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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

PREPARATION OF FE FILLED MULTIWALLED CARBON NANOTUBES BY CVD METHOD AND DEVELOPMENT OF MULTIFUNCTIONAL NANOCOMPOSITES TECHNOLOGY

Specialty:	2203.01 – Electronics
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Applicant:	**Rovshan Farhad Hasanov**

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Scientific supervisor:
Doctor of Sciences in Physics and Mathematics
Rasim Baba Jabbarov

Official opponents:
Doctor of Sciences in Physics, Associate Professor
Tahir Djumshud Ibrahimov

Doctor of Sciences in Physics and Mathematics, Professor
Vaqif Ali Maharramov

Candidate of Sciences in Physics and Mathematics, Associate Professor
Elshan Fayaz Nasirov

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Chairman of the Dissertation Council:
Active member of ANAS, Doctor of Sciences in Physics and Mathematics, Professor
Nazim Timur Mammadov

Scientific Secretary of the Dissertation Council:
Doctor of Sciences in Physics, Associate Professor
Rafiga Zabil Mehdiyeva

Chairman of scientific seminar:
Doctor of Sciences in Physics and Mathematics, Associate Professor
Ayaz Hidayat Bayramov

GENERAL CHARACTERISTICS OF WORK

Relevance and degree of development of the topic. In modern times, the field of nanotechnology is considered one of the leading scientific fields, as it combines knowledge in the fields of physics, chemistry, biology, medicine, computer science and technology. The simplest definition of nanotechnology is "nanomaterial technology". In this regard, this technology can be widely used in the creation of various types of nanomaterials and nano-devices. Due to their superior mechanical and physical properties, carbon nanomaterials have been in the spotlight for many years, and carbon nanotechnology is one of the priorities of a constantly evolving science. The application of carbon nanomaterials in industry, agriculture and medicine has led to significant improvements in these areas. New technologies require faster-responsive electronic devices, smaller integrated circuits, and lower power consumption. Nanotubes and nanowires are at the forefront of the list of innovative materials that meet such requirements. Among the carbon modifications, one of the most widely used materials in the field of nanotechnology is Carbon Nanotubes (CNT). CNTs have different properties from other carbon allotropes, such as graphite and diamond, and have been the subject of global research since their discovery, thanks to their superior properties as well as their interesting applications. Thus, due to its electrical, mechanical, thermal, magnetic, chemical, structural properties, the application of CNTs in various fields is of great practical importance. According to the number of external walls and atomic structure, CNTs are divided into single-walled, double-walled and multi-walled types. In addition to both metal and semiconductor properties, CNTs have a strong effect on the electrical, mechanical strength, absorption and many other properties of polymers. There are several technologies (technological methods) for the production of carbon nanostructures: arc discharge, laser ablation, chemical vapor deposition - CVD, etc. One of the methods that is considered to be economically and practically effective among the methods of obtaining is the Catalytic CVD (CCVD) method. Multi-walled CNTs are synthesized using mixtures such as ferrocene, nickellocene, and cobaltocene, which play a catalytic role in the formation of nanotubes by the aerosol-based CVD method. CNTs prepared by this method are added to dielectric, catalyst, polymer materials in order to increase their strength and conductivity, and the resulting nanocomposite material has a number of important properties and advantages. Thus, one of the main applications of CNTs is the preparation of conductive and structural composites. The application of CNT-based polymer nanocomposite layers in nanoelectronics, sensor technology, aerospace, etc. is being studied.

In the dissertation, despite the spread of scientific research on the synthesis and study of CNTs, the study of such nanotubes by various methods, new nanocomposites based on them by modern methods is of great interest for the creation of more efficient electronic converters in this area.

Object and subject of research.

The object of research in the dissertation is the study of multi-walled CNTs synthesized using Aerosol-based Chemical Vapor Deposition method, then purified, functionalized and dispersed in polymers by two-factor mechanical method for the preparation of CNT-based polymer nanocomposite material.

The purpose and objectives of the research.

The purpose of the research is the synthesis of multi-walled carbon nanotubes (MWCNTs) by the method of Catalytic (Aerosol-based) Chemical Vapor Deposition (CVD), the production of polymer nanocomposites (CNT / PNC) based on them and application of such materials in nanoelectronics.

The following tasks have been fulfilled to achieve the set goal:

- A new method for the synthesis of CNTs - Aerosol-based CVD method was used. In the process, various carbon sources and experimental conditions were used to grow fairly long, smooth, small-diameter CNTs. Our experiments have shown that CNTs synthesized by this method cannot be grown without a catalyst.
- In this dissertation the optimal synthesis conditions for the growth of high quality CNTs using iron as a catalyst were

studied. Thus, the optimal ripening temperature of the CNTs we studied was determined to be in the range of: 830 – 1000 ℃. At the same time, the low synthesis temperature reduces the productivity of CNTs. In addition, low temperatures (T<840 °C) in the reactor reduced the amount of product produced, while high temperatures (T>950 °C) led to the formation of pyrolytic carbon or other carbon structures.

- The CNTs we synthesized were examined by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersed X-Ray Spectroscopy (EDRS), X-Ray Diffraction (RD), Raman Spectroscopy (RS) analysis methods, and here the surface morphology characteristics such as size (diameter, length), degree of purity, element composition, number of walls (coatings), structural, amorphous and crystalline phases were studied.
- Chemical and two-factor mechanical dispersion methods were used for the preparation of electrically conductive polymer nanocomposite materials, for the dispersion of CNTs in the polymer matrix. The study found that the two-factor mechanical method developed by us for the production of polymer nanocomposites containing CNTs is superior to the chemical method, which is a difficult, complicated, inconvenient and not effective method.
- The technology of preparation of CNT-based polymer (polydimethylsiloxane (PDMS) and epoxy resin polymers) composites with different percentages (1%, 2%, 3%, 5%) was implemented through both chemical and two-factor mechanical dispersion methods, and the electrical properties of these nanocomposites have been studied.
- The specific electrical conductivity of MWCNT/PP, MWCNT/Chitosan and MWCNT/Epoxy resin-based thin-layer composites obtained by solution and dispersion methods was studied.

Research methods.

Research methods include: study of surface morphology, dimensions (diameter, length), number of walls of CNTs by means of SEM and TEM analysis methods; study of purity and element composition, as well as amorphous and crystalline phases by EDRS and Raman Spectroscopy analysis, structure of CNTs (monocrystalline, polycrystalline) by X-ray diffraction analysis, investigation of electrical properties of CNT-based polymer nanocomposites using Hiresta-UPMCP - HT450 device.

Basic scientific theses put forward to defend:

1. Proposing a new method, which is economically and practically profitable in the synthesis (formation) of multi-walled CNTs, depending on the efficiency of production methods and maturation technology - Aerosol-assisted CVD method;
2. Investigation of optimal synthesis conditions for the production of high-quality MWCNTs in the aerosol-based CVD method, using iron as a catalyst and various carbon sources (organic solvents);
3. Study of the optimal synthesis conditions for the production of high-quality MWCNTs in the Aerosol-assisted CVD, using Azerbaijani oil fractions as a carbon source;
4. Investigation of optimal synthesis conditions for the production of high quality multi-walled CNTs using an Azerbaijani oil fraction as a carbon source in an aerosol-based CVD equipment;
5. In all three cases, the study of a number of properties of the formed CNTs through various analytical methods;
6. Purification process of synthesized CNTs and dispersion within the polymer matrix;
7. Preparation technologies for the of electrically conductive CNT/Polymer nanocomposites and study of the electrical properties of these composites.

The scientific novelty of the research.

The scientific novelty of the work is the study of methods for obtaining CNTs and technologies for the production of polymer nanocomposites based on CNTs. In this regard, for the first time, the following works have been done:

- Carbon (Electric) Arc Discharge - In the processes carried out by the methods of discharge and laser spraying, due to the mixed nature of the technology of obtaining multi-walled CNTs, a new method for their synthesis - Aerosol-based CVD method was proposed.

- In the process carried out by this method, carbohydrate liquids were selected as a suitable solution for aerosol, and as a result of continuous inflow of carbon source during the experiment, the production volume of the product was increased up to 10 times.

- Ferrocene / sulfur / xylene solution was used as a carbon source in the process of synthesis of CNTs by aerosol-based CVD method. It has been found that the addition of sulfur or sulfur-containing compounds to the reaction solution as maturation promoters affects the number of walls, surface morphology and electrical properties of the synthesized CNTs. The presence of large amounts of sulfur (S_2) in the reagent mixture leads to the formation of amorphous carbon, and the small amount leads to the formation of MWCNTs and carbon fibers.

- In addition, in order to determine the suitability of cheap and heavy tonnage raw materials, Azerbaijani oil as a source of carbon in the process of synthesis of CDNBs by aerosol-based CBC method: Heavy gasoline fraction (C_7 - C_{11}); Reactive fuel fraction (C_9 - C_{16}); Fractions such as diesel fuel fraction (C_{14} - C_{25}) were used. It was found that when distilled fractions of Azerbaijani oil are used, the obtained MWCNTs are formed under atmospheric pressure only as a result of the gasoline fraction. In this process, the purification phase of the synthesized MWCNTs was carried out by means of ultrasonic washing using organic solvents (cyclohexane, toluene) and burning in a muffle furnace at air temperature $T = 420\ ^\circ C$ for half an hour.

- In the preparation of CNT/Polymer nanocomposites, using both chemical and two-factor mechanical dispersion methods, two types of composites were prepared on the basis of CNTs with different percentages: CNT/PDMS and CNT/Epoxy resin nanocomposites.

- When using the chemical method for dispersion of CNTs in PDMS, it was observed that agglomerates are insignificant in CNT/PDMS nanocomposites prepared by chemical method in different percentages of CNTs (1%, 3%, 5% and 7%), it also indicates that the dispersion is good. In PDMS, the electrical conductivity ($< 10^{-6}$ S/m) is very low, although the dispersion is good in samples with 1% and 3% ratios of CNTs. The electrical conductivity of CNTs is increasing rapidly, starting at 3%.

- Samples obtained by the two- factor mechanical method show such good electrical properties in PDMS that even 1% of the CNTs. SEM analysis of the same percentage (5%) of CNT samples in PDMS shows that CNTs separated by mechanical action are homogeneously distributed in the polymer without strong destructive effect, and a second (after dispersion) agglomeration process occurs. This fact significantly affected the electrical properties of nanocomposites. In fact, it can be shown that the electrical conductivity of CNT/PDMS nanocomposites containing 5% CNTs obtained by the two-factor mechanical method is $10^3 - 10^5$ times higher (stronger) than the electrical conductivity of nanocomposites of the same composition obtained by the chemical method.

Theoretical and practical significance of the research.

The extraordinary properties of CNTs make them interesting, leading and superior in the fields of microelectronics, nanoelectronics, spintronics, optics, materials science, mechanics and biology. The inclusion of CNTs in small amounts in polymer composites allows to maintain not only its strength and mechanical modulus, but also its chemical resistance, thermal and electrical conductivity, as well as dimensional stability. The CNTs included in the polymer matrix improve the electrical conductivity of the composite. This allows for energy storage and rechargeable batteries with additional active materials. In biosensors, CNT/Polymer nanocomposites show better results because the electron permeability and ion mass permeability are faster.

CNTs are mainly used in the field of nanoelectronics, energy storage devices, energy converters, thermoelectric and photoelectric devices, field emission displays and radiation sources, nanoscale semiconductor transistors, nanoelectromechanical systems, etc. covers a wide range of applications such as. CNT-based polymer nanocomposites display elastic electrodes, electronic paper, antistatic coating, bulletproof jackets, protective clothing, etc. are potentially alternative materials for applications such as they could be applied in many areas, such as air transport, automobiles, construction and the oil industry.

The obtained scientific results are also useful in the development of the physics of nanocomposites and electron converters based on them.

Approbation and application.

The main results of the dissertation were presented at the international "Academician GB Abdullayev Centenary International Conference and School Modern Trends in Condensed Matter Physics" (NASA, Institute of Physics, Azerbaijan Journal of Physics, 2018) conference, as well as "Fabrication, Properties and Applications of Nano-Materials and Nano-Devices International Conference, Italy, 2019" abroad conference.

10 scientific works on the topic of the dissertation (1 article in an international conference material, 2 theses in foreign conference materials, 1 article in a foreign journal with impact factor of 1.43, 2 articles in a foreign journal with impact factor of 1.42, 1 article in a foreign journal with impact factor of 0.97, 3 articles in national journals) was published.

The name of the organization in which the dissertation was carried out: The dissertation work was carried out in the 2.2 "Bio Nanostructures Physics" laboratory of the Institute of Physics of the Azerbaijan National Academy of Sciences.

Structure and scope of the dissertation. The dissertation consists of an introduction, five chapters, main results and a list of 120 references. The work consists of 160 computer printed pages, consisting of 54 figures, 2 tables and 171753 symbols.

THE CONTENT OF THE WORK

The introduction substantiates the relevance of the topic, the scientific purpose of the dissertation, its scientific and practical significance, the obtained scientific novelty, the main theses put to defense, the approbation, structure and summary of the research.

First chapter "Carbon nanotubes (CNT) and CNT-based polymer nanocomposite's (CNT/PNC) application areas" gives general information about CNTs, their structure, number of outer walls and types according to atomic structure, as well as the technology of processing of CNT-based polymer nanocomposites (CNT/PNC) in different applications. As is well known, CNTs are cylindrical, graphite-laden graphite-coated graphite sheets. As we know, since graphene is a graphite-containing carbon monolayer, this layer rolls in several forms to form different types of CNTs. In general, according to the number of external walls and atomic structure, CNTs are divided into three parts: single-walled, double-walled and multi-walled. Single-walled CNTs are nanotubes made of a coated graphene layer with a diameter of 1 to 3 nm. In addition, single-walled CNTs are a very important type of CNT in terms of electrical properties and can be shaped as a cylindrical roll of a single layer of graphite. Double-walled CNTs consist of two concentric carbon nanotubes, which connect the inner tube to the inner tube. Multi-walled CNTs are nanotubes consisting of coated layers of graphene with a diameter of 8 to 50 nm, depending on the number of graphene tubes. In other words, multi-walled CNTs are also understood as a collection of concentric single-walled CNTs of different diameters. As we know, in CNTs, as in graphite, there is a sp^2-bonds (hybridization state), in which each atom is connected with three other neighboring atoms. In addition, the type of CNTs depends on the orientation of the cylindrical bending of the graphene layer. This can be expressed by a quantity that determines how the graphene layer is bent - a vector called the chirality vector (Ch). The concept of chirality is one of the key factors in determining the electrical properties of CNTs. CNTs have a number of electrical, thermal, and structural properties, and these properties can vary depending on the physical design of the CNTs. The chirality vector is defined by two integers (n, m) and is expressed in the following equation:

$$C_{ch} = na_1 + ma_2 \qquad (1)$$

Where n and m are integers, the vectors a_1 and a_2 are the unit vectors of the two-dimensional lattice created by the graphene layer. The direction of the axis of the CNTs is perpendicular to this chiral vector. The angle between the chirality vector and the zig-zag nanotube axis is called the chirality angle (θ). Depending on the cylindrical bending of the graphene layer, there are the following types of CNTs:

1) For armchairs CNTs: $n = m$ ($\theta = 30°$);
2) For Zig-Zag-shaped CNTs: $n = 0$, $m = 0$ ($\theta = 0°$);
3) For Chiral CNTs: $n \neq m$ ($0° < \theta < 30°$).

The pair of integers (n, m) determines the chirality of CNTs, as well as affects the optical, mechanical and electronic properties of CNTs. In general, depending on the diameter of the tube and the angle of rotation, CNTs with an “armchair” structure have metallic properties, and “zig-zag” and “chiral” CNTs have a metallic, semiconductor and dielectric properties. "Armchair" and "zig-zag" tubular structures have a high degree of symmetry. This condition is based on the arrangement of hexagons around a circle. In practice, the most common "chiral" tube structure can exist in two opposite forms. For CNTs, the length of the carbon-carbon bond is: a_{cc}=0.1421 nm, and the distance between the layers is: 0.34 nm = 3.4 Å. Polymer nanocomposites (PNCs), which consist of polymer matrices and additives, including thermoplastics, thermosetting materials and elastomers, are an important group of materials that are economically viable for many technical applications. To obtain (produce) composites, two or more materials with unique properties are combined. For example, high-modulus carbon fibers or silicon dioxide (SiO_2) particles are added to the polymer to produce reinforcing PNCs that exhibit high mechanical properties such as durability, modulus and breaking hardness. In addition, the use of micron-sized fillers poses a number of challenges in optimizing the properties of PNCs. In general, the traditional filler content in PNCs is usually in the range of 10 to 70% (varies). This, in turn, results in the acquisition of a composite with a high density and high material value. Unlike PNCs, which contain micro-sized fillers, the inclusion of nano-sized CNTs in the polymer system results in a short distance between the fillers. In this regard, the properties of composites can be modified depending on the low filler content. As it is known, CNTs are considered to be a strong and rigid fiber, and their excellent mechanical properties are combined with physical properties, creating favorable conditions for potential applications of CNT/PNKs. As for the technology of CNT/PNCs processing, this type of composites is used in structural materials, electromagnetic materials, electroacoustics, chemistry, mechanical engineering, nanoelectronics, hydrogen accumulators, interconnectors, energy storage devices (supercapacitors, Li-ion batteries) It is widely used in medicine (label delivery of medicines, multifunctional nanocontainer). Additionally, mechanical, electrical, thermal and optical properties of the synthesized CNTs and CNT/PNCs are studied, and due to these properties, the modulus of elasticity, surface tension resistance, current density, electrical and thermal conductivity, etc. such characteristics are being investigated. We know that CNTs have a high aspect and a large surface area, as well as significantly superior and leading mechanical strength (durability), so their aspect ratio is 1000 times higher than other carbon-based materials (graphite, diamond, fullerene). Theoretical and experimental calculations have shown that, in general, the value of the Young's modulus of CNTs is in the range of 270-950 TPa, and the tensile strength is very high, ranging from 11 to 63 GPa. The high value of the elasticity (Young) module makes CNTs useful in the construction of scanning microscope probes. The elasticity of CNTs has a certain extent, and under the influence of very strong forces, CNTs can be permanently deformed. In addition, CNTs have very interesting electrical properties. Depending on the internal structure of CNTs and its interaction with other objects, the electrical properties of individual CNTs are characterized by quantities such as resistance, capacitance and inductance. The CNTs are affected by the electrical carrier inside, the defect scattering and the lattice vibrations. Like nano-sized graphite structures, CNTs are of great interest not only for their electrical and mechanical properties, but also for their thermal properties. All CNTs have a feature known as "ballistic conductivity" and are expected to have excellent thermal conductivity along the length of the tube and also to be good insulators in the lateral direction of the tube axis. The thermal conductivity of CNTs has been studied theoretically and experimentally. Thus, it is shown that the thermal conductivity of single-walled CNTs is more than 200 W/m×K, and the thermal conductivity of multi-walled CNTs is more than 3000 W/m×K. The temperature stability of CNTs is estimated at 2800°C in vacuum and about 750°C in air. Adding only 1% of pure and functional CNTs to different materials can double the thermal conductivity of the material. This suggests that polymer nanocomposite materials based on CNTs may be useful for thermal management applications in industry. The specific heat capacity of a substance (C(T)) is a sensitive probe for low-energy excitation. In general, in three-dimensional graphite, two-dimensional graphene, and CNTs, phonons have dominant excitation states. In this regard, the specific heat capacity of phonons - C_{ph} is superior to C(T) at high temperatures. The specific heat capacity (C_{ph}) of phonons depends on the density of phonon levels (ρ(ω)) and, depending on the temperature of each phonon level, can be obtained by integrating ρ(ω):

$$C_{ph} = \int k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\left(\frac{\hbar\omega}{k_B T}\right)}\rho(\omega)d\omega}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)} \qquad (2)$$

As is known from the science of materials science, the optical properties of CNTs include their important properties such as optical absorption, photoluminescence, fluorescence and Raman spectroscopy. It should be noted that the methods of optical absorption, photoluminescence and Raman spectroscopy, non-tubular carbon content, structure (chirality) and structural defects of synthesized CNTs allow to quickly and reliably characterize the quality of CNTs. These properties, like optical, mechanical and electrical properties, determine virtually any property. With the emergence of CNTs around the world, there have been numerous opportunities to study the properties of CNT/PNKs. Mechanical, electrical, thermal, optical, etc. properties of nanocomposites filled with CNTs have been significantly improved compared to pure polymers. As is well known, a number of factors, such as the nature of the polymer matrix, the aspect ratio (length/diameter ratio) of the CNTs, the reprocessing process (eg, covalent functionalization, polymer or surfactants surface coating), and the processing method used, have a decisive effect in determining the properties of the formed nanocomposites. The electrical conductivity of polymers can be increased by the addition of conductive fillers to them, including various types of carbon fibers, carbon black and graphite. Unlike other carbon-based fillers, CNTs, with their high conductivity (>> 10^{-10} S/m) and low aspect ratio (length/diameter ratio), led researchers to produce electrically conductive nanocomposites filled with CNTs. The combination of CNTs (insertion into the composite) causes the formation of electrical conductivity within the insulating matrix. This can be mainly attributed to the formation of three-dimensional electrical networks in a thermosetting matrix. Thus, a tunneling effect of electrons occurs between the dispersed filler particles. Due to the carrier properties of CNTs, they are used as an electrically conductive filler in epoxy resin composites. Such composites typically have a percolation boundary. The theory of leakage refers to the explanation of the electrical conductivity properties of (organized) composites consisting of a conductive filler and an insulating matrix. As the permeability of the filler gradually increases, the composite metal undergoes a dielectric transition. Thus, the critical filler composition is called the leakage limit. In this case, the measured electrical conductivity of the composite increases by several orders of magnitude due to the formation of continuous electronic conduction and conductive networks. In such case, the load-carrying capacity (ie, leakage limit) of the filler with critical conductivity for the matrix-filler combination (combination) is calculated by the following formula:

$$\sigma = \sigma_0(v - v_c)^{t} \qquad (3)$$

Where σ is the electrical conductivity of the composite, σ_0 is the characteristic conductivity, v is the volume ratio of the filler, v_c is the volume ratio at the leakage limit, and t is the critical coefficient (indicator). Thus, it follows that both the leakage limit and the maximum permeability of the composite are highly dependent on the type of nano-sized carbon-containing filler and the degree of dispersion.

In the second chapter, "Methods of obtaining the CNTs", the methods of obtaining CNTs are classified according to physical process and high temperature factors, cleaning stage, features, advantages and necessity of these methods are discussed, as well as their growth by the Aerosol-assisted Chemical Vapor Deposition, which is a modern method of growth used in the dissertation. In 1996, the Chemical Vapor Deposition (CVD) method became one of the traditional methods for the synthesis of large-scale production of CNTs. This method has the ability to synthesize a large number of CNTs and control the direction of growth technology on the substrate. In this process, mixtures of hydrocarbon gas (ethylene, methane or acetylene) and process gas (ammonia, nitrogen, hydrogen) interact under the influence of atmospheric pressure and in a reaction chamber placed on a metal substrate heated to a temperature of 700 – 900°C. The CNTs are formed as a result of the decomposition and deposition of hydrocarbon gas grow on a metal base. The use of catalysts and the preparation of the substrate are important factors in the CVD method. This substrate plays an important role in determining the nature and type of grown CNTs. Si element, quartz glass (SiO_2) and aluminum oxide (Al_2O_3) compounds are widely used as base material. Catalysts are metal nanoparticles similar to Fe, Co, and Ni, and they can deposit on a metal substrate by electron beam evaporation, physical dusting, or solution deposition. Porous Si substrate is an ideal substrate for growing individual-oriented CNTs on large surfaces. The diameter of the CNTs depends on the size of the catalyst particles. For this reason, the catalyst-based deposition method must be used correctly and carefully to obtain the desired result. As we know, in aerosol-assisted CVD method various additives are being used and it is one of the few methods of obtaining CNTs. With this method, the grown CNTs tend to have many advantages for the preparation of catalytic materials with the use of various acids where chemical cleaning process is not required. This technology is based on the aerosol injection of the solution into the reactor and thermal decomposition at high temperatures (830 – 1000°C) (Figure 1). In this process, air was evacuated from the system and Ar/H_2 gas mixtures were used as the carrier gas. In addition, Azerbaijani oil fractions (heavy gasoline fraction, jet fuel fraction, diesel fuel fraction) were used as a carbon source in the synthesis of CNTs in the new Aerosol-assisted CVD method. It should be noted that the synthesis processes were carried out under: 930°C and atmospheric pressure, as well as lower (10-30 kPa) pressure. In all experiments, ferrocene ($Fe(C_5H_5)_2$) was mixed with an organic solvent with a concentration of n=20 mg/ml and used as a catalyst. In an experiment conducted under standard conditions, the synthesized CNBs were cleaned from the tubes without any chemical assistance. However, the process of cleaning of CNTs synthesized using Azerbaijani oil fractions included: 1) Washing in organic solvents (cyclohexane, toluene) using ultrasonic device; 2) Annealing in a muffle furnace at atmospheric conditions at a temperature of 420°C for half an hour.

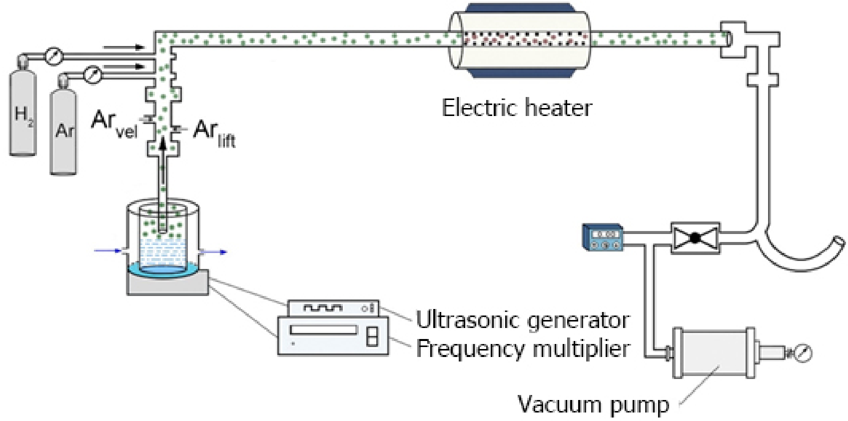


Figure 1. General description of the aerosol-assisted CVD equipment.

The third chapter, "Characterization of CNTs", describes the process of cultivation of synthesized CNTs and research (analysis) using different methods of characterization. Each sample (CNT) was synthesized under different conditions and analyzed. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis methods were used to determine the surface morphology, geometric parameters (diameter, length, number of walls) and the position of the iron (Fe) in the obtained CNTs. The structure of CNTs was studied by X-ray diffraction (RD) analysis

(Figure 2). Characterization was performed using a diffractometer ω-2θ. The purity, amorphous and crystalline phases of the CNT samples were analyzed by Raman spectroscopy (RS) (Figure 3). A green laser beam with wavelength λ = 532 nm was used to excite the sample. The beam was sent from a 50x lens. All measurements were made at room temperature. The Raman signal was collected by the back-thinned Charge Coupled Device (CCD). The synthesis of CNTs in an aerosol-assisted CVD unit was performed using a cyclohexane solvent as a carbon source and a ferrocene concentration with n = 20 mg/ml. As a result, the temperature in the hot area of the reactor was changed and its effect on the characteristics of the obtained CNTs was analyzed.

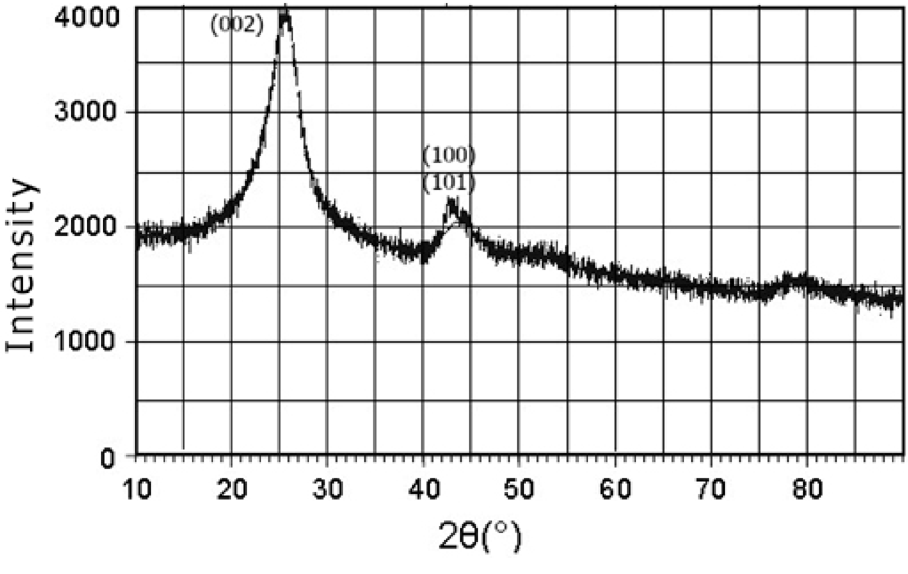


Figure 2. X-Ray diffraction spectra of MWCNTs grown at T = 840 °C.

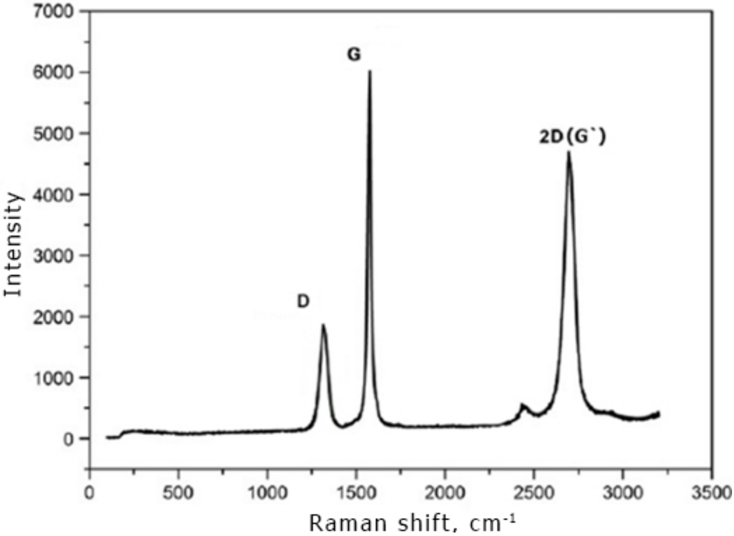
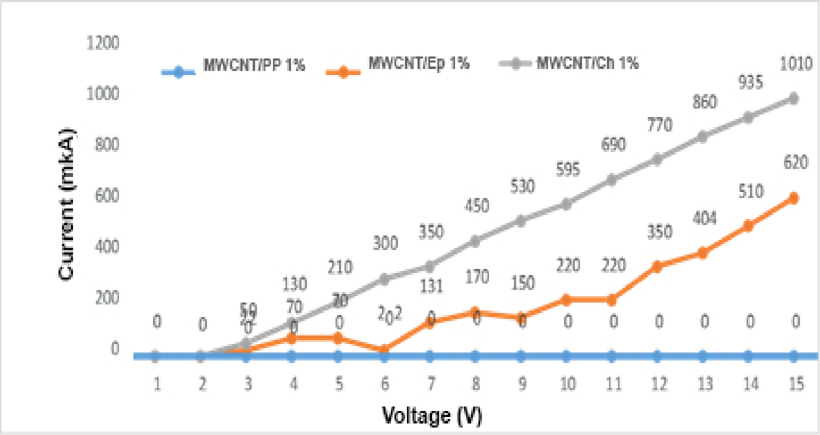


Figure 3. Raman scattering spectra of MWCNTs grown at T = 840 °C.

The fourth chapter "Functionalization and dispersion of CNTs" discusses the functionalization and dispersion of synthesized CNTs, types of functionalization process (chemical (covalent), physical (non-covalent)), the role of polymers and surfactants in the functioning of CNTs, as well as the technology of preparation of CNT-based polymer nanocomposites using chemical and two-factor mechanical dispersion methods, the study of electrical properties of this type of composites are shown. As it is known, the dispersion of CNTs means the inclusion of CNTs in the polymer matrix and their distribution in a certain equilibrium on a single surface within the polymer matrix. Functionalization is the process of adding new functions, properties, abilities and properties to a material as a result of changing the surface chemistry of the material. The process of functionalization is carried out as a result of the addition of molecules or nanoparticles to the surface of the substance, by chemical bonding or adsorption. A number of studies have focused on the production of CNT-based polymer nanocomposites (CNT/Polymer Nanocomposites) for functional and structural applications. Thus, the main problem of widespread synthesis methods was the process of production of CNTs contaminated with metal and amorphous mixtures, as well as with different diameters and chirality. However, the potential of CNTs to be used as reinforcements was severely limited due to weak interphase interactions and Van der Vaals interaction forces between CNTs and the polymer matrix. In addition, CNTs differ significantly from conventional filler dispersions, such as spherical particles and carbon fibers, because of their nano-scale scale, small diameter, high aspect ratio (>1000), and large surface area. Also, industrial CNTs are supplied in a mixed group. This leads to difficulties during the dispersion process. Thus, the solution to these problems is to improve the methods for modifying the surface properties of CNTs. These approaches can be simply divided into chemical (covalent) and physical (non-covalent) functionalization types, which exist as interactions between CNTs and active substances. Chemical functionalization is based on the covalent bonding of functional groups associated with the carbon form of CNTs. This process can be performed on the end caps of the CNTs or on the side walls with a large number of defects. This is directly related to the covalent functionality of the side walls of the CNTs, the change of hybridization from sp^2 to sp^3, and at the same time the loss of the π-conjugation system present in the graphene layer. Chemically functional CNTs, together with many polymers, can form strong phase bonds. This gives CNT-based nanocomposites high mechanical and functional properties. In general, the use of covalent methods to functionalize CNTs can provide their surface with suitable functional groups. However, due to a number of shortcomings of covalent methods, we switch to non-covalent functionalization. The advantage of the non-covalent functionalization method is that in this method, the "combined bind" system in the side walls of the CNTs does not collapse, which, in turn, does not affect the final structural properties of the material. In addition, the non-covalent functionalization method is an alternative method for regulating the inter-phasal properties of CNTs. However, in addition to polymers, surfactants are also used in the operation of CNTs. Recently, one of the main directions in the development of the nanotechnology industry has been the development of polymer nanocomposite materials with new properties as a result of the addition of nanoscale components. In this regard, CNTs with unique physical and chemical properties were considered as a promising material for the production of electrically conductive nanocomposites. The inclusion of CNTs in a polymer matrix and their distribution (dispersion) on a single surface within this matrix not only converts CNTs into electrically conductive material, but also increases their thermal conductivity and strength by several magnitudes. The difficulty in the production of polymer composites with high quality and permeability was due to the need for even distribution of nanocarbon material on a single surface in the polymer matrix and a high dispersion condition. Given the tendency of CNTs to form agglomerates, it is necessary to develop different processing methods for the dispersion of CNTs. These methods also differ sharply from each other, depending on the nature of the polymer material and the type of CNTs (functional or non-functional, single-walled or multi-walled, etc.). CNTs with - OH, - CHOH, - COOH and other functional groups are often compatible with the corresponding polymers that form a single composition of CNT-based polymer nanocomposites (CNT/Polymer Nanocomposite). Thus, the use of non-functional CNTs (NFCNTs) in the polymer modification process is more cost-effective than functionalized CNTs (FCNTs). In addition, NFCNTs differ from FCNTs due to their effective modifying properties (e.g. high electrical conductivity), which are drastically reduced in the process of functionalization (modification) of CNTs. Thus, two types of composites with different percentages were used in the production of CNT-based polymer nanocomposites, using both chemical and two-factor mechanical dispersion methods: CNT/PDMS and CNT/Epoxy resin composites. The electrical properties of nanocomposites have been studied by Hiresta - UPMCP - HT450. Under the applied voltage (U), after obtaining the full current intensity (I), the electrical conductivity of nanocomposites is calculated according to Ohm's law by the following formula: $\sigma_{com} = (I/U) \times (D/S)$, where, D - is the distance between two electrodes, and S is the section area of the electrode.

In the fifth chapter, "Study of thin layers of CNT-based polymer nanocomposites (CNT/PNC) for next-generation electronics", the technology of obtaining CNT-based polymer nanocomposites using different types of polymers, preparation of thin layers of such materials, volt-ampere characteristics (VA) The study of the application of thin layers of CNT-based polymer nanocomposites as a new generation electronics material is being discussed. New technologies require electronic devices that respond faster, smaller integrated circuits, and lower power consumption. CNT s and CNT -based polymers are on the list of innovative materials that meet such requirements. However, their separate use limits their application. CNT s have a strong effect on the electrical, strength and absorption properties of polymers. Polymers, in turn, expand the application of CNT s in the form of a thin layer. At present, the application of CNT/polymer nanocomposite layers in nanoelectronics, sensor technology, aerospace, medicine and other fields is being studied. Here, thin layers of MWCNT / Epoxy, MWCNT/PP, MWCNT/Chitosan type composites were prepared using epoxy, polypropylene (PP) and chitosan polymers. CNT/Epoxy composites are used in a number of applications: automotive, aerospace, radar absorption material, electromagnetic interference protector, electronics, biomedical devices and wind turbine blades. The properties of epoxy resin polymer and CNT/Epoxy nanocomposite are important to investigate their potential applications. CNT/PP nanocomposites have superior thermal stability compared to polyolefin materials. The electrical and thermal conductivity of CNT/PP composites increases with the addition of CNTs that form a conductive network in the polymer matrix. Application of CNT/Chitosan composites includes biomedical (tissue engineering, targeted delivery of biosensors and pharmaceuticals) and wastewater. These nanobiocomposites are expected to have numerous potential applications in tissue engineering and drug delivery. The conductivity of the samples was determined by the two-probe method. The technology of the two-probe method is in the specific resistance of a material is determined by measuring its resistance and physical dimensions. In this case, the material is cut into rectangles of length (l), height (h) and width (a). Metal contacts are attached to both sides of the sample. This method is called the two-probe method because the contacts are fixed on both sides during the measurement. A voltage source is applied to the sample, and as a result, current begins to flow from the sample. An amperemeter (A) connected in series to the circuit measures the current (I) flowing through the sample. As mentioned earlier, it has been observed from the electrical properties of composite layers prepared by the incorporation of MWCNTs into polymers in small proportions that MWCNTs have a significant effect on the change of electrical properties of polymers from dielectric to conductive. The IV characteristics of the samples at constant voltage was determined and the conductivity was calculated based on the results obtained (Figure 4). In addition, the uniformity of the CNTs in the obtained layers is demonstrated by the fact that the IVs tested in different parts are the same by changing the position of the contacts along the entire surface, and at the same time the measurements made by placing the contacts at the end points of the samples give the same result. Thus, the electrical conductivities of the composite layers were determined by measurements and calculations using two the probe method (Table).



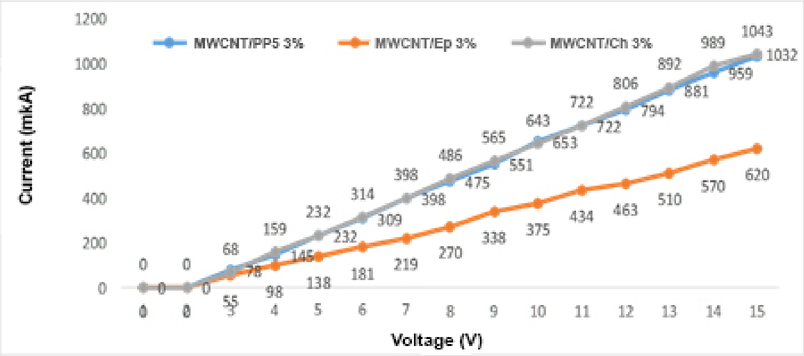


Figure 4. IV characteristics of 1% and 3% MWCNT / polymer composite layers.

Table. Specific electrical conductivity of CNT / polymer composite layers.

CNT/Polymer composites	Electrical conductivity S·m^{-1} 1% of the sample	Electrical conductivity S·m^{-1} 3% of the sample
MWCNT/Chitosan	$2.3 \cdot 10^6$	$2.4 \cdot 10^6$
MWCNT/PP	–	$2.3 \cdot 10^6$
MWCNT/Epoxy	$1.2 \cdot 10^6$	$1.3 \cdot 10^6$

RESULT

1. High-purity CNTs were grown using various carbon sources, catalysts and synthesis temperatures (T = 830-1000°C) and the optimal mode of Aerosol-assisted Chemical Vapor Deposition (A-CVD) method was found.

2. From the results of X-ray diffraction and Raman spectroscopy analyzes, it was determined that the intensity of the peak points D (defect) and G (graphite) in the samples of MWCNT grown at T = 840 ℃ is smaller than the ratio I_D / I_G, which confirmed the absence of amorphous carbon and defects between the CNTs.

3. The location of Fe nanoparticles being not only at the tips of CNTs, but also along their length (inner canal of CNTs) was determined by the results of TEM, SEM and EDRS analyzes. In the samples, Fe nanoparticles are predominantly located at the tips, which forms the diameter of the CNTs.

4. During the deposition of CNTs synthesized by the ACVD method using ferrocene/sulphur/xylene solution, it was observed that the addition of sulfur to the reaction solution leads to a decrease in the number of walls of the resulting CNTs.

5. The presence of double-walled and multi-walled CNTs was determined by SEM, TEM and Raman spectroscopy.

6. When using only distilled oil fractions of Azerbaijani oil (Heavy gasoline fraction (C_7 - C_{11}); Jet fuel fraction (C_9 - C_{16}); Diesel fuel fraction (C_{14} - C_{25})) as a carbon source, it was determined that CNTs are only formed resulting from gasoline fraction under atmospheric pressure.

7. For the preparation of nanocomposites, a new two – factor mechanical method has been developed that is highly optimized (improved) for the dispersion of MWCNBs in a polymer matrix. SEM analysis and electrical measurements have shown that non-functional

MWCNBs are better dispersed within the polymer matrix by a two-factor mechanical method, as opposed to the chemical method.

8. It was shown that the electrical conductivity of samples obtained by the two-factor mechanical method is 10^3-10^5 times higher than that obtained by the chemical method.

9. The incorporation of 1% and 3% of MWCNTs into dielectric polymers (epoxy, polypropylene, chitosan) using dissolution and dispersion methods results in the formation of MWCNB/Polymer composite layers with a thickness of 50 µm.

THE LIST OF THE WORKS PUBLISHED ON THE TOPIC OF THE DISSERTATION

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Address: Institute of Physics, H. Javid ave. 131, Baku, AZ1143, Azerbaijan.

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