

*Georgiy Kozlov<sup>1</sup>, Boris Dzhangurazov<sup>1</sup>, Gennady Zaikov<sup>2</sup>  
and Abdulakh Mikitaev<sup>1</sup>*

## THE NANOCOMPOSITES POLYETHYLENE/ORGANOCLAY PERMEABILITY TO GAS DESCRIPTION WITHIN THE FRAMEWORKS OF PERCOLATION AND MULTIFRACTAL MODELS

<sup>1</sup> *Kabardino-Balkarian State University; 173, Chernyshevsky str., 360004 Nal'chik, Russian Federation*

<sup>2</sup> *N.M. Emanuel Institute of Biochemical Physics of Russian Academy of Sciences*

*4, Kosygin str., 119334 Moscow, Russian Federation*

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**Abstract.** It has been shown that permeability to gas coefficient reduction at the layered nanofiller introduction in polyethylene is due to polymer matrix fraction decrease, which is accessible for gas transport processes. Two models (percolation and multifractal ones) are offered for this reduction quantitative description.

**Keywords:** nanocomposite, organoclay, permeability to gas, interfacial regions, percolation and multifractal models.

### 1. Introduction

For the last 15 years nanocomposites polymer/organoclay elaboration causes great interest because of their physical and mechanical properties essential improvement in comparison with the initial matrix polymer at small (no more than 10 mas %) nanofiller contents [1, 2]. The essential reduction of permeability to gas coefficient  $P$  is one of the indicated changes of these nanocomposites properties. So, in a number of papers [3-7] it has been shown, that the introduction of montmorillonite in polyethylenes at volume contents of the latter 0.005–0.035 decreases the value  $P$  in several times in comparison with the initial matrix polymer. The analysis of this effect fulfilled by the authors of the indicated papers, assumes that permeability to gas coefficient reduction is related to essential increase of gas molecules way winding at diffusion through a nanocomposite film, containing montmorillonite anisotropic particles, but not to matrix polyethylene structure change at nanofiller (montmorillonite) introduction. As a rule while describing this effect the models where the main parameter is a ratio of montmorillonite platelet, *i.e.* its anisotropic were used [4, 8]. However there are also other models describing this effect and taking into

consideration characteristics of both nanocomposite structure and gas-penetrant molecule structure. For example, the multifractal model [9] allows a quantitative estimation of gas-penetrant molecules way winding degree through a polymer material. Therefore the purpose of the present paper is structural analysis of permeability to gas coefficient reduction effect for nanocomposites low density polyethylene/montmorillonite [7] with percolation and multifractal models usage.

### 2. Experimental

Low density polyethylene (LDPE) of El-Lene industrial mark, LD1905F with a melt flow index 5 g/10 min and density 0.919 g/cm<sup>3</sup> was used as a matrix polymer. Purified Na<sup>+</sup>-montmorillonite of Bentolite H mark (MMT) was used as a nanofiller. To prepare the organoclay, MMT was mixed with di(hydrogenated tallowalkyl) dimethyl ammonium chloride. Polyethylene grafted maleic anhydride was applied as a compatibilizing agent [7].

Nanocomposites LDPE/MMT were prepared by the components mixing in melt using twin-screw extruder Thermo Haake Rheomex RTW at temperature of 433 K and screw speed of 150 rpm [7].

Tensile tests were performed by using a mechanical testing machine Instron, model 5567, at temperature of 293 K and strain rate  $\sim 2 \cdot 10^{-2}$  s<sup>-1</sup>. For each test, 10 film specimens (50–60  $\mu$ m thickness) were used [7].

The measurements of permeability to gas coefficient for initial LDPE and nanocomposites LDPE/MMT were performed using Oxygen Permeation Analyzer (model 8501) with automatic recording of the indicated parameter [7].

### 3. Results and Discussion

The authors [10] proposed the percolation relationship for polymer composites reinforcement degree  $E_c/E_m$  description:

$$\frac{E_c}{E_m} = 1 + 11j_n^{1.7} \quad (1)$$

where  $E_c$  and  $E_m$  are elasticity moduli of composite and matrix polymer, relatively:  $j_n$  is filler volume contents.

The following modification of the Eq. (1) was offered for polymer nanocomposites [11]:

$$\frac{E_n}{E_m} = 1 + 11(j_n + j_{if})^{1.7} \quad (2)$$

where  $E_n$  is a nanocomposite elasticity modulus,  $j_{if}$  is an interfacial regions relative fraction.

The nanofiller volume fraction  $j_n$  was determined according to the known equation [11]:

$$j_n = \frac{W_n}{r_n} \quad (3)$$

where  $W_n$  is a nanofiller mass contents,  $r_n$  is montmorillonite density equal approximately to  $2000 \text{ kg/m}^3$  [4].

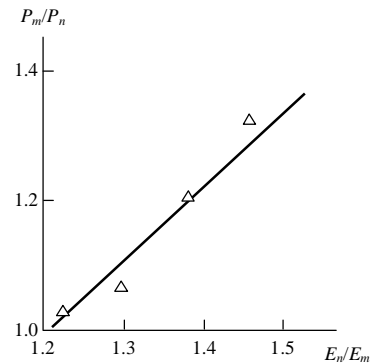
As a rule, the increase of nanofiller contents  $j_n$  (or  $W_n$ ) is accompanied by  $E_n$  enhancement and reduction of permeability to gas coefficient  $P_n$  for nanocomposites in comparison with similar parameter for matrix polymer  $P_m$ . Since at the deduction of the Eq. (1) derivation regulations were applied, which are true in gas transport processes case as well (nanofiller critical concentration absence, much lower nanofiller permeability to gas coefficient in comparison with  $P_m$ ), then the equation (2) can be used for permeability to gas coefficient relative change description in the following form:

$$\frac{P_m}{P_n} = 1 + 11(j_n + j_{if})^{1.7} \quad (4)$$

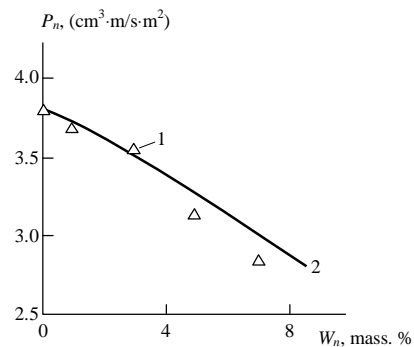
where the total value  $(j_n + j_{if})$  can be obtained by mechanical testing results according to the Eq. (2).

The comparison of Eqs. (2) and (4) shows that  $E_n/E_m$  increase should be accompanied by  $P_m/P_n$  enhancement or  $P_n$  reduction. In Fig. 1 the relation between reinforcement degree  $E_n/E_m$  and relative permeability to gas coefficient  $P_m/P_n$  is adduced, which turns out to be linear with a slope close to one. However, this correlation does not pass through coordinates origin and at  $E_n/E_m \approx 1.22$  the value  $P_m/P_n = 1$ , i.e. at MMT small contents the value  $P_n$  is close to permeability to gas coefficient for matrix polymer. The indicated circumstance makes necessary the Eq. (4) modification as follows:

$$\frac{P_m}{P_n} = 0.78 + 11(j_n + j_{if})^{1.7} \quad (5)$$



**Fig. 1.** The comparison of relative coefficient of gas permeability  $P_m/P_n$  and reinforcement degree  $E_n/E_m$  for nanocomposites LDPE/MMT



**Fig. 2.** The comparison of the experimental (1) and calculated (2) according to the Eq. (5) dependences of permeability to gas coefficient  $P_n$  on organoclay mass contents  $W_n$  for nanocomposites LDPE/MMT

The comparison of the experimental and calculated in accordance with the Eq. (5) (percolation model) dependences of permeability to gas coefficient  $P_n$  as a function of nanofiller mass contents  $W_n$  for nanocomposites LDPE/MMT is shown in Fig. 2. As it follows from this comparison, the Eq. (5) gives precise enough description of permeability to gas coefficient for the studied nanocomposites at nanofiller contents growth (the theory and experiment average discrepancy makes up 3 %).

Another variant of nanocomposites permeability to gas coefficient  $P_n$  calculation assumes a gas transport multifractal model [9] usage. The indicated model allows to determine the value  $P_n$  as follows:

$$P_n = P_m \alpha_{ac} D_{ch} \quad (6)$$

where  $\alpha_{ac}$  is a polymer nanocomposite relative fraction, accessible for gas transport processes,  $D_{ch}$  is fractal dimension of a polymer chain section between its fixation points (chemical cross-linking nodes, physical entanglements, clusters, etc.), which characterizes molecular mobility level in the polymer [9].

The authors [12] proposed the following equation for semicrystalline polymers permeability to gas coefficient estimation:

$$P = \frac{P_{am}}{tb} \quad (7)$$

where  $P_{am}$  is permeability to gas coefficient of completely amorphous polymer,  $t$  is a nonlinearity (winding) coefficient, which is due to the difficulty of gas-penetrant molecules transport ways between crystallites,  $b$  is the so-called polymer chains immobility coefficient.

The direct similarity between nanocomposites and semicrystalline polymers consists in the fact that both indicated polymer materials classes have regions, impenetrable for transport processes (nanofiller and crystallites, accordingly). Therefore the indicated processes are realized through a polymer matrix and amorphous phase, respectively. Hence, from the relationships (6) and (7) can be written:

$$P_m \sim P_{am} \quad (8)$$

$$t = \frac{1}{a_{ac}} \quad (9)$$

$$b = \frac{1}{D_{ch}} \quad (10)$$

Thus, the offered treatment assumes in general case not only nonlinearity coefficient  $t$  change because of nanofiller introduction, but polymer matrix structure change in virtue of coefficient  $b$  variation, depending on its molecular mobility level [9].

Let us consider estimation methods of parameters, included in the Eq. (6). The value  $P_m$  is accepted equal to value  $P$  for LDPE. As it is known [11], in the polymer nanocomposites a nanofiller and surrounded its particles interfacial regions with relative fractions  $j_n$  and  $j_{if}$ , relatively (see also the Eq. (5)) will be impenetrable for gas transport processes. Then the polymer matrix relative fraction  $a$  can be estimated as follows:

$$a = 1 - j_n - j_{if} \quad (11)$$

In its turn, the following relation between values  $j_n$  and  $j_{if}$  exists for the layered silicates [11]:

$$j_{if} = 1.910j_n \quad (12)$$

for exfoliated organoclay and

$$j_{if} = 0.955j_n \quad (13)$$

for an intercalated one.

The nanocomposites polymer matrix fraction, accessible for oxygen permeability,  $a_{ac}$  is determined according to the equation [9]:

$$a_{ac} = a^{d_{o_2}} \quad (14)$$

where  $d_{o_2}$  is an oxygen molecule diameter, which is equal to 2.9 Å [13].

Dimension  $D_{ch}$  can be determined with the aid of the following equation [14]:

$$\frac{2}{j_{cl}} = C_{\infty}^{D_{ch}} \quad (15)$$

where  $j_{cl}$  is a polymer matrix of relative fraction of local order domains (clusters),  $C_{\infty}$  is a characteristic ratio, which is a polymer chain statistical flexibility indicator [15].

For parameters  $j_{cl}$  and  $C_{\infty}$  estimation it is necessary to determine the fractal (Hausdorff) dimension of nanocomposites structure  $d_f$ , that can be made according to the equation [16]:

$$d_f = (d-1)(1+n) \quad (16)$$

where  $d$  is the dimension of Euclidean space, in which fractal is considered (it is obvious, that in our case  $d = 3$ ),  $\nu$  is the Poisson's ration, estimated according to mechanical tests results with the aid of the relationship [17]:

$$\frac{S_Y}{E_n} = \frac{1-2\nu}{6(1+\nu)} \quad (17)$$

where  $S_Y$  is a nanocomposites yield stress.

Further the value  $C_{\infty}$  can be calculated according to the equation [14]:

$$C_{\infty} = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3} \quad (18)$$

Then value  $j_{cl}$  was determined, by using the following formula [14]:

$$d_f = 3 - 6 \left( \frac{j_{cl}}{C_{\infty} S} \right)^{1/2} \quad (19)$$

where  $S$  is  $\phi$  macromolecule cross-sectional area, which is equal to 14.4 Å<sup>2</sup> for polyethylenes [18].

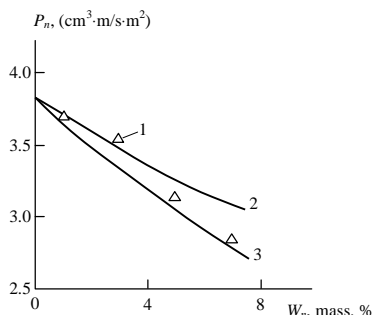
The crystallinity degree  $K$  of the studied nanocomposites can be estimated according to the equation [19]:

$$K = 0.32C_{\infty}^{1/3} \quad (20)$$

As estimations according to the Eqs. (15) and (20) have shown, the values  $D_{ch}$  and  $K$  change insignificantly ( $D_{ch} = 1.73-1.75$ ,  $K = 0.49-0.51$ ), therefore for the studied nanocomposites the Eq. (6) is simplified up to:

$$P_n = P_m (1 - j_n - j_{if})^{d_{o_2}} \quad (21)$$

In Fig. 3 the comparison of the experimental and calculated according to the Eq. (21) (multifractal model) in supposition of both exfoliated and intercalated layered silicate dependences  $P_n(W_n)$  for nanocomposites LDPE/MMT is adduced. As one can see, the multifractal model of gas transport processes also gives a good correspondence with the experiment (the theory and experiment average discrepancy makes up 3 %).



**Fig. 3.** The comparison of the experimental (1) and calculated (2, 3) according to the Eq. (21) in supposition of intercalated (2) and exfoliated (3) nanofiller dependences of permeability to gas coefficient  $P_n$  on organoclay mass contents  $W_n$  for nanocomposites LDPE/MMT

## 4. Conclusions

The layered nanofiller introduction in low density polyethylene results to gas coefficient reduction in the received nanocomposites permeability. The fulfilled structural analysis of this effect demonstrated, that the indicated reduction was due to the decrease of polymer matrix relative fraction, accessible for the gas transport process, in virtue of both nanofiller introduction and interfacial regions formation. Both used theoretical models (percolation and multifractal ones) give correct quantitative description of permeability to gas coefficient reduction at nanofiller contents increasing.

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## ОПИС ГАЗОПРОНИКНОСТІ НАНОКОМПЗИТИВ ПОЛІЕТИЛЕН/ОРГАНОГЛИНА В РАМКАХ ПЕРКОЛЯЦІЙНОЇ ТА МУЛЬТИФРАКТАЛЬНОЇ МОДЕЛЕЙ

**Анотація.** Запропоновано дві моделі для кількісного опису зниження коефіцієнта газопроникності (перколяційна та мультифрактальна) при введенні шарового нанонаповнювача в поліетилен. Показано, що зниження коефіцієнта газопроникності викликане зменшенням частки полімерної матриці, доступної для процесів газоперенесення.

**Ключові слова:** нанокмпозит, органоглина, газопроникність, міжфазові області, перколяційна і мультифрактальна моделі.