

## Influence of nanodiamonds on the structure and thermophysical properties of polyethylene glycol-based systems

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The structure features and properties of nanocomposites based on polyethylene glycol (PEG) and nanodiamonds were investigated using the methods of X-ray diffraction, differential scanning calorimetry and optical microscopy. Systems based on crystalline PEG and detonation synthesized nanodiamonds were prepared by ultrasonic dispersion in melt. It has been shown that the structure and properties of PEG-based nanocomposites are significantly dependent on the content of the nanofillers. It was found that in the concentration range of 1–1.5 % nanofiller in the system, structural and thermophysical characteristics, such as crystallinity, effective crystallite size and melting temperature, exhibit extreme behavior. At these concentrations, the particles of nanodiamonds have the largest surface of polymer-filler interaction. The concentration dependence of the thermal conductivity coefficient exhibits percolation-like behavior. This effect is observed when the content of nanodiamonds is 1 % and is confirmed by optical microscopy data. The phenomenon of a step-like increase in thermal conductivity is explained by the formation of a structural network of filler particles in the PEG matrix.

**Keywords:** nanodiamonds, nanocomposites, polyethylene glycol, X-ray diffraction, differential scanning calorimetry, thermal conductivity.

**Вплив наноалмазів на структуру та теплофізичні властивості систем на основі поліетиленгліколю.** *Е.А.Лисенков, І.П.Лисенкова*

Досліджено структуру та властивості нанокомпозитів на основі поліетиленгліколю (ПЕГ) та наноалмазів. Системи на основі наноалмазів детонаційного синтезу та кристалічного ПЕГ одержано методом ультразвукового диспергування у розплаві. Показано, що структура та властивості нанокомпозитів на основі ПЕГ істотно залежать від вмісту нанонаповнювача. Встановлено, що у діапазоні концентрацій 1–1,5 % нанонаповнювача у системі структурні та теплофізичні характеристики, такі як ступінь кристалічності, ефективний розмір кристалітів та температура плавлення, проявляють екстремальну поведінку. При цій концентрації частинки наноалмазів мають найбільшу поверхню взаємодії полімер-наповнювач. Концентраційна залежність коефіцієнта теплопровідності проявляє перколяційно подібну поведінку. Цей ефект спостерігається при вмісті наноалмазів рівному 1 % і підтверджується даними оптичної мікроскопії. Явище сходинкоподібного зростання теплопровідності пояснюється утворенням структурної сітки із частинок наповнювача у матриці ПЕГ.

Исследованы структуры и свойства нанокомпозитов на основе полиэтиленгликоля (ПЭГ) и наноалмазов. Системы на основе наноалмазов детонационного синтеза и кристаллического ПЭГ получены методом ультразвукового диспергирования в расплаве. Показано, что структура и свойства нанокомпозитов на основе ПЭГ существенно зависят от содержания наполнителя. Установлено, что в диапазоне концентраций 1–1,5 % нанонаполнителя в системе структурные и теплофизические характеристики, такие как степень кристалличес-

ности, эффективный размер кристаллитов и температура плавления, проявляют экстремальное поведение. При этой концентрации частицы наноалмазов имеют наибольшую поверхность взаимодействия полимер-наполнитель. Концентрационная зависимость коэффициента теплопроводности проявляет перколяционноподобное поведение. Этот эффект наблюдается при содержании наноалмазов, равном 1 %, и подтверждается данными оптической микроскопии. Явление ступенеобразного роста теплопроводности объясняется образованием структурной сетки из частиц наполнителя в матрице ПЭГ.

## 1. Introduction

In the last decade, polymer nanocomposites, as a new class of functional materials, have been the subject of intense research [1, 2]. The rapid research of these materials is explained by the fact that they have improved functional properties (mechanical stability, durability and thermostability) compared to unfilled polymers. The improvement of the polymer characteristics occurs already with the introduction of a small amount of filler (~ 1–3 %) [3]. In addition to their applied nature, polymer nanocomposite systems are of fundamental interest. Nano-scale fillers have a very large specific surface area, but the mechanism of their influence on the polymer matrix is not fully understood. Recent studies in this area have focused on the improvement of synthesis methods and characterization of the physical properties of polymer nanocomposites [4].

Today, one of the most promising fillers for creating polymer nanocomposite materials is carbon nanofillers, such as carbon nanotubes, graphene, fullerenes, and nanodiamonds [5–7]. Among carbon fillers, nano-diamonds (ND) are of particular interest, which are characterized by extremely high mechanical strength and high thermal conductivity [6]. The advantages of ND are their non-toxicity and biocompatibility [8], which allows them to be used to create advanced biomedical materials [9].

Polymer nanocomposites containing nanodiamonds have improved functional characteristics and are used in various fields of production. For example, with the introduction of 1 % ND, Young's modulus of the nanocomposites based on polyvinyl alcohol increased 2.5 times compared to the unfilled matrix [10].

With an increase in the filler content, the thermal conductivity coefficient of such nanocomposites sharply increases, significantly exceeding the calculated values, especially at a low ND content. Song et al. [11] reports on the creation of polymer nanocomposite materials based on cellulose and ND with a maximum thermal conductivity of 5.37 W/m·K. However, there are works that state that when 5 % ND was introduced

into the polyvinyl alcohol matrix, the thermal conductivity of the system was 0.18 W/m·K, even when the content of nano-filler reached 5 % [10]. Also, the influence of ND on the structure and thermophysical properties of polymer nanocomposites has not been fully established. Various authors report that the introduction of ND leads to an increase in the crystallinity of the thermoplastic polymer matrix [12, 13]; however, for the majority of polymer nanocomposites, the crystallinity decreases with the introduction of nano-fillers such as carbon nano-tubes and montmorillonite [14]. Consequently, the effect of ND on the structure and thermophysical properties of polymer nanocomposites requires a deeper study. To solve this fundamental problem, we studied a polyethylene glycol-nanodiamond system, which is, for example, potential material for biomedical applications and nanocomposites with increased photo-oxidation resistance and long service life [13].

## 2. Experimental

Polyethylene glycol (PEG-1000) HO[–CH<sub>2</sub>–CH<sub>2</sub>–O–]<sub>n</sub>H ( $n \approx 22$ ) with a molecular mass of  $M_w = 1000$  (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 dehydrated by heating in vacuum (2 mm) at residual pressure  $p = 270$  Pa and temperature  $T = 363$  K during 5 h.

Ultradispersed nano-diamonds (UDND) ("ALIT" Ltd., Ukraine) with a spherical shape were used as a filler. UDNDs are formed when unbalanced oxygen explosives detonate in the absence of additional carbon sources. The average particle size of UDND is near 20 nm and the specific surface area is 200 m<sup>2</sup>/g.

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 frequency of 22 kHz and the output power of 150 W. A series of samples with the content of UDND in the range of 0.5–5 wt.% (hereinafter, %) were investigated.

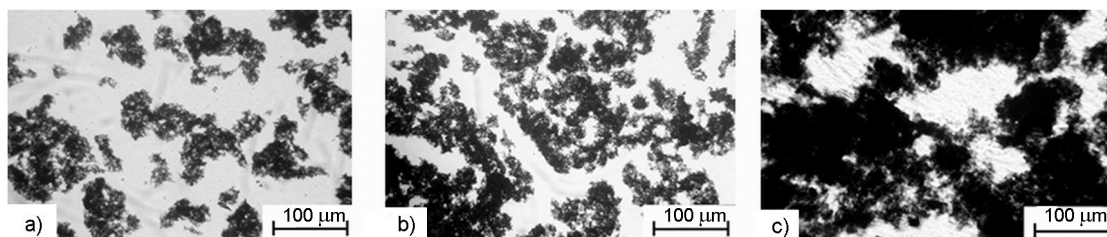


Fig. 1. Micrographs of the nanocomposites based on PEG. UDNDs content: a) 0.5 %; b) 1 %; c) 2 %.

The structure of composite at a small spatial scale was investigated using a wide angle X-ray diffraction (XRD) instrument DRON-2 (Bourestnik, Inc., St. Petersburg, Russia) with  $\text{Cu K}\alpha$  source of emission at a wavelength  $\lambda = 0.154$  nm.

The effective crystallite size  $L$  in the PEG-1000 based nanocomposites was estimated from the Scherrer equation, which can be used if the crystal is smaller than 100 nm [15]

$$L = \alpha\lambda / \beta \cos\theta_m, \quad (1)$$

where  $\alpha$  is the coefficient accounting for the form of the correlation zone (it is close to unity,  $\alpha \approx 0.9$ ),  $\beta$  is the full width of a peak at half-maximum (FWHM) expressed in radians of  $2\theta$  (width measured in  $2\theta$  degrees and then multiplied by  $\pi/180$ ),  $\theta_m$  is a half of the diffraction angle corresponding to the position of the scattering peak. For calculation of  $L$ , the most intensive maximum in the XRD pattern was used.

XRD patterns were used also for derivation of the relative fractional crystallinity of PEG-1000 based nanocomposites,  $\chi_{XRD}$ , defined as the ratio [16]:

$$\chi_{XRD} = Q_c / Q_t. \quad (2)$$

Here,  $Q_c$  is the part of area under the diffraction peak that correspond to the crystalline structure and  $Q_t$  is the total area under of the diffraction peak.

We obtained endothermic curves of melting by means of a Perkin Elmer DSC-2 differential scanning calorimeter (Germany; modified and equipped with an IFA GMBH, Ulm, software). The samples (20–30 mg) were packed in aluminium pans. Each sample was examined in the temperature range from 270 to 370 K at 2 K/min. The fractional crystallinity of PEG-1000 based nanocomposites,  $\chi_{DSC}$ , was calculated as

$$\chi_{DSC} = \Delta H_m / \Delta H_m^0, \quad (3)$$

where  $\Delta H_m$  is the heat of melting of the nanocomposite under investigation and  $\Delta H_m^0$  is the heat of melting of 100 % crystalline polymer (= 165.5 J/g [17]).

The thermal conductivity of the specimens was measured by an IT- $\lambda$ -400 heat conduction meter. To raise the accuracy, the measurements were repeated three times with each specimen with subsequent averaging of the results. The error of measurements was less than 5 %.

An optical microscope (Ningbo Sunny Instruments Co., Ltd, China) with a digital device mounted into its eyepiece and connected with a computer was used for obtaining micro-images. The specimens were placed in a glass cell 100  $\mu\text{m}$  thick and their images were recorded with a magnification of  $\times 40$ .

### 3. Results and discussion

#### 3.1. Structural features of the PEG-UDNDs system

For most polymer nanocomposites, with an increase in filler content, interactions between individual nanoparticles become stronger than polymer-filler interactions. As a result, in such systems, a structural percolation transition is observed at some threshold concentration of nanoparticles. In this case, the nanoparticles or their aggregates form a network that permeates the entire volume of the material.

Microscopic images of PEG-based nanocomposites with different concentrations of UDND in the range from 0.5 % to 2 % at  $T = 343$  K are shown in Fig. 1. It can be seen that when the UDND content is lower than the percolation threshold ( $< 1$  %), nano-diamonds form single clusters that do not connect. At concentrations near the percolation threshold ( $\approx 1$  %), UDNDs begin to form large agglomerates. Upon reaching the percolation concentration, a continuous percolation cluster is formed. At concentrations greater than 1 %, the UDND clusters begin to grow, forming a percolation net-

work. Such a low percolation threshold is typical for most of the studied polymer — nanodiamond systems [10, 18, 19].

Fig. 2 shows the XRD patterns of the system based on PEG and UDNDs. Presence of sharp (crystalline) and broad (amorphous) peaks for all the samples confirms the two-phase morphology [20]. As can be seen, the patterns of PEG-UDNDs nanocomposites consist of two major crystalline peaks at  $2\theta \approx 19^\circ$  ( $d = 4.63 \text{ \AA}$ ) and  $2\theta \approx 23.1^\circ$  ( $d = 3.80 \text{ \AA}$ ). Since the PEG-UDNDs nanocomposites have a crystalline structure, it is possible to calculate their effective crystallite size using the Scherrer Eq. (1). Table 1 shows the FWHM values, peak positions and calculated using Eq. (1) crystallite size for the PEG-based systems. To calculate the effective crystallite size for each nanocomposite, the half-width of the most intense maximum ( $2\theta \approx 23.1^\circ$ ) was used.

Table 1 shows that the angular position of the crystalline peaks of PEG-1000 is practically unchanged. When filled with UDND, their half-widths are almost unchanged, however, their weak extreme dependence on the content of the nanofiller is observed. For this reason, the effective crystallite size (Table 1) also exhibits a weak extreme dependence. This indicates that the introduction of UDNDs slightly affects the formation of crystallites by PEG macromolecules during crystallization.

For a more detailed analysis of the effect of the content of nanoscale fillers on the structure of nanocomposites based on PEG-1000, the relative crystallinity  $\chi_{XRD}$  of these systems was evaluated. To estimate the relative crystallinity of the samples, Eq. (2) was used. The calculated values of the relative degree of crystallinity for the systems based on PEG-1000 are given in Table 1. It is seen that the introduction of the filler, although it has little effect on the effective size of the crystallites, but has a significant effect on the degree of crystallinity of PEG. This fact can be explained by the large spe-

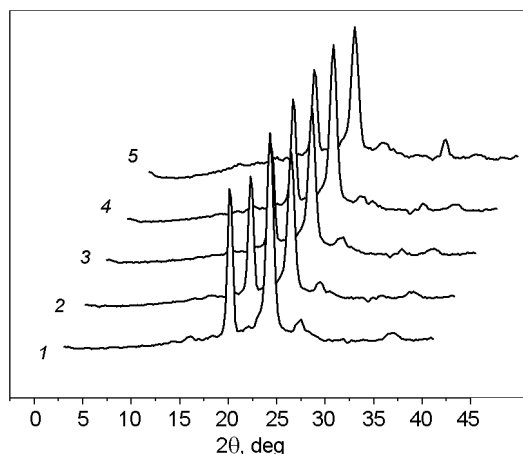


Fig. 2. Wide-angle X-ray diffraction patterns for unfilled PEG-1000 (1) and systems filled with UDND: 0.5 % (2); 1.5 % (3); 3 % (4); 5 % (5). For clarity, the curves are shifted along the x-axis.

cific surface of the UDNDs and the peculiarities of the packing of their particles.

### 3.2. Thermophysical properties of the PEG-UDNDs system

In the next stage of studying the influence of UDND content on the structure and properties of nanocomposites based on PEG-1000, their thermophysical properties were investigated. Fig. 3 shows the melting endotherms of the PEG-based nanocomposites obtained by the DSC method, and Table 2 shows the basic thermophysical characteristics.

Fig. 3 and Table 2 show that the introduction of nanodiamond particles has a significant effect on the polymer matrix of PEG-1000. It can be seen that the melting point of the studied systems exhibits extreme behavior. With an increase of the UDND content, the melting point first decreases, reaching a minimum value at the filler content of 1 %, and then increases again. Similar effects were observed in the literature for example, for PEG-1000 and laponite based nanocomposite systems. The

Table 1. Structural characteristics of nanocomposites based on PEG-1000

Sample	$\theta_m, \pm 0.1^\circ$	$\beta^\circ, \pm 0.05^\circ$	$L, \text{ nm} \pm 0.05 \text{ nm}$	$\chi_{XRD}, \% \pm 0.1 \%$
PEG-1000	23.1	0.70	12.70	58.6
PEG-0.5 % UDNDs	23.1	0.75	12.50	49.8
PEG-1 % UDNDs	23.1	0.80	12.35	44.7
PEG-3 % UDNDs	23.1	0.75	12.50	46.2
PEG-5 % UDNDs	23.2	0.70	12.70	49.0

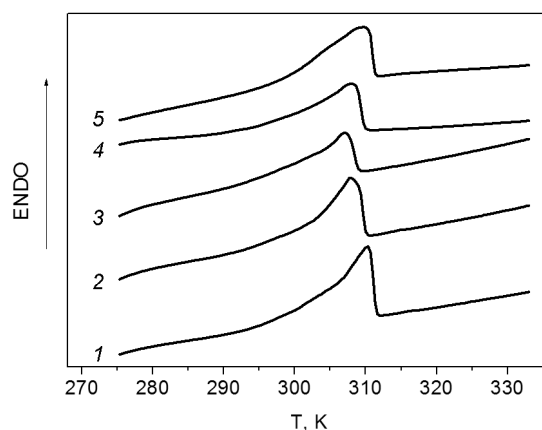


Fig. 3. DSC curves for unfilled PEG-1000 (1) and systems filled with UDNDs: 0.5 % (2); 1.5 % (3); 3 % (4); 5 % (5).

authors explain these effects by forming nanoparticles in a structural network [21].

From the thermophysical data, the crystallinity of the PEG-based nanocomposites was calculated using Eq. (3). Table 2 presents the values of crystallinity calculated by Eq. (3). It can be seen that  $\chi_{DSC}$  also exhibits extreme behavior and reaches a minimum value at the UDND content of 1 % in the system. It should be noted that the degree of crystallinity determined by different methods differs in absolute values, although it shows a similar dependence on the content of the filler. This is because the DSC method allows one to determine the true crystallinity, while X-Ray diffraction and Eq. (2) [16] give relative crystallinity.

To explain the influence of UDND on the structural and thermophysical features of the polymer matrix, all the results obtained are summarized in Fig. 4. Fig. 4 shows that the studied parameters exhibit extreme behavior with a minimum in the concentration range of the filler from 1 % to 1.5 %.

At a low content of UDND ( $< 1$  %), the developed surface of the filler impedes the processes of thermal motion of molecules of the polymer matrix and, thus, affects its thermophysical properties. At a UDND con-

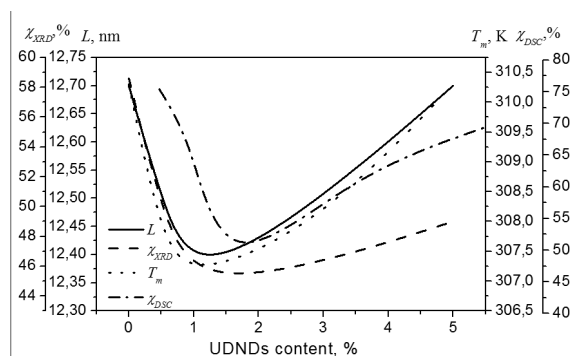


Fig. 4. The effective crystalline size, melting temperature and crystallinity vs. UDNDs content for PEG-based systems.

centration of 1 %, the crystallinity and melting point decrease, and a network is formed, similar to the percolation network of carbon nanotubes [22]. These data not only correlate with the literature data, but are also confirmed by the results of optical microscopy (Fig. 1). When the content of the filler is greater than 1 %, the nanoparticles begin to form aggregates (possibly not wetted by the matrix); this leads to a decrease in the surface of the filler, which is able to interact with the matrix. As the concentration of the filler increases above the percolation threshold, the structural and thermophysical characteristics of the composites practically change to the values corresponding to the unfilled PEG-1000 matrix.

### 3.3. Thermal conductivity of PEG-UDNDs systems

One of the main thermophysical characteristics of nanocomposite materials is thermal conductivity, which depends on many factors. In particular, the value of the thermal conductivity of polymer-nanodiamond systems is highly dependent on the quality of contacts between the filler particles, which can either conduct heat or dissipate it. Fig. 5 shows the experimental results of the dependence of the thermal conductivity coefficient on the content of filler for PEG-UDND nanocomposites. It is seen that the concentration

Table 2. Thermophysical characteristics of nanocomposites based on PEG-1000

Sample	$T_m$ , K $\pm 0.1$ K	$\Delta H_m$ , J/g $\pm 0.1$ J/g	$\chi_{DSC}$ , $\pm 0,1$ %
PEG	310.3	124.8	75.4
PEG + 0.5 % UDNDs	307.7	111.2	67.1
PEG + 1 % UDNDs	307.0	74.1	44.7
PEG + 3 % UDNDs	308.0	102.8	62.1
PEG + 5 % UDNDs	310.3	114.7	69.3

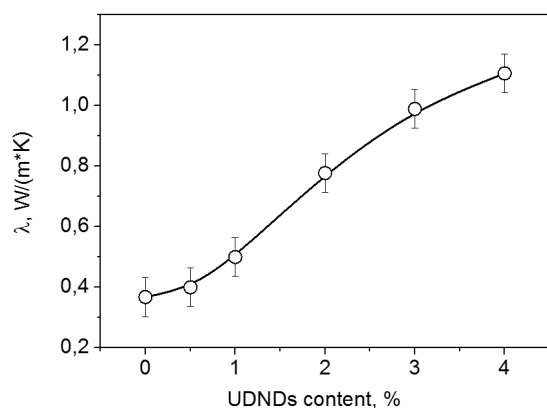


Fig. 5. Thermal conductivity vs. UDNDs content for PEG-based systems.

dependence of the thermal conductivity coefficient is nonlinear. The increase in thermal conductivity is related to the contribution of UDND to the thermal conductivity of nanocomposites, which are characterized by a much higher coefficient of thermal conductivity ( $\lambda = 50\text{--}500$  W/m·K) [23] compared to the polymer matrix of PEG ( $\lambda = 0.4$  W/m·K) [24].

Achievement of the thermal conductivity values of the nanocomposite commensurate with the thermal conductivity of nanodiamond is hindered by the presence of a developed polymer-nanofiller interface, and the energy loss due to the low thermal conductivity of the contacts is of decisive importance [25]. The sharp increase in the coefficient of thermal conductivity in the concentration range of 1–1.5 % UDND is due to the percolation process, in which nanodiamonds form a heat-conducting network in the polymer matrix. These data correlate well with the results of optical microscopy, structural and thermophysical characteristics, which confirm the structural change in the UDND concentration range from 1 % to 1.5 %. It should be noted that with the UDND content of 5 %, the thermal conductivity of the system increases to 1.1 W/m·K, which makes this material promising for practical application in the field of thermal power equipment.

#### 4. Conclusions

The effect of nanodiamond filler on the structure and properties of polymer nanocomposites based on polyethylene glycol was studied. It was found that the introduction of UDNDs leads to a change in the structure of the polymer matrix. These changes affect the microstructure: filler particles

form a continuous cluster of their aggregates at a UDND concentration of 1 %. The effect of nanoparticles on the formation of PEG crystallites has been also revealed. From the DSC data, it can be seen that the introduction of UDNDs leads to an extreme change in the crystallinity of the system, which first decreases and then increases. This extreme behavior is observed for both the melting temperature and the effective crystallite size. The crystallinity and other characteristics are minimal in the UDND concentration range of 1–1.5 %. Based on thermal conductivity studies, it has been shown that an increase in the content of filler leads to a nonlinear change in the coefficient of thermal conductivity of polymer nanocomposites based on PEG. Concentration dependence of thermal conductivity has a percolation-like behavior. The most rapid change in thermal conductivity is observed in the concentration range of 1–1.5 %; this correlates well with the change of other studied characteristics and is explained by the formation of a thermal conductive network of filler particles and their aggregates.

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