Chapter 7

AN INFLUENCE OF MICA SURFACE ON MODEL REACTION OF REETHERIFICATION

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ABSTRACT

The applicability of scaling approach for analysis of mica catalytic activity in model reaction of reetherification is shown. The change of space dimension, in which passing reaction, essentially influences on its intensity. For reaction rate increase is required raising of both Euclidean space dimension and diffusivity of reagents.

Keywords: Polyether, reetherification, catalysis, mica, reaction kinetics, scaling approach.

INTRODUCTION

Composite polymeric materials with improved properties find wide applicability in modern technology. One of the most progressive trends of filled materials making, where the filler defines synthesis kinetics, structure and properties of final product and at the same time performs the role of catalyst, is polymer's synthesis in the presence of inorganic fillers [1, 2].

Saturated complex polyethers, particular polybutylenetherephtalate (PBT), are used as enginiring thermoplasts, having a good thermo- and wear stability, excellent performance. These properties allow also to apply them as a matrix material for polymer composites [3]. One of the perspective ways of effective filler-catalysts searching is kinetic study of reetherification model reaction, performed in the presence of various inorganic compounds. The elucidation on the example of model system of the most effective filler-catalysts number allows to use them for receiving filled PBT and compare catalytic activity of filler and traditional catalysts.

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The catalysis process reflects a complex interconnection between chemical and geometric parameters of surface. That is why the purpose of the present paper is clarification of influence of filler-catalyst (mica) surface structure on kinetics of reetherification model reaction.

EXPERIMENTAL

The reetherification model reaction kinetics of methylbenzoate by heptanole-1 in mica presence is studied at 443 K. Mica catalytic activity is estimated on the dependence conversion degree-time (*Q-t*) at twentieth multiple of heptanole-1 excess and mica contents 30 mass. % in calculation on the methylbenzoate [2].

The reetherification kinetics is studied on the gas chromatograph "Biokhrom" with using as internal standard diphenyloxide according to the earlier described method [1].

The mica flagopit with polydispersity 0.749 and average probable particles size 0.23×10^{-6} m is used. The initial mica (conditional designation NMM) and also mica chemically modified by sodium hydroxide (SMM) and sulphur acid (AMM) were applied.

RESULTS AND DISCUSSION

For influence analysis of mica surface on reetherification reaction the scaling approach is used [4]. As an example let's consider the reaction in which particles P of a chemical substance diffuse in the medium, containing the randomly located static nonsaturated traps T. By the contact of a particle P with a trap T, the particle disappears. Nonsaturation of a trap means that the reaction P+T→T can repeat itself an infinite number of times. It is usually considered that the concentration of particles and traps is large or the reaction occurs at intersive stirring, and the process can be considered as the classical reaction of the first order. In this case, it is possible to consider that the concentration decay of particles c decreases with time *t* as [4]:

$$c(t) \approx \exp(-At) \tag{1}$$

where *A* is constant, proportional to the trap concentration.

However, if the concentration of the randomly located traps is small, with necessity exist space areas (reaction medium), practically free from traps. The particles getting into these areas can reach the traps only during a rather long period of time and, hence, the decrease of their number in the reaction course will be slower. The formal analysis of this problem shows that the concentration of particles falls down under the law [4]:

$$c(t) \sim \exp\left(-Bt^{d/(d+2)}\right) \tag{2}$$

being dependent on the space dimension *d* (*B* is constant).

It is necessary to mark, that the singular dependence on time in the equation (2) appears simultaneously with large-scale fluctuations (inhomogeneity) of traps density. If the traps can move, their mobility averages the influence of spatial heterogeneity, so the assumptions resulting to (1) will be carried out better. It was shown, that in this case the concentration of the particles drops under the combined law [4]:

$$c(t) \sim \exp(-At)\exp\left(-Bt^{d/(d+2)}\right) \tag{3}$$

where A is proportional to the traps diffusivity.

Since the reetherification reaction elapses with intensive stirring due to both passing of inert gas through reactive medium and mechanical stirring ("scavenger" reaction [5]), then for theoretical description of reagents concentration decay $c(t)(=1-Q)$ with time t we use the relationship (3). In Fig. 1-3 the fit of theory and experiment for reetherification reactions without mica (Fig. 1), in the presence of NMM (Fig. 2) and AMM (Fig. 3) is shown. The data for SMM are analogous to the shown in Fig. 2 results for NMM and therefore are not shown. Two space dimensions d are used, in which the reaction elapses: $d=2$ and $d=3$. As can be see reetherification reaction without mica is approximately equally described by both cases, but better correspondence is reached by using $d=3$. For reaction in the presence of NMM (and SMM) the space transition from $d=3$ to $d=2$ is observed, i.e., such transition assumes elapsing of reetherification reaction on the flat surface (the mica surface dimension $d_{sp}=2$ [6]) of filler-catalyst. And at last in case of AMM the space dimension becomes again equal to 3.
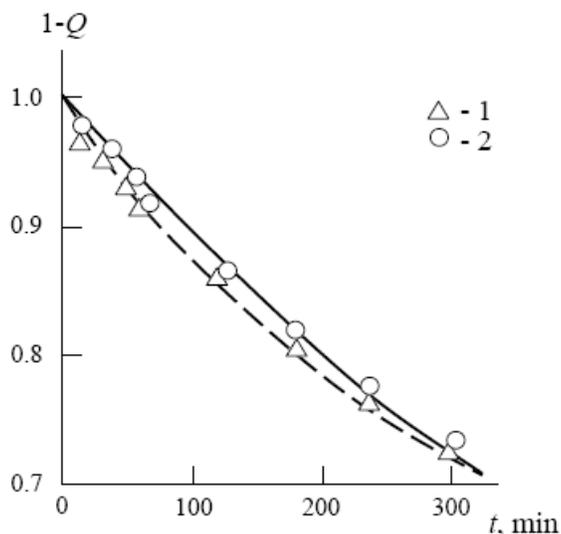

Figure 1. The dependences (1-Q) on t, corresponding to the relationship (3), for reetherification reaction without mica at d=2 (1) and d=3 (2). Solid line is experimental data
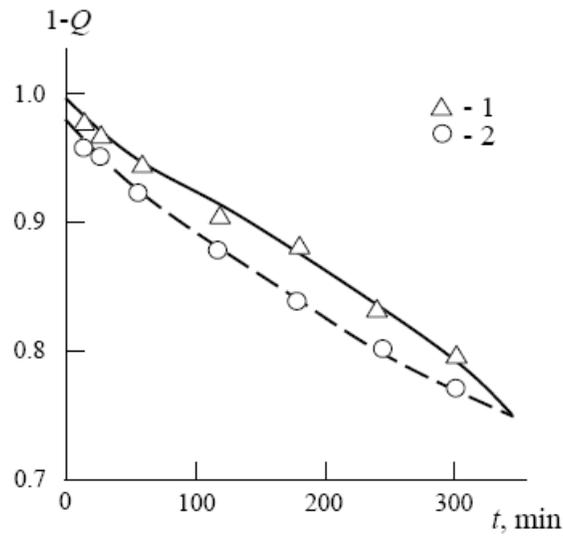
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Figure 2. The dependences (1-Q) on t, corresponding to the relationship (3), for reetherification reaction in presence of NMM. The notation is the same, as in a Fig. 1
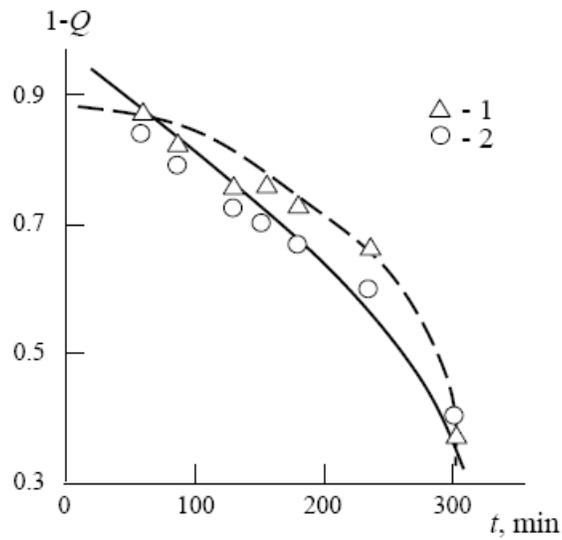

Figure 3. The dependences (1-Q) on t, corresponding to the relationship (3), for reetherification reaction in presence of AMM. The notation is the same, as in a Fig. 1

Let's consider physical principles of mentioned dimension changes and, hence, space type in which considered reaction elapses. The value d_{sp} for three mica types can be estimated with the aid of the relationship [7]:

$$k_{2KT} \sim t^{(1-d_{sp})/2} \qquad\qquad (4)$$

where k_{2KT} is catalysis rate constant of the second order accepting according to the data of paper [2]. The constant in the relationship (4) can be determined at condition $d_{sp}=2.0$ for NMM [6].

In table 1 the relationship (3) constants are accepted at which using the best correspondence with experiment (A, B and d) is obtained and the values d_{sp} are also estimated according to the equation (4). As can be seen, mica processing by sodium hydroxide practically does not change the value d_{sp} for SMM in comparison with the initial mica NMM, whereas processing by sulphur acid results to the fact, that AMM surface becomes fractal object with dimension $d_{sp}=2.23$. If the values d_{sp} for NMM and SMM characterize the essence of Euclidean surface and, hence, are considered in $d=2$, then for AMM fractal surface with $d_{sp}>2$ can be considered only in Euclidean space with $d=3$, that is observed according to the data of Fig. 3 and Table 1. The increase d_{sp} for AMM in comparison with similar value for NMM and SMM completely co-ordinates with specific surface raising S_u for the first ($S_u \approx 21.3$ and 18.4 m^2/g, accordingly [2]).

The space dimension change results to variation of reactive medium effective volume V_{ef}, in which reaction can elapse. The value V_{ef} is determined as that [8]:

$$V_{ef} = L^{d_{ef}} \varepsilon^{3-d_{ef}} \tag{5}$$

where L is upper limit of fractal behaviour, ε is measurement scale, d_{ef} is effective medium dimension.

**Table 1. The characteristics of filler-catalyst (mica),
applied in model reaction of reetherification**

Mica	d	$A \times 10^4$	$B \times 10^3$	d_{sp}	V_{ef}, relative units
Is not	3	5.2	5.0	-	8
NMM	2	5.2	4.0	2.0	2
SMM	2	4.8	3.9	1.964	2
AMM	3	10.0	10.0	2.230	8

The estimation V_{ef} according to the equation (5) at arbitrary values $L=2$, $\varepsilon=0.5$ and condition $d_{ef}=d$ shows essential distinction of effective volume for considered reactions (table 1). As it has been noted above, the constant A in the relationship (3) is proportional to traps diffusivity [4, 5]. It is necessary to wait, that the increase both V_{ef} and A (traps diffusivity) results to the conversion degree Q raising of reetherification reaction. In Fig. 4 the dependence of value Q at $t=300$ min. on product AV_{ef} (in relative units) for studied reactions confirmed this assumption is shown. The pointed dependence is linear, i.e., factors A and V_{ef} have equal influence degree on value Q, and passes through coordinates origin, i.e., obvious condition is observed: at $A=0$ or $V_{ef}=0$ $Q=0$.

The expounded above results allow to explain the kinetics of reetherification model reaction. In Fig. 5 kinetic curves Q-t for four studied reactions are shown. They are all linear, i.e., reetherification reaction elapses in Euclidean space with dimension $d=2$ or $d=3$ (see table 1). The reaction without mica occupies intermediate position because of a larger dimension d, but relatively small diffusivity.
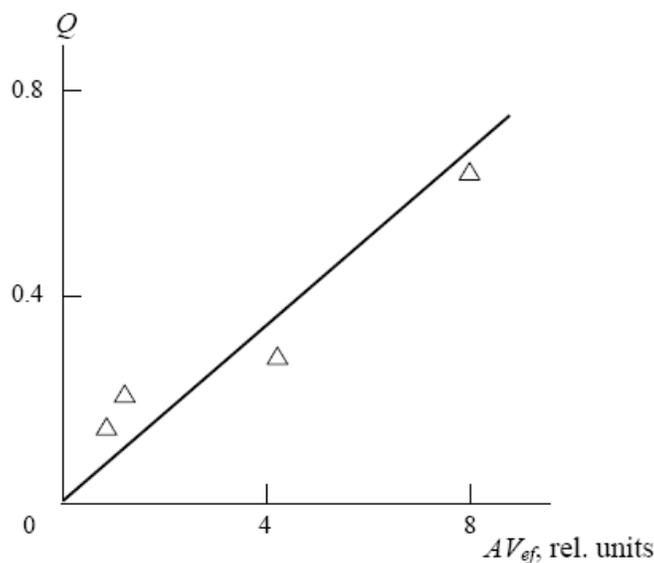
Figure 4. The dependence of conversion degree Q at t=300 min on product AV_{ef} for reetherification reactions
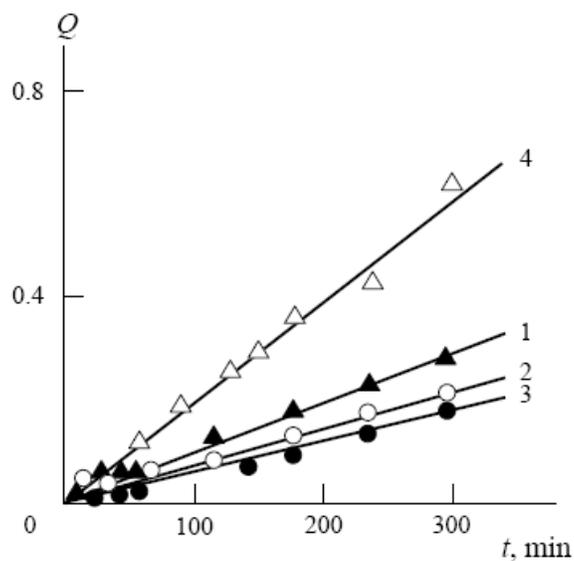

Figure 5. Kinetic curves conversion degree-time (Q-t) for reetherification reactions without mica (1) and in presence of NMM (2), SMM (3), AMM (4)

Introduction in reactive medium NMM and SMM results to the decrease of both d and A, that reduces the reaction intensity. And at last, for reetherification reaction in the presence of AMM are obtained the largest values of both d (d=3) and A (diffusivity), by virtue of which this reaction elapses much more rapidly than the rest. Also let's note, that coefficient B in the relationship (3) is proportional to reactive sites number of reagents [5] and its value is the largest for reetherification reaction in the presence of AMM (Table 1).

CONCLUSION

Therefore, the results of present paper have shown the applicability of scaling approach for analysis of mica catalytic activity in model reaction of reetherification. The change of space dimension, in which the reaction passes, essentially influences on its intensity. For reaction rate increase is required raising of both Euclidean space dimension and diffusivity of reagents.

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Chapter 8

THE INTERRELATION OF ELASTICITY MODULUS AND AMORPHOUS CHAIN'S TIGHTNESS FOR NANOCOMPOSITES BASED ON THE POLYPROPYLENE

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ABSTRACT

The interrelation of elasticity modulus and amorphous chain's tightness characterized by fractal dimension of chain part between its fixation points for nanocomposites based on the polypropylene is shown. This assumes the polymeric matrix structure change in comparison with initial polymer: the role of densely-packed regions for it is played by interphase areas. An offered fractal model allows estimation of elasticity modulus limiting values.

Keywords: Nanocomposite; polypropylene; elasticity modulus; amorphous chain tightness; fractal analysis.

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INTRODUCTION

At present time it is assumed [1], that the elasticity modulus E of semi-crystalline polymers is controled by structure (topology) of noncrystalline areas. The authors [2] were offered the model, according which value E increases at amplification of chains tightness in amorphous areas (amorphous chains) of the mentioned polymers. This model was applied succesfully for description of elasticity modulus behaviour of compositions based on the high density polyethylene modified by highly dispersed mixture Fe/FeO [1]. However, the degree of amorphous chains tightness can also be experessed within the framework of fractal analysis using for this dimension D of chain part between its fixation point (physical entanglements, chemical cross-linking nodes and so on) [3]. The value D is varied in limits $1<D\leq2$ and at $D=1$ the chain is fully streched between its fixation points (mobility of this chain part is freezed). At $D=2$ the chain has maximally possible mobility which is typical for rubber state of polymers [3]. This allows enough simple and adequate description of amorphous chains tightness degree with the aid of dimension D. The purpose of present paper is to give the development of fractal analoque of model [2] and with its aid to receive the description of behaviour of elasticity modulus of nanocomposites based on the polypropylene.

EXPERIMENTAL

The data of paper [4] for nanocomposites based on industrial isotactic polypropylene (PP) of manufacture Shell Co. is used. As a filler natural clay Na^+-montmorillonite is used modified by four modificators, with volume contents φ_f=0.025, 0.050 and 0.10. The more detailed description of nanocomposites in paper [4] is cited. Specimens for mechanical testing in the form of dog-bone with base lenght 10 mm and thichness 0.2 mm were produced by pressing from the melt at 473 K. The tension testing was made at temperatures 293 and 373 K and strain rate 8.3×10^{-3} s^{-1} [4].

RESULTS AND DISCUSSION

As it is known [4], Na^+-montmorillonite is layered silicate the plates of which have smaller thichness than their width and length. Therefore it is assumed, that the structure of nanocomposite having that filler besides actually Na^+-montmorillonite has crystalline regions, amorphous (rubber) phase and interfacial areas. In this case reinforcement degree E_c/E_m can be written in the following form [5]

$$\frac{E_c}{E_m} = \left[1+11\left(\varphi_f + \varphi_{int}\right)^{1.7}\right] \tag{1}$$

where E_c and E_m are elasticity modulus of nanocomposite and matrix polymer accordingly, φ_{int} – relative fraction of interfacial areas. The equation (1) allows to determine the φ_{int} value on the base of experimental values E_c, E_m and φ_f.

The calculation of dimension D was made according to following method. First of all fractal (Hausdorff) dimension of nanocomposite structure d_f was determined according to the equation [3]

$$d_f = (d-1)(1+\nu) \tag{2}$$

where d is dimension of Euclidean space, in which the fractal is considered (obviously, in our case $d=3$), ν is Poisson's ratio estimated on the mechanical testing results with the aid of relationship [1]

$$\frac{\sigma_Y}{E} = \frac{1-2\nu}{6(1+\nu)} \tag{3}$$

where σ_Y is yielding stress.

The value of characteristic ratio C_∞, which is the indicator of polymeric chain statistical flexibility, is determined according to the following equation [3]

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

Orthorhombic crystallinity degree K of polymer is connected with parameter C_∞ by the equation [6]

$$K = 0.32C_\infty^{1/3} \tag{5}$$

Now the value of fractal dimension D can be calculated with the aid of the following equation [7]

$$\frac{2(1-K)}{\varphi_{int}} = C_\infty^D \tag{6}$$

In a Fig. 1 the dependences of elasticity modulus E_c on dimension D at two mentioned above testing temperatures T for nanocomposites based on the PP are shown. Just as it was expected, linear increase of E_c at decrease D or amplification of amorphous chains tightness is observed. Two various straight lines for two testing temperatures are obtained, according which the maximally reached values E_c^{max} can be determined: at $T=293$ K $E_c^{max}=1.16$ GPa, at $T=373$ K $E_c^{max}=0.53$ GPa. It should be noted, that one of the advantages of fractal analysis is availability of precisely determined dimension limits (for example, $1<D\leq2$ [7]), that allows estimation of limiting values of any property. The data of Fig. 1 allow to receive analytical relationship between E_c and D in the following form

$$E_c = E_c^{max} - E_c^{max}(D-1) \text{ or} \tag{7}$$
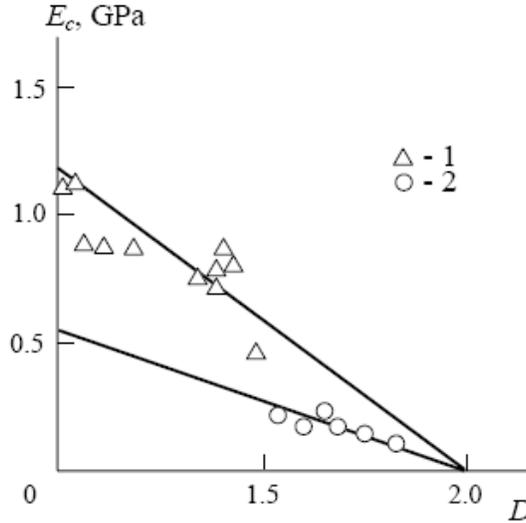
$$E_c = E_c^{max}(2-D) \tag{8}$$

Figure. 1. The elasticity modulus E_c vs. fractal dimension of chain part between interfacial areas D at testing temperatures 293 (1) and 373 K (2) for nanocomposites based on the polypropylene

CONCLUSION

Therefore, the results of the present paper showed interrelation of elasticity modulus and amorphous chains tightness characterized by fractal dimension of chain part between its fixation points for nanocomposites based on the semi-crystalline polypropylene. This assumes the polymeric matrix structure change in comparison with initial polymer: the role of densely-packed regions for it is played by interfacial areas. An offered fractal model allows estimation of elasticity modulus limiting values.

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Chapter 9

STRUCTURE FORMATION OF POLYMER NANOCOMPOSITES BASED ON POLYPROPYLENE

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ABSTRACT

It is shown, that the structure formation of nanocomposites based on the polypropylene takes in Euclidean space with dimension d=3. Within the framework of the offered for these material structural model is shown identity of local order regions, interfacial areas and crystalline β-phase. This model allows quantitative description of nanocomposites properties.

Keywords: Nanocomposite; polypropylene; structure; Euclidean space; local order; crystalline β-phase.

INTRODUCTION

The introduction of disperce filler in polymeric matrix changes significantly properties of the last [1]. This fact is well known, but there are definite difficulties with its quantitative estimation. For particulate-filled composites polyhydroxiether-graphite (PHE-Gr) was found the structure fractal dimension d_f increase from 2.6 to 2.8 within the volume content of filler interval φ_f=0-0.09. This structure change is accompanied by corresponding increase of composites mechanical characteristics (elasticity modulus, yielding stress, fracture stress and so on) [2]. The mentioned change of composites PHE-Gr structure is due to its formation in fractal space, which creates a filler network of particles (particle aggregates) [3,4]. As studies

of mechanical properties of nanocomposites based on the polypropylene (PP), filled by modified natural clay (NC) Na^+-montmorillonite in interval $\varphi_f=0.025-0.10$, show that for them elasticity modulus raising is not observed and yielding stress and strength are even a little decreased [5]. Proceeded from these differences of mechanical properties behaviour of composites PHE-Gr and nanocomposites based on the PP, presents interest of the study of structural changes, due to introduction of layered filler and determines mechanical behaviour of nanocomposites, that is the purpose of present paper.

EXPERIMENTAL

The data of paper [5] for nanocomposites based on the isotactic industrial PP (Shell Co.), filled by Na^+-montmorillonite with last contents $\varphi_f=0.025$, 0.050 and 0.10 were used. As modificators: dioctadecyldimethyl ammonium bromide (DODAB) plus block-copolymer polyethyleneoxide-polyethylene (PEO-PE) (conventional sign of nanocomposite PP-NC-1); PEO-PE (PP-NC-2); DODAB plus PEO-PE with isobutylene (PP-NC-3); PEO-PE plus isobutylene (PP-NC-4) are used. The detailed description of specimens preparation methodics is cited in the paper [5].

The mechanical tests were made on film specimens with length 10 mm, width 3 mm and thickness 0.2 mm, prepared by pressing from melt at 473 K. The tests were made at temperature 293 K and strain rate 8.3×10^{-3} s^{-1} [5].

The experimental values d_f(d_f^e) were determined according to the equation [6]

$$d_f^e = (d-1)(1+\nu) \tag{1}$$

where d is dimension of Euclidean space, in which a fractal is considered (obviously, in our case $d=3$), ν is Poisson's ratio, the value of which can be estimated on mechanical testing results with the aid of the relationship [7]

$$\frac{\sigma_Y}{E} = \frac{1-2\nu}{6(1+\nu)} \tag{2}$$

where σ_Y is yielding stress, E is elasticity modulus.

RESULTS AND DISCUSSION

As it is mentioned above, the change d_f at increase φ_f for composites PHE-Gr is due to formation of polymeric matrix structure in fractal space with dimension D_{lat} [3,4]. The value can be determined with the aid of the following equation [8]

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$$\nu_F = \frac{3}{2 + D_{lat}} \tag{3}$$

where ν_F is Flory exponent connected with dimension d_f in the linear polymers case by the following relationship [9]

$$\nu_F = \frac{1.5}{d_f} \tag{4}$$

The calculation of value d_f^e according to the equation (1) shows this dimension variation within the limits 2.678-2.739 with average value 2.709. The estimation D_{lat} according to the equation (3) give in this case the value ~ 3.42, that is does not correspond to condition $D_{lat} \leq 3$, which is common for all objects in three-dimensional Euclidean space [6]. Therefore, it is necessary to assume $D_{lat}=3$ and value d_f in this case is equal to 2.5 according to the equation (3). This value d_f is excellently coordinated with calculation according to the equation (1) for initial PP (d_f^e =2.518). Thus, the cited estimations allow to assume, that the formation of structure of initial PP and polymeric matrix of nanocomposites on its basis is realized in the three-dimensional Euclidean space, and increase d_f^e for nanocomposites in comparison with PP is due to introduction of the filler. It is necessary to mark, that at condition $D_{lat}<3$ (structure formation in fractal space) the decrease d_f in comparison with $D_{lat}=3$ for nanocomposites in comparison with initial PP must take place, that contradicts to experimental data.

Let's consider physical base of the mentioned increase d_f^e. As it is shown in paper [5], the introduction of layered filler (Na^+-montmorillonite) in PP results to the formation of crystalline β-phase, the crystallites of which have primary orientation inseparably connected with flat texture of siliceous layers, on which they are crystallized. This allows to consider mentioned crystallites both as local order regions, and as interfacial areas at the same time. Let's perform quantitative estimation of these regions contents at both of their definitions. The relative fraction of local order regions (clusters) φ_{cl} for semi-crystalline polymers can be calculated according to the following percolation relationship [9]

$$\varphi_{cl} = 0.03(1 - K)(T_m - T)^{0.55} \tag{5}$$

where K is orthorhombic crystallinity degree, T_m and T are temperature of melting and testing accordingly.

For PP $T_m \approx 440$ K [10] and value K can be determined according to the equation [11]

$$K = 0.32 C_\infty^{1/3} \tag{6}$$

where C_∞ is characteristic ratio, which is an indicator of polymer chain statistical flexibility [12] and connected with dimension d_f by the relationship [9]

$$C_\infty = \frac{2d_f}{d(d-1)(d-d_f)} + \frac{4}{3} \qquad (7)$$

The relative fraction of interfacial areas φ_{inf} was calculated with the aid of the equation [13]

$$\frac{E_c}{E_m} = 1 + 11\left(\varphi_f + \varphi_{inf}\right) \qquad (8)$$

where E_c and E_m are elasticity modulus of composite and matrix polymer, accordingly.

The connection between dimension d_f and crystallinity degree is defined by the following empirical approximation [11]

$$d_f = 2 + K \qquad (9)$$

It is obvious, that for the studied nanocomposites with appreciation of crystalline β-phase formation the following version of the equation (9) should be written

$$d_f = 2 + K + \varphi_{inf} \qquad (10)$$

According to the equation (10) the formation of nanocomposites structure in fractal space, defining decrease d_f, must decrease value K, that also does not correspond to the experiment.

In Fig. 1 the comparison of dimensions d_f^e and d_f^T calculated according to the equations (1) and (10), accordingly, is shown. As can be seen, between these values d_f the good correspondence is received (average discrepancy by fractional part of dimensions, which performs main information about structure, is equal to 4.6 %). This allows to assume, that the structure of nanocomposites based on the PP consists of the following structural regions: orthorhombic crystallites, amorphous phase, filler and crystalline β-phase, forming interfacial areas. Let's note, that the calculation φ_{inf} according to the equation (8) and nanocomposites crystallinity degree rise in comparison with initial PP [5] give close values: ~ 0.15-0.20.

Another method of calculation of theoretical value $d_f (d_f^T)$ gives the following equation [9]

$$d_f^T = 3 - 6\left(\frac{\varphi_{cl}}{SC_\infty}\right)^{1/2} \qquad (11)$$

where S is cross-section area of macromolecule, which is equal to 34.27 Å^2 for PP [14].

In Fig. 2 the dependence d_f^T on φ_f calculated according to the equation (4) for PP and according to the equation (11) for nanocomposites based on the PP at φ_{cl} estimated according to the equation (5) is shown. The comparison with experimental data for four groups of nanocomposites and initial PP shows correctness of this estimation.
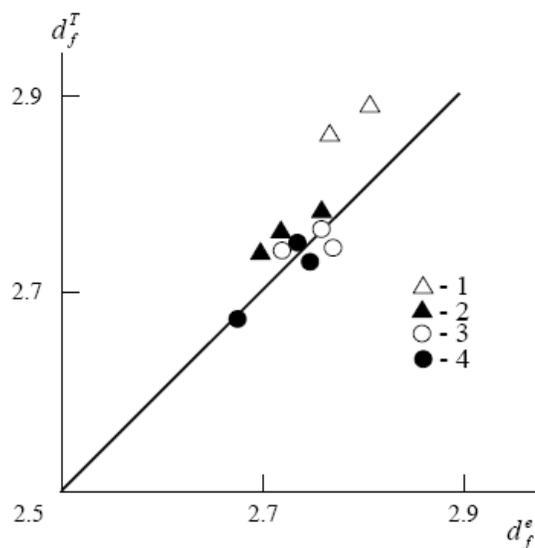

Figure 1. The comparison of experimental d_f^e and calculated according to the equation (10) d_f^T values of structure fractal dimension for nanocomposites PP-NC-1 (1), PP-NC-2 (2), PP-NC-3 (3) and PP-NC-4 (4)
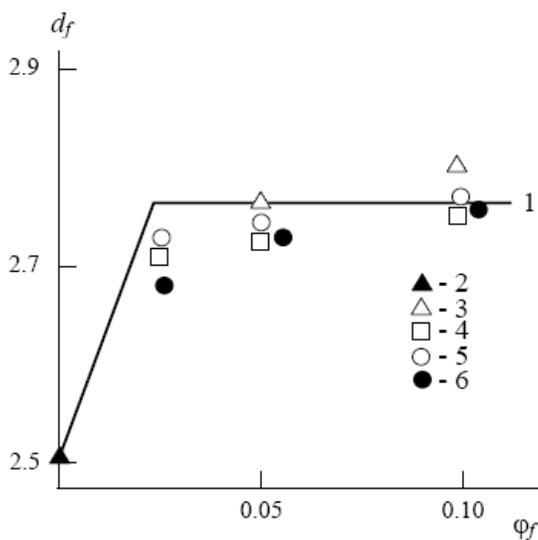

Figure 2. The comparison of calculated according to the equations (4) and (11) (1) and experimental (2-6) the dependences of fractal dimension d_f on filler contents φ_f for PP (2), PP-NC-1 (3), PP-NC-2 (4), PP-NC-3 (5) and PP-NC-4 (6)

CONCLUSION

Therefore, the results of the present paper showed, that the structure formation of nanocomposites based on the polypropylene takes place in Euclidean space with dimension d=3. Within the framework of offered for these materials structural model is shown identity of local order regions, interfacial areas and crystalline β-phase. This model allows quantitative description of nanocomposites properties.

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