kozlov G. and Zaikov G.: Structure of the polymer amorphous state. Brill Academic Publishers, Utrecht-Boston 2004.

[4] Richardson M. (Ed.): Polymer Engineering Composites. Applied Science Publishers LTD, London 1979.

[5] Ahmed S. and Jones F.: J. Mater. Sci., 1990, **25**, 4933.

[6] Vasserman A. and Kovarskiy A.: Spinovye metki i zondy v fiziko-khimii polimerov. Nauka, Moskwa 1986.

[7] Kozlov G., Shogenov V. and Mikitaev A.: Inzhenerno-Fizicheskiy Zh., 1998, **71**, 1012.

[8] Aharoni S.: Macromolecules, 1985, **18**, 2624.

[9] Wu S.: J. Polymer Sci. B, 1989, **27**, 723.

[10] Aharoni S.M.: Macromolecules, 1983, **16**, 1722.

[11] Budtov V.: Fizicheskaya khimiya rastvorov polimerov. Khimiya, Sankt-Peterburg 1992.

[12] Kozlov G. and Novikov V.: Sinergetika i fraktal'nyi analiz schitykh polimerov. Klassika, Moskwa 1998.

[13] Balankin A.: Sinergetika deformiruemogo tela. Izd-vo Ministerstva oborony SSSR, Moskwa 1991.

[14] Kozlov G. and Sanditov D.: Angarmonicheskie efekty i fiziko-mechanicheskie svoistva polimerov. Nauka, Novosibirsk 1994.

[15] Kozlov G. and Aloev V.: Teoriya perkolyatsii v fiziko-khimii polimerov. Polygraphservis i T., Nal'chik 2005.

[16] Aloev V. and Kozlov G.: Fizika orientatsionnykh yavleniy v polimernyh materialah. Polygraphservis i T., Nal'chik 2002.

ПОЛІМЕРИ ЯК ПРИРОДНІ НАНОКОМПОЗИТИ. 1. СТРУКТУРНА МОДЕЛЬ ЗМІЦНЕННЯ

Анотація. *Запропоновано структурне оброблення аморфного склоподібного полікарбонату як природного нанокомпозиту. Показано, що міцність полікарбонатів повністю визначається їх структурою, яка описана в межах локальної моделі. Встановлено значне збільшення запасу міцності для аморфних склоподібних полімерів.*

Ключові слова: *полікарбонат, нанокомпозит, структура в твердому стані, ЕПР, зміцнення.*