

## Features of Structural Organization of Nanodiamonds in the Polyethylene Glycol Matrix

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(Received 14 April 2020; revised manuscript received 15 August 2020; published online 25 August 2020)

Polymeric nanocomposites containing nanodiamonds are attractive multifunctional materials with a growing range of applications. Since the microstructure of the system determines its properties, it is an important task to establish the features of structure formation of nanodiamonds in the polymer matrix. The structural features of nanocomposites based on polyethylene glycol (PEG) and ultradispersed nanodiamonds (UDNDs) were investigated using the methods of wide-angle and small-angle X-ray scattering. Systems based on nanodiamonds of detonation synthesis and crystalline PEG were prepared by ultrasonic dispersion in melt. The studied UDNDs are found to be polydispersed particles with a narrow size distribution. The average radius of the UDNDs primary particles is 20 nm. It is shown that as the content of nanodiamonds in the system increases, the aggregation processes increase. The structure of such systems is well described within the model with multilevel fractal aggregation. Fractal analysis identified the type of fractal aggregates of each structural level and determined their sizes. Depending on the content of the filler in the system, particles of UDNDs form different types of aggregates. At low filler content, dense mass fractal aggregates and surface aggregates with a smooth surface are formed. At high contents, dense aggregates of surface-fractal type with a rough surface are formed. It is established that aggregates with an average size of 60-75 nm are formed at the first structural level, and aggregates with an average size of 225-240 nm are formed at the second level.

**Keywords:** Nanodiamonds, Nanocomposites, Polyethylene glycol, X-ray diffraction, Fractal structures.

DOI: [10.21272/jnep.12\(4\).04006](https://doi.org/10.21272/jnep.12(4).04006)

PACS numbers: 61.46.Hk, 81.07.Bc, 61.05.cf

### 1. INTRODUCTION

In recent years, particular interest has been given to the study of the structure and properties of nanosystems. Increasing attention to them is primarily related to the observation in their exploration of a set of new unique properties (compared to macrosystems), which makes their use extremely promising in nanotechnology [1]. The properties of nanosystems are determined not only by the size of the clusters or nanoparticles, but also by the methods of their organization. The nature of the structural organization of such systems depends both on the nature of the nanoparticles (as well as the matrix in which they are distributed) and on the method of their production.

Nanodiamonds (NDs) are an allotropic form of carbon nanomaterials characterized by unique physical, mechanical, thermal, optical and biocompatible properties [2]. The NDs particles are preferably spherical, having a diamond core and a graphite outer shell. In addition, the NDs particles have a highly reactive surface that surrounds their diamond core and contains a variety of functional groups. In the case of detonation synthesis of NDs, oxygen-containing groups such as carboxylic acids, esters, ethers, lactones and amines may be present on their surfaces. In addition, the NDs surface is partially covered by thin layers of graphite or graphene structures [3].

Due to such unique structure and properties of NDs, they are, in fact, promising for the development of multifunctional polymer composites [4]. However, for the creation of nanocomposite materials with specified functional characteristics, it is important to establish the structure of such systems, since the structural or-

ganization of nanoparticles in the polymer matrix determines the final properties of the material [5]. Despite the large number of publications devoted to NDs, there are almost no works that have examined the structural organization of NDs particles in the polymer matrix. Instead, there is a study of the features of NDs structure formation in low molecular weight media. For example, Ozawa et al. obtained a number of highly dispersed particles of NDs in various protic and aprotic solvents, including water. Dispersion of particles by ultrasonic disintegration in high-polar alcohols and polar or hydrocarbon solvents allowed to obtain nanosuspensions with a particle size from 4 to 100 nm [6].

It was reported that NDs are characterized by a complex multilevel fractal-like structure that exhibits self-similarity at scale change (scale-invariance) [7]. In addition to the higher-level agglomerates (10  $\mu\text{m}$ ), the fractal structure consists of aggregates of various levels classified as secondary sizes (2-3  $\mu\text{m}$ ) and primary sizes (100-200 nm), including primary particles (4-5 nm).

Kovarik et al. investigated the structural organization of NDs in systems based on deionized water and dimethylformamide prepared by ultrasonic dispersion or centrifugation [8]. It is shown that NDs form aggregates in the liquid medium. The size of aggregates varies in the range from 61 to 73 nm and strongly depends on the type of solvent and the particle content.

Therefore, the purpose of this work was to establish the character and features of the structural organization of NDs particles in a polymer matrix. To solve this problem, a PEG-1000 matrix was selected, which has unique properties such as low melting temperature and melt viscosity, which makes it easier to enter the

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filler, and a crystalline structure that allows to fix the NDs in the matrix [9].

## 2. EXPERIMENTAL PART

### 2.1 Materials

Polyethylene glycol (PEG) HO[–CH<sub>2</sub>–CH<sub>2</sub>–O–]<sub>n</sub>H ( $n \approx 22$ ) with a molecular mass  $M_w = 1000$  (Aldrich) was used as a polymer matrix. Its density at  $T = 293$  K was  $\rho_n = 1093$  kg/m<sup>3</sup>. PEG-1000 is a solid. Before using PEG-1000 was dewatered by heating in vacuum (2 mm) at residual pressure  $p = 270$  Pa and temperature  $T = 363$  K during 5 h.

Ultradispersed nanodiamonds (UDNDs) („ALIT” Ltd., Ukraine) with a spherical shape were used as a filler. UDNDs are formed by an explosion of unbalanced oxygen explosives in the absence of extra sources of carbon. The average particle size of UDNDs is near 20 nm and the specific surface area is 200 m<sup>2</sup>/g.

### 2.2 Preparation of Composite Materials

The composites were obtained by adding the appropriate weights of filler to PEG-1000 at  $T = 363$  K (viscosity is 30 mPa·s) with subsequent 5 min sonication of the mixture using a UZDN-2T ultrasonic disperser at a frequency of 22 kHz and the output power of 150 W. The series of samples with content of UDNDs within 0.5-3 wt. % (thereafter %) were investigated.

### 2.3 Testing and Characterization

The structure of the composite at a small spatial scale was investigated using wide-angle X-ray scattering (WAXS) instrument DRON-2 with CuK<sub>α</sub> source of emission at a wavelength  $\lambda = 0.154$  nm.

The small-angle X-ray scattering (SAXS) experiments were performed using a Kratky camera. The emission from the copper anode was monochromated by the total internal reflection and a nickel filter. The intensity curves were recorded in the step-scanning mode of the scintillation detector. The FFSAXS package was used to smooth out the SAXS curves, to correct them for parasitic scattering and to make a desmearing procedure. The SAXS curves were recorded in the range of scattering angles from 0.03 to 4° corresponding to the wave vector,  $q$ , of 0.022-2.86 nm<sup>-1</sup> ( $q = 4\pi\sin\theta/\lambda$ ,  $\theta$  is one half of the scattering angle,  $\lambda$  is the wavelength of the X-ray radiation). The Origin 9.0 program package was used to determine the structural parameters and modelling of the SAXS curves.

## 3. RESULTS AND DISCUSSION

Fig. 1 shows a wide-angle diffraction pattern of the investigated UDNDs. The source of the diffuse scattering component observed in the region of scattering angles up to 10° is most likely the presence of a significant proportion of disordered carbon material, in which the distances between adjacent graphite layers vary from one to tens and hundreds of nanometers. It should be noted that the presence of a maximum at a 44° angle is explained by the scattering from the crystal lattice of diamond (111) [10].

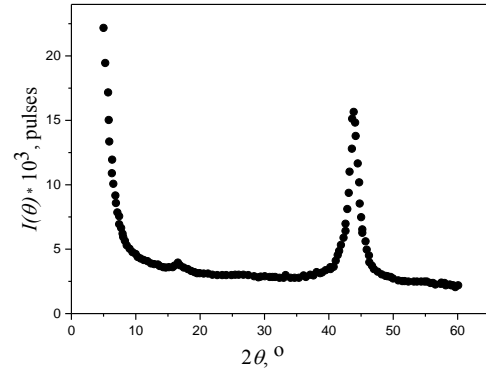


Fig. 1 – The WAXS curve of the original powder UDNDs

To determine the size of UDNDs particles and the nature of their spatial distribution, the method of SAXS was used.

The SAXS curves on a logarithmic scale for the UDNDs output powder are shown in Fig. 2. It is seen that the scattering intensity of the test sample decreases with a slope close to  $-3.5$ , from the minimally recorded value of the wave vector to  $q \approx 0.05$  nm<sup>-1</sup>. Then there is the so-called "Guinier region", in which there is a smooth change in the slope of the curve. After this area, the scattering intensity begins to increase. This increase corresponds to the contribution of the tail part of the so-called WAXS which is caused by the close ordering in the spatial arrangement of adjacent atoms and atomic groups of the studied material, which corresponds to a range of distances from tenths to 1-2 nm.

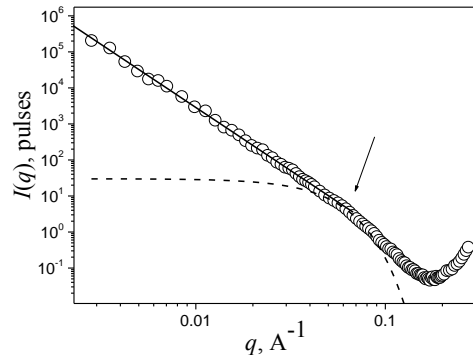


Fig. 2 – The SAXS curve for the UDNDs powder. Blank circles show experimental data, dashed line – Guinier contribution. The arrow shows the "Guinier region"

The slope of the SAXS curve of the initial UDNDs powder  $-3.5$  is obviously due to the spatial distribution of the nanoscale regions whose density is different from the average value for the material [11].

To determine the size of UDNDs particles, we used the Guinier approximation, which determines the dependence of the intensity of particle scattering  $I(q)$  on the wave vector  $q$  [12]:

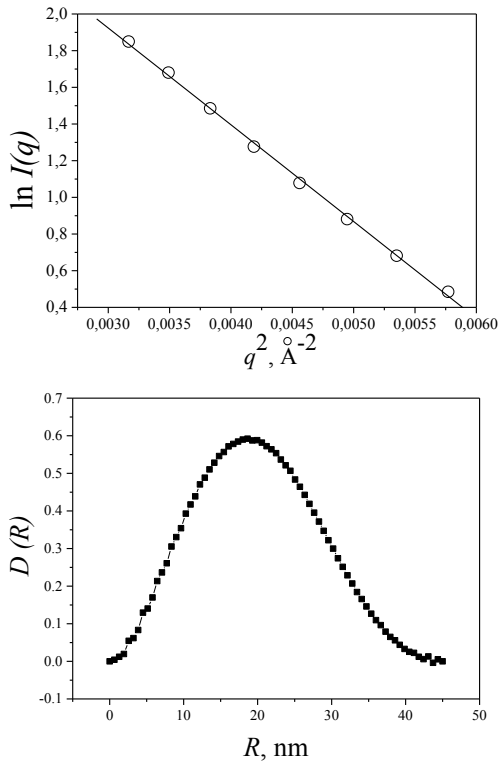
$$I(q) = I_0 \exp\left(-\frac{(qR_g)^2}{3}\right), \quad (1)$$

where  $I_0$  is the scattering intensity at zero angle;  $R_g$  is the radius of gyration of the particle. To determine  $R_g$ ,

the curve in Fig. 2 is built in the coordinates of Guinier equation ( $\ln I(q)$  vs.  $q^2$ ). The result of the approximation is shown in Fig. 3a. It is found that for the UDNDs  $R_g$  is equal to 15 nm. Assuming that the UDNDs particles have a spherical shape, one can determine their geometric radius using the next equation [12]:

$$R = \sqrt{\frac{5}{3}} R_g. \quad (2)$$

Therefore, the geometric radius of the UDNDs particles is approximately 20 nm. Using the approximation data and Eq. (1), the contribution of the scattering intensity from spherical particles to the total intensity was calculated. This contribution (Guinier contribution) is shown by the dotted line in Fig. 2. Fig. 2 shows that the Guinier curve coincides with the general curve only in a certain region. This is evidence of the aggregation of UDNDs particles at a higher scale.



**Fig. 3** – SAXS data for the UDNDs powder in the Guinier coordinates (a); distribution over the radii of the UDNDs particles (b)

Using the experimental data shown in Fig. 1 and the GNOM calculation program [13], the particle size distribution of the UDNDs was obtained. In software calculations, we used the hard-sphere form factor. The results are shown in Fig. 3b. It is seen that the distribution curve is unimodal with a maximum of about 18-20 nm, which correlates well with the results obtained by the approximation of the Guinier equation (1).

To determine the type of structural organization of UDNDs in a PEG matrix, profiles of their small angle X-ray scattering were obtained and analyzed. The curves are shown in Fig. 4 in double logarithmic coordinates for their analysis in terms of fractal-cluster organization of the structure.

It is known that the intensity of X-ray scattering on fractal type structures is described by the following power law [11]:

$$I(q) \sim q^{-\alpha}. \quad (3)$$

Information on the construction of fractal-like aggregates can be obtained from the fractal dimension ( $D$ ) which is determined by the slope of the straight section of the curve ( $\alpha$ ) [14].

The fractal dimension of the mass fractal ( $D_f$ ) varies within  $1 < D_f < 3$ . The greater the value of  $D_f$ , the more compact the fractal object is. The fractal dimension of the surface fractal ( $D_s$ ) varies within  $2 < D_s < 3$  and is given by the equation  $D_s = 6 - D$ . The higher the value of  $D_s$ , the rougher the surface of the fractal object is. If the dimension of space  $D$  is non-integer, then the structure of such objects is described by fractal geometry [15].

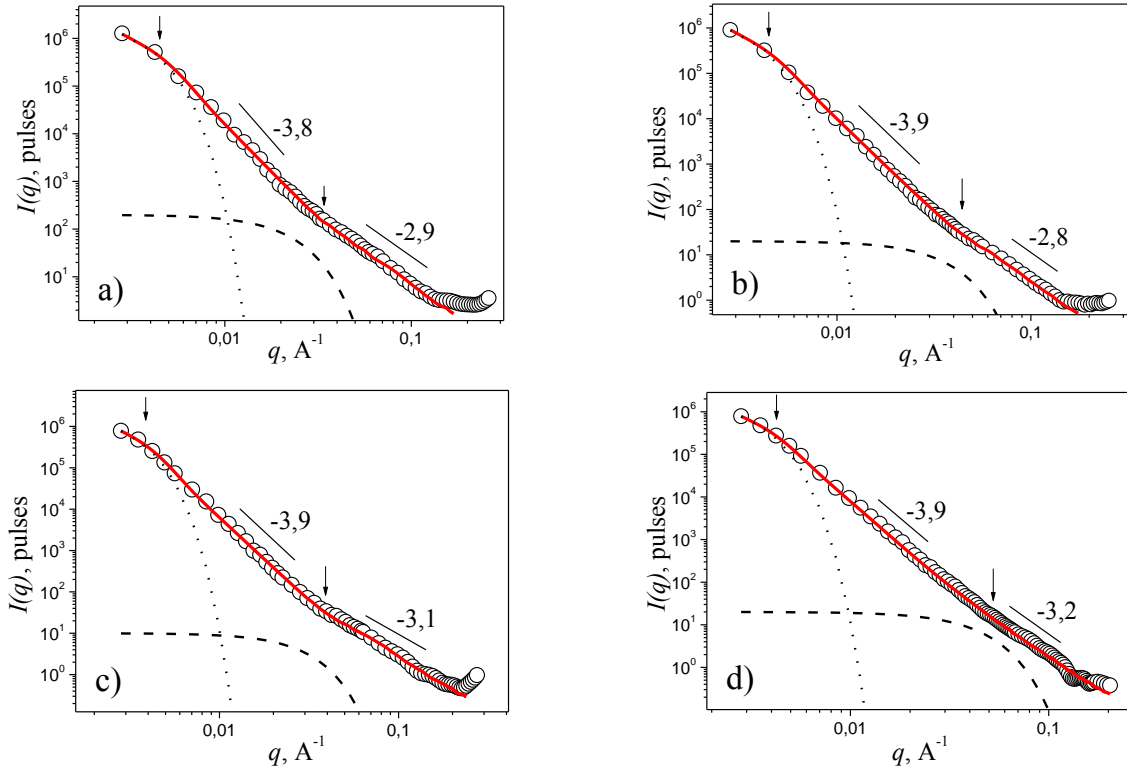
The obtained results show that all SAXS curves for nanocomposite systems with different UDNDs content are characterized by a two-level fractal structural organization. The slope of the linear sections and the corresponding values of the fractal dimension of the structural formations are given in Table 1.

To determine the true size of fractal aggregates, we use the method of global unified power functions developed by G. Beaucage [16]. Using this method, efficient diagnostics of nanosystems of various types is carried out by scattering modelling of multilevel fractal structures [17]. As a result of fitting the model curves to the experimental ones, the structural parameters of the material, such as the type of fractal aggregates (mass or surface), fractal dimension, aggregate sizes and the number of lower-level primary particles in higher-level fractal aggregates, are determined. The following equations are used to describe an arbitrary number of interrelated structural levels:

$$I(q) = \sum_{i=1}^n \left( G_i \exp\left(\frac{-q^2 R_{g_i}^2}{3}\right) + B_i \exp\left(\frac{-q^2 R_{g_{(i+1)}}^2}{3}\right) \times \left[ \left[ \text{erf}\left(\frac{q R_{g_i}}{\sqrt{6}}\right) \right]^3 / q \right]^{P_i} \right), \quad (4)$$

where  $G_i$  is the coefficient on the Guinier ratio for the  $i$ -th level;  $B_i$  is the coefficient for the Porod term for the degree-dependence of the logarithm of the intensity on the logarithm of the wave vector;  $P_i$  is the exponent that determines the fractal dimension of the aggregates of the  $i$ -th level;  $R_{g_i}$  is the radius of inertia of the fractal aggregate of the  $i$ -th level. Assuming that the units are spherical, we can determine their average radius as  $R = 1.29 R_g$  [14].

Fig. 4 shows the SAXS curves for systems containing different amounts of UDNDs modelled by Eq. (4). Fig. 4 shows that the model well describes the experimental data, which allows us to determine the parameters of Eq. (4) with sufficient accuracy. The characteristic dimensions of the structural formations determined by the simulation are given in Table 1.

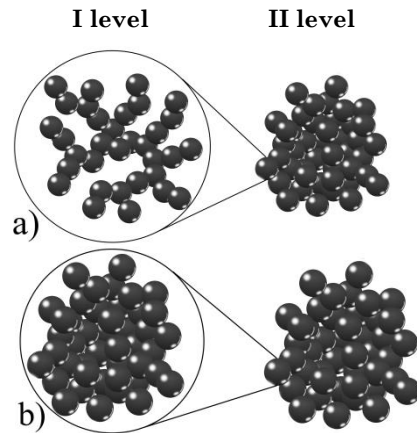


**Fig. 4** – SAXS curves for PEG-based nanocomposites containing 0.5 % (a), 1 % (b), 1.5 % (c) and 3 % (d) of UDNDs modelled in the frame of the Beaucage equation. The arrows show the Guinier region. Blank points are experimental data, red solid line is the model, dashed line is the first Guinier contribution, dotted line is the second Guinier contribution

**Table 1** – Parameters of the fractal structure of PEG and UDNDs systems

$w, \%$	Str. level	Type	$a$	$D$	$R_g, \text{nm}$	$R, \text{nm}$
0.5	I	M	-2.9	2.9	59.4	74.9
	II	S	-3.8	2.2	186.2	240.1
1	I	M	-2.8	2.8	55.6	70.9
	II	S	-3.9	2.1	179.7	232.2
1.5	I	S	-3.1	2.9	52.3	68.0
	II	S	-3.9	2.1	178.1	230.1
3	I	S	-3.2	2.8	46.4	59.8
	II	S	-3.9	2.1	173.2	224.3

The obtained results made it possible to estimate the mechanisms of structure formation of NDs particles. Depending on the content of the filler, structures with different fractal organization are formed. Thus, a system containing 0.5 % and 1 % UDNDs is characterized by a two-level hierarchical structure of type  $M \rightarrow S$ , which is schematically presented in Fig. 5a. The results show that the fractals of the first structural aggregation level for the studied systems are mass-type with an average size of 71-75 nm. Such values correlate well with the values obtained for deionized water-ND systems [8]. However, at the second level, the NDs particles form surface-fractal aggregates with an average size of 230-240 nm. It should be noted that the fractal dimension values for mass-fractal structures of the first hierarchical level are close to 3, which is evidence of their compactness and density. The values of fractal dimension for surface-fractal structures of the first hierarchical level are close to 3, which indicates a very rough surface of aggregates. The value of the fractal dimension for the surface-



**Fig. 5** – Schematic representation of the structural organization of UDNDs particles in the PEG matrix. UDNDs content: 0.5 % and 1 % (a), 1.5 % and 3 % (b)

As the content of the filler in the system increases, the nature of fractal aggregation changes. For a system containing 1.5 % and 3 % UDNDs, a hierarchical structure of type  $S \rightarrow S$  is observed, which is schematically presented in Fig. 5b. Unlike a system containing 0.5 % and 1 % UDNDs, surface-fractal aggregates with an average size of 60-68 nm are formed at the first level. At the second level, the NDs particles form surface-fractal aggregates with an average size of 224-230 nm. The fractal dimension values for the surface-fractal structures of the first hierarchical level are close to 3, which indicates a very rough surface of aggregates. The value of the fractal dimension for the surface-

fractal structures of the second hierarchical level is 2.1, which indicates a radically different nature of the surface of aggregates, which varies from rough to smooth. It should be noted that there is a tendency to reduce the average size of aggregates with increasing content of UDNDs in the system, which is probably due to the compaction of fluffier structures.

Therefore, in the studied systems there is a change in the nature of aggregation from  $M \rightarrow S$  to  $S \rightarrow S$  when the content of the filler is 1-1.5 %. This change is likely to be due to the formation of the UDNDs particles by a structural percolation cluster that permeates the entire volume of the system. Achieving the percolation threshold at such a relatively low filler content is characteristic of PEG-based systems and carbon nanofillers [18, 19]. When the content of the filler is lower than the percolation threshold ( $< 1.5\%$ ), the growth of branched clusters is observed, which is gradually compacted. At high filler content, compact aggregates are formed characterized by a rough fractal surface. At the same time, the surface in such clusters is large enough that it is possible to use UDNDs as a reinforcing component in materials with improved mechanical properties.

#### 4. CONCLUSIONS

As a result of the researches, the features of NDs particles structuring in the PEG matrix have been stud-

ied. The sizes of primary particles of the powder of UDNDs were determined. It was found that the studied particles are polydispersed, the average particle radius is about 20 nm. The nature of aggregation of the filler nanoparticles was investigated by the method of small-angle X-ray scattering. All studied nanocomposites are characterized by two-level fractal aggregation. To effectively diagnose the studied nanosystems we use the Beaucage approach, which is based on modelling the scattering of the system by means of multilevel fractal structures. Fractal analysis of X-ray curves showed that when the filler content in the system increases, the nature of fractal aggregation changes. For systems with different contents of NDs, a hierarchical structure is observed, at which both mass and surface fractal aggregates can be formed at different levels. The scheme of multilevel fractal organization of UDNDs is proposed depending on the content of the filler. Using the simulation, the dimensions of the units at each structural level were calculated. Thus, at the first level, aggregates with an average size of 60-75 nm are formed; at the second level, UDNDs particles form aggregates with an average size of 225-240 nm. There is a tendency to reduce the average size of aggregates with an increase in the content of UDNDs in the system, which is probably due to the compaction of fluffier structures.

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#### Особливості структурної організації наноалмазів у матриці поліетиленгліколю

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Полімерні нанокомпозити, які містять наноалмази, привертають все більшу увагу через зростання областей їх застосування. Оскільки мікроструктура системи визначає її властивості, важливим завданням є встановлення особливостей структуроутворення у полімерній матриці. Методами ширококутового та малокутового розсіювання рентгенівських променів досліджено структурні особливості нанокомпозитів на основі поліетиленгліколю (ПЕГ) та ультрадисперсних наноалмазів (УДНА). Системи на основі наноалмазів детонаційного синтезу та кристалічного ПЕГ готувалися методом ультразвукового диспергування у розплаві. Виявлено, що досліджувані УДНА є полідисперсними частинками із вузьким розподілом за розмірами. Середній радіус первинних частинок УДНА становить

20 нм. Показано, що зі збільшенням вмісту наноалмазів у системі посилюються процеси агрегації. Структура таких систем добре описується в рамках моделі з багаторівневою фрактальною агрегацією. За допомогою фрактального аналізу ідентифіковано тип фрактальних агрегатів кожного структурного рівня та визначено їх розміри. Залежно від вмісту наповнювача у системі, частинки УДНА утворюють різний тип агрегатів. При низькому вмісті наповнювача утворюються щільні масово-фрактальні агрегати та поверхневі агрегати із гладкою поверхнею. При високому вмісті утворюються щільні агрегати поверхнево-фрактального типу із шорсткою поверхнею. Встановлено, що на першому структурному рівні утворюються агрегати із середнім розміром 60-75 нм, на другому рівні частинки УДНА формують агрегати із середнім розміром 225-240 нм.

**Ключові слова:** Наноалмази, Нанокompозити, Поліетиленгліколь, Рентгеноструктурний аналіз, Фрактальні структури.