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## QUANTUM CHEMICAL STUDY ON THE INTERACTION OF CARBON NANOTUBE WITH POLYETHYLENE AND POLYPROPYLENE OLIGOMERS

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*The results of the study on the properties of carbon nanotubes-polymer nanocomposites have shown that the use of nanotubes (CNT) to fill the polymer matrices of different species significantly alter their physical properties compared to the original polymers. However, the influence of CNT on the properties of nanocomposites obtained at the molecular level has not been completely ascertained yet. Therefore, the purpose of this work was to examine the interaction of CNT with fragments of polymers with the same nature, but the different structure, for example, polyethylene and polypropylene using quantum chemistry.*

*By method of density functional theory with the exchange-correlation functional B3LYP, the basis set 6-31G(d,p) and the Grimme dispersion correction, the energy values have been calculated of interaction between carbon nanotube fragments and oligomers of polyethylene and polypropylene, the most probable structures of their intermolecular complexes being optimized.*

*A graphene-like plane of 40 carbon atoms and 16 atoms of hydrogen was chosen as a model for the outer surface of the multi-walled nanotubes (MWNT). In addition to the above described, two larger models were used, with the general formula  $C_{54}H_{18}$  and  $C_{96}H_{24}$  in order to take into account the dimensional effect of the surface of the nanotube fragment model on the interaction energy.*

*It has been found that the interaction energy of a carbon nanotube fragment with an oligomer of polypropylene is greater, compared with polyethylene, which is consistent with the experimental data on melting temperatures of pure polymers and nanotube-polymer composites.*

*The polymer with an outer surface of a carbon nanotube forms an intermolecular complex do not bound covalently and retained by intermolecular dispersion forces. Oligomers of polymeric matters and nanotube surfaces in nanocomposites formed are located closer to each other than separate polymeric links between them.*

**Keywords:** *nanocomposite, carbon nanotube, polyethylene, polypropylene, density functional theory method, cluster approximation, dispersion forces of interaction*

### INTRODUCTION

One of the most promising directions for the development of modern science is nanotechnology [1]. Development of the principles of obtaining polymer nanocomposites is actual [2], the creation of which is based on fundamental research of physico-chemical processes of formation of materials and their structure at the atomic level, which ensures the possibility of obtaining nanocomposites with predefined functional properties. A number of papers shows the effectiveness of using compounds of different chemical nature, having a uniform size as modifiers of polymer matrices [3–5].

In recent times, as a filler, carbon nanotubes are often used, which are cylinders formed by

coagulation of graphite mesh surfaces [5, 6], considered to be an ideal reinforcement material for polymers [7]. To ensure the uniform distribution of CNT in the polymer matrix, surface-active substances are selected that prevent the formation of carbon nanotubes agglomerates [8].

It has been found that the addition of 1 to 5 wt. % of nanotubes to thermoplastic polymers increases the elasticity and strength of the material by 36–42 % [9].

However, the inclusion of carbon nanotubes in the polyethylene matrix in small amounts (up to 5 % by weight) leads to a nonmonotonic change in both degrees of crystallinity of the polymer matrix, the electrophysical and

thermodynamic properties [10]. In this paper, it is also found that the leakage threshold in polyethylene - CNT systems is determined by experimental data on electrical conductivity, is within 0.0015–0.0020 in volumetric lobes. In this case, the content of CNT up to 2 wt. % increases the temperature of thermooxidative degradation of the polymer by almost 60 °C. The greater degree of CNT deagglomeration, the more significant effect of CNT on the structure and properties of the composite. Polypropylene-carbon nanotubes (PP - CNT) composites were described in [11], and features were examined of their structure, melting and crystallization processes, mechanical, electro- and thermophysical characteristics. It is shown that the presence of CNT in a composite of PP - CNT for insignificant content (up to 2 wt. %) leads to a nonmonotonic change in the degree of crystallinity of the PP, as in the previous case [10], which is most clearly reflected in the thermophysical properties. It has been found that the content of 0.5–5.0 wt. % CNT results in the formation of a continuous grid with CNT lead to a significant increase in the compression strength, reduction of the deformation rate, increase in electrical conductivity to five orders of magnitude with a slight increase in the thermal conductivity.

Carbon nanotubes in polymer matrices significantly affect electrical conductivity, viscosity moving another transport properties. In particular, in [12] a study was carried out on the complex permittivity and electrical conductivity both in the ultrahigh-frequency range (9 GHz) and at low frequencies (0.1, 1, and 10 kHz) of two systems of polytetrafluoroethylene-multilayered carbon nanotubes, output and dispersed in an aqueous medium. It has been found that the introduction of dispersed nanotubes into a polymer reduces the percolation threshold from 4.5 to 2.6 % due to the uniform distribution of the filler in the polymer, which leads to an increase in the interphase surface of the interaction of polymer-carbon nanotubes, which manifests itself in increasing the values of the real and imaginary components of the complex dielectric constant. In another paper [13], studies on the electrophysical properties of polymeric composites (PCs) filled with MWNTs synthesized on the surface of the basalt scales based on polychlorotrifluoroethylene in the ultrahigh frequency range and at low frequencies. It

is shown that the values of the real and imaginary components of the complex permittivity in the ultrahigh-frequency range and the electrical conductivity at low frequencies are nonlinearly dependent on the bulk content of MWNT in the PC.

It is also necessary to study the structural, thermal, and electrophysical characteristics of polymer composite materials based on polypropylene and polytetrafluoroethylene filled with multilayered carbon nanotubes and fine silica [14]. In this work, deviations were detected of heat and electrical conductivity from the additive values for low-filled (up to 1.5 % by weight) materials correlated with the degree of crystallinity of polymers. It was found that reducing the size of aggregates of nanotubes in a polymer matrix can significantly reduce the percolation threshold and increase absorption of electromagnetic energy by nanocomposites in the ultrahigh frequency range by increasing the phase separation surface.

The results of the study on the properties of CNT - polymer nanocomposites have shown that the use of nanotubes to fill the polymer matrices of different species significantly alter their physical properties compared to the original polymers. However, the influence of CNT on the properties of nanocomposites obtained at the molecular level has not yet been completely ascertained.

The interaction and properties of composites of organic polymers with nanotubes are successfully investigated by methods of computer simulation [15–19]. In addition, the interaction of nitrogen-containing molecules (1,1-diamino-2,2-dinitroethylene, hexahydro-1,3,5-trinitro-*s*-triazine, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, 3,3'-azo-bis(6-amino-1,2,4,5-tetrazine, 3,6-diazido-1,2,4,5-tetrazine *etc.*) with single-carbon nanotubes of small diameter (up to 1.0 nm), it has been found that the interaction energy of the molecule-off-piecemeal complex is dependent on the dispersion forces between the molecules and carbon nanostructures, and also, in some cases, on Coulomb interactions due to charge transfer and intermolecular H-bonds. In [21], the importance of proper consideration in quantum chemical simulation, the influence of  $sp^2$ -hybridized carbon atoms on the formation energy and the geometric parameters of intermolecular complexes of organic molecules

and carbon nanotubes or graphene-like planes are discussed. Also, in our previous article [22] it is shown that when molecules are adsorbed physically on a carbon nanotube, a substantial redistribution of electron density between them occurs in contrast to chemisorption in the case of the formation of covalent bonds between a molecule and a nanotube. Consequently, the above considerations suggest the successful use of quantum chemistry to study the interaction of fragments of polymers with carbon nanostructures. Therefore, the purpose of this work was to examine the interaction of CNT with fragments of polymers of the same nature, but different structure, for example, polyethylene and polypropylene using quantum chemistry.

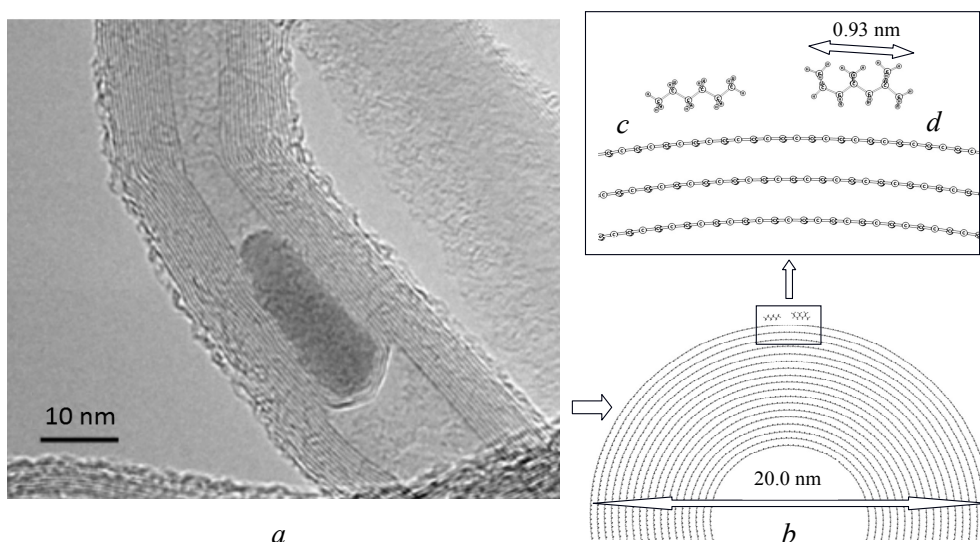
#### OBJECTS AND METHODS OF EXAMINATION

Within the framework of the density functional theory (DFT) with the functional B3LYP [23, 24] and the basis set 6-31G(d,p), the modeling of "fragment of the outer surface of a multilayer carbon nanotube with oligomers" containing one, two, and three elementary units (further monomers, dimers, and trimers) of polymers such as polyethylene and polypropylene, for which there are available experimental physical properties [10, 11]. The calculations used the GAMESS (US) program [25].

In order to take into account the dispersion effects of binding [26, 27] that arise in the formation of non-covalent intermolecular complexes, the dispersion correction Grimme D3 [28, 29] was taken into account in the intermolecular interaction energy calculations.

The choice of the DFT-D method, namely, B3LYP-D3 for our study, can be justified by the fact that it is not time-consuming, compared to the calculations using the B97D or wB97XD functionality. According to the literature data [30–32], all three methods give comparable results with respect to geometric parameters and binding energy for objects similar to ours.

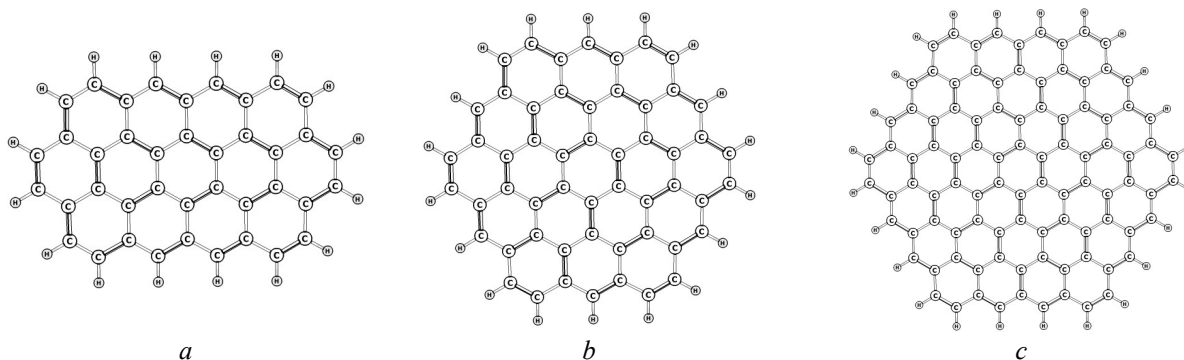
When creating nanocomposites based on polyethylene and polypropylene, multilayer nanotubes were used that had an outer diameter of 10 to 20 nm [10, 11] (Fig. 1 *a*). As shown by the results of the simulation of a cross section of a nanotube with the diameter of 20 nm (Fig. 1 *b*), it turned out that when the fragments of a small size, approximately 0.93 nm (trimers) of selected polymers interact, the outer surface of the nanotube looks almost without a positive curvature of the cylinder (see Fig. 1 *d*), which allows us to consider as a result of the interaction of small size oligomers of these polymers with the outer surface of MWNT as intermolecular complexes of oligomers of selected polymers with a graphene-like plane.



**Fig. 1.** Comparison of the size of a typical multilayer nanotube with those of the oligomers of selected polymers: *a* – TEM image of a fragment of a multilayer carbon nanotube [11], *b* – a transverse section of a carbon nanotube, *c* – a polyethylene trimer, and *d* – a polypropylene trimer

Therefore, a graphene-like plane of 40 carbon atoms (Fig. 1 *a*) was chosen as a model for the outer surface of the MWNT, as was done in [15]. In this case, the distance between the most remote carbon atoms in this graphene-like cluster is 1.2 nm. Therefore, to equalize uncompensated valences and to preserve  $sp^2$ -hybridization at carbon atoms, 16 atoms of

hydrogen, one to each carbon atom were added to peripheral atoms (see Fig. 2 *a*). In addition, in order to take into account the dimensional effect of the surface of the nanotube fragment model on the interaction energy, in addition to the above described, two larger models were used, the general formula  $C_{54}H_{18}$  and  $C_{96}H_{24}$  (Fig. 2 *b, c*).



**Fig. 2.** Models for the fragment of the outer surface of a multilayer carbon nanotube by the gross composition: *a* –  $C_{40}H_{16}$ , *b* –  $C_{54}H_{18}$ , *c* –  $C_{96}H_{24}$

Equilibrium spatial structures of reagent molecules and reaction products were found by minimizing the gradient norm to 0.0001 Hartree. The stationary power minima of relative structures is proved by the absence of negative eigenvalues of Hesse matrices (matrices of force constants) [33].

## RESULTS AND DISCUSSION

**Examination of the interaction between polyethylene and polypropylene oligomers.** It is known [34–36] that for thermoplastic polymers, the intermolecular binding energy between their structural units correlates with the melting temperature of the corresponding matter. In the study of intermolecular interactions of the fragments of polymers with the outer surface of carbon nanotubes, magnitudes of the energy of intermolecular interaction of the fragment of polymers of different sizes for polyethylene polymers (Fig. 3 *a–c*) and polypropylene (Fig. 3 *d–f*) were estimated. Fig. 3 shows the most probable intermolecular complexes, the total energies of which were minimal. In addition, we have shown that, regardless of the size of the fragment of polymers of polyethylene and polypropylene, the average distance between the carbon atoms is about 0.390 nm, which

indicates the absence of chemical bonding between different oligomers [35].

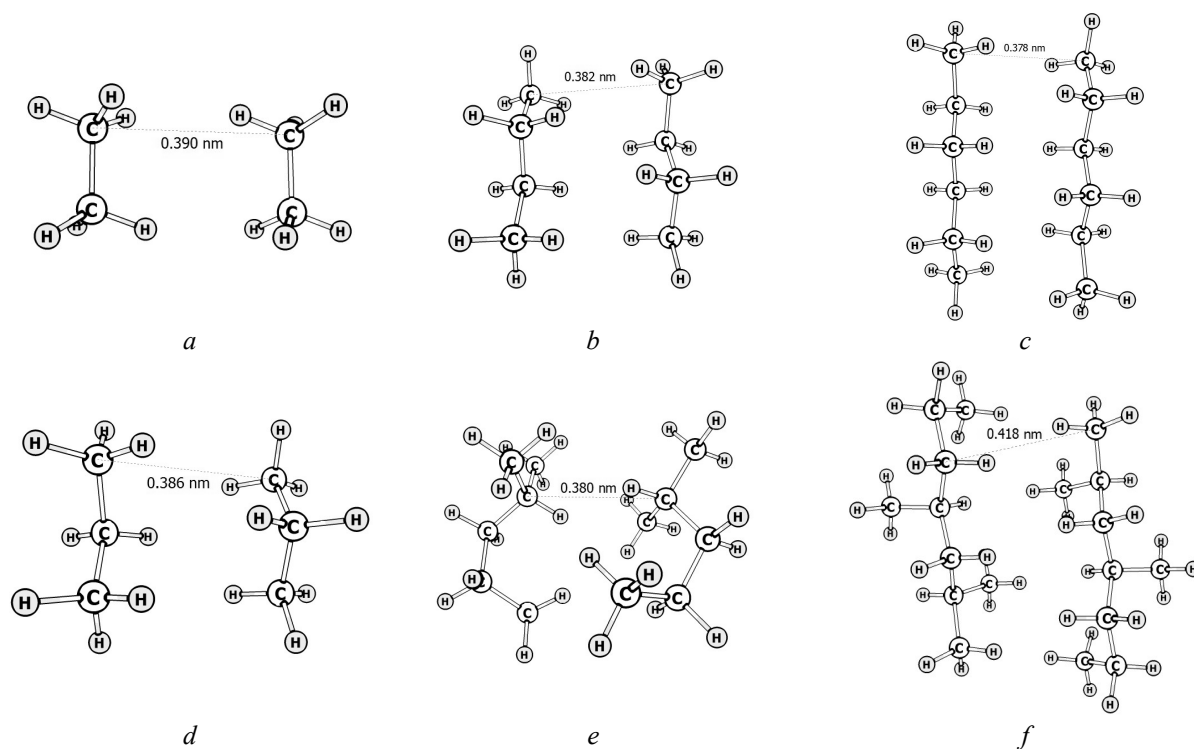
The results of the analysis of calculations are shown in Fig. 6 *a*, from which it is evident that the energy of interaction between two identical monomers for polyethylene (Fig. 3 *a*) is  $-8.0$  kJ/mol, and for polypropylene (Fig. 3 *d*)  $-14.4$  kJ/mol, respectively. With an increase in the size of the oligomeric units to two for each of the polymers (Fig. 3 *b, e*), the energy of their interaction is also twice as high, while the energy is  $-20.3$  and  $-25.9$  kJ/mol, respectively. By increasing the size of the oligomers studied by another (Fig. 3 *c, f*), the energy of the intermolecular interaction increases (Fig. 4): for polyethylene it is  $-32.9$  kJ/mol, and for polypropylene it is  $40.6$  kJ/mol. In this case, for a linear chain of polyethylene, an increase in the length of the fragments that interact with each other results in a monotonical decrease in the distance between the oligomers (0.390, 0.382, 0.378 nm). This is also consistent with the energy of interaction per number of elemental links of the polymer. In particular, for the complex depicted in Fig. 3 *b* (consisting of two double-polymer units) to find out this value, it is necessary to divide  $-20.3$  kJ/mol into two and we so obtain the value of  $-10.1$  kJ/mol, which is

2 kJ/mol less than the similar value for a complex of two monomeric parts of polyethylene ( $-8.0$  kJ/mol). For the complex consisting of two trimers (Fig. 3 c), this value is even larger and is divided into three ( $-32.9/3 = -11.0$  kJ/mol).

For polypropylene, a similar trend of change in distance is not observed. The energy of intermolecular interaction per one elementary polypropylene link also does not increase with an increase in the number of elementary units: compared to the complex consisting of polypropylene monomers and having the intermolecular interaction energy value of  $-14.4$  kJ/mol. For a link consisting of two elementary units, this value is  $-26.0/2 =$

$-13.0$  kJ/mol and for the trimeric polypropylene fragment  $-40.6/3 = -13.5$  kJ/mol, respectively. This can be explained by the fact that polypropylene has a more complex structure (the presence of a methyl group in each elementary chain), compared with polyethylene.

Consequently, with an increase in the number of elemental units in the polypropylene oligomer, the energy per polypropylene unit will not differ by more than 3 kJ/mol from the above considered quantities. Therefore, for the study of intermolecular interaction between individual groups of polymeric units, it is enough to use oligomers consisting of two or three elementary units.



**Fig. 3.** The most probable intermolecular complexes of polyethylene oligomers (a–c) and polypropylene (d–f)

Consequently, based on the analysis of the calculation results, it can be argued that, regardless of the size of the fragments of these polymers, comparing the value of intermolecular energy for the same number of elementary units of these two polymers, the polypropylene fragments are more tightly bound than those of polyethylene, which means that in order to disconnect the polypropylene links, which are connected by non-covalent bonds, more energy is needed than for polyethylene. The calculation results obtained are consistent with experimental

data on the melting temperature of polymers, since the melting temperature of the polyethylene is  $120\text{--}140^\circ\text{C}$ , and for polypropylene this value is higher ( $130$  to  $170^\circ\text{C}$  as dependent on the polymer grade [37–40]).

**Interaction of fragments of a carbon nanotube with polyethylene oligomers.** In connection with the choice of a graphene-like plane as a fragment of the outer surface of a nanotube interacting with polyethylene oligomers, it is crucially important to confirm the reliability of the calculated energy values of

intermolecular interaction. Therefore, intermolecular complexes with different amounts of polymeric units (one, two, three) and graphene-shaped planes of various sizes ( $C_{40}H_{16}$ ,  $C_{54}H_{18}$ , and  $C_{96}H_{24}$ , Fig. 4) were modeled.

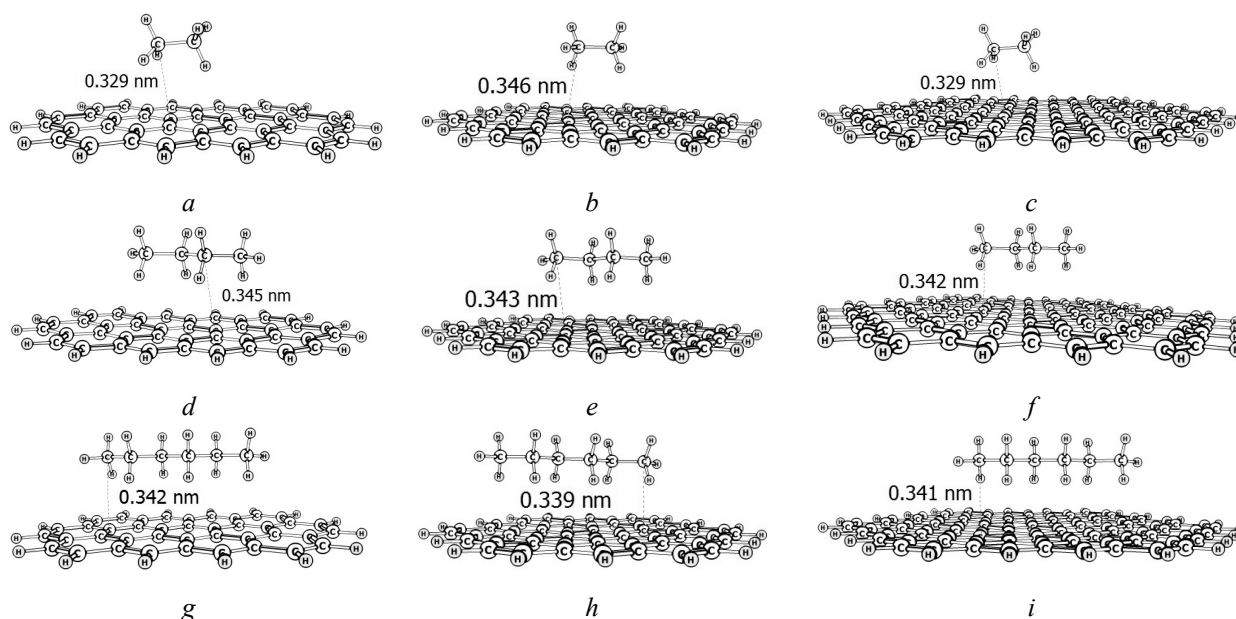
For complexes where the fragment of the outer surface of a nanotube has the smallest graphene cluster  $C_{40}H_{16}$  (Fig. 4 *a, d, g*), the intermolecular distance between of the fragment of polymers and the graphene-shaped plane increases slightly from 0.329 to 0.345 nm with an increase in the size of the fragment of polymers from monomer to dimer, and for the trimer this value is slightly reduced to 0.342 nm. The energy of the intermolecular interaction of the polyethylene monomer with the graphene plane is  $-31.5$  kJ/mol, for dimer this value is  $-54.6$  kJ/mol, and for the trimer  $-80.4$  kJ/mol (Fig. 6 *b*). For intermolecular complexes with the graphene-like cluster  $C_{54}H_{18}$  (Fig. 4, *b, e, h*), a tendency arises to decrease the intermolecular distance due to an increase in the size of the polyethylene fragments (0.346 nm for the monomer, 0.343 nm for the monomer, and 0.339 nm for the trimer).

The energy of the intermolecular interaction between the polyethylene monomer and the  $C_{54}H_{18}$  cluster is 30.0 kJ/mol, which is 1.5 kJ/mol less than the value for the complex

with the  $C_{40}H_{16}$  cluster. For dimer, this value is  $-56.4$  kJ/mol, that is, the energy per polymeric link is slightly smaller than the value for the monomer ( $-28.2$  kJ/mol).

When using as a fragment of the outer surface of a carbon nanotube of a graphene-like cluster, the gross composition of  $C_{96}H_{24}$ , no similar tendency arises in shortening the distance compared to the length of the oligomeric chain in previous case with the  $C_{54}H_{18}$  cluster. For the polyethylene monomer complex, the intermolecular distance is the smallest (0.329 nm, see Fig. 4 *c*), and is similar to that in the complex monomer of polyethylene ( $C_{40}H_{16}$ , Fig. 4 *a*), unlike that for the complex with dimer (Fig. 4 *f*). The energy of intermolecular interaction for the monomer is 33.0 kJ/mol, for the dimer  $-57.4$  kJ/mol, and for the trimer 81.3 kJ/mol.

Comparing the distances between the carbon atoms for the complexes between two identical oligomers (Fig. 3) and the distance between the graphene planes and the carbon atoms of polyethylene fragments (Fig. 4), it is seen that, regardless of the size of the graphene cluster, this distance is approximately 0.05 nm smaller than similar value for the complexes consisting of two fragments of polyethylene (Fig. 4 *a-c*).



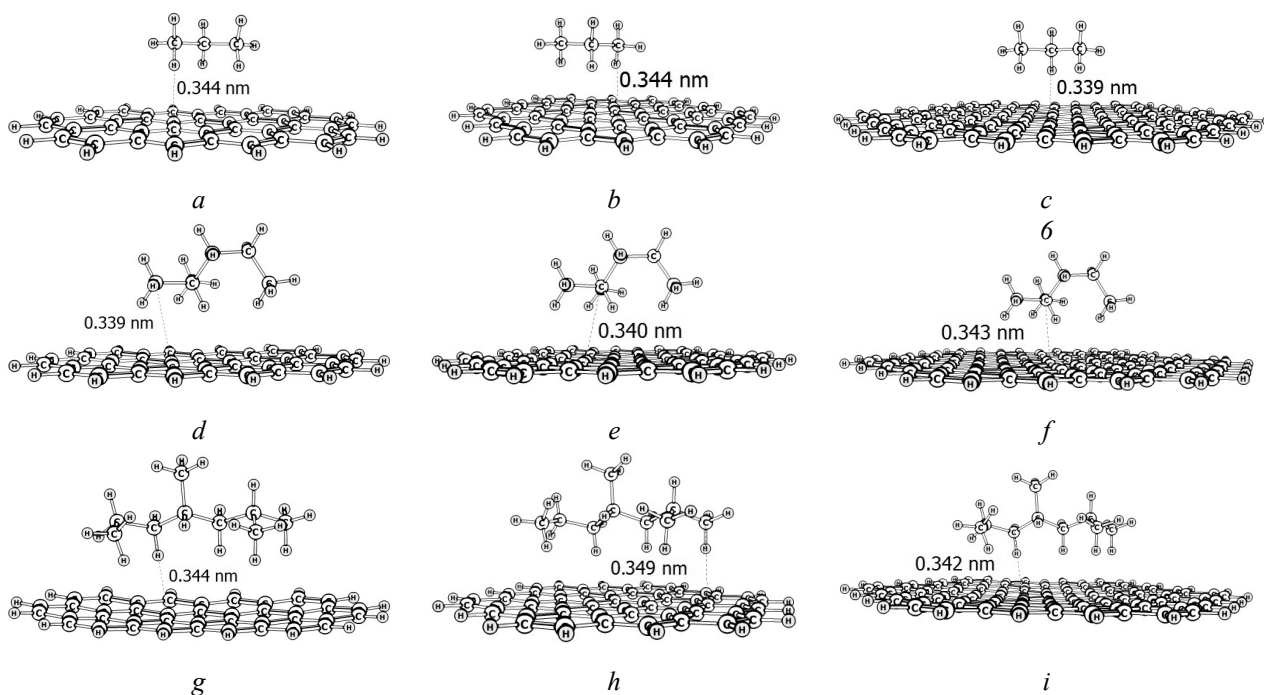
**Fig. 4.** The structure of different length of polyethylene fragments in intermolecular complexes with graphene-like clusters of different sizes, modeling a fragment of the outer surface of a carbon nanotube

**Interaction of a fragment of a carbon nanotube with polypropylene oligomers.** In the study of the interaction of polypropylene oligomers with fragments of the outer surface of a carbon nanotube, the same three graphene-like clusters were used, as for oligomers of polyethylene with CNT. These intermolecular complexes are depicted in Fig. 5.

For complexes of polypropylene monomer with graphene-like clusters of different sizes, as shown in Fig. 5 *a, c*, the distance between the carbon atoms of the monomer and the graphene-like plane almost does not change, in contrast to the similar value for the complex with polyethylene, and make up 0.34 nm. This is probably due to the larger size of the monomer of polypropylene compared with polyethylene. The energy of the intermolecular interaction for

the monomer with the smallest carbon cluster ( $C_{40}H_{16}$ ) is  $-41.3$  kJ/mol. Increasing the size of the cluster to  $C_{54}H_{18}$  results in an increase in the energy of the interaction, which in this case has a value of  $-45.0$  kJ/mol, and a further increase in the size of the graphene-like plane to  $C_{96}H_{24}$  increases the magnitude of the intermolecular interaction energy to  $-46.3$  kJ/mol (Fig. 6 *b*).

Considering the interaction of graphene-like clusters of different sizes with a two-link polypropylene oligomer, it can be seen that increasing the size of the carbon cluster increases the inter-molecular distance from 0.339 nm for the  $C_{40}H_{16}$  cluster, 0.340 nm for  $C_{54}H_{18}$  and 0.343 nm for  $C_{96}H_{24}$  (Fig. 5 *d-f*). This distance is almost the same as for a complex with a monomer (Fig. 5 *a-c*).



**Fig. 5.** The structure of different length polypropylene fragments in intermolecular complexes with graphene-like clusters of different sizes, which simulate a fragment of the outer surface of a carbon nanotube

The energy of intermolecular interaction for a complex with the smallest graphene-like cluster and dimer is  $-66.4$  kJ/mol, and for the dimer oligomer of polypropylene with a larger cluster ( $C_{54}H_{18}$ ), the interaction energy is  $-69.3$  kJ/mol (Fig. 6). The energy of the interaction of dimer with a graphene-like cluster of maximum size  $C_{96}H_{24}$  has an even greater absolute value of  $-71.0$  kJ/mol.

With an increase in the size of the graphene-like cluster up to  $C_{54}H_{18}$  for a complex with a trimer, the binding energy of 1.6 kJ/mol is greater than that for trimer and  $C_{40}H_{16}$  ( $-89.2$  kJ/mol), which is not consistent with the fact of increasing the intermolecular distance in these complexes, as can be seen in Fig. 5 *g, h*.

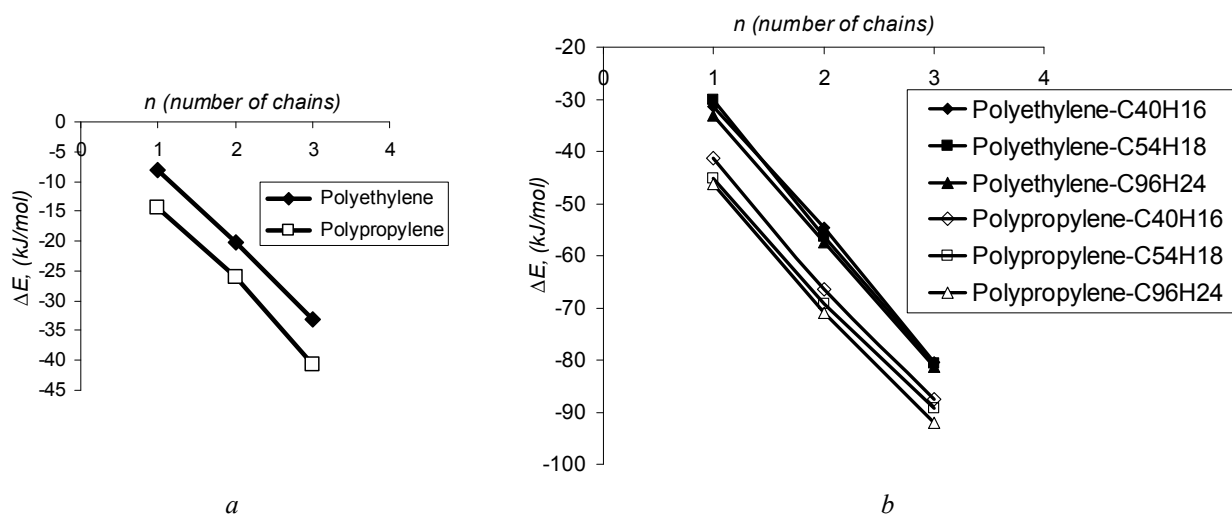
Using the maximum size of the  $C_{96}H_{24}$  cluster in the intermolecular complex with the

trimer slightly increases the energy of the intermolecular interaction ( $-92.1$  kJ/mol) compared with those for smaller clusters ( $C_{40}H_{16}$  and  $C_{54}H_{18}$ ).

To illustrate the dependence of the binding energy on the size of the graphene-like cluster and on the number of polymeric units for polyethylene and polypropylene, graphic dependences were plotted shown in Fig. 6. It can be seen from these that both lines for the pure polymers (Fig. 6 *a*) and for their nanocomposites (Fig. 6 *b*) show the dependences of the intermolecular interaction energy on the number

of elementary units in the oligomers of these materials are parallel to each other, indicating a direct proportional dependence and the fact that these lines will not intersect with the increase in both the lengths of these oligomers and the size of the graphene-like cluster simulating the outer surface of the multilayer carbon nanotube.

The summary Table shows the numerical values of intermolecular binding energy between two identical oligomers for polyethylene and polypropylene, as well as for their complexes with graphene-like clusters of different sizes.



**Fig. 6.** The dependence of the energy of intermolecular interaction on the number of interacting units for polyethylene and polypropylene: (a) for pure polymers and (b) for nanocomposites with different fragments of the outer surface of carbon nanotubes

**Table.** Intermolecular binding energy values for pure polymers and nanocomposites (kJ/mol)

Number of links in the oligomer	Pure polymers		Nanocomposites					
	Polyethylene	Polypropylene	Polyethylene			Polypropylene		
			$C_{40}H_{16}$	$C_{54}H_{18}$	$C_{96}H_{24}$	$C_{40}H_{16}$	$C_{54}H_{18}$	$C_{96}H_{24}$
1	-8.0	-14.4	-31.5	-30.0	-33.0	-41.3	-45.1	-46.3
2	-20.3	-25.9	-54.6	-56.4	-57.4	-66.4	-69.3	-71.0
3	-33.0	-40.6	-80.5	-80.6	-81.3	-87.6	-89.2	-92.1

Comparing these data (Table), it can be seen that irrespective of the size of the graphene-like clusters, the intermolecular interaction between the graphene-like cluster and the fragments of polyethylene and polypropylene is greater than those for the pair of these fragments with each other. Consequently, it can be argued that the introduction of carbon nanotubes into polyethylene or polypropylene increases the

strength and melting point of the resulting nanocomposites compared to pure polymers, which is confirmed by experimental data [10, 11].

It can be seen from Fig. 6 and Table that for pure polymers and for their nanocomposites (CNT-polymer), the energy of intermolecular interaction is greater for polypropylene than for polyethylene.



## CONCLUSIONS

According to the results of simulation, due to addition of multilayered nanotubes to polyethylene and polypropylene, the energy of intermolecular CNT - polymer interaction increases, what is consistent with the increase in the melting temperature of the nanocomposites obtained. The energy of intermolecular interaction for polymer-carbon nanotube complexes is greater by 18.9 kJ/mol for polyethylene, and by 22.5 kJ/mol for polypropylene, as compared to those of pure polymers.

The fragment of polymer with an outer surface of a carbon nanotube forms an

intermolecular complex not bound covalently and retained by intermolecular dispersion forces. Oligomers of polymeric matters and nanotube surfaces in nanocomposites formed are placed closer to each other than separate polymeric links between them.

The magnitude of the energy of interaction between a carbon nanotube fragment and polypropylene oligomers is much greater than that of polyethylene, which is consistent with experimental data on greater strength and thermal stability of polypropylene-based nanocomposite than on polyethylene-based ones.

## Квантовохімічне дослідження взаємодії вуглецевої нанотрубки з олігомерами поліетилену і поліпропілену

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*Результати вивчення властивостей наноконкомпозитів вуглецеві нанотрубки - полімер показали, що використання вуглецевих нанотрубок (ВНТ) для наповнення полімерних матриць різних видів суттєво змінює їх фізичні властивості в порівнянні з вихідними полімерами. Однак, вплив ВНТ на властивості одержаних наноконкомпозитів на молекулярному рівні остаточно не з'ясовано, тому метою даної роботи було дослідити взаємодію ВНТ з олігомерами полімерів однакової природи, але децю відмінної будови на прикладі поліетилену і поліпропілену методами квантової хімії.*

*Методом теорії функціоналу густини з обмінно-кореляційним функціоналом B3LYP, базисним набором 6-31G(d,p) і дисперсійною поправкою Грімме розраховані величини енергії взаємодії фрагментів вуглецевої нанотрубки з олігомерами поліетилену та поліпропілену, оптимізовані найбільш ймовірні структури їх міжмолекулярних комплексів.*

*За модель зовнішньої поверхні багатощарових вуглецевих нанотрубок (БШВНТ) було вибрано графеноподібну площину складом  $C_{40}H_{16}$ . Для врахування розмірного ефекту поверхні моделі фрагменту нанотрубки на енергію взаємодії, крім вище описаної, було використано дві моделі більшого розміру, загальною формулою  $C_{54}H_{18}$  і  $C_{96}H_{24}$ .*

*Встановлено, що величина енергії взаємодії фрагмента вуглецевої нанотрубки з олігомером поліпропілену більша, в порівнянні з поліетиленом, що узгоджується з експериментальними даними щодо температур плавлення чистих полімерів і композитів нанотрубка-полімер.*

*Полімер з зовнішньою поверхнею вуглецевої нанотрубки утворює міжмолекулярний комплекс, який не зв'язаний ковалентно і утримується міжмолекулярними дисперсійними силами. Олігомери полімерів і поверхні нанотрубки в утворених наноконкомпозитах розміщуються ближче один до одного, ніж окремі полімерні ланки між собою.*

**Ключові слова:** *наноконкомпозит, вуглецева нанотрубка, поліетилен, поліпропілен, метод теорії функціоналу густини, кластерне наближення, дисперсійні сили взаємодії*

## Квантовохимическое исследование взаимодействия углеродной нанотрубки с олигомерами полиэтилена и полипропилена

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Результаты изучения свойств нанокompозитов углеродные нанотрубки - полимер показали, что использование углеродных нанотрубок (УНТ) для наполнения полимерных матриц различных видов существенно изменяют их физические свойства по сравнению с исходными полимерами. Однако, влияние УНТ на свойства полученных нанокompозитов на молекулярном уровне окончательно не выяснено, поэтому целью данной работы было исследовать взаимодействие УНТ с олигомерами полимеров одинаковой природы, но несколько различного строения на примере полиэтилена и полипропилена методами квантовой химии.

Методом теории функционала плотности с обменно-корреляционным функционалом  $B3LYP$ , базисным набором  $6-31G(d,p)$  и дисперсионной поправкой Гримме рассчитаны величины энергии взаимодействия фрагментов углеродной нанотрубки с олигомерами полиэтилена и полипропилена, оптимизированы наиболее вероятные структуры их межмолекулярных комплексов.

В качестве модели внешней поверхности многослойных углеродных нанотрубок (МСУНТ) была выбрана графеноподобная плоскость состава  $C_{40}H_{16}$ . Для учета размерного эффекта поверхности модели фрагмента нанотрубки на энергию взаимодействия, кроме выше описанной, были использованы две модели большего размера, общей формулой  $C_{54}H_{18}$  и  $C_{96}H_{24}$ .

Установлено, что величина энергии взаимодействия фрагмента углеродной нанотрубки с олигомером полипропилена больше, по сравнению с полиэтиленом, что согласуется с экспериментальными данными температурам плавления чистых полимеров и композитов нанотрубка-полимер.

Полимер с внешней поверхностью углеродной нанотрубки образует межмолекулярный комплекс, который не связан ковалентно и удерживается межмолекулярными дисперсионными силами. Олигомеры полимеров и поверхность нанотрубки образованных нанокompозитов размещаются ближе друг к другу, чем отдельные полимерные звенья между собой.

**Ключевые слова:** нанокompозит, углеродная нанотрубка, полиэтилен, полипропилен, метод теории функционала плотности, кластерное приближение, дисперсионные силы взаимодействия

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