Article

Nanocomposite Material Based on Polyvinyl Alcohol Modified with Carbon Nanotubes: Mechanism of Formation and Electronic Energy Structure

Lusine Elbakyan [1,*] , Irina Zaporotskova [1] and David Hayrapetyan [2]

[1] Institute of Priority Technologies, Volgograd State University, 100 Prospect Universitetsky, Volgograd 400062, Russia
[2] Institute of Engineering and Physics, Russian-Armenian University, 123 Hovsep Emin St., Yerevan 0051, Armenia
[*] Correspondence: elbakyanlusine90@gmail.com

Abstract: The physical chemistry of surface phenomena in polymers is an important issue when studying the interaction of polymers with solid surfaces. This is due to the fact that most of the modern polymer materials are heterogeneous systems with highly developed phase separation surfaces. An example of such materials can be reinforced plastic, filled thermoplastics, reinforced rubber, paint coatings, etc. Polymer adsorption at the boundary of the phase separation process in solids plays an important role in the reinforcing effect of fillers, adhesion, gluing and obtaining composite materials with high strength properties. Compositions based on polyvinyl alcohol (PVA) modified with carbon nanotubes (CNTs) can be used as an interesting and informative system for studying the structure and properties of polymer nanocomposites, especially in a highly oriented state. PVA has one of the simplest chemical structure among the polymers, containing a functional (hydroxyl) group capable of participating in interphase interactions. In turn, carbon nanotubes with unique strength properties are currently products of industrial production, which makes it possible to control and modify their properties. To prove the possibility of creating new composite materials with improved strength characteristics, the mechanisms of interaction between PVA and CNTs are studied by modeling the adsorption processes of a polymer fragment on the outer surface of single-layer carbon nanotubes of different chirality, performed within the framework of the modern DFT calculation method. The main adsorption characteristics of the process and the features of the electron energy structure of the resulting composite systems are determined.

Keywords: carbon nanotubes; polymer nanocomposite; polyvinyl alcohol; adsorption interaction; electronic energy structure; density functional theory calculations

1. Introduction

Polymer materials are used in the automotive industry, aircraft, ship and rocket engineering, medicine and pharmacology, the oil industry, household appliances and construction due to their unique properties, such as low density, high plasticity, elasticity, thermal and wear resistance, chemical and radiation resistance, low electrical and thermal conductivity, crack resistance in conditions of high-intensity loads, etc. Nowadays, the sphere of use of polymer materials is constantly growing. In this regard, there is a need to improve their physicochemical, operational, conductive and other characteristics.

The problem of creating new types of polymer composite materials is becoming quite relevant. These are the so-called polymer nanocomposites, in which the level of dispersion of the filler or reinforcing element lies in the nanometer size range, which in some cases makes it possible to create materials with new performance properties.

Carbon nanotubes (CNTs) are widely used as electrically conductive fillers due to the inherent properties of this material. CNT has outstanding electrical and thermal

conductivity values. In addition, the high aspect ratio of CNTs can reduce the thermal contact resistance between the CNTs and the polymer matrix, allowing the composites to exhibit excellent electrical conductivity and thermal performance. Carbon nanotubes with a complex of unique properties (sorption, strength, etc.) can be used as such a filler. Currently, they are products of industrial production. This makes it possible to control the properties of the obtained materials [1–5]. Therefore, it is possible to propose the creation of new composite materials obtained by modifying polymers with carbon nanotubes to improve their physicochemical properties and, as a result, contribute their entry to the consumer market. The created polymer nanocomposite materials based on carbon nanotubes will enable us to combine the advantages of the polymer material and the unique strength properties of CNTs, and the resulting composite materials will be characterized by low weight, cheapness, ease of production and storage. Although there are quite a large number of works devoted to the study of the structure and properties of nanostructured composites [6–10], the range of tasks that need to be solved is still very wide, since the objects that can be attributed to nanocomposites are extremely diverse and numerous.

One of the main aspects of obtaining composite-material doped CNTs is an equal distribution of CNTs into the polymer matrix. Many attempts have been made to incorporate CNTs into various polymer matrices. The polymer matrix must be selected as a material to provide the desired physical, mechanical or chemical properties of the final composite product.

Well-known and inexpensive polymers can act as a matrix polymer, for example, polyvinyl alcohol (PVA), which is widely used in many fields [11,12]. PVA, among the polymers, has one of the simplest chemical structures, containing a functional (hydroxyl) group capable of participating in interphase interactions. The introduction of carbon nanotubes into this polymer will improve its operational characteristics and ensure the creation of better-quality products based on it.

In order to establish the mechanisms occurring in the composite between CNTs and PVA, and to prove the possibility of doping the polymer matrix with carbon nanotubes, we have performed theoretical quantum chemical studies of the interaction of single-layer carbon nanotubes with fragments of polyvinyl alcohol, which have not been conducted to date. This determines the relevance of this work.

2. Material and Methods

2.1. Investigated Material

A polymer material based on polyvinyl alcohol was selected as the object of research. Polyvinyl alcohol (PVA) is a non-expensive, hydrophilic, non-toxic, stable and thermoplastic polymer. Among the various properties of PVA, the ability of this alcohol to impart adhesive properties to materials stands out. Polyvinyl alcohol-based adhesive is characterized by high density and viscosity. It is used in the process of packaging production and tailoring, among others. It is resistant to gasoline, oils and acids, which makes it an indispensable component in the production of building materials and protective coatings. The production of polyvinyl alcohol helps doctors to perform blood transfusions and perform fixations while collecting samples. Another rather important advantage of this polymer is its ability to easily mix with fillers. This greatly expands its scope of application, since in recent years, polymer composite materials have become very popular; these are materials that, in addition to the main component called the matrix, include other components in certain ratios, otherwise called fillers, which differ from the matrix in properties.

2.2. «Polymer Nanofill» System

It is known that the properties of a polymer composite material are determined not only by the properties of the matrix and the filler, but also by the filler–matrix interaction process. However, obtaining new polymeric nanocomposite materials with predictable and reproducible properties is difficult due to the high tendency of uncontrolled aggregation of the nanodispersed elements. It is obvious that in order to solve these problems and to

reveal the general principles of controlling the dispersion of nanofillers in polymer matrices, a detailed systematic study of the structure and properties of such composites is necessary, using the examples of "model" objects with well-characterized components that allow for the optimization of the properties of the polymer nanofiller system as a whole.

The introduction of CNTs into polymer materials as a filler is an important mean of regulation of the physical and chemical properties of polymers [13,14]. As it is known, CNTs are among the most promising nanomaterials due to their mechanical, electrical, thermal and sorption properties. This allows them to be used as fillers in order to create new materials with a unique set of consumer and operational properties. However, it should be noted that carbon nanotubes with the highest surface energy show an increased ability to stick together and form conglomerates. In this case, the effect of improving the electrophysical characteristics of the matrix material, characteristic of uniformly distributed carbon nanotubes, is not achieved. This negatively affects the properties of the resulting composite. A number of studies [15,16] have proven that the use of ultrasonic vibrations ensures the uniform dispersion of carbon nanotubes in a polymer matrix.

The introduction of CNTs into the polymer matrix can provide the possibility of using polymer materials in electronics. The electrical properties of CNTs are an important parameter. The usage of CNTs for various purposes depends on these properties. There are several factors to determine the electrical conductivity of CNTs: the type of CNTs (single-layer or multi-layer), the density of defects, the existence (or absence) of adsorbed molecules and—one of the most important—chirality (symmetry groups that a particular nanotube belongs to). According to many experimental studies, the usage of CNTs as a conductive filler in a polymer matrix leads to very low thresholds of CNT concentrations, where a noticeable current flow begins, in contrast to the theoretical values predicted by percolation theory [15–18]. Thus, a noticeable conductivity in the dielectric matrix of the polymer is already observed at CNT concentrations from 0.0001 to a few percent, while the percolation theory predicts about 16% [10]. This makes it possible to control the electrical properties of initially dielectric polymers over a wide range with small perturbations of volumetric physical properties, such as strength and flexibility [15–17].

3. Theory/Calculation

Methods of modern quantum chemistry are widely used in solving a variety of physical and chemical problems and are not only used for the interpretation of experimental data, but also for assessing the possibility of existence and predicting the physicochemical properties of new chemical compounds, including those based on carbon nanotubes. Quantum chemistry methods help to estimate the stability of various CNT derivatives and choose those that may be of theoretical or practical interest.

The density functional theory methods have been widely used in the ab initio modeling of nanostructures. The essence of this method lies in the use of electron density distributions in the description of atomic–molecular systems. The density functional theory (DFT) is used to study the features of the electronic energy structure of a nanocomposite based on PVA doped with carbon nanotubes, and the mechanisms of interaction between CNTs and fragments of polyvinyl alcohol [19]. The essence of this method lies in the use of electron density distributions in the description of atomic–molecular systems. Thus, according to DFT, all the electronic properties of the system, including energy, can be obtained from the electron density $\rho(r)$, without knowledge of the wave functions. Therefore, the electron energy in the DFT method can be calculated as:

$$E[\rho] = T[\rho] + V_{en}[\rho] + V_{ee}[\rho] \qquad (1)$$

where:

$T[\rho]$—Kinetic energy;

$V_{en}[\rho]$—Potential energy of electron–nuclear interactions;

$V_{ee}[\rho]$—Energy of interelectronic interactions.

The energy of interelectronic interactions can be represented as

$$V_{ee}[\rho] = V_{Coul}[\rho] + V_{xc}[\rho] \tag{2}$$

where $V_{Coul}[\rho]$ is the energy of the Coulomb interaction between an electron and $V_{xc}[\rho]$ is the exchange correlation energy.

A hybrid method of approximation, named the B3LYP method, was used to study the system. The B3LYP method gives accurate results for energetics, structure and vibrational properties of molecules and solids. Based on its superior performance in numerous energy assessments of small molecules, BLYP is the most widely used method. The B3LYP reproduces the geometries of smaller and larger molecules very well.

The main advantage of the B3LYP method is its high accuracy. Calculations were carried out using a basis set of type 3-21G. This functionality with the selected basis set is well adapted to the selected systems. One very economical, small split valence basis set is the 3-21G basis set. The non-valence electrons are described by single basis functions composed of a contraction of three Gaussians. Each valence electron is described by two basis functions. The first of these basis functions is composed of two Gaussian primitives, while the second consists of a single uncontracted Gaussian primitive [20–22].

4. Results and Discussion

4.1. The Effect of Adsorption of Polyvinyl Alcohol on the Surface of Carbon Nanotubes

To predict the possibility of creating a new composite material, the problem of the adsorption activity of the polymer material under study in relation to carbon nanotube is of fundamental importance. To study this process, we carried out theoretical studies of the interaction of a structural unit of a nanomaterial—polyvinyl alcohol (PVA)—with the CNT surface via quantum chemical modeling in the Gaussian software product using the DFT calculation method. A model of a CNT molecular cluster with boundary pseudo-atoms was used. This model allows you to select a certain section of the extended nanotube system and perform the necessary calculations specifically for it. The cluster length was chosen so as to avoid the influence of edge effects on the process. Pseudo-atoms were used to compensate for broken chemical bonds at the cluster boundary. In the case under consideration, hydrogen atoms playing the role of pseudo-atoms are well suited for this role.

We calculated the energy characteristics of the adsorption processes of one monomeric link (C_2H_4O) of polyvinyl alcohol on single-layer CNTs of the achiral type of two types: (a) "arm chair" of the chiral indices (6,6); (b) "zig-zag" of the chiral indices (9,0). Table 1 presents the main parameters of the CNTs under consideration and the lengths of the molecular clusters considered by us. The diameters of the selected nanotubes were calculated using the formula:

$$D = \frac{\sqrt{3}}{\pi} d_0 \sqrt{m^2 + mn + n^2} \tag{3}$$

where $d_0 = 0.142$ nm and represents the distance between adjacent carbon atoms in the graphite plane; and (m, n) represents the chiral indices of single-layer carbon nanotubes.

Table 1. The main parameters of CNTs.

Types of CNTs	Diameter D, nm	Chirality Angle, α	CNT Cluster Length, nm/Number of Atoms	Type of Conductivity
(6,6)	0.814	30	24.4/264	Metal
(9,0)	0.705	0	23.9/234	Metal

The geometry of two types of nanotubes, (6,6) and (9,0), as well as the geometry of the polyvinyl alcohol monomer itself, were previously optimized. The process of adsorption of the C_2H_4O fragment of polyvinyl alcohol to the central part of the CNT cluster was modeled by approaching the molecule stepwise to the selected carbon atom of

the nanotube perpendicular to the CNT surface (the straight line of monomer displacement is perpendicular to the longitudinal axis of the nanotube). In the structure of the PVA monomer, the most active centers were chosen, which are capable of providing a stable bond of the fragment under study with the surface of nanotubes of the "arm chair" (6,6) and "zig-zag" (9,0) types: center 1 is an oxygen atom, center 2 is a hydrogen atom (Figure 1). In this case, in the case of center 2, two variants of monomer orientation relative to CNTs are considered: the monomer plane is perpendicular to the CNT axis and parallel to the CNT axis (Figure 2a–c).
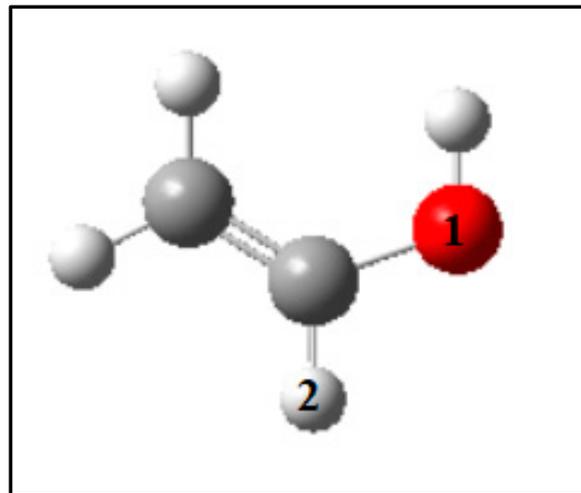

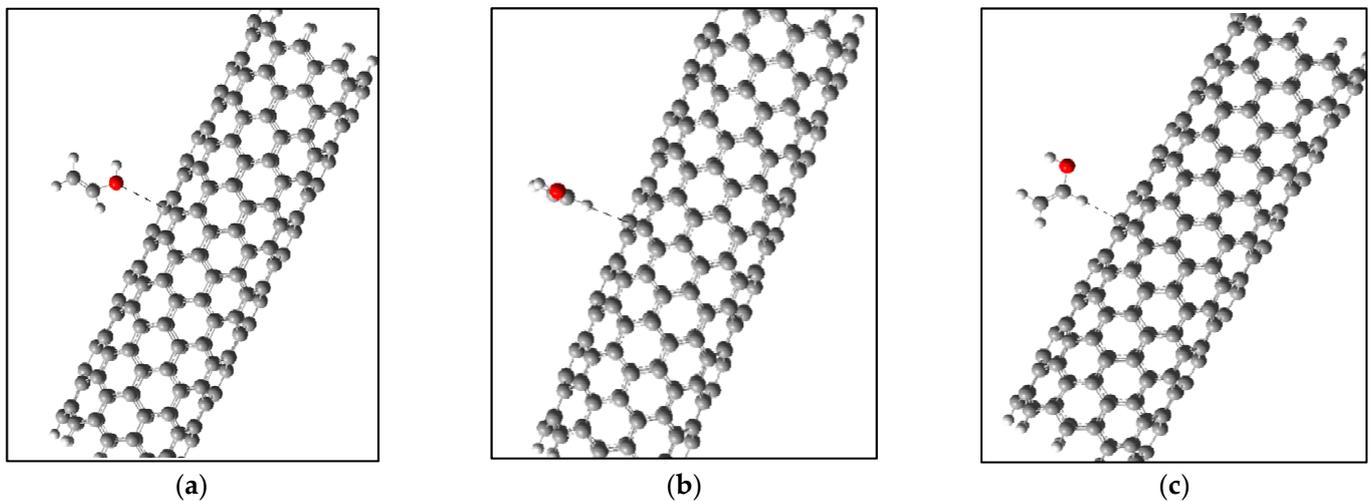**Figure 1.** Active centers in the structure of the PVA monomer.

Figure 2. Variants of the orientation of the monomer relative to the CNT, which are considered in the study on the example of CNT (9,0): (**a**) the active center 1 is an oxygen atom; (**b**) the active center 2 is a hydrogen atom (the plane of the monomer is perpendicular to the axis of CNT); (**c**) the active center 2 is a hydrogen atom (the plane of the monomer is directed along the axis CNT).

As a result of the performed calculations, the energy values of the systems at each step were obtained, which made it possible to construct curves of the dependence of the interaction energy on the distance between the selected monomer and the CNT (Figure 3).
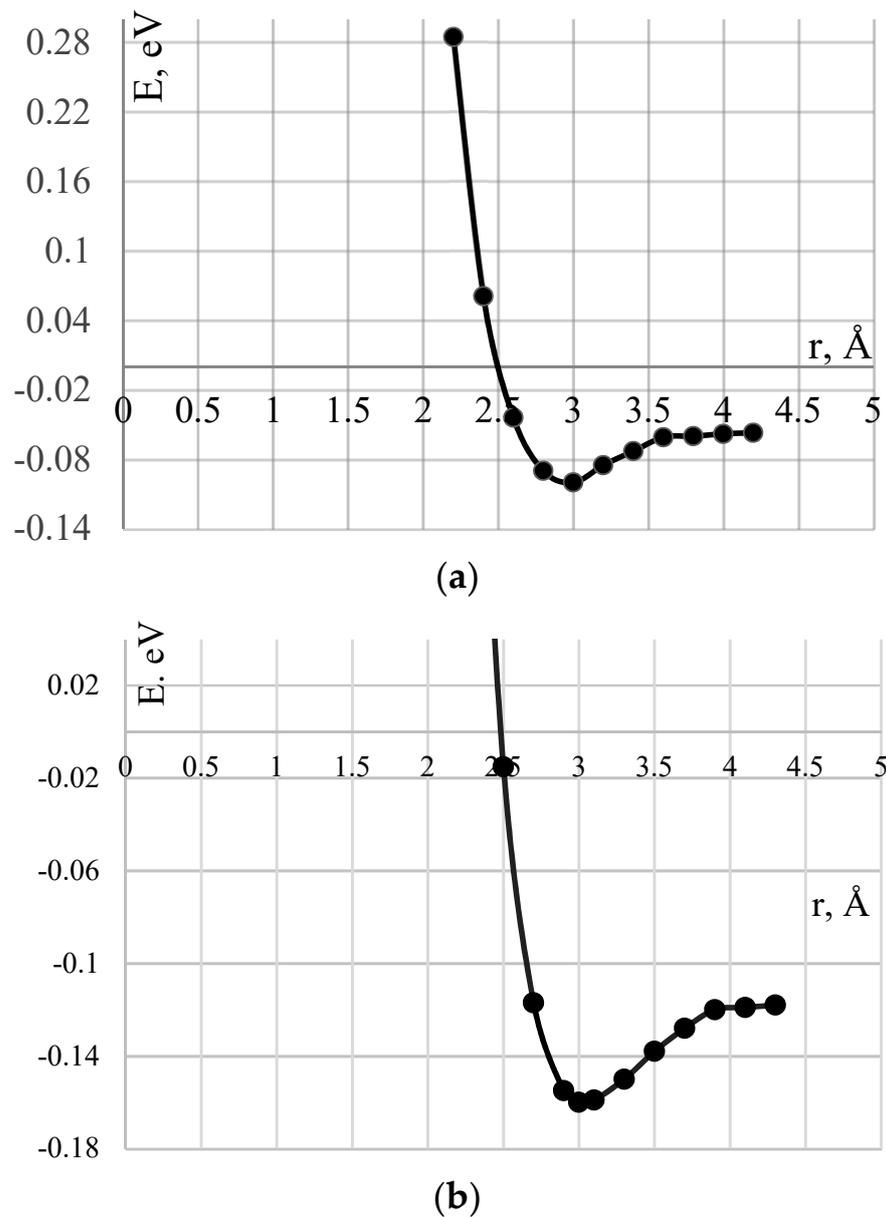
Figure 3. Energy curves of the interaction of the C_2H_4O monomer: (**a**) with CNT type (9,0) using active center 1—oxygen atom (option 1), (**b**) with CNT type (6,6) using active center 1—oxygen atom (option 1).

It is established that each curve has a minimum corresponding to the interaction at certain distances. The adsorption energy was calculated as the difference between the total energies of the adsorption complex and the sum of the energies of noninteracting CNTs and the monomer under study (C_2H_4O):

$$\Delta E_a = E_{ad.k.} - (E_{CNT} + E_{mol}) \tag{4}$$

where:

$E_{ad.k.}$—The energy of the adsorption complex obtained as a result of calculations;

E_{CNT}—The energy of the CNT;

E_{mol}—The energy of the C_2H_4O.

The values of ΔE_a revealed the physical interaction (adsorption) of the C_2H_4O monomer with a CNT cluster of type (6,6) (Table 2):

Table 2. The results of adsorption interaction of PVA monomer C_2H_4O on the outer surface of CNTs.

Types of CNTs	Active Center	Adsorption Distance, R_{ad}, Å	Adsorption Energy, ΔE_a, eV
(6,6)	1	3.0	0.16
(6,6)	2 (the plane of the monomer is perpendicular to the CNT axis)	2.8	0.14
(6,6)	2 (the plane of the monomer is directed along the CNT axis)	2.7	0.07
(9,0)	1	3.0	0.1
(9,0)	2 (the plane of the monomer is perpendicular to the CNT axis)	2.9	0.08
(9,0)	2 (the plane of the monomer is directed along the CNT axis)	2.6	0.05

(1) The energy value during the interaction between C_2H_4O and the CNT using active center (1) turned out to be 0.16 eV, with an adsorption distance of Rad = 3.0 Å.

(2) The value of the adsorption energy during interaction with active center (2) was 0.14 eV at a distance of Rad = 2.8 Å (if the plane of the monomer was perpendicular to the CNT axis) and 0.07 eV at a distance of Rad = 2.7 Å (if the plane of the monomer was directed along the CNT axis).

In the case of interaction of the C_2H_4O monomer with a CNT cluster of type (9,0), the values of ΔEa also confirmed the realization of the physical adsorption of the fragment on the surface of the nanotube (Table 2):

(1) The value of the adsorption energy at the interaction of active center (1) was 0.1 eV, with an adsorption distance of Rad = 3.0 Å.

(2) The value of the adsorption energy at the interaction of active center (2) was 0.08 eV at an adsorption distance of Rad = 2.9 Å (if the plane of the monomer was perpendicular to the CNT axis) and 0.05 eV at a distance of Rad = 2.6 Å (if the plane of the monomer was directed along the CNT axis).

Therefore, the established interaction of the structural unit of the polymer PVS with the surface of achiral single-layer carbon nanotubes of the "arm chair" and "zig-zag" type explains the mechanism of creating a composite polymer material based on polyvinyl alcohol reinforced with nanotubes during the adsorption interaction of the polymer with CNT, leading to the creation of stable complexes.

It is important to know how the process of interaction of carbon nanotubes with a fragment of PVA containing several structural units of polyvinyl alcohol occurs. For that purpose, based on the results of the theoretical studies presented above, we have performed DFT calculations of the interaction processes of single-layer carbon nanotubes (6,6) and (9,0), with a polymer fragment $[-CH_2CH(OH)-]_n$, where n is the number of structural units. In our case, *n* = 16 was chosen. A polyvinyl alcohol fragment consisting of 16 monomer units was also previously optimized. Calculations were carried out within the framework of density functional theory at the level of B3LYP/3-21G theory. Figure 4a shows the structure of this PVA fragment after optimization, performed in the GaussView software package.

To simulate the process of adsorption interaction, the oxygen atom isolated in Figure 2a was selected as the active center in the structure of the polymer compound. The choice of the active center is due to the previously obtained results on the study of the adsorption of the PVA monomer on the surface of carbon nanotubes. The interaction process was modeled based on the step-by-step approximation of the PVA fragment to the carbon atom on the surfaces of the selected types of nanotubes with a step of 0.1 Å. A molecular cluster

model was used to model nanotubes. The carbon atom that the fragment [-CH$_2$CH(OH)-] was approaching was located approximately in the middle of the cluster, which made it possible to avoid edge effects. Figure 2b shows a model of an interacting nanotube (6,6) and a fragment of PVA. The energy curves of the interaction process "CNT+PVA" was a result of the calculations performed (Figure 5).
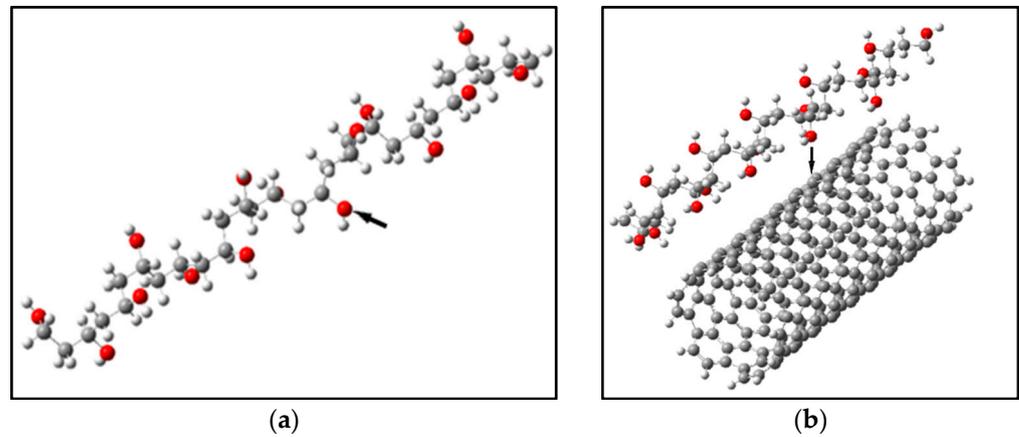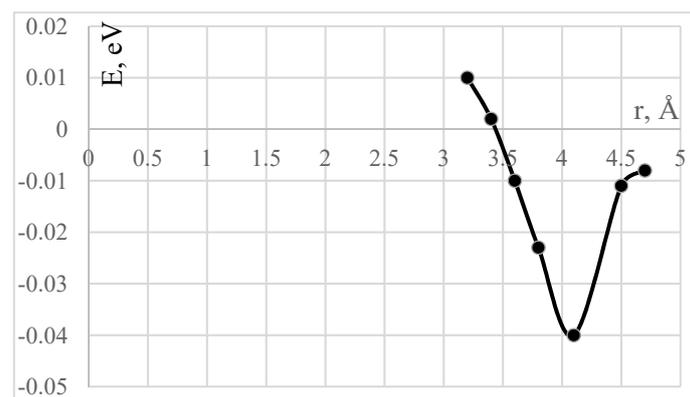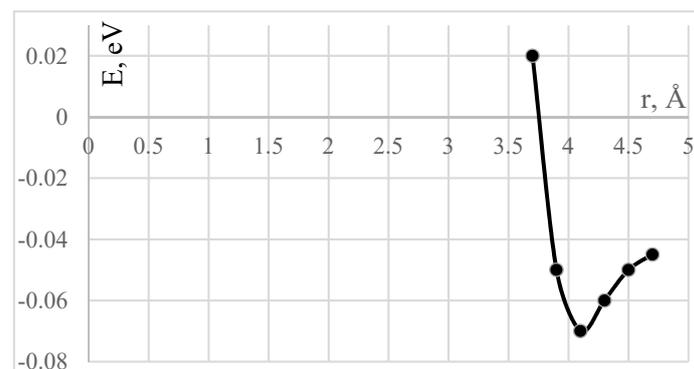

(**a**)   (**b**)

Figure 4. (**a**) A fragment of the PVA, consisting of 16 structural units (monomers), after optimization; (**b**) a model of the interacting system "CNT (6,6) + PVA".

(**a**)

(**b**)

Figure 5. Energy curves of the interaction of the polymer cluster [-CH2CH(OH)-]16: (**a**) with CNT (6,6), using active center 1—oxygen atom (option 1); (**b**) with CNT (9,0), using active center 1—oxygen atom (option 1).

The value of the adsorption energy during the interaction of PVA by active center (1) with CNT (6,6) was about 0.04 eV, and the adsorption distance was Rad = 4.1 Å, whereas CNT (9,0) displayed 0.07 eV at a distance Rad = 4.1 Å (Table 3).

Table 3. The results of adsorption interaction of PVA fragment $[-CH_2CH(OH)-]_{16}$ on the outer surface of carbon nanotubes.

Types of CNTs	Active Center	Adsorption Distance, R_{ad}, Å	Adsorption Energy, ΔE_a, eV
(6,6)	1	4.1	0.04
(9,0)	1	4.1	0.07

The results obtained indicate that the selected carbon nanotubes can form complexes with a PVA fragment containing several structural units while the resulting complexes are stable. Interaction distances are characteristic of physical adsorption.

4.2. Features of the Electron Energy Structure of Polymer Nanocomposites Based on Polyvinyl Alcohol and Carbon Nanotubes

The analysis of the electron energy structure of complexes formed by CNTs of various types and a fragment of PVA $[-CH_2CH(OH)-]_{16}$ has been performed. For the study, nanotubules that showed the maximum sorption activity against PVS were selected. The band gap ΔEg was chosen as the quantity that determines the electronic properties of the carbon nanotube.

The band gap was calculated as the difference between the energy of the Highest Occupied Molecular Orbital (HOMO) and the energy of the Lowest Unoccupied Molecular Orbital (LUMO):

$$\Delta Eg = E_{LUMO} - E_{HOMO} \tag{5}$$

An analysis of the band gap width ΔEg of adsorption complexes found that the system is a semiconductor by type of conductivity (the value of ΔEg varies from 1.175 eV to 1.307 eV for different complexes). Thus, the introduction of CNTs into the polymer matrix of PVA, which is a dielectric by type of conductivity, leads to the appearance of semiconducting properties in the resulting polymer nanocomposite. The values of the orbital energies were calculated using the program "Gaussview", which is a set of routines used in combination with the main program "Gaussian" [23].

The values of ΔEg are given in Table 4; the visualization of the single-electron energy levels of polymer clusters and the "PVA + CNT" is shown in Figure 6.

Table 4. The results of the analysis of the band gap width ΔEg of adsorption complexes.

Types of CNTs	Connection Option (Active PVA Center)	The Forbidden Zone Width ΔEg, eV
(6,6)	oxygen atom	1.175
(9,0)	oxygen atom	1.307

Therefore, the results obtained allow us to predict the possibility of using nanocomposites based on polyvinyl alcohol doped with carbon nanotubes as a material used in micro- and nanoelectronics devices with semiconductor properties.
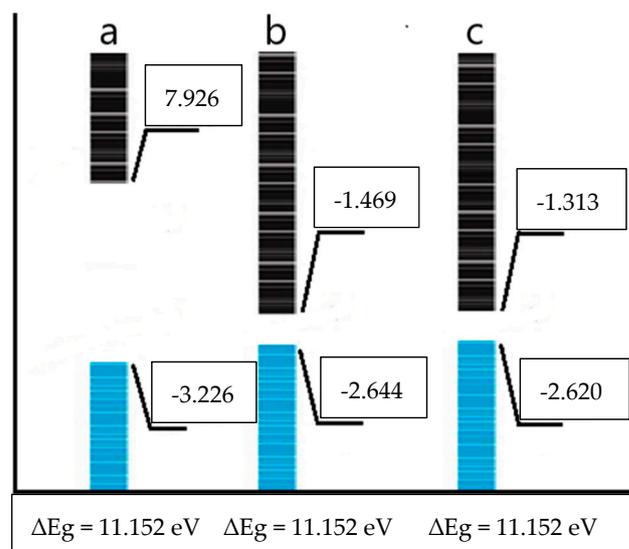
Figure 6. Visualization of single-electron energy levels of polymer clusters and the "PVA + CNT" system: (**a**) PVA; (**b**) PVA + CNT (6,6); (**c**) PVA + CNT (9,0).

5. Conclusions

(1) Based on theoretical calculations performed using the DFT method, the adsorption activity of the structural unit of the polyvinyl alcohol polymer against single-layer carbon nanotubes of two types (6,6) and (9,0) has been proven. The most effective centers of the selected fragment were established: in all cases, it turned out to be an oxygen atom of the examined monomer. The results that have been obtained prove that the main mechanism for obtaining stable polymer complexes based on polyvinyl alcohol doped with carbon nanotubes is the adsorption interaction of the structural components of the PVA polymer with single-layer carbon nanotubes.

(2) To confirm the possibility of creating polymer composite materials based on polyvinyl alcohol reinforced with carbon nanotubes, theoretical calculations of the adsorption interaction process between carbon nanotubes and a PVS fragment containing several structural units of polyvinyl alcohol ($n = 16$) were carried out. The results obtained confirm the possibility of creating stable complexes—polymer composite materials based on polyvinyl alcohol doped with carbon nanotubes. Interaction distances are characteristic of physical adsorption.

(3) The features of the electron energy structure of a polymer nanocomposite based on polyvinyl alcohol doped with carbon nanotubes have been studied and analyzed. It is established that the width of the band gap of the adsorption complexes, defined as the energy difference between the Lowest Unoccupied Molecular Orbital (E_{LUMO}) and the Highest Occupied Molecular Orbital (E_{HOMO}), by the type of conductivity allows the created nanocomposite to be attributed to semiconductors, which distinguishes it from the original polymer with dielectric conductivity. The results obtained make it possible to predict the creation of new composite polymer materials with variable conductive properties and their application in micro- and nanoelectronic applications.

Author Contributions: Conceptualization, I.Z. and D.H.; methodology, I.Z. and L.E.; validation, I.Z. and D.H.; formal analysis, D.H.; investigation, L.E.; data curation, I.Z.; writing—original draft preparation, L.E.; writing—review and editing, I.Z.; supervision, L.E.; funding acquisition, I.Z. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lu, D.; Huo, Y.; Jiang, Z.; Zhong, J. Carbon nanotube polymer nanocomposites coated aggregate enabled highly conductive concrete for structural health monitoring. *J. Carbon* **2023**, *206*, 340–350. [CrossRef]
2. Zhao, X.; Zhang, J.; Lv, K.; Kong, N.; Shao, Y.; Tao, J. Carbon nanotubes boosts the toughness and conductivity of wet-spun MXene fibers for fiber-shaped super capacitors. *Carbon* **2022**, *200*, 38–46. [CrossRef]
3. Kharche, G.; Lokavarapu, B.R. Static buckling analysis of single walled carbon nanotube. *Mater. Proc.* 2023, *in press*. [CrossRef]
4. Zaporotskova, I.V. *Carbon and Non-Carbon Nanomaterials and Composite Structures Based on Them: Structure and Electronic Properties*; VolSU Publishing House: Volgograd, Russia, 2009; p. 490.
5. Dyachkov, P.N. Carbon nanotubes: Structure, properties, applications. *Binomial* **2005**, *196*, 36.
6. Hasnain, M.S.; Nayak, A.K. Nanocomposites for improved orthopedic and bone tissue engineering applications. In *Applications of Nanocomposite Materials in Orthopedics*; Series in Biomaterials; Elsevier: Amsterdam, The Netherlands, 2019; pp. 145–177.
7. Shi, D.; Guo, Z.; Bedford, N. Nanocomposites. In *Nanomaterials and Devices (Micro and Nano Technologies)*; William Andrew: Norwich, NY, USA, 2015; pp. 293–315.
8. Kausar, A. Sensing Materials: Nanocomposites. In *Encyclopedia of Sensors and Biosensors*; Elsevier: Amsterdam, The Netherlands, 2023; Volume 2, pp. 305–315.
9. de Oliveira, A.D.; Beatrice, C.A.G. Polymer Nanocomposites with Different Types of Nanofiller. In *Nanocomposites—Recent Evolutions*; Intechopen: London, UK, 2019; p. 230.
10. Chebil, A.; Doudou, B.B.; Dridi, C.; Dammak, M. Synthesis characterization, optical and electrical properties of polyvinyl alcohol/multi-walled carbon nanotube nanocomposites: A composition dependence study. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* **2019**, *243*, 125–130. [CrossRef]
11. Tyagi, V.; Thakur, A. Carboxymethyl cellulose-polyvinyl alcohol based materials: A review. *Mater. Today Proc.* 2023. [CrossRef]
12. Khazaei, S.; Mozaffari, S.A.; Ebrahimi, F. Polyvinyl alcohol as a crucial omissible polymer to fabricate an impedimetric glucose biosensor based on hierarchical 3D-NPZnO/chitosan. *Carbohydr. Polym.* **2021**, *266*, 118105. [CrossRef] [PubMed]
13. Pogorelov, T.V. Quantum Chemical Calculations Using the Gaussian Software Package and the Gaussview Graphics Editor. *Append. Phys.-Mat.* **2000**, *76*, 2868–2870.
14. Xie, X.-L.; Mai, Y.-W.; Zhou, X.-P. Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Mater. Sci. Eng. R Rep.* **2005**, *49*, 89–112. [CrossRef]
15. Zaporotskova, I.V.; Elbakyan, L.S. Obtaining New Dental Materials Reinforced with Carbon Nanotubes. *J. Nano-Electron. Phys.* **2014**, *6*, 03008-1–03008-3.
16. Elbakyan, L.S.; Zaporotskova, I.V.; Belonenko, M.B. Nanocomposites based on polymethylmethacrylate doped with carbon nanotubes: Some electrophysical studies. *J. Perspect. Mater.* **2017**, *4*, 16–22.
17. Sandler, J.K.W.; Kirk, J.E.; Kinloch, I.A.; Shaffer, M.S.P.; Windle, A.H. Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites. *Polymer* **2003**, *44*, 5893–5899. [CrossRef]
18. Ramasubramaniam, R.; Chen, J.; Liu, H. Homogeneous carbon nanotube/polymer composites for electrical applications. *Appl. Phys. Lett.* **2003**, *83*, 2928–2930. [CrossRef]
19. Scher, H.; Zallen, R. Critical density in percolation processes. *J. Chem. Phys.* **1970**, *53*, 3759–3761. [CrossRef]
20. Gordon, M.S.; Binkley, J.S.; Pople, J.A.; Pietro, W.J.; Hehre, W.J. Self-Consistent Molecular Orbital Methods. 22. Small Split-Valence Basis Sets for Second-Row Elements. *J. Am. Chem. Soc.* **1982**, *104*, 2797. [CrossRef]
21. Koch, W.; Holthausen, M.C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley: Hoboken, NJ, USA, 2001.
22. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E. *Gaussian 09, Revision A.1*; Gaussian, Inc.: Wallingford, CT, USA, 2009.
23. Elbakyan, L.S. *Quantum Chemical Calculations Using THE Gaussian Software Package and the Gaussview Graphics Editor: Textbook*; Publishing House of the VolSU: Volgograd, Russia, 2022; p. 81.