Original paper

Studying the interaction of polyacrylonitrile oligomer chains with carbon fillers

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Abstract: The dependence of the adhesion energy of the polyacrylonitrile oligomeric chain on the surfaces of carbon nanoparticles such as carbon nanotubes and graphene is studied in the framework of full atomistic molecular mechanics simulation using the polymer consistent force field and the open part of the condensed-phase optimized molecular potentials for atomistic simulation studies force field. The length of the polyacrylonitrile oligomer chain, the number of layers in the graphene nanoparticle, the diameter of the carbon nanotube, and the type and density of the modifier molecules on the surface of the graphene are the main parameters of the calculations. The graphene nanoparticle is taken as a limiting case corresponding to the large-diameter carbon nanotube. N-(2-aminoethyl) carbamoyl, nitrocyclohexane, benzamide, and dinitrobiphenyl are selected as surface modifiers. It is shown that with an increase in the number of layers and diameter of carbon nanotubes, the adhesion energy of the polyacrylonitrile oligomer chain increases, which allows us to consider multiwalled carbon nanotube with large diameters as a preferred filler for polyacrylonitrile. The estimates obtained also show that when surface modifiers are used, it is possible to increase the adhesion energy of polyacrylonitrile only in the case of low surface modifier densities.

Keywords: polyacrylonitrile, carbon fibers, carbon nanotubes, graphene, computer simulation.

1. Introduction

Today, carbon fibers (CF) are widely used in the production of high-tech composite materials for aerospace, automotive, chemical equipment, and other applications where a combination of high strength, lightweight, high heat resistance, and chemical inertness is required [1, 2]. It is a unique material consisting of almost pure carbon (the content of which reaches 95-99% by weight), forming fibrillar and ribbon-shaped graphene-like structures, which are produced by multistage heat treatment of synthetic precursor fibers. According to the literature [1-11], the properties of CFs can be controlled by varying conditions of formation of precursor fibers and their composition.

The highest-strength carbon fibers are usually produced on the basis of polyacrylonitrile (PAN) [1-7]. This is explained by the fact that PAN has a high carbon content in its composition (~63 wt%) and, due to the presence of nitrile side groups, can undergo cyclization reactions at high temperatures [1, 3-6] with the formation of ladder-like and graphene-like structures. It is believed that to obtain high-modulus carbon fibers it is necessary to arrange these structures parallel to the fiber axis. Therefore, in the stage of obtaining precursors, they are drawn several times, which makes it possible to achieve a high level of ordering of polymer chains, which leads to an increase in the degree of crystallinity of the

fiber and, as a consequence, the modulus of elasticity. Fillers based on various nanoparticles (NPs) are also used as orienting templates for polymer chains and as initiators of crystallinity growth. To date, carbon nanotubes (CNTs) and graphene are thought to be the most suitable fillers for PAN-derived carbon fibers [4, 6-16].

The influence of carbon fillers has been studied in many experimental works dedicated to the optimization of the properties of PAN-based carbon fibers. However, such works generally focus on revealing the effect of only one type of filler, e. g. single wall [12, 13] and multiwall [9, 14, 15] carbon nanotubes or graphene [10, 11]. Very few studies have compared fibers prepared with different types of fillers [8, 16]. This can be explained by the difficulty of carrying out experimental studies in parallel with the synthesis of the fillers, the adjustment of the conditions for obtaining the precursors, and their transformation into carbon fibers. In this case, the use of computer simulation with simplified models allows us to partially fill the gap in the systematic study of the compatibility of carbon fillers with polyacrylonitrile. It should be noted that the articles presenting the results of the polyacrylonitrile simulation are devoted to the study of a narrow range of issues: the interaction of PAN with solvents [17], the behavior of a single oligomer chain in solution [18], and the interaction of PAN with small-diameter single-walled carbon nanotubes in solution [19]. We can also mention works on the carbonization of PAN [20-23]. At the same time, there are no works devoted to a comparative study of the properties of different carbon fillers.

In this work, we investigated the question of which type of carbon filler is most suitable for PAN. To get the answer, we calculated the adhesion energy of PAN (E_A) on the surface of graphene and CNTs using the molecular mechanics method [24]. Separately, the influence of different surface modifiers on the interaction of the polymer with the filler was considered.

2. Model and calculation method

All calculations were carried out within the framework of fully atomistic molecular mechanics [24]. The initial construction of the molecular systems was carried out using a Nanoobjects module from a MULTICOMP package [25], and time-consuming calculations were carried out using the LAMMPS package [26]. Since the peculiarities of parameterization of interactions of molecular systems can significantly affect the simulation results, we used two Class 2 valence force fields (VFFs) to verify the results obtained: the polymer consistent force field (PCFF) [27] and open parameters for the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) VFFs [28]. The PCFF VFF is the most widely used for the simulation of polymer materials, while the COMPASS VFF is considered to be the most accurate since its

parameterization is based on quantum-mechanical calculations from the first principles. However, only a small part of its parameters is freely available.

The following parameters were used in the calculations: the degree of polymerization of PAN (number of comonomers L), the diameter (d) of CNTs, the number of layers forming NPs of CNTs and graphene (n), and the type and density of the surface modifier of graphene NPs. These parameters were used to construct models of PAN, CNT, and graphene. Syndiotactic PAN oligomers were constructed from 6, 8, 10, 12, and 14 acrylonitrile monomers. Graphene NPs were built as stacks of n graphene sheets with dimensions of 38,34×38,34 Å^2. The distance between adjacent sheets was set to 3,3 Å (corresponding to the equilibrium configuration of the NPs), and the number of layers n varied from 1 to 7. To study the effect of surface modification of carbon fillers on PAN adhesion energy, we prepared models of graphene NPs with grafted surfaces. The following compounds were used as surface modifiers: N-(2-aminoethyl)carbamoyl, nitrocyclohexane, benzamide, and dinitrobiphenyl. Two grafting densities of 2% and 5% of the total number of carbon atoms on the NP surface were used. An example of a three-layer graphene NP with nitrocyclohexane on the surface is shown in Figure 1. The set of CNT models included NPs with a length of 38,34 Å and a diameter d from 20 to 140 Å with a fixed number of layers n equal to 3. The number of CNT layers was chosen on the basis of the results of the study of the dependence of the adhesion energy of PAN on the graphene surface as a function of the number of layers in the NPs.

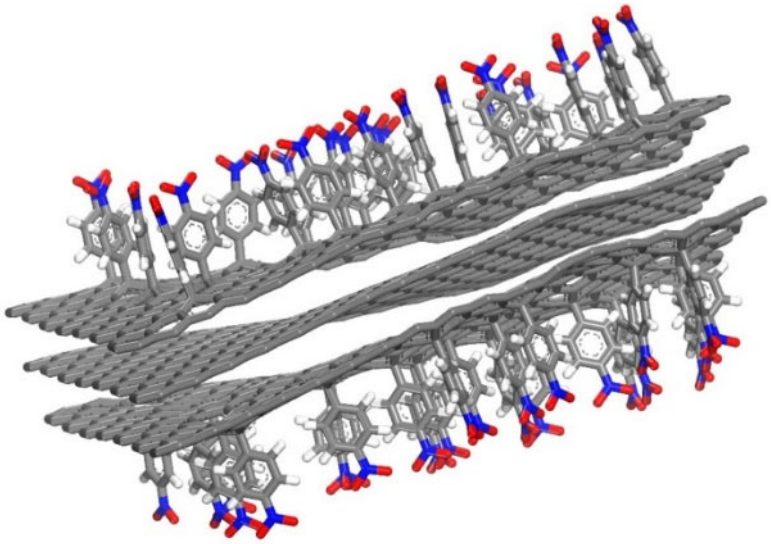

Fig. 1. An example of the three-layer nitrocyclohexane modified graphene of 38,34×38,34 Å^2 in size with the 5% grafting density.

Before calculating the adhesion energy of PAN for each set of parameters, a geometry optimization procedure was performed for the PAN chains and the selected nanoparticle using the FIRE algorithm [29] for 50,000 steps with an

energy convergence threshold of 0,001 kJ/mol. Then, for each molecular model, a short relaxation using molecular dynamics was performed with a step of 0,5 ps in the *NVE* and *NVT* ensembles (at T = 300 K) with a duration of 0,1 ns to obtain equilibrium configurations.

Since the adhesion energy (E_A) characterizes the intensity of the intermolecular interactions and can be interpreted as a change in the potential energy of the prepared system (PAN on the NP surface) and a system where all components are separated by an infinite distance, the following algorithm was used to calculate the E_A. The first step was to construct a system consisting of an oligomeric PAN chain with the number of monomers L and a selected NP. The chain was placed parallel to the NP surface so that its center of mass was close to the center of the graphene NP or half the length of the CNT (along the axis of symmetry). The average distance between the oligomer chain and NP atoms was chosen to be 2 Å (relative to the surface or a modifier on the NP surface) to avoid the overlap of neighboring atoms. In the second step, the geometry of the prepared system was optimized using the FIRE algorithm. In the third step, the system was relaxed in the *NVE* ensemble until the total energy of the system reached an equilibrium value. In the fourth step, the system was also relaxed in the *NVT* ensemble at T = 300 K for 0,5 ns, which is sufficient for the temperature and potential energy of the system to reach a well-defined mean value. The relaxation was then continued for 0,5 ns (productive computation), with the potential energy values of the entire system, filler, and oligomer chain, stored with a step of 0,01 ns for subsequent averaging. Examples of two prepared systems, PAN/CNT and PAN/graphene, are shown in Fig. 2.

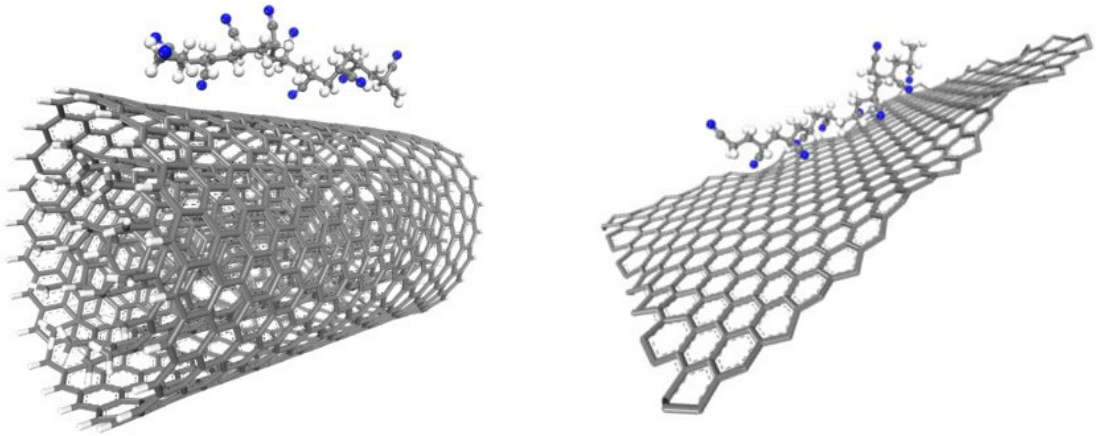

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Fig. 2. Examples of two prepared systems: PAN oligomer chain of 10 units near the surface of (a) three-walled CNT NP (length 38,34 Å, diameter d = 20,0 Å) and (b) graphene NP (n = 1) of 38,34×38,34 Å^2 in size.

Construction of statistically independent configurations was performed using an «annealing» procedure. The temperature of the systems gradually

increased from 300 K to 400 K over 0,1 ns and then decreased back to 300 K. The maximum temperature value of 400 K was chosen to avoid system destruction. At the end of the annealing cycle, a new equilibration of the system was performed in the *NVT* ensemble at a temperature of 300 K for 0,5 ns. The relaxation of the system was then continued to calculate the average values of the potential energies.

The adhesion energy $E_A(L,i)$ of each prepared system (obtained in i-th annealing cycle) normalized to the molecular weight of PAN (specific adhesion energy) was calculated using the following equation

$$E_A(L,i) = (E_{Full}(L,i) - E_{PAN}(L) - E_{NP}) / M_{PAN}(L),$$

where L is the number of monomers in the oligomeric chain, $M_{PAN}(L)$ is its molecular weight, $E_{Full}(L,i)$ is the total energy of the system at the i-th step of the annealing cycle, $E_{PAN}(L)$ and E_{NP} are the average energies of the isolated oligomeric PAN chains and NP. The $E_A(L,i)$ values were used to calculate the average $E_A(L)$ values. For each set of parameters, 1,000 annealing cycles were performed (i.e., 1,000 independent configurations were built).

3. Calculation results

To study the effect of chain length on $E_A(L)$, oligomer chains with the number of monomers L = 6-14 and three-layer graphene NP were used. The results obtained are shown in Fig. 3. The behavior of $E_A(L)$ allows us to conclude that within the error range the adhesion energy is practically independent of the chain length, so L = 10 was chosen for all subsequent calculations.

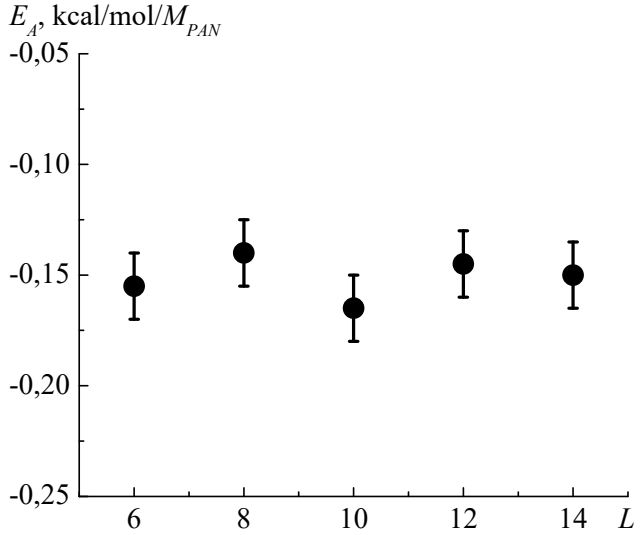

Fig. 3. The specific adhesion energy of PAN (E_A) to the surface of graphene NPs as a function of the number of units L of the oligomer chain. The NP consists of three graphene sheets of 38,34×38,34 Å^2 in size. VFF PCFF.

Next, we investigate the influence of the number of layers in graphene NPs on the specific adhesion energy $E_A(10) \equiv E_A$. In Fig. 4, E_A is plotted as a function of n. It can be seen that the adhesion energy in the modulus increases with increasing n and tends to saturate at $n > 4$. Because graphene NPs were taken as the limiting model of infinite-radius CNTs, this result indicates that multiwalled CNTs should interact more strongly with the polymer matrix compared to single-walled ones.

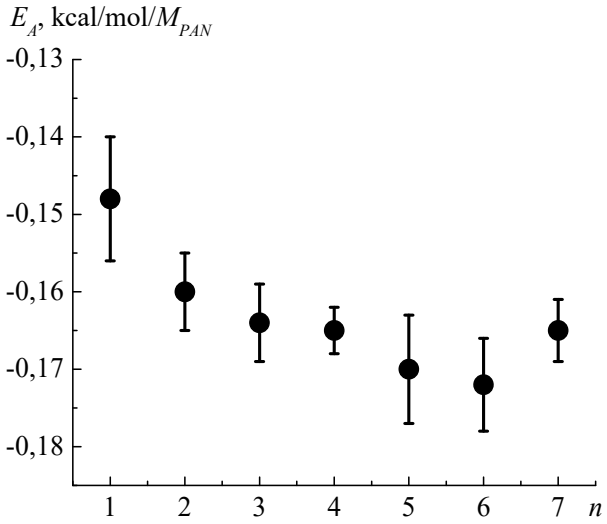

Fig. 4. The specific adhesion energy of PAN (E_A) with L = 10 on the graphene surface as a function of the number of NP layers. The NP consists of n sheets of 38,34×38,34 Å^2 in size. VFF PCFF.

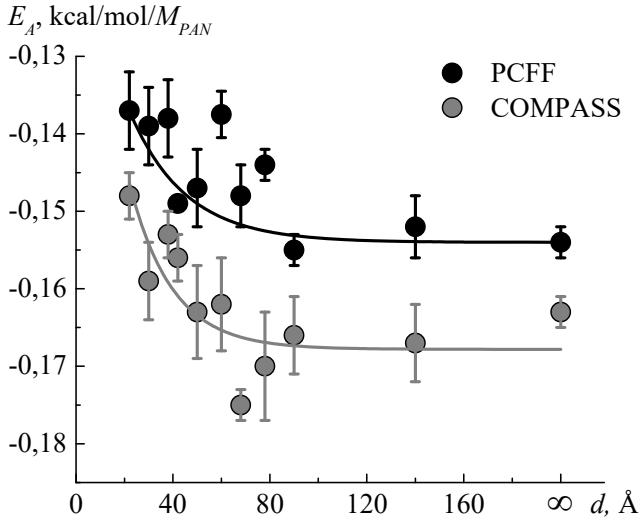

Fig. 5. The PAN adhesion energy (E_A) with L = 10 as a function of the diameter of a three-walled CNT of length 38,34 Å for VFFs COMPASS and PCFF. The rightmost points correspond to the values of the adhesion energy of PAN on the surface of three-layer graphene. This system was used as a reference system.

To study the effect of the CNT radius on the interaction between the

polymer and the filler, a set of three-layer NPs with fixed lengths and different radii was used. In this case, three-layer graphene NPs were used as reference systems, i. e. CNTs with an infinite radius. Figure 5 shows that with increasing CNT diameter, the E_A values reach saturation and tend to the results obtained for three-layer graphene. This allows us to conclude that large-diameter multiwalled CNTs should interact more strongly with PAN than small-diameter single- and double-walled CNTs. To control the influence of the choice of VFF, calculations were performed with two VFFs: PCFF and COMPASS. According to the results shown in Fig. 5, the selected VFFs give similar values of E_A, differing by 0,015 kcal/mol. Thus, to analyze the interaction of PAN with carbon fillers, it is sufficient to perform calculations with one of the selected VFFs.

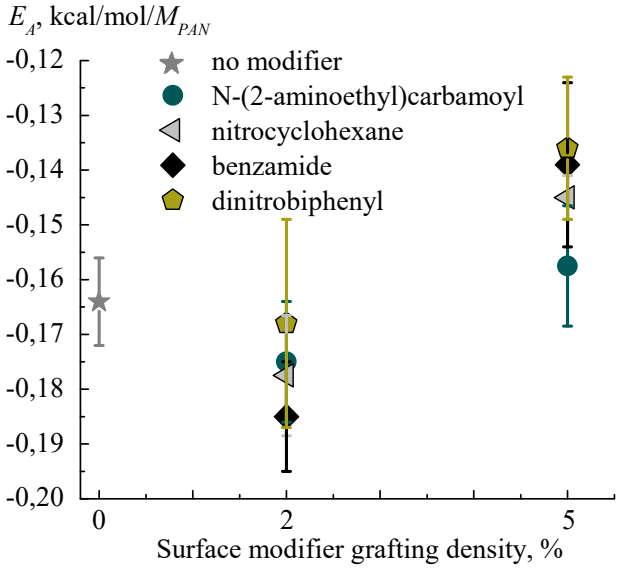

Fig. 6. Adhesion energies of PAN (E_A) to graphene NPs as a function of the type of surface modifier and its grafting density. PAN chain length L = 10. N-(2-aminoethyl)carbamoyl, nitrocyclohexane, benzamide, and dinitrobiphenyl were used as modifiers. Graphene NP of size 38,34×38,34 Å^2 with n = 3 was used. VFF PCFF. The values obtained for NPs without modifiers were used as reference values for E_A.

In the final stage of our investigation, we evaluated the effect of the presence of a surface modifier on the three-layer graphene NPs on the interaction of carbon fillers with PAN. Figure 6 shows the E_A calculated for different surface modifiers as a function of their grafting density. NP without surface modification was used as a reference system. The modifiers selected were N-(2-aminoethyl)carbamoyl, nitrocyclohexane, benzamide, and dinitrobiphenyl. The figure shows that at a grafting density of 2%, the adhesion energy is higher than that of NPs without modifiers. However, as the modifier density increases, the adhesion energy decreases compared to the reference system. According to visual analysis, this is explained by the fact that the

surface modifier can act as a steric hindrance, see Fig. 7. It can be concluded that the most energetically favorable case is a low modifier density on the surface. In this case, a fragment of the polymer chain can be in contact with both the filler surface and the modifier groups.

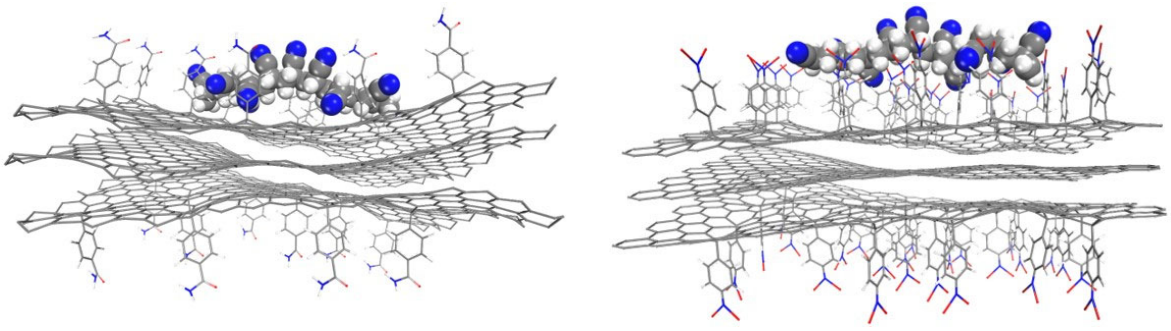

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Fig. 7. An example of graphene NPs (side view) with grafted: (a) benzamide (with a surface density of 2%), and (b) nitrocyclohexane (5%). The NPs are constructed from three graphene sheets of size 38,34×38,34 Å^2 and are shown as wire models. Figures show an oligomer chain of PAN with $L = 10$.

4. Conclusions

Thus, in this work, we evaluated the dependence of the adhesion energy of PAN on the surfaces of CNTs and graphene, depending on the length of the oligomer chain, the number of filler layers, the diameter of the CNTs, and the presence of different modifiers on the graphene surface. Graphene concerning CNTs was taken as a reference system of CNTs of infinite diameter to reveal the effect of the influence of the lengths of the oligomer chains, the number of layers in the carbon filler, and the presence of the surface modifier. The calculations were performed with the fully atomistic molecular mechanics method using two variants of VFFs. The results obtained show that PAN has a high affinity for different types of carbon fillers. At the same time, multiwalled CNTs with large diameters can be considered as a preferred filler because they interact more strongly with the polymer compared to single-walled CNTs and CNTs with smaller diameters. This is indirectly consistent with the results of studies investigating the properties of polyacrylonitrile-based carbon fibers and different types of carbon nanotubes [8]. The results obtained also show that, when using the surface modifier, it is possible to increase the adhesion energy of PAN only in the case of low graft densities of carbon fillers surface. Although our calculations show that multiwalled graphene should interact more strongly with PANs than CNTs, we prefer multiwalled carbon nanotubes because (due to their geometric properties) they are more easily ordered along the fiber axis than graphene by pressing the spinning solution through a spinneret and subsequent repeated drawing of the formed fiber. As a result, they can act as an orientation template for the ordering of PANs in the fiber and contribute to the production

of stronger carbon fibers.

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Изучение взаимодействия олигомерных цепей полиакрилонитрила с углеродными наполнителями

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Аннотация: В рамках полноатомного молекулярно-механического моделирования с использованием двух валентно-силовых полей: полимерного согласованного силового поля и открытой части оптимизированных молекулярных потенциалов конденсированной фазы для атомистического моделирования исследована зависимость энергии адгезии олигомерных цепей полиакрилонитрила к поверхности углеродных наночастиц, таких как нанотрубки и графен. В качестве основных параметров для расчетов выбраны: длина олигомерной цепи полиакрилонитрила, количество слоев в наночастице графена, диаметр углеродной нанотрубки, а также тип и плотность молекул модификатора на поверхности графена. Графен рассматривался как предельный случай – углеродной нанотрубки большого диаметра. В качестве модификаторов поверхности выбраны N-(2-аминоэтил)карбамоил, нитроциклогексан, бензамид и динитробифенил. Показано, что с увеличением числа слоев и диаметра углеродной нанотрубки энергия адгезии полиакрилонитрила возрастает, что позволяет рассматривать многослойные углеродные нанотрубки больших диаметров в качестве предпочтительного наполнителя для полиакрилонитрила. Полученные результаты также показывают, что поверхностный модификатор может увеличить энергию адгезии полиакрилонитрила в случае малых значений плотности прививки модификатора.

Ключевые слова: полиакрилонитрил, углеродные волокна, углеродные нанотрубки, графен, компьютерное моделирование.

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