Polymer nanocomposites are widely used in various high-tech industries. Due to the combination of the elasticity of the matrix and the strength of the inorganic filler, they have improved functional characteristics compared to unfilled polymers. The article is devoted to determining the effect of carbon nanotubes (CNT) on the microstructure and properties of polymeric nanocomposite materials for 3D printing based on polycarbonate. As a result of this work, a series of composite materials was manufactured using a piston extruder. Their microstructure and functional characteristics were investigated using methods of optical microscopy, thermophysical, electrical and mechanical analysis. It was found that CNTs form clusters in the polymer matrix, which form a percolation network at a content of 0.5–0.8%. This feature of the structure formation of CNTs provided an abrupt increase in the functional characteristics of the materials obtained. It is shown that with an increase in the filler content in the system to 3%, the thermal conductivity rapidly increases to 1.22 W/(m·K). A similar effect is observed for the electrical conductivity, which increases by seven orders of magnitude from $10^{-12}$ to $10^{-5}$ S/cm at 3% CNT content in the system, exhibiting percolation behavior. With the introduction of CNTs, the crystallinity degree of the polymer matrix decreases by almost 15%, due to the fact that the developed surface of the nanotubes creates steric hindrances for polycarbonate macromolecules. This effect almost negates the reinforcing effect of nanotubes; therefore, the mechanical tensile strength with the introduction of 3% CNTs increases by only 21% compared to the unfilled matrix. In terms of their functional characteristics, the obtained materials are promising for the creation of filaments for 3D printing on their basis.

Keywords: polymer nanocomposites, carbon nanotubes, thermal conductivity, electrical conductivity, tensile strength, polycarbonate

1. Introduction

Polymer nanocomposites, as a new class of materials consisting of a polymer matrix and inorganic nanosized filler dispersed in it, have been the subject of intensive research over the past decade [1]. Due to the combination of the elasticity of the matrix and the strength of the inorganic filler, they have improved functional characteristics compared to unfilled polymers. To create new nanocomposite materials, many natural polymers, synthetic polymers, biopolymers and elastomers and inorganic nanoparticles of various types, nature and properties are used. However, the optimal selection of a polymer-nanoparticle pair, the combination of which provides the required final properties of nanocomposites, depends on the field of application of such materials [1].

Over the past two decades, 3D printing technologies using polymer filament materials have attracted considerable attention from scientists [2–7]. As a material for this technology, classical thermoplastic polymers are used, for example, polylactic acid (PLA) [2], Acrylonitrile butadiene styrene (ABS) [3], polycarbonate (PC) [4], polyamide (nylon) [5], etc. However, the process manufacturing parts using 3D printing technology using classical polymers has its own problems, the main one of which is the limited properties of polymeric materials. As it is known, the properties of a printed object directly depend on the properties of polymer filaments. Therefore, it became necessary to develop new materials with improved mechanical, physical, electrical, magnetic properties for the manufacture of functional components for various industries. To solve this problem, nanocomposite polymer materials are used to create filaments [6].

Therefore, an urgent task is to create nanocomposite polymer materials based on classical polymer matrices modified with inorganic nanofillers. In the future, this will make it possible to create filaments on their basis, improve the print quality and increase the necessary properties of the printed object.
2. Literature review and problem statement

The final properties of composite polymer materials are largely influenced by the size of the filler particles. Thus, in [7], the authors studied the effect of the size of filler microparticles on the viscosity and mechanical properties of composites based on thermoplastic elastomer and steel powder. It was found that the introduction of particles of a larger diameter worsened the mechanical characteristics of the material and made it impossible to use such materials for printing. This was due to large aggregates of filler particles that created defects in the polymer matrix. Subsequently, the efforts of scientists were aimed at introducing a smaller filler for its uniform distribution in the polymer. Thus, in [8], the effect of micro- and nanosized particles on the mechanical properties of polymer materials based on ABS was studied. It is shown that the introduction of a nanofiller (SiO$_2$ and carbon nanotubes) increases the thermal shock resistance and improves the strength of materials in comparison with the introduction of microfillers (ZrB$_2$ and Al). The authors suggested that the introduction of nanosized filler is more effective for improving the functional characteristics of materials; however, the mechanism of the reinforced effect of the filler remains not fully understood.

In addition to the size of the filler particles, the properties of composite polymer materials significantly affect their type. To create such systems, carbon-based nanomaterials, ceramic and metal powders, glassy fillers, minerals, etc. are used. [nine]. However, to ensure the required physical properties, the type of filler must be selected individually for solving a specific problem. One of the most promising are nanosized carbon materials (carbon nanotubes (CNT), graphene, nanodiamonds), which provide improved mechanical, electrical, and thermal properties [10]. But the issues of manufacturing materials containing carbon nanofillers remained insufficiently covered. The reason for this may be problems associated with the distribution of the inorganic filler within the polymer matrix and its aggregation ability.

For carbon nanomaterials introduced into a polymer matrix, the characteristic phenomenon of percolation, which consists in an abrupt increase in the properties of the material with the introduction of a critical filler content. For example, the introduction of CNTs into a polyethylene oxide matrix leads to an increase in electrical conductivity by more than two orders of magnitude [11]. In this case, percolation behavior is observed, in which clusters with CNTs at a content of 0.5 % form an electrically conductive network inside the polymer matrix. However, the increase in conductivity is negligible compared to other systems. The reason for this may be the intense aggregation of CNTs in the polyethylene oxide matrix. In contrast to systems based on polyethylene oxide, a rather large jump in electrical conductivity was observed for the PLA-CNT system [12]. Thus, the electrical conductivity of such a system increased from 10$^{-9}$ to 10$^{-2}$ S/cm, while the percolation threshold was 0.25 0.5 %. However, the percolation behavior for other, besides electrical conductivity, properties of the system has not been established. The introduction of CNTs abruptly changes the thermal conductivity of nanocomposite materials. For example, in [13], with the introduction of 0.6 % VHT, the thermal conductivity of a material based on polyethylene oxide increased from 0.3 to 0.8 W/(m·K), exhibiting percolation behavior. In addition, the introduction of CNTs makes and reinforces the effect on the polymer matrix, however, the increase in mechanical properties is less pronounced in comparison with electrical conductivity. In [14], the mechanical properties of materials based on ABS and carbon nanotubes were studied. It is shown that the introduction of 3 % CNTs in a polymer matrix leads to an increase in Young's modulus in the system by 10 %. However, the authors did not observe a jump-like (percolation) behavior of the mechanical properties. The reason for this is probably the imperfection of the methods for introducing nanosupply into the polymer matrix.

Thus, the existing studies devoted to the study of the microstructure and properties of nanocomposite systems filled with carbon nanotubes do not answer many questions devoted to the creation of materials with improved characteristics. Further development will require research to determine the effect of the nanofiller on the functional properties of polymer systems when using new methods of manufacturing such nanocomposite materials.

3. The aim and objectives of research

The aim of research is to determine the effect of carbon nanotubes on the microstructure and functional properties of polycarbonate-based polymeric nanocomposite materials, manufactured using a piston extruder. This will make it possible to establish the content of nanotubes, at which the functional characteristics acquire high values, and to create materials that will be promising as filaments for 3D printing.

To achieve this aim, the following objectives were solved:

- to investigate the microstructure of materials based on polycarbonate and carbon nanotubes;
- to establish the effect of the filler on the electrical properties of the manufactured materials;
- to investigate the effect of the filler on the thermophysical characteristics of the materials obtained;
- to establish the features of the influence of the filler on the physical and mechanical characteristics of the created materials.

4. Materials and methods of research

4.1. Investigated materials used in the experiment

Polycarbonate (PC) ($M_w$~45,000), manufactured by Merk (Germany). The melting point is in the range 490–520 K, the glass transition temperature is 416 K, the density at 25 °C is 1.2–1.22 g/cm$^3$. PC is non-toxic, heat and chemical resistant.

Carbon nanotubes produced by JSC Spetsmash (Ukraine) were used as a filler. The CNTs that were used to obtain polymer nanocomposites were multilayer and manufactured by the CVD (chemical vapor deposition) method [15]. The filler contained a small amount of mineral impurities, the content of which was not more than 0.1 %. Carbon nanotubes had a specific surface area of 190 m$^2$/g, an outer diameter of 20 nm, a length (5÷10) μm, and a length-to-diameter ratio $L/d=250±170$.

4.2. Technique for the manufacture of the materials

Composite samples were prepared by the extrusion method (mechanical grinding in the melt) using a piston extruder, followed by cooling according to n. v. [16]. The filler content was varied within (1–3) mass % (further – %). The main advantage of piston extruders over
screw extruders is the ability to vary the mixing time of the filler particles with the molten polymer matrix, after which the test sample can be formed in the form of either a plate or a thread.

The procedure for obtaining the studied materials based on polycarbonate and carbon nanotubes is given below. Previously, all the original components of the polymer composite material were mixed mechanically. After that, the resulting mixture of components was loaded into the cylindrical base of the extruder (Fig. 1). The installation was heated to a temperature of 570 K. When the piston part of the extruder rotated in the melt of the polymer composite, very high shear stresses are created, and aggregates with CNTs are destroyed.

Thermophysical studies were performed in a dry air atmosphere using an upgraded Perkin Elmer DSC-2 instrument (Germany). The temperature range was from 265 K to 550 K, the heating rate was 2 K/min, the research method was modulated differential scanning calorimetry (DSC). The procedure for obtaining the studied materials based on polycarbonate and carbon nanotubes is given below. Previously, all the original components of the polymer composite material were mixed mechanically. After that, the resulting mixture of components was loaded into the cylindrical base of the extruder (Fig. 1). The installation was heated to a temperature of 570 K. When the piston part of the extruder rotated in the melt of the polymer composite, very high shear stresses are created, and aggregates with CNTs are destroyed.

The measurement error was 5 %, which is reflected in the graph of the dependence of thermal conductivity on the content of the filler. Studies were carried out at a temperature of 303 K. The measurement error was no more than 3 %.

It was found experimentally that the most uniform mixing of filler particles in the matrix occurs within 10 minutes. After this time, hole 4 was opened and the pressure on the composite was increased by the piston. In this case, the melt of the polymer composite passed through a hole ∼2 mm in diameter, forming filamentary specimens.

4.3. Methods for studying the functional properties of the obtained composite materials

The study of the microstructure of the obtained materials was carried out using a SIGETA MB-303 digital optical microscope (Ukraine) equipped with a SIGETA DCM-800 digital video camera (Ukraine). To conduct research, materials in a molten state were placed between two plane-parallel glass plates, the gap between which was 80 μm. To obtain information on the fractality of the structure of clusters with CNTs, the obtained micrographs were processed using the ImageJ v1.41 program. Cluster analysis was performed using the Hoshen-Kopelman algorithm [17].

To study thermal conductivity, the method of dynamic calorimetry was used, implemented on the IT-κ-400 device (Kazakhstan). To increase the accuracy, the measuring cell was modified by mounting several additional thermocouples. The studies were carried out at a temperature of 303 K. The measurement error was 5 %, which is reflected in the graph of the dependence of thermal conductivity on the content of the filler.

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The electrical conductivity of the materials under study was measured using an E7-20 immittance meter (Belarus). The sample was placed in a measuring cell, which consisted of two electrodes. The studies were carried out at an alternating current at a frequency of 1 kHz and 293 K.

In this work, a study of tensile fracture stresses was carried out according to (tensile strength). The dimensions of the samples were examined: length l=100±2 mm, diameter d=2±0.3 mm. The study of the effect of filler content on tensile strength was carried out using an automated tensile testing machine UM-5 (Ukraine) (modified with high-precision pressure and displacement sensors) at a load speed v=5 N/s. The measurement error was no more than 3 %.

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5. The results of studies of the effect of filler on the microstructure and functional properties of polycarbonate-based materials

5.1. Study of the microstructure of nanocomposite materials based on polycarbonate and carbon nanotubes

Polymer systems that contain carbon nanotubes have their own microstructure features. First of all, this is due to the fact that there are strong gravitational forces between CNTs, so they tend to form aggregates. Another feature of such systems is the formation of a percolation grid of units. All these features can be established using the method of high-resolution optical microscopy.

Micrographs for PC-CNT systems with a nanotube content of 0.1 % to 1 % at T=303 K are shown in Fig. 2.

From Fig. 2 it can be seen that when the content of CNTs is close to the percolation threshold (0.1–0.5 %), the nanotubes form separate clusters and do not interconnect. At concentrations near the percolation threshold (>0.8 %), CNTs begin to form large agglomerates.

To assess the degree of space filling and the morphology of clusters from nanotubes, the values of the fractal dimension d were calculated. In this study, the fractal dimension is calculated using the “box-counting” algorithm by counting the number of squares of size L required to overlap aggregates with a perimeter N[18]:
The main requirement of the image processing program is binary images, so all micrographs were converted to black and white format. In this case, the value of the fractal dimension for two-dimensional objects \( d_f^2 \) was obtained. For the transition to three-dimensional objects, the following formula was proposed in [18]:

\[
d_f^3 = d_f^2 + 1,
\]

where \( d_f^2 \) – fractal dimension of two-dimensional aggregates; \( d_f^3 \) – fractal dimension of two-dimensional aggregates.

5. 2. Influence of carbon nanotubes on the electrical properties of polycarbonate-based systems

Most polymer systems containing CNTs are characterized by an abrupt change in properties, in particular in electrical conductivity. Therefore, their behavior is often described within the framework of the scaling approach of the theory of critical percolation. [19]. Using the percolation theory approach, the concentration dependence of the electrical conductivity of PC-CNT systems can be described by the scaling equation [20]:

\[
\sigma \propto (\phi - \phi_c)^t \text{ at } \phi > \phi_c
\]

where \( \sigma \) – electrical conductivity of the nanocomposite material; \( \phi \) – CNT concentration; \( \phi_c \) – percolation threshold (critical concentration of CNTs); \( t \) – critical index of electrical conductivity.

Fig. 3 shows the concentration dependence of electrical conductivity for the studied PC-CNT systems at a current frequency of 1 kHz.

From Fig. 3, it can be seen that in the concentration range from 0.5 to 1 %, the electrical conductivity of the system changes abruptly. Such a change in properties is more likely associated with the phenomenon of percolation. With a content of 1 % carbon nanotubes in the system, the electrical conductivity is seven orders of magnitude higher than the electrical conductivity to the percolation threshold.

5. 3. Influence of carbon nanotubes on the thermophysical properties of polycarbonate-based systems

Differential scanning calorimetry provides detailed information on the change in the thermophysical characteristics and the degree of crystallinity of the polymer matrix when a filler is introduced into the system. Fig. 3 shows the results of calorimetric studies for the materials obtained. The studies were carried out in the most informative temperature range from 265 to 550 K. From Fig. 4 it is possible to see that the introduction of CNTs affects the thermophysical characteristics of nanocomposite materials. On the plots of the \( C_p(T) \) dependence (Fig. 4), for all the systems under study, one endothermic maximum is observed, which is responsible for the melting of the crystalline phase of PS [21].
used. The degree of crystallinity is calculated using data obtained from various techniques, such as X-ray diffraction analysis or infrared spectroscopy. However, the degree of crystallinity can be calculated most accurately using the thermophysical studies according to formula (4) [22]:

\[ \chi_c = \frac{\Delta H_m}{\Delta H_{m,C}} \times 100 \% \]  

(4)

where \( \Delta H_m \) – measured enthalpy of melting, \( \Delta H_{m,C} \) – enthalpy of melting of 100 % crystalline polymer (for PC, \( \Delta H_{m,C} = 134.3 \text{ J/g} \) [23]).

Fig. 5 shows the concentration dependencies of the thermal conductivity for materials based on PC-CNT. Fig. 5 shows that the dependence \( \lambda(\phi) \) is nonlinear. The increase in the thermal conductivity is abrupt. This rapid growth is due to the introduction of CNTs, which have orders of magnitude higher thermal conductivity compared to the polymer matrix [24].

An abrupt change in the properties of a system, including thermal conductivity, is described within the framework of the scaling approach of the theory of critical percolation. Using the percolation theory approach, the concentration dependence of the thermal conductivity of the obtained nanocomposite materials (\( \lambda_{eff} \)) can be described using the scaling equation [25]:

\[ \lambda_{eff} = (\phi - \phi_c)^k \text{, at } \phi > \phi_c \]  

(5)

where \( \phi \) – content of the heat-conducting filler (CNT); \( \phi_c \) – critical concentration of nanotubes (percolation threshold); \( k \) – critical index of thermal conductivity.

Fig. 6 shows the dependence of the tensile strength on the content of carbon nanotubes. From the dependence of the strength on the CNT concentration, it can be seen that with an increase in the filler content, the tensile strength of the system increases. At the same time, with a content of 3 % in the material, the tensile strength increases by 21 %.

5.4. Influence of carbon nanotubes on the physical and mechanical characteristics of the created materials polycarbonate-based materials

To study the effect of the filler on the mechanical characteristics of the PC-CNT system, the tensile strength of the obtained materials was studied.

6. Discussion of the results of the effect of the filler on the functional properties of polymer composite materials

The specific features of CNT structuring in a polymer matrix play a key role in the acquisition of the final properties of the created material. Therefore, their installation is a very important stage in the study of the material polycarbonate-carbon nanotubes. As can be seen from Fig. 2 structures that form clusters with CNTs significantly depend on the content of nanotubes. The micrographs show aggregates that exist separately at low filler concentrations, and at high concentrations form a network throughout the material. When the percolation concentration is reached (0.8 %), a continuous percolation cluster is formed (Fig. 2). It can be seen that at concentrations exceeding (1 %), clusters with CNTs enlarge, forming a network. Compared to other types of fillers, a low percolation threshold (less than 1 %) is quite typical for materials containing CNTs. This is explained by the shape anisometry of carbon nanotubes, which are of great importance for the ratio of length to diameter [26].

From the analysis of the fractal dimension, it was found that the fractal dimension increases with an increase in the content of the filler in the material. The \( d_f \) value ranges from 2 (in the case of flat aggregates) to 3 (in the case of dense aggregates). At 3 % CNT content, the fractal dimension of the systems is 2.9, which indicates the formation of dense and rough aggregates from nanotubes.

The electrical properties of nanocomposites depend on the type of nanoparticles, their shape, size, the method of intro-
duction, and the method of arrangement in the polymer matrix [19]. However, the filler content has the greatest influence on many properties of polymeric materials. When filling a polymer matrix, its properties can change dramatically at certain critical filler concentrations. This behavior of the properties of nanocomposites with a change in the filler content is well described within the framework of the percolation theory [27].

To determine the critical index and percolation threshold, the concentration dependence of the electrical conductivity (Fig. 3) was modeled using (3). According to the simulation results, it was found that the percolation threshold was 0.8 %, and \( t = 2.23 \pm 0.12 \). The critical index value indicates the formation of a three-dimensional network with CNTs inside the material. The value of \( \varphi_c \) is very close to the values of the percolation threshold for similar polycarbonate-CNT systems (0.5 %) [28] and polyester-CNT systems (0.45 %) [29].

The calculated value of the \( t \) index in terms of its value turned out to be slightly higher than the theoretical value of \( t = 2 \). According to [27], if particles of an electrically conductive medium, they form a percolation cluster, then \( t = 2 \). In this case, the value of the critical index \( t \) is very close to the theoretical, which indicates the uniformity of the distribution of nanotubes within the polymer matrix.

Fig. 4 and Table 1 show that CNTs affect the polymer matrix of PC. Thus, the melting point of nanocomposites increases with increasing filler content. In the presence of CNTs, which act as nucleation centers for crystallites, smaller crystallites are formed, which require more energy to melt. In this case, the amplifying effect of nanotubes on the structure of the polymeric matrix of PC is traced. The values of the crystallinity degree for the investigated systems, calculated according to (4), are given in Table 1. This tendency to change the crystallinity of the matrix is opposite to the change in the melting point of the system. It is shown that the introduction of CNTs into a polymer matrix leads to a decrease in the PC crystallinity by 15 %, which in turn can affect the mechanical properties of the materials obtained.

Compared with a jump in electrical conductivity by several orders of magnitude with a CNT content of up to 3 %, the thermal conductivity of the PC-CNT system increases several times and reaches a value of 1.22 W/(m·K). Achievement of thermal conductivity values of the nanocomposite commensurate with the thermal conductivity of nanotubes is hindered by the presence of a developed polymer-filler interface, and the decisive factor is the energy loss due to the low thermal conductivity of the contacts [30]. A sharp increase in the thermal conductivity coefficient at a concentration of 0.8 % of CNTs is associated with the percolation process, in which nanotubes form a heat-conducting network in the polymer matrix.

Using the method of least squares and (5) to describe the experimental data on the concentration dependence of thermal conductivity (Fig. 5), let's determine the value of the percolation threshold \( \varphi_c \), and the critical index \( k \). The value of the thermal conductivity percolation threshold for the PC-CNT system is 0.8 %, and \( k = 0.38 \pm 0.06 \). The percolation threshold was found to be lower than for most polymer-CNT systems.

It is because of the decrease in the crystallinity of the polymer matrix that the reinforcing effect of carbon nanotubes on the polymer matrix is suppressed. Fig. 6 shows that with an increase in the filler content, the tensile strength of the studied systems increases, but this increase is insignificant and is only 21 %. It can be assumed that there are two competing processes inside the material: the formation of a reinforcing mesh from the filler and the destruction of the solid crystalline structure of PC.

Polymer nanocomposites based on polycarbonate and CNTs are promising for creating materials for 3D printing. Their prospects are associated with an improved complex of their characteristics in comparison with unfilled PCs. The materials obtained are more heat-resistant, have higher thermal and electrical conductivity and mechanical strength.

The research carried out concerns the study of the effect of carbon nanotubes on the microstructure and some functional properties of polymer composites. This work only evaluates the prospects of using the created nanocomposite materials as filaments for 3D printing technologies. Other characteristics important specifically for filaments, such as temperature and concentration dependences of melt viscosity, melt flow rate, and hardening rate will be the subject of our next publications.

Further development of this study will consist in the experimental confirmation of the possibility of using PC-CNT materials as filaments. It is also planned to directly manufacture such filamentous materials, 3D print various objects and study the complex of their physical and mechanical properties. The creation of filaments based on other plastic thermoplastic polymer matrices filled with carbon nanotubes will also be of considerable interest.

### 7. Conclusions

1. It has been found that CNTs introduced into the composition of the PS matrix, at a content of 0.8 %, form a percolation network that permeates the entire volume of the material. Thus, a change in the structure leads to a significant increase in the functional characteristics of the obtained materials.

2. It has been revealed that the introduction of 3 % fillers leads to a significant increase in electrical conductivity (about 7 orders of magnitude), thermal conductivity (more than 5 times) and mechanical tensile strength (about 20 %) of the materials under study. This rapid growth is due to their percolation behavior.

3. It has been shown that the introduction of fillers leads to an increase in the melting temperatures of PC-based systems. This is a consequence of the nucleation function of CNTs, which act as nucleation centers for the crystalline phase. The degree of crystallinity of the polymer matrix is reduced by 15 %, which leads to suppression of the effect of matrix reinforcement and a rapid increase in mechanical strength.

4. It has been shown that the functional characteristics of the material based on PC and 3 % CNTs are significantly higher than in unfilled matrices. The developed materials have improved functional characteristics compared to unmodified polycarbonate. The combination of improved properties makes the use of such composite materials promising for the creation of filaments for 3D printing.

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