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THE BEHAVIOUR FEATURES OF POLYMER NANOCOMPOSITES FILLED WITH CALCIUM CARBONATE

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Abstract. The most typical behaviour features of polymer nanocomposites filled with dispersed calcium carbonate were considered. The quantitative analysis was carried out within the frameworks of structural model: the cluster model of polymers amorphous state structure and fractal analysis. It has been shown that all changes of the considered nanocomposites properties were defined by polymeric matrix structure variations, which are due to nanofiller introduction.

Keywords: polymer, nanocomposite, elasticity modulus, interfacial adhesion, yield, plasticity, fractal analysis.

1. Introduction

Lately a scientists' interest to particulate-filled polymer nanocomposites, where the nanofiller is calcium carbonate has been increased. Nanocomposites on the basis of polyethylene [1-8], polypropylene [9, 10], poly(vinyl chloride) [11, 12], butadiene rubber [13] *etc.* were studied. These studies of nanocomposites polymer/calcium carbonate allow to reveal a number of their specific features, which do not correspond to the known ones at present for polymer composites. Let us note some of them. The elasticity modulus enhancement at calcium carbonate (CaCO_3) introduction in the mentioned matrices is usually small even at using of binding agents [9] and for polypropylene it makes up no more than 50 % at CaCO_3 contents of 40 mas %. Let us remind that similar processing of mineral microfillers allows to increase an elasticity modulus of epoxy polymer by 300–400 % at the same filler content [14]. Secondly, CaCO_3 contents increasing does not practically increase nanocomposites yield stress and sometimes even reduces it [5, 6]. But the most interesting feature of the considered nanocomposites is their plasticity, characterized by either

limiting strain at failure ϵ_f [12], or impact toughness A_p [5, 6, 9, 13], at CaCO_3 contents growth increasing, which often has an extreme character. Let us remind that brittleness of polymers at the introduction of various fillers into them (including nanofillers [11]) is one of the most essential deficiencies of polymer composites in general [14]. And at last, melts of nanocomposites filled with CaCO_3 often discover an anomalous behaviour [15]. A sufficiently large number of works [1-13, 15] which have mainly a qualitative character, taking into consideration characteristics of secondary structures obtained at specimens fracture but giving no interrelation with nanocomposites neat structure were devoted to these features of the mentioned nanocomposites study. Therefore the purpose of the present paper is quantitative analysis of the indicated effects on the example of polymer nanocomposites filled with calcium carbonate.

2. Experimental

Homopolymer of polypropylene (PP) of mark F1 supplied by the Langang Petrochemical Company, China, was used as the polymeric matrix. The dispersed CaCO_3 was purchased from Solvay firm, particles size makes up 70 nm, nanofiller contents vary within the limits of 0–40 mas %. CaCO_3 particles were treated by 1 mas % of coupling agent liquid silane of mark KH550, *g*-aminopropyl triethoxy silane, supplied by the firm Hengda, China [9].

Nanocomposites PP/ CaCO_3 were prepared in a screw extruder with a length/diameter ratio of 32, and a screw diameter of 25 mm (T55J-25/32, China) at the temperature of 503 K and screw rotation rate of 140 rpm. Then the prepared nanocomposites were palletized and the obtained pellets were molded in Nissei PS40E5ASE casting machine into two types of specimens for

mechanical tests: the samples for the tests on the three-pointed bending have a shape of rectangular bars with the length of 80 mm, the width of 10 mm and the thickness of 4 mm; samples for impact testing have the same shape, analogous width thickness and length of 60 mm. On the last ones V-shaped notch with the length of 2 mm and the tip radius of 0.25 mm was marked.

Flexural tests were made on the apparatus Shimadzu AG-10TA Universal Testing Machine at the temperature of 293 K and the crosshead speed of 2 mm/min. Impact tests were made according to the Izod method at the rate of 3.5 m/s. The reported data were average value of five individual measurements [9].

3. Results and Discussion

As the data of paper [9] have shown, the contents of CaCO_3 W_f increasing within the range of 0–40 mas % results to nanocomposites elasticity modulus E_n enhancement from 1387 up to 2086 MPa, *i.e.* approximately in 1.5 times. The fractal conception of polymer composites elasticity [16] supposes that this parameter increasing is due to modification (“disturbance”) of polymeric matrix structure at the filler introduction. The indicated disturbance degree can be characterized by the excess energy localization regions dimension D_f , connected with fractal (Hausdorff) dimension d_f of composites structure according to the Eq. (1) [17]:

$$D_f = 1 + \frac{1}{3 - d_f} \quad (1)$$

In its turn, the value d_f is determined according to the following relationship [17]:

$$d_f = (d - 1)(1 + n) \quad (2)$$

where d is the dimension of the Euclidean space, in which a fractal is considered (obviously, in our case $d = 3$), n is the Poisson’s ratio, estimated according to the mechanical tests results with the aid of the formula [18]:

$$\frac{s_Y}{E} = \frac{1 - 2n}{6(1 + n)} \quad (3)$$

where s_Y is the yield stress, E is the elasticity modulus.

In Fig. 1 the dependences $E_n(D_f)$ for four nanocomposites are added: PP/ CaCO_3 , poly(vinyl chloride)/calcium carbonate (PVC/ CaCO_3) with CaCO_3 particles size of 44 nm, the high density polyethylene/calcium carbonate (HDPE/ CaCO_3) with particles sizes of 50 and 1200 nm. As it can be seen, all indicated correlations are described by linear dependences with different slope. Obtaining of common correlation for all indicated polymer materials is possible by normalization of the adduced straight lines in Fig. 1 by the means of ratio E_{pol}/E_{PP} , where E_{pol} and E_{PP} are elasticity modulus of arbitrary matrix polymer and PP, respectively. Then the

adduced elasticity modulus E_n^{red} of the nanocomposite is described by the following generalized formula:

$$E_n^{red} = 0.32 \left(\frac{E_{pol}}{E_{PP}} \right) (D_f - 1) \quad (4)$$

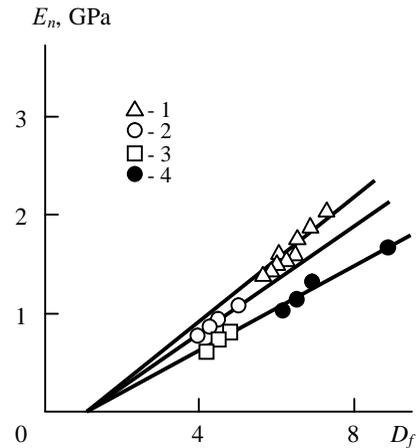


Fig. 1. The dependences of elasticity modulus E_n on fractal dimension D_f for nanocomposites on the basis of PP (diameter of CaCO_3 nanoparticles $D_p = 70$ nm) (1); HDPE ($D_p = 50$ nm) (2); HDPE ($D_p = 1200$ nm) (3) and PVC ($D_p = 44$ nm) (4)

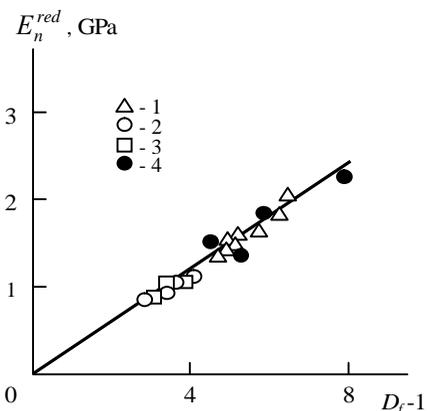


Fig. 2. The dependence of reduced elasticity modulus E_n^{red} of nanocomposites, calculated according to the Eq. (4), on fractal dimension D_f . Conventional signs are the same that in Fig. 1.

The adduced correlation $E_n^{red}(D_f - 1)$ in Fig. 2 corresponding to the Eq. (4), confirms its correctness. Let us note, that the indicated equation allows to determine the upper limiting value of nanocomposite elasticity modulus at the condition that values E_{pol} and E_{PP} are known (it is naturally that not only PP can be used as a basic one, but any other polymer as well). As it is known [17], for the real physical objects the maximum value $d_f = 2.95$. From the Eq. (1) it is followed that corresponding to its maximum value $D_f = 21$. For example, if for PVC $E_{pol} = 1150$ MPa [12], then this means according to the Eq. (4), that maximum attainable

for nanocomposites PVC/CaCO₃ value E_n is equal to ~ 5300 MPa. Therefore, particulate-filled polymer nanocomposites obey the general laws, obtained earlier for particulate-filled microcomposites.

The authors [19] obtained the following equation, showing the dependence of reinforcement degree E_n/E_m for particulate-filled nanocomposites on their main characteristics:

$$\frac{E_n}{E_m} = \frac{0.19W_f l_{st}}{D_p^{1/2}} \quad (5)$$

where E_m is the elasticity modulus of matrix polymer, W_f is the nanofiller mass contents, l_{st} is the length of statistical segment of polymeric matrix, D_p is the nanofiller particles diameter.

The value l_{st} can be determined according to the formula [20]:

$$l_{st} = C_\infty l_0 \quad (6)$$

where C_∞ is the characteristic ratio, l_0 is the length of the main chain skeletal bond. For PP one should accept: $C_\infty = 6$, $l_0 = 1.54 \text{ \AA}$ [21].

In Table 1 the comparison of the obtained experimentally (E_n/E_m) and calculated according to the Eq. (5) ($(E_n/E_m)^T$) values of reinforcement degree for nanocomposites PP/CaCO₃ is adduced. As one can see, sufficiently good correspondence of the theory and experiment is obtained (the average discrepancy of (E_n/E_m) and ($(E_n/E_m)^T$) makes up 8.4 %), but for all nanocomposites the condition (E_n/E_m) < ($(E_n/E_m)^T$) is fulfilled. According to the Eq. (5) such effect can be given by nanoparticles aggregation, i.e. D_p increasing. Using experimental values of reinforcement degree, real sizes of nanofiller particles aggregates D_p^{agr} can be calculated, the dependence of which on the filling mass degree W_f in Fig. 3 is adduced. The data of this figure demonstrate rather strong aggregation of nanofiller particles at small W_f (≤ 10 mas %) and its small degree at $W_f \geq 20$ mas %. Such unexpected correlation (it is usually considered that the stronger aggregation the higher filler contents [16]) can be explained by nanocomposites melt viscosity h change, since in this state only nanofiller particles aggregation is possible. In Fig. 4 the dependence of melt relative viscosity for nano-

composites PP/CaCO₃ h/h_0 (h_0 is the neat matrix polymer melt viscosity), calculated according to the Einstein's formula (7) [22] on CaCO₃ contents is adduced.

$$\frac{h}{h_0} = 1 + \frac{2.5W_f}{1-W_f} \quad (7)$$

As it follows from Fig. 4 plot, at $W_f \approx 10$ mas % relative viscosity gradient increases essentially (about twice) for large CaCO₃ contents. This means that relatively low nanocomposites PP/CaCO₃ melt viscosity at small W_f allows rather high nanofiller particles mobility degree in the melt that facilitates their aggregation, since nanoparticles in general have high specific surface, promoting to their strong agglomeration [10, 23]. A melt viscosity enhancement at $W_f > 10$ mas % reduces nanofiller particles mobility in the melt, making their aggregation difficult (compare Figs. 3 and 4). The similar anomalous effect of the melt viscosity change as a function of W_f for nanocomposites PP/CaCO₃ was observed in the work [15]. It is significant that, as it has been expected, nanofiller particles aggregation degree influences nanocomposites elasticity modulus E_n . In Fig. 5 the dependence $E_n(W_f)$ is adduced, which corresponds completely to Figs. 3 and 4 data. As one can see, in the range of $W_f = 0-10$ mas %, where nanofiller particles aggregation is relatively high (Fig. 3) and the melt relative viscosity is small (Fig. 4), E_n growth at W_f increase occurs much slower than in the range of $W_f > 10$ mas %.

Let us consider further the reasons of the yield stress σ_Y of relatively small increasing of particulate-filled nanocomposites in comparison with their elasticity modulus E_n . So, for nanocomposites PP/CaCO₃ at E_n increasing by 50 % σ_Y enhancement only by 10 % is observed [9] and for nanocomposites HDPE/CaCO₃ W_f increasing W_f up to 20 mas % results in σ_Y reduction in comparison with such nanocomposites with CaCO₃ smaller contents [5, 6]. The similar picture is observed for nanocomposites PVC/CaCO₃ [12]. Within the frameworks of the cluster model of polymers amorphous state structure yield stress σ_Y is determined by the following equation [16, 24]:

$$s_Y = \frac{Gbr_d^{1/2}}{2p} \quad (8)$$

Table 1

The structural and mechanical characteristics of nanocomposites PP/CaCO₃

W_f , mas %	E_n/E_m	$(E_n/E_m)^T$	d_f	φ_{cl}	G , MPa	σ_Y , MPa	s_Y^T , MPa
0	1	1	2.787	0.194	498	35.4	36.8
2	1.025	1.040	2.792	0.189	509	35.4	37.1
4	1.047	1.060	2.795	0.183	519	35.6	37.3
6	1.060	1.120	2.796	0.181	525	35.8	37.5
8	1.071	1.160	2.796	0.181	531	36.1	37.3
10	1.108	1.200	2.800	0.174	549	36.4	38.0
20	1.243	1.400	2.816	0.148	612	37.5	39.2
30	1.347	1.600	2.826	0.132	661	38.2	39.2
40	1.504	1.800	2.840	0.112	735	39.2	39.4

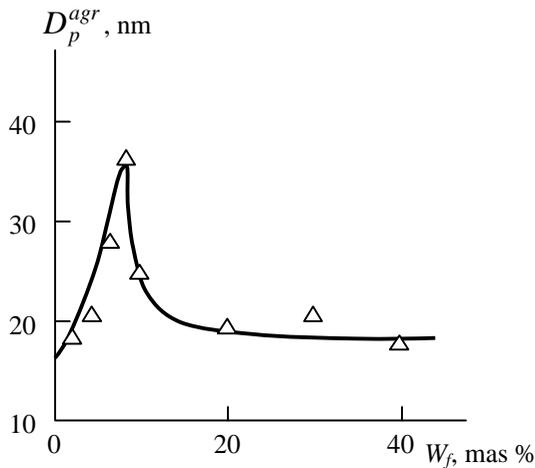


Fig. 3. The dependence of diameter of nanofiller particles aggregates D_p^{agr} on mass contents of CaCO_3 W_f for nanocomposites PP/ CaCO_3

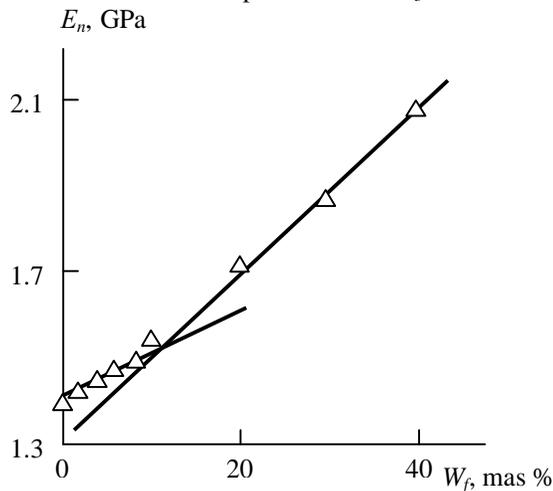


Fig. 5. The dependence of elasticity modulus E_n on CaCO_3 mass contents W_f for nanocomposites PP/ CaCO_3

where G is the shearing modulus, b is the Burgers vector, ρ_d is the structure linear defects density (analog of dislocations for crystalline lattices).

Let us consider parameters estimation methods, which are included in the Eq. (8). The value G is determined as follows [17]:

$$G = \frac{E_n}{d_f} \quad (9)$$

and the Burgers vector b – according to the empirical equation [16, 24]:

$$b = \left(\frac{62.5}{C_\infty} \right)^{1/2}, \text{ \AA} \quad (10)$$

For polymers as structure linear defects the segments of macromolecules, included in densely-packed

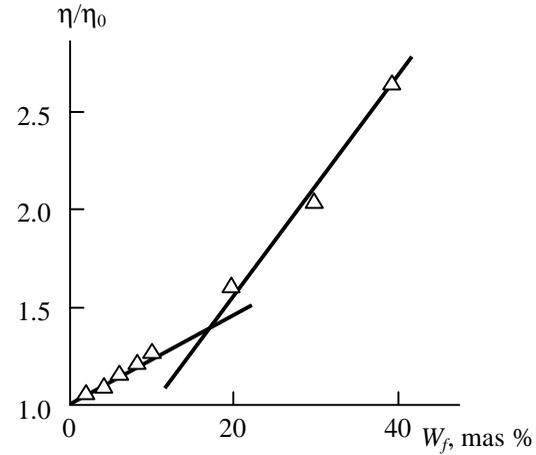


Fig. 4. The dependence of melt relative viscosity h/h_0 , calculated according to the Eq. (7), on CaCO_3 mass contents W_f for nanocomposites PP/ CaCO_3

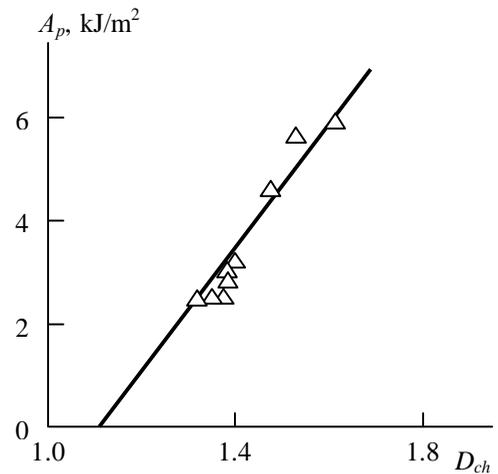


Fig. 6. The dependence of impact toughness A_p on fractal dimension D_{ch} of chain part between clusters for nanocomposites PP/ CaCO_3

regions are accepted, which for nanocomposites with semicrystalline matrix are crystallites, local order regions (clusters) and interphase regions [23]. Relative fraction of the last ϕ_{if} can be estimated with the aid of the equation [23]:

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

The estimations according to the Eq. (11) have shown practical absence of interphase regions in nanocomposites PP/ CaCO_3 . These estimations are confirmed experimentally by the data of atomic force microscopy on the example of nanocomposites HDPE/ CaCO_3 [5]. In itself the fact of practical absence of interphase regions in nanocomposites PP/ CaCO_3 speaks for rather low level of interfacial adhesion nanofiller-

polymeric matrix despite coupling agent usage [23]. The authors [25] show that in case of ideal adhesion between the filler and the polymeric matrix the dependence $E_n/E_m(W_f)$ was described by the Kerner's equation, which can be approximated by the following relationship:

$$\frac{E_n}{E_m} = 1 + 11.6W_f - 44.4W_f^2 + 96.3W_f^3 \quad (12)$$

The other similar relationship (the Guth's equation), used for estimation of composites reinforcement degree in case of ideal adhesion, has the form [12]:

$$\frac{E_n}{E_m} = 1 + 2.5W_f + 14.1W_f^2 \quad (13)$$

The Eqs (12) and (13) give close values of E_n/E_m at $W_f = 40 \text{ mas } \%$ (or $W_f = 0.4$) for nanocomposites PP/CaCO₃: 4.70 and 4.46, that correspond to elasticity modulus $E_n = 6.52$ and 6.18 GPa, respectively. Since the experimental E_n value at the indicated CaCO₃ content is equal to 2.09 GPa [9], then this comparison confirms the conclusion about the low level of the interfacial adhesion for these nanocomposites, which was made above.

Therefore, for the studied nanocomposites one should accept segments, included in crystallites and clusters with relative fractions K (crystallinity degree) and φ_{cl} , respectively, as the structure linear defects. K value for PP is equal to 0.50 [9] and the value φ_{cl} can be estimated with the aid of the equation [24]:

$$d_f = 3 - 6 \left(\frac{j_{cl}}{C_\infty S} \right)^{1/2} \quad (14)$$

where S is the cross-sectional area of macromolecule, which is equal to 34.3 \AA^2 for PP [26].

Further the value ρ_d is calculated according to the following formula [16]:

$$r_d = \frac{K + j_{cl}}{S} \quad (15)$$

In Table 1 the comparison of experimental σ_Y and calculated according to the equation (8) s_Y^T yield stress values for nanocomposites PP/CaCO₃ is adduced and the necessary for such calculation values d_f , j_{cl} and G are given as well. As one can see, a good correspondence of the theory and the experiment is obtained (the average discrepancy of σ_Y and s_Y^T makes up 3.6%). Let us note the polymeric matrix structure, characterized by the dimension d_f , small change – at $W_f = 40 \text{ mas } \%$ it makes up by the fractional part of d_f (which gives the main information about the structure) only 6.7% . For comparison, in case of composites polyhydroxiether/graphite at the same filler content d_f change is equal to 32.8% , i.e. approximately in 5 times more [16]. Antilate change of parameters G and j_{cl} , defining the value σ_Y in the Eq. (8) is also significant. Hence, σ_Y weak increase at

W_f growth for nanocomposites PP/CaCO₃ is due to a compensating effect of antilate change of parameters G and j_{cl} (or ρ_d).

In conclusion let us consider nanocomposites PP/CaCO₃ plasticity increasing effect at W_f growth on the example of the impact toughness A_p , which at $W_f = 40 \text{ mas } \%$ raises in 2.4 times in comparison with neat PP. As Kausch shows [27], the polymer molecular mobility increasing is always accompanied by its plasticity (impact toughness) growth. Within the frameworks of fractal analysis the molecular mobility level can be estimated with the aid of fractal dimension D_{ch} of the chain part between its fixation points (cross-linking nodes, physical entanglements, clusters, etc.) [28]. The value D_{ch} can be calculated with the aid of the Eq. (16) [28]:

$$\frac{2}{j_{cl}} = C_\infty^{D_{ch}} \quad (16)$$

In Fig. 6 the dependence $A_p(D_{ch})$ is adduced, which has an expected form: enhancement of the molecular mobility level, characterized by the dimension D_{ch} , results to the growth of nanocomposites plasticity, characterized by their impact toughness A_p . Let us note, that D_{ch} and, consequently, A_p increase is due to the local order level reduction in the amorphous phase of the polymeric matrix, i.e. j_{cl} decrease at W_f growth (Table 1), in other words, by polymeric matrix structure “disturbance” at nanofiller introduction.

The fractal analysis application allows to estimate the maximum attainable A_p value. So, from Fig. 6 plot it follows that for nanocomposites PP/CaCO₃ at maximum $D_{ch} = 2$ the limiting magnitude of the impact toughness is equal to 10.4 kJ/m^2 .

4. Conclusions

Therefore, the quantitative analysis of particulate-filled polymer nanocomposites main features within the frameworks of the fractal analysis and the cluster model of the polymers amorphous state structure performed in the present paper allows to elucidate the following structural causes of the indicated features:

1. The relatively small reinforcement degree of polymer nanocomposites, filled with calcium carbonate, is due to low level of interfacial adhesion polymer-CaCO₃, despite the coupling agent using. Nanofiller particles aggregation plays a definite role in this aspect.
2. The weak increasing of nanocomposites yield stress at CaCO₃ contents growth is due to the compensating effect of the shear modulus change and relative fraction of polymeric matrix local order regions.
3. The melts viscosity anomalous behaviour of nanocomposites, filled with CaCO₃, is due to a strong tendency to aggregation of nanofiller particles in virtue of

their high specific surface at small nanofiller contents and, as a consequence, nanoparticles high mobility. CaCO_3 contents increase raises essentially the melt viscosity, reduces the nanofiller particles mobility and decreases their aggregation degree.

4. The plasticity, characterized by the impact toughness, increasing for nanocomposites PP/ CaCO_3 is due to the polymeric matrix structure “disturbance” at nanofiller introduction and, as a consequence, to the growth of molecular mobility level.

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ОСОБЛИВОСТІ ПОВЕДІНКИ НАПОВНЕНИХ КАРБОНАТОМ КАЛЬЦІЮ ПОЛІМЕРНИХ НАНОКОМПЗИТІВ

Анотація. Розглянуті найбільш типові особливості поведінки полімерних нанокмпозитів наповнених дисперсним карбонатом кальцію. Проведено кількісний аналіз в рамках структурної моделі: кластерна модель аморфної структури полімерів і фрактальний аналіз. Показано, що всі зміни у властивостях розглянутих нанокмпозитів визначені зміною структури полімерної матриці через введення нанонаповнювача.

Ключові слова: полімер, нанокмпозит, модуль пружності, міжфазова адгезія, пластичність, фрактальний аналіз.