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Functional properties of polymer composite materials based on polypropylene, carbon nanotubes and silver nanoparticles for transportation systems

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Abstract

Due to its unique characteristics, the creation of polymer nanocomposite materials opens wide prospects for their use in transportation systems. The influence of carbon nanotubes (CNT) and silver nanoparticles (SN) on the functional properties of polymer composites based on polypropylene (PP) was studied using the methods of impedance spectroscopy, differential scanning calorimetry, and mechanical analysis. It is shown that the introduction of nanofillers leads to a decrease in the degree of crystallinity and the melting temperature of polypropylene-based systems, which is a consequence of the destruction or increase in the defectivity of the crystalline structure of the polymer matrix under the influence of inorganic nanoparticles. Due to a more developed surface, SN have a greater influence, compared to CNT, on the thermophysical characteristics of the studied materials. At a filler content of 0.5 %, the crystallinity of unfilled PP, which is 72.1 %, decreases to 64.7 % in the case of CNT filling and to 53.4 % in the case of SN filling. An extreme change in the electrical conductivity of polymer composites is observed, which is a consequence of the formation of a percolation cluster in the polymer matrix, a mesh of filler that permeates the entire volume of the material. The maximum electrical conductivity is observed at a filler content of 2 %. For the PP-CNT system, the maximum electrical conductivity is 10^{-5} S/cm, and for the PP-SN system, it is 10^{-9} S/cm. An extreme change in the electrical conductivity of polymer composites is observed, which is a consequence of the formation of a percolation cluster in the polymer matrix, a network of filler that permeates the entire volume of the material. As a result of conducted studies of electrical conductivity, the percolation threshold was determined, which for these systems filled with CNT is 0.5 %, and for systems containing SN is 0.82 %. An increase in mechanical strength was recorded, which for PP-CNT systems increases by approximately 50 %, and for PP-SN systems by about 30 %. The obtained properties make the studied materials promising for use in transportation systems.

Keywords: *carbon nanotubes, mechanical strength, percolation, polypropylene, silver nanoparticles.*

Introduction

Polymer composite materials (PCM) have been the subject of intensive research for the past twenty years. Considerable interest in this type of systems is caused by their unique properties, which arise due to the combination of flexible organic and rigid inorganic components [1]. One of the most promising fields of application of polymer composite materials are transportation systems.

Pipeline systems using reinforced polymer composites are more reliable and resistant to highly corrosive liquids at various pressures, temperatures, adverse soil and weather conditions (especially for oil exploration, desalination, chemical plants, fire mains, dredging, transport water, etc.). Composite pipes are commonly used in oil transportation, where resistance to crude oil, paraffin formation, and the ability to withstand relatively high pressures are required.

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Polyolefins, which are characterized by high resistance to aggressive environments, are used as a basis for the creation of PCM for transportation systems. One of such polymers is polypropylene (PP) – a thermoplastic polymer that is widely used in the plastics industry. It is endowed with excellent chemical resistance, effective mechanical properties, high temperature of thermal deformation, excellent rigidity, electrical insulation, significant resistance to coagulation and ease of forming [2]. Due to low production costs, PP is often used in many industries. Polypropylene has a crystalline structure with a high level of rigidity and a high melting point compared to other commercial thermoplastics.

Various inorganic fillers, in particular nanofillers, are used to create PCM with functional characteristics that are necessary for transportation systems. Among the most promising fillers are carbon particles (carbon nanotubes (CNT), thermally expanded graphite, soot, nanodiamonds) and metal nanoparticles (iron, silver, copper) [3–6]. The combination of polypropylene matrix and carbon nanotubes leads to a number of unique properties of such systems. So, for example, Sahli and others established that the introduction of CNT into the PP system can increase the heat resistance of nanocomposites due to the interaction between the outer walls of CNT and the crystal structures of PP [7]. Moreover, the formation of barrier with CNT prevents mass transfer and provides thermal insulation and protects the base polymer from the heat source. In their work, Stanciu et al. studied in detail a system based on PP and up to 5 wt. % CNT [8]. It is established that the addition of CNT does not significantly change the melting and crystallization behavior of PP-CNT nanocomposites. The effect of CNT on melt shear viscosity is more pronounced at low shear rates. However, with the addition of up to 5 wt. % CNT, the nanocomposite still behaves as a non-Newtonian fluid. The thermal conductivity coefficient, depending on pressure, CNT content, and temperature, did not exceed 0.35 W/m·K. The PP-CNT nanocomposite is not electrically conductive up to 3 wt. %, while after reaching the percolation threshold, the nanocomposite with 5 wt. % becomes semiconductive with an electrical conductivity of 1−10 S/m. Tensile modulus, breaking strength, and stress at break increase, while elongation at break decreases significantly with increasing CNT content.

Coppola et al. showed that PCM based on PP and CNT have wide practical applications, in particular as strain gauges for health monitoring [9]. Such sensors were tested in the mode of 3-point bending, recording the change in impedance as the load increased. It is shown that PP-CNT nanocomposite foils with 5 wt. % CNT demonstrate significant advantages compared to materials based on other matrices and fillers.

In contrast to other fillers, the introduction of silver nanoparticles into the composition of PCM based on polypropylene leads to the occurrence of new unique properties [10]. The authors showed that the introduction of silver nanoparticles into the composition of the polypropylene foil improves the properties of thermal degradation and crystallization. In addition, such systems show high antimicrobial activity of the foil substrate against gram-negative (Escherichia coli) and gram-positive (Staphylococcus aureus) bacteria. They noted that the nanocomposite, which contains 0.4 % of silver nanoparticles, shows dramatically improved antibacterial properties due to the release of active oxygen forms and Ag+ ion diffusion processes. Similar effects were recorded by the authors of works [11, 12].

Therefore, the analysis of the literature showed, that the study of the effect of different types of nanofillers on the functional properties of polymer materials, especially for transportation systems, is quite up-to-date. That's why, the purpose of our work was to study the influence of carbon nanotubes and silver nanoparticles on the electrical, thermophysical and mechanical properties of polymer composite materials based on polypropylene. Achieving this goal involves fulfillment of the following tasks:

1. Production of a number of polymer composite materials based on polypropylene filled with carbon nanotubes and silver nanoparticles by extrusion method using a piston extruder.
2. Conducting electrical researches to study the electrical and dielectric characteristics of the obtained materials.
3. Study of thermophysical characteristics, namely thermal conductivity and heat capacity, of PP-nanofiller systems and their analysis.
4. Conducting mechanical tests for PP-based materials.

Objects and methods of research

Materials based on polypropylene filled with carbon nanotubes and silver nanoparticles were used for the research.

Polymer matrix. Polypropylene (PP), produced by SABIC®HDPE Eurotrubplast Holding Company Ltd Trusthose (Saudi Arabia), was chosen as the polymer matrix for the preparation of experimental samples ($T_m \approx 437$ K).

Multiwalled carbon nanotubes. Multiwalled CNT produced by «Spetsmash» Ltd (Ukraine) are made of ethylene by chemical vapor deposition (CVD). The content of mineral impurities was no more than 0.1%. CNT contained functional groups on the surface, the content of which was determined by titration. Specific surface area – 190 m^2/g, outer diameter – 20 nm, length (5–10) μm, aspect ratio L/d ≈ 250 ± 170.

Silver nanoparticles. Ag(0) nanoparticles were synthesized by restoration of Ag(I) ions within $AgNO_3$ with trisodium citrate in the presence of ion-containing oligomer of hyperbranched structure HB-([SO_3]-[HMim+])$_{32}$, that we developed, as their surface stabilizer. To 0.941 g (0.002202 equiv) of HB-([SO_3]-[HMim+])$_{32}$ in 22 ml of water was added 0.125 g (0.000734 equiv) of $AgNO_3$ in 8 ml of water, the mixture was stirred for 10 min at room temperature, added 0.731 g (0.002833 equiv) of $C_6H_5O_7Na_3$ in 30 ml of water and stirred for another 10 min. Next, the temperature of the solution was raised to 100°C and boiled it with a returned condenser for 1 hour. At the same time, the color of the solution was changing from yellow to brown. The solution was filtered, the water was evaporated at 70–75 °C, the obtained product as a brown sediment was vacuumed at a residual pressure of 1–3 mm Hg and a temperature of 75–80 °C, washed with ethanol and dried in a vacuum (1–3 mm Hg) at 75-80 °C. Product yield is 0.868 g (85.2 %). The obtained product is a brown powder soluble in water and insoluble in organic solvents.

The composite samples were produced by the method of extrusion (mechanical grinding in the melt) using a piston extruder followed by cooling under normal conditions. The content of the filler was varied within (1–5) wt. % (further – %). The main advantage of piston extruders over screw extruders is the ability to vary the time of mixing 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 manufacturing technology of the studied materials is given in the work [13].

The electrical properties were investigated by the method of impedance spectroscopy, implemented on the basis of the immittance meter E7-20. At the same time, the real (Z') and imaginary (Z") parts of the impedance were measured in the frequency range from 10 Hz to 1 MHz. The thickness of the samples was 100 μm.

The study of the temperature dependences of the heat flow was carried out in a dry air atmosphere in the temperature range from –70 to 200 °C at a heating rate of 10 °C/min by the method of differential scanning calorimetry (DSC) on the DSC-60 Plus device (Japan). The absolute error in determining the temperature of phase and relaxation transitions was 0.1 °C.

The study of the damaging stresses under static tension was carried out in the work. Dimensions of the studied samples: length l=100±2 mm, diameter d=2±0.3 mm. The study of the effect of the filler content on the tensile strength was carried out using an automated tensile machine UM-5 (Ukraine) (modified with high-precision pressure and displacement sensors) at a loading rate of υ=5 N/s. The measurement error was no more than 3 %.

Results and discussion

To establish the influence of nanofillers of different nature on the functional characteristics of polymer nanocomposite materials, studies of their electrophysical, thermophysical and mechanical properties were conducted.

Electrophysical properties of PCM

Since carbon nanotubes and silver particles have high electrical conductivity, it was necessary to study the effect of these nanoparticles on the electrical properties of PCM based on PP. For this purpose, the dependence of electrical characteristics of materials on frequency was studied by the method of impedance spectroscopy. In Fig. 1 the concentration dependences of electrical conductivity for various fillers are given.

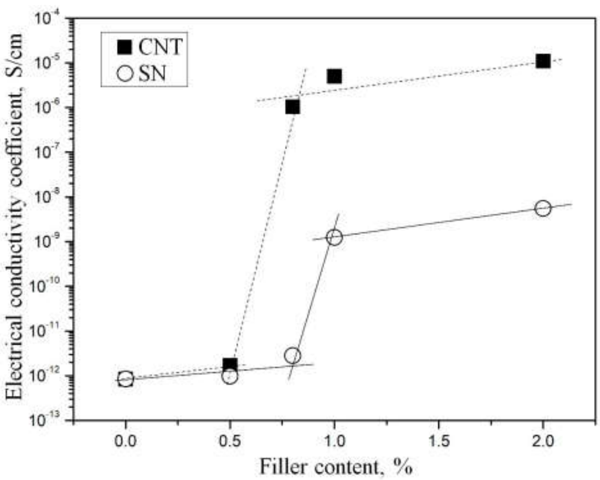


Figure 1 – Dependence of electrical conductivity at a frequency of 1 kHz on the content of nanoparticles of different types for polypropylene-based systems

Figure 1 shows that the qualitative behavior of electrical conductivity is similar, but some differences are observed. For example, the maximum electrical conductivity for PP-CNT systems with a 2 % filler content is 10^{-5} S/cm, while for systems with the same SN content, this value is 10^{-9} S/cm. However, it is worth noting that the obtained level of electrical conductivity of materials filled with SN is significantly lower than the electrical conductivity of PCM with CNT. This is because the silver nanoparticles have been stabilized by an ionic liquid, which is essentially a hyperbranched polymer. The polymer creates a shell around the particle, which prevents the direct passage of charge carriers through the silver particles.

In the concentration range from 0.5 to 0.75 % for PCM with CNT and from 0.8 to 1 % for PCM with SN, the electrical conductivity of the systems changes abruptly. Such a change in properties is more likely associated with the phenomenon of percolation. Analyzing the data of Fig. 1, percolation thresholds (φ_c) were determined as a part of the percolation theory scaling approach. For the PP-CNT systems φ_c = 0.5 %, and for the PP-SN system – φ_c = 0.82 %. With a content of 1 % of carbon nanotubes in the system, the electrical conductivity is seven orders of magnitude higher than the electrical conductivity up to the percolation threshold, and in the case of silver nanoparticles – by three orders of magnitude. These data indicate the formation of a reinforcing mesh from filler nanoparticles inside the studied materials, which in the future will contribute to a rapid growth in mechanical characteristics.

Thermophysical properties of PCM

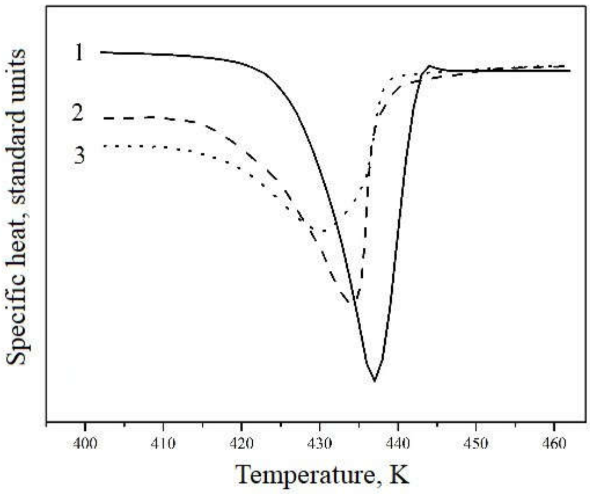
In order to establish the influence of different types of fillers on the thermophysical characteristics and the degree of crystallinity of the polymer matrix, the samples were examined by DSC method. Figure 2 shows the results of DSC studies for PP-based composites in the temperature range from 400 to 465 K, since this is the most informative interval in which the melting process of the polymer is observed. From the analysis of the data shown in Fig. 2, it can be seen that the amount of introduced filler significantly affects the thermophysical characteristics of polymer-filled systems. On the graph is observed one endothermic maximum, which indicates the melting of the PP crystalline phase.

Table 1 shows the main thermophysical characteristics of the PP-nanofiller system.

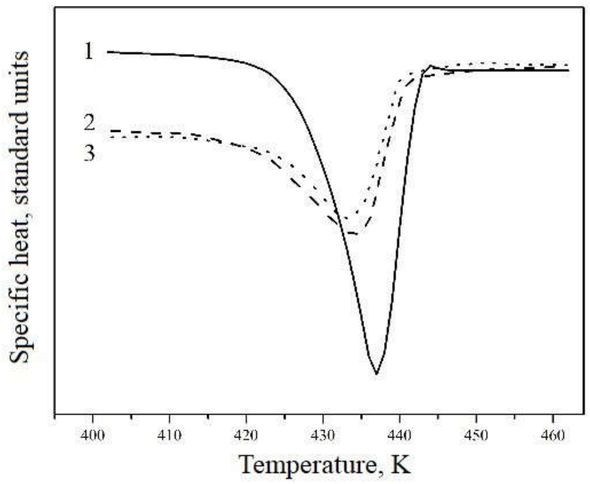
Table 1 – Thermophysical characteristics of nanocomposites based on PP and nanofillers

Name	T_m, °C	ΔH_m, J/g	χ_c, %
PP	437.2	122.57	72.1
PP+0.5 % CNT	434.1	109.99	64.7
PP+1.0 % CNT	430.5	87.38	51.4
PP+0.5 % SN	434.0	90.78	53.4
PP+1.0 % SN	432.6	90.44	53.2

Table 1 shows that different types of nanofillers have different effects on the polymer matrix of partially crystalline PP. Thus, the melting point of composites decreases with increasing filler content. Analyzing the DSC graphs in Fig. 2a and 2b, it can be observed that in the presence of SN, smaller crystallites are formed, in contrast to crystallites in the presence of CNT, which require less energy to melt. At the same time, the structure of the polymer matrix becomes more defective.



a)



b)

1 – 0 %; 2 – 0.5 %; 3 – 1 %

Figure 2 – Temperature dependence of the specific heat for PCM based on PP filled with CNT (*a*) and SN (*b*)

The degree of crystallinity (χ_C) is one of the key characteristics of polymers and indicates the proportion of crystalline areas in the polymer. The degree of crystallinity of the studied systems can be calculated from the thermophysical data presented in Fig. 2, using the formula (1):

$$\chi_C = \frac{\Delta H_m}{\Delta H_{m,C}} \cdot 100\ \% , \qquad (1)$$

where ΔH_m is measured melting enthalpy, $\Delta H_{m,c}$ is melting enthalpy of 100 % crystalline polymer (for PP, $\Delta H_{m,c} =$ 170 J/g [14]).

The values of the degree of crystallinity for the investigated systems, calculated according to formula (1), are given in the Table 1. This trend of change in crystallinity of the matrix correlates well with a decrease in the melting point of the system. It can be seen that the introduction of nanofillers into the polymer matrix leads to a significant decrease in the crystallinity of PP. However, depending on the type of filler, this effect is different. It can be seen that the introduction of SN suppresses the crystallinity of the polymer matrix more than the introduction of CNT. Such effect is associated with the hyperbranched shell of silver nanoparticles, which forms a developed surface and creates steric barriers for PP macromolecules that cannot form a crystal.

Mechanical properties of PCM

In addition to the influence on the microstructure and thermophysical properties, the modification of the PP matrix with the help of nanoparticles of various types leads to a significant improvement in the mechanical characteristics of the obtained materials.

To study the influence of the filler on the mechanical characteristics of PCM based on PP and nanofiller, the tensile strength of the obtained materials was studied. Figure 3 shows the dependence of the tensile strength (σ_{st}) on the filler content. From the obtained dependence, it can be seen that the tensile strength of both systems increases with an increase in the filler content. At the same time, with a content of 2 % in the PP-CNT material, the tensile strength increases by about 50 %, while in PCM filled with SN, the increase is about 30 %.

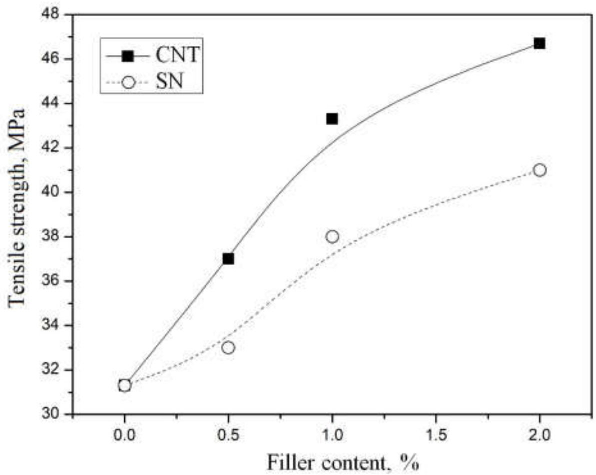


Figure 3 – Dependence of tensile strength on the content of nanofiller for PP-based systems

Fig. 3 shows that with increasing filler content, the tensile strength of the studied systems increases from 31.3 MPa for unfilled PP to 46.7 MPa for the PP-2 % CNT system and to 41 MPa for the PP-2 % SN system. The increase in mechanical characteristics in the obtained materials can be explained by the contribution of the filler, which has greater strength than the polymer matrix. Fig. 3 also shows that the increase in mechanical tensile strength is non-linear. In the area of filler concentrations up to 1 %, an abrupt increase in strength is observed. This is explained by the formation inside the material of a reinforcing mesh made of filler particles, which, during interaction with each other and the matrix, significantly strengthen its mechanical characteristics. The obtained mechanical characteristics make the studied materials promising for use in transportation systems.

Conclusions

As a result of the work, the effect of carbon nanotubes and silver nanoparticles on the functional properties of polypropylene-based polymer composites was investigated. It is shown that the introduction of different types of nanofillers leads to a decrease in the degree of crystallinity and melting temperature of systems based on polypropylene, which is a consequence of the destruction or increase in the defectivity of the crystalline structure of the polymer matrix under the influence of the developed surface of nanoparticles. It was established that the use of carbon nanotubes for polymer matrices leads to an extreme effect on the electrical and mechanical properties in composites at their ultra-low concentrations (~0.5–1 %). The extreme change in the properties of polymer composites is a consequence of the formation of a percolation cluster by nanoparticles in the polymer matrix, i.e. a mesh of filler that permeates the entire volume of the material. This process can be described within the framework of percolation theory. As a result of conducted studies of electrical conductivity, the percolation threshold was determined, which is 0.5 % for PP-CNT materials, while it is 0.82 % for the PP-SN system. A non-linear increase in the mechanical strength of the studied systems was recorded, which is a consequence of the formation of a reinforcing mesh from the filler inside the polymer matrix. It is shown that the mechanical strength increases by 50 % when filled with CNT and by 30 % when filled with SN.

Therefore, the use of different types of nanofillers made it possible to obtain polymer composite materials, which, according to their characteristics, are promising for use in transportation systems. The prospect of further development of this direction is the study of a wider range of properties of systems of the polymer-filler type. Systems containing SN are potential antimicrobial materials. Also, systems containing CNT have great prospects as materials for shielding electromagnetic radiation.

The article presents the results of research carried out within the framework of the state budget research topics "Creation of new multifunctional nanocomposite polymer materials containing carbon nanotubes" (state registration number 0121U100658) and "Development of innovative technologies for the creation of the latest silver-containing antimicrobial nanocomposite polymer materials with specified multifunctional characteristics for special purposes" (state registration number 0122U002326), financed by the Ministry of Education and Science of Ukraine.

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Функціональні властивості полімерних композитних матеріалів на основі поліпропілену, вуглецевих нанотрубок та наночастинок срібла для систем транспортування

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Завдяки своїм унікальним характеристикам, створення полімерних нанокомпозитних матеріалів відкриває широкі перспективи для використання їх у системах транспортування. Методами імпедансної спектроскопії, диференціально сканувальної калориметрії та механічного аналізу було вивчено вплив вуглецевих нанотрубок (ВНТ) та наночастинок срібла (НС) на функціональні властивості полімерних композитів на основі поліпропілену (ПП). Показано, що введення нанонаповнювачів приводить до зниження ступеня кристалічності та температури плавлення систем на основі поліпропілену, що є наслідком руйнування або зростання дефектності кристалічної структури полімерної матриці під впливом неорганічних наночастинок. Завдяки більш розвиненій поверхні, НС мають більший вплив, порівняно із ВНТ, на теплофізичні характеристики досліджуваних матеріалів. При вмісті 0.5 % наповнювача кристалічність ненаповненого ПП, яка становить 72.1 % знижується до 64.7 % у випадку наповнення ВНТ та до 53.4 % у випадку наповнення НС. Спостерігається екстремальна зміна електропровідності полімерних композитів, що є наслідком утворення у полімерній матриці перколяційного кластеру, тобто сітки із наповнювача, яка пронизує весь об’єм матеріалу. Максимальна електропровідність спостерігається при вмісті наповнювача, який становить 2 %. Для системи ПП-ВНТ максимальна електропровідність становить 10^{-5} См/см, а для системи ПП-НС – 10^{-9} См/см. У результаті проведених досліджень електропровідності було визначено поріг перколяції, який для даних систем, наповнених ВНТ становить 0.5 %, а для систем які містять НС – 0.82 %. Зафіксовано зростання механічної міцності, яка для систем ПП-ВНТ збільшується приблизно на 50 %, а для систем ПП-НС близько 30 %. Отримані властивості робить досліджувані матеріали перспективним для застосуванні у системах транспортування.

Ключові слова: *вуглецеві нанотрубки, механічна міцність, наночастинки срібла, перколяція, поліпропілен.*