Georgiy Kozlov[1], Zarema Aphashagova[1], Akhmed Malamatov[1] and Gennady Zaikov[2]

THE STRUCTURAL MODEL OF IMPACT TOUGHNESS
OF PARTICULATE-FILLED POLYMER NANOCOMPOSITES

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

Abstract. A quantitative structural model of particulate-filled polymer composites impact toughness, based on the fractal analysis ideas, was offered. The model demonstrated good correspondence with the experimental data. It has been shown that the action of nanofiller as nucleator, resulting in crystallinity degree and amorphous phase structure change, exert the main influence on impact toughness value.

Keywords: nanocomposite, polyethylene, calcium carbonate, structure, fractal analysis, impact toughness.

1. Introduction

The authors of the papers [1, 2] found out that the introduction of particulate nanofiller (calcium carbonate, $CaCO_3$) in high density polyethylene (HDPE) results in about 20 % increase of nanocomposite $HDPE/CaCO_3$ impact toughness A_p as compared with neat polymer. The authors [1, 2] fulfilled the detailed fractographic analysis of this effect and explained the observed A_p increase by nanocomposite $HDPE/CaCO_3$ plastic deformation mechanism change in comparison with neat HDPE. Without going into detail of the mentioned analysis, doubts regarding its correctness appear. In Fig. 1 the schematic diagrams of load-time (*P-t*) are adduced for two cases of polymeric materials samples fracture: by instable (a) and stable cracks (b). As it is known [3], A_p value is characterized by the area under *P-t* diagram, which gives mechanical energy consumed at samples fracture. The polymeric materials macroscopic fracture process, defined by the magistral crack propagation, begins at the greatest load *P*. From *P-t* schematic diagrams it follows that fracture process proper exerts practically no influence on the value A_p in case of crack instable propagation and only partial influence – in case of stable crack. Although the authors [1, 2] performed impact testing on the

instrumented apparatus, allowing to obtain diagrams *P-t*, these diagrams were not adduced. Besides, the structural aspect of fracture process in papers [1, 2] is being considered with secondary structures (crazes, shearing zones, *etc.*) using. Their interconnection with neat non-deformed material structure is purely speculative. It is obvious that with such analysis method it is impossible to obtain structure-properties quantitative relationships (which is the main task of polymer physics [4]). Therefore the purpose of the present paper is quantitative structural analysis of HDPE and nanocomposite $HDPE/CaCO_3$ impact testing results within the frameworks of fractal models.
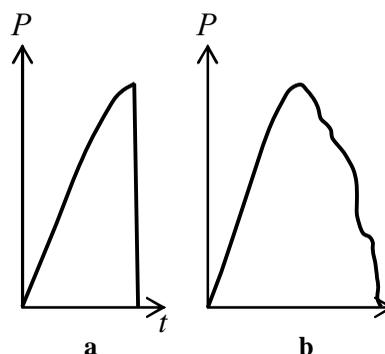
Fig. 1. Schematic diagrams of load-time (*P-t*) in instrumented impact tests. The fracture by instable (a) and stable (b) cracks.

2. Experimental

The experimental data were accepted according to the paper [2]. High density polyethylene with the molecular number and average weight of $1.46 \cdot 10^4$ and $5.50 \cdot 10^4$, respectively, was used as binding. Powder-like $CaCO_3$ with particles size of 50–60 nm was used as a nanofiller. $CaCO_3$ content makes 5 mas %.

The impact tests were carried out by Izod method on samples sized 63×12.7×3.0 mm. The samples have a notch with the length of 2.5 mm and tip radius of 0.1 mm. The tests were carried out on impact tester Tinius Olsen (Model 899) with impact velocity 1 m/s in the testing temperature range of 233–293 K.

The samples crystallinity degree K was determined with the help of differential scanning calorimetry (DSC).

3. Results and Discussion

As is known [5], the fractal dimension d_f is the most general informant of an object structure (in our case – polymeric material) and the true structural characteristic, describing structure elements distribution in space. The value d_f can be determined according to the equation [6]:

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

where j_{cl} is a relative fraction of local order domains (clusters) in polymeric material structure, C_∞ is characteristic ratio, which is equal to 7 for polyethylenes [7], S is macromolecule cross-sectional area, which is equal to 14.3 Å^2 for HDPE [8].

The j_{cl} value is determined according to the following percolation relationship [9]:

$$j_{cl} = 0.03(1 - K)(T_m - T)^{0.55} \tag{2}$$

where K is cristallinity degree, equal to 0.48 and 0.55 for neat HDPE and nanocomposite HDPE/CaCO$_3$, respectively [2], T_m is melting temperature, equal to ~ 406 and 405 K for the mentioned materials, respectively [2], T is testing temperature.

Let us note that d_f calculation according to Eq. (1) gives values, corresponding to other methods of this parameter estimation. So the value d_f can be calculated alternatively according to the following equation [10]:

$$d_f = (d - 1)(1 + n) \tag{3}$$

where d is dimension of Euclidean space, in which fractal is considered (it is obvious, that in our case $d = 3$), ν is Poisson's ratio, estimated with the aid of the relationship [11]:

$$\frac{s_Y}{E} = \frac{1 - 2n}{6(1 + n)} \tag{4}$$

where σ_Y is yield stress, E is elasticity modulus.

The estimations according to Eqs. (1) and (4) have given the following d_f values at the testing temperature of 293 K: 2.73 and 2.68 for HDPE and 2.75 and 2.73 for nanocomposite HDPE/CaCO$_3$. As one can see, a good enough correspondence is obtained – the discrepancy by d_f fractional part, which has the main information amount about structure, does not exceed 7 %.

In Fig. 2 the dependence $A_p(d_f)$ for the studied polymeric materials is adduced, which has turned out to be linear, common for the neat HDPE and nanocomposite HDPE/CaCO$_3$ and is described by the following empirical correlation:

$$A_p = 13.5(d_f - 2.5), \qquad \text{kJ/m}^2 \tag{5}$$

From Eq. (5) it follows that at $d_f = 2.5$ the value $A_p = 0$. The mentioned fractal dimension corresponds to the ideally brittle fracture condition [10], that defines the condition $A_p = 0$. For real solids the greatest fractal dimension of their structure is equal to 2.95 [10], which allows to determine the greatest value of A_p according to Eq. (5), which is equal to ~ 6.1 kJ/m^2.
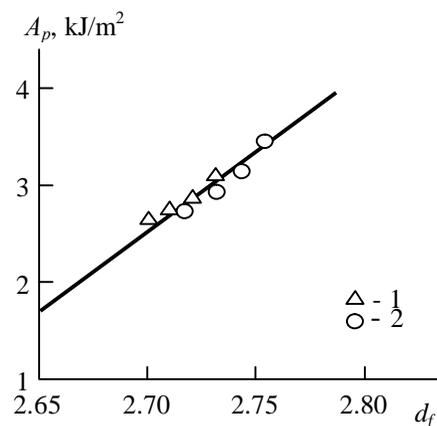
Fig. 2. The dependence of impact toughness A_p on structure fractal dimension d_f for HDPE (1) and nanocomposite HDPE/CaCO$_3$ (2)

As Kausch has shown [12], energy dissipation at an impact grows at polymeric materials molecular mobility level increase. Within the frameworks of fractal analysis this level can be characterized with the aid of the fractal dimension D_{ch} of a polymer chain part between its fixation points (chemical crosslinks, physical entanglements nodes, clusters, *etc*.) [6]. Such analysis method was applied successfully for the value A_p description in case of particulate-filled nanocomposites phenylone/*b*-sialone [13]. The D_{ch} value can be determined with the aid of the following equation [6]:

$$D_{ch} = \frac{\ln N_{cl}}{\ln(4 - d_f) - \ln(3 - d_f)} \tag{6}$$

where N_{cl} is a statistical segments number per chain part between clusters, which is determined as follows.

Firstly the density of physical entanglements cluster network ν_{cl} is determined [6]:

$$n_{cl} = \frac{j_{cl}}{C_\infty l_0 S} \tag{7}$$

where l_0 is the main chain skeletal bond length, which is equal to 1.54 Å for polyethylenes [7].

Then the estimation of polymer chains total length per polymer volume unit L was carried out as follows [6]:

$$L = S^{-1} \tag{8}$$

The chain part length between clusters L_{cl} is determined according to the equation [6]:

$$L_{cl} = \frac{2L}{n_{cl}} \tag{9}$$

The statistical segment length l_{st} is determined as follows [14]:

$$l_{st} = l_0 C_\infty \tag{10}$$

And at last the value N_{cl} can be determined as ratio [6]:

$$N_{cl} = \frac{L_{cl}}{l_{st}} \tag{11}$$

In Fig. 3 the dependence of impact toughness A_p on fractal dimension D_{ch} for the studied materials is adduced. As it should be expected, A_p growth at D_{ch} increase is observed and is analytically described by the following relationship:

$$A_p = 6.75\left(D_{ch} - 1\right), \qquad \text{kJ/m}^2 \tag{12}$$

The Eq. (12) allows to determine the greatest value A_p for the studied materials at the condition $D_{ch} = 2.0$: this value is equal to 6.75 kJ/m^2, that is close to the cited above estimation according to the Eq. (5) – the average discrepancy makes less than 10 %.

Let us consider the condition of zero impact toughness reached at $d_f = 2.50$, but not at $d_f = 2.0$ ($2.0 \leq d_f \leq 3.0$ [10]). As it is known [15], at j_{cl} growth irrespective of its causes the polymers structure in general and HDPE in particular reaches its quasiequilibrium state, when j_{cl} growth is balanced by entropic tightness of polymer chains and then ceases. As it was shown in paper [15], for HDPE dimension of the structure quasiequilibrium state was equal to 2.50. The calculation according to the adduced above methods (the Eqs. (2) and (6)-(11)) shows that in this case $D_{ch} \approx 1.0$ and, consequently, polymeric material becomes ideally brittle.

Using the Eqs. (5) and (12) allows to estimate the theoretical values of A_p^T and compare them with the experimental magnitudes A_p of this parameter. Such comparison is presented in Fig. 4, from which good correspondence of theory and experiment follows (for calculation according to the Eq. (5) the average discrepancy of A_p^T and A_p makes 3.5 %, according to the Eq. (12) – 3.9 % that is essentially lower than the usual error of impact toughness experimental determination, which makes ~ 10 %).
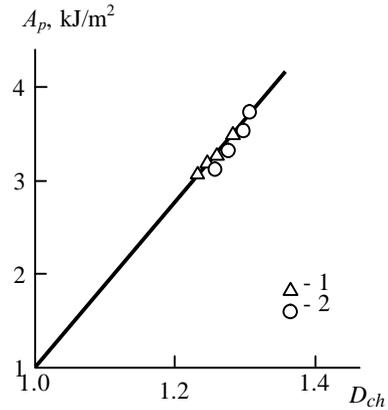
Fig. 3. The dependence of impact toughness A_p on fractal dimension D_{ch} of chain part between clusters for HDPE (1) and nanocomposite HDPE/CaCO$_3$ (2)
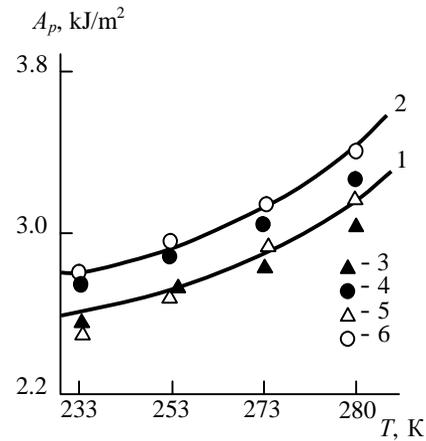
Fig. 4. The comparison of experimental (1, 2) and calculated according to the Eqs. (5) (3, 4) and (12) (5, 6) temperature dependences of impact toughness A_p for HDPE (1, 3, 5) and nanocomposite HDPE/CaCO$_3$ (2, 4, 6)

Let us consider the physical grounds of impact toughness increasing effect for nanocomposite HDPE/CaCO$_3$ in comparison with matrix polymer HDPE. The A_p increase, as follows from the plots of Figs. 2 and 3, is defined by enhancement of dimensions d_f and D_{ch}, respectively. In its turn, as it follows from the Eqs. (1) and (6), the mentioned dimension enhancement is defined by j_{cl} reduction, since molecular characteristics C_∞ and S are accepted constants. The j_{cl} reduction, as follows from the Eq. (2), depends only on crystallinity degree K raising, since the values T_m for HDPE and nanocomposite HDPE/CaCO$_3$ are practically the same. This means that the increasing A_p effect for nanocomposites HDPE/CaCO$_3$ in comparison with matrix polymer is due to the action of nanofiller CaCO$_3$ as nucleator, promoting K enhancement [1, 2].

4. Conclusions

Therefore, the quantitative correlation of impact toughness of high density polyethylene and particulate-filled nanocomposite on its basis with structural characteristics of these materials is obtained within the frameworks of fractal analysis. The impact toughness enhancement is due to the action of nanofiller as nucleator and corresponding change of amorphous phase structure. The theoretical calculation showed good correspondence to the experimental data.

References

[1] Tanniru M. and Misra R.: Mater. Sci. Eng., 2005, **A405**, 178.
[2] Deshmane C., Yuan Q. and Misra R.: Mater. Sci. Eng., 2007, **A452-453**, 592.
[3] Bucknall C.: Toughened Plastics. Applied Science, London 1977.
[4] Bartenev G. and Frenkel S.: Fizika Polimerov. Khimiya, Leningrad 1990.
[5] Kuseev I., Samigullin G., Kulikov D. and Zakirnichnaya M.: Slozhnye Sistemy v Prirode i Tekhnike. Izd-vo ISNTU, Ufa 1997.
[6] Kozlov G. and Novikov V.: Uspekhi Fizicheskich Nauk, 2001, **171**, 717.
[7] Aharoni S.: Macromolecules, 1983, **16**, 1722.
[8] Aharoni S.: Macromolecules, 1985, **18**, 2624.
[9] Kozlov G., Gazaev M., Novikov V. and Mikitaev A.: Pis'ma v Zh. Tekhnicheskoi Fiziki, 1996, **22**, 31.
[10] Balankin A.: Sinergetika Deformiruemogo Tela. Izd-vo Ministersva oborony SSSR, Moskwa 1991.
[11] Kozlov G. and Sanditov D.: Angarmonicheskie Effekty i Fiziko-Mekhanicheskie Svoistva Polimerov. Nauka, Novosibirsk 1994.
[12] Kausch H.: Polymer Fracture. Springer-Verlag, Berlin, Heidelberg, New York 1978.
[13] Aphashagova Z., Kozlov G., Burya A. and Malamatov A.: Materialy Khar'kovskoy Nanotekhnologicheskoy Assamblei, Khar'kov 2007, 204.
[14] Wu S.: J. Polymer Sci. B, 1989, **27**, 723.
[15] Kozlov G. and Zaikov G. (Eds.): Fractals and Local Order in Polymeric Materials. Nova Science Publishers, Inc., New York 2001.

СТРУКТУРНА МОДЕЛЬ УДАРНОЇ В'ЯЗКОСТІ ДИСПЕРСНО-НАПОВНЕНИХ ПОЛІМЕРНИХ НАНОКОМПОЗИТІВ

Анотація. *Запропоновано кількісну структурну модель ударної в'язкості дисперсно-наповнених полімерних нанокомпозитів на основі уявлень фрактального аналізу. Вказана модель добре узгоджується з експериментальними даними. Показано, що основний вплив на величину ударної в'язкості має дія наповнювача як утворювача зародків, що призводить до зміни ступеня кристалічності і структури аморфної фази.*

Ключові слова: *нанокомпозит, поліетилен, карбонат кальцію, структура, фрактальний аналіз, ударна в'язкість.*