Yu.V. Hrebelna [1], E.M. Demianenko [1], M.I. Terets [1], A.G. Grebenyuk [1], Yu.I. Sementsov [1, 2], N.V. Sigareva [1], S.M. Makhno [1, 2], M.T. Kartel [1, 2]

THEORETICAL STUDY ON THE INTERACTION OF POLYCHLOROTRIFLUOROETHYLENE FRAGMENTS WITH GRAPHENE-LIKE PLANES

[1] *Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine*
17 General Naumov Str., Kyiv, 03164, Ukraine, E-mail: teretsmariya@gmail.com
[2] *Ningbo Sino-Ukrainian New Materials Industrial Technologies Institute, Kechuang*
Building, N777 Zhongguan road, Ningbo, 315211, China

The interaction of graphene with fragments of polychlorotrifluoroethylene (PCTFE) has been studied by quantum chemistry methods. Within the frameworks of the density functional theory with B3LYP exchange-correlation functional, 6-31G(d,p) basis set and the Grimme dispersion correction, and the second order Møller-Plesset perturbation theory (MP2), the values of the interaction energy of graphene with polychlorotrifluoroethylene oligomers were calculated and the most probable structures of their intermolecular complexes were optimized. As a graphene model, graphene-like planes (GLP) of different sizes were chosen, namely: $C_{40}H_{16}$, $C_{54}H_{18}$ and $C_{96}H_{24}$.

Oligomers of polychlorotrifluoroethylene and graphene-like planes in the formed nanocomposites are located closer to each other than individual polymer links.

When comparing the results of calculations by the B3LYP-D3/6-31G(d,p) and MP2/6-31G(d,p) methods, both in the case of interactions of polychlorotrifluoroethylene oligomers with each other and intermolecular complexes of polychlorotrifluoroethylene oligomers and graphene-like planes, it has been found that the second order Møller-Plesset method is characterized by a larger intermolecular distance and a lower energy of intermolecular interactions compared to the method of the density functional theory with the Grimme dispersion correction, which is explained by the fact that the MP2 method does not fully take into account the relatively small components of dispersion interactions.

Analysis of the calculation results using quantum chemistry methods shows that the addition of graphene-like planes to the polychlorotrifluoroethylene polymer leads to an increase in the intermolecular interaction energy, regardless of the calculation method used and the sizes of polychlorotrifluoroethylene oligomers and graphene-like planes. This may indicate greater strength and thermal stability of the nanocomposite based on graphene-like planes with polychlorotrifluoroethylene oligomers.

The zero value of the Gibbs free energy ΔG_{react} for the interaction of two dimers with each other is characteristic at 270 K, and the similar value of the interaction of the PCTFE dimer with GLP is at a much higher temperature (420 K). This fact reflects the growth in thermostability of nanocomposites as compared to the polymer itself.

***Keywords:** nanocomposite, graphene, graphene-like plane, polychlorotrifluoroethylene, density functional theory method, cluster approximation*

INTRODUCTION

Creation of new composite materials modified with carbon nanomaterials is a promising direction of modern science [1]. The development of the principles of obtaining polymer nanocomposites [2] is relevant, the creation of which is based on fundamental research of the physical and chemical processes of the formation of materials and their structure at the atomic level, which provides the possibility of obtaining nanocomposites with predetermined functional properties.

Nanocomposites with predetermined properties, as evidenced by the literature, can be created in a wide variety of ways, in particular, in the interaction of sp^2-hybridized carbon materials with inorganic compounds and metals [3–4], with polymers [5–6].

In a number of works, the effectiveness of using compounds of different chemical nature with nanoscale dimensions as modifiers of polymer matrices has been shown [7–8].

Novadays, graphene is often used as a filler [9–10]. In particular, the thickness of graphene is equal to one carbon atom, which makes it the thinnest material known today [11–13]. The theoretical Young's modulus of graphene is 1.0 TPa, and the intrinsic tensile strength is

130 GPa, which means that the mechanical properties of graphene are special. In addition, graphene has some other excellent properties, such as high specific surface area, electrical conductivity, and thermal conductivity [14].

Nanocomposites based on carbon materials and, in particular, graphene and polychlorotrifluoroethylene (PCTFE) have special electrical and mechanical properties [15–16]. It is known that PCTFE is a thermoplastic chlorofluoropolymer with the molecular formula $(CF_2CClF)_n$. PCTFE is a homopolymer of chlorotrifluoroethylene (CTFE), while PCTFE is a homopolymer of tetrafluoroethylene. Monomers of the former differ from monomers of the latter structurally, so that a chlorine atom replaces one of the fluorine atoms. Therefore, each repeating unit of PCTFE contains a chlorine atom instead of a fluorine atom. This explains the lower flexibility of the PCTFE chain and, therefore, the higher glass transition temperature. PTFE has a higher melting point and is more crystalline than PCTFE, but the latter is more strong and rigid. PCTFE has high tensile strength. It is non-flammable and has heat resistance up to 175 °C, including a low coefficient of thermal expansion. The glass transition temperature is about 45 °C [17].

PCTFE has the lowest rate of water vapor transmission among all plastics, so it is used to obtain anti-corrosion coatings on metal, glass, porcelain, ceramics (in the form of a suspension), obtaining films and sheets for anti-corrosion covers of containers, equipment, manufacture of gaskets and seals. As an anti-corrosion coating, PTFE-3 is significantly superior to polytetrafluoroethylene (PTFE) and many other materials. The diffusion coefficient in PCTFE is about 100 times less than in PTFE. Coatings made of it are practically non-diffusion. Its water absorption is practically zero [18]. PTFE does not absorb visible light. But under the influence of high-energy radiation, it breaks down like PTFE. Fluoroplast-3 can be used as a transparent film [19].

The presence of a chlorine atom in PCTFE, which has a larger atomic radius than fluorine, prevents the close packing possible in PTFE. This leads to a relatively lower melting point among fluoropolymers, around 210–215 °C [20]. PCTFE is resistant to the influence of most chemicals and oxidants, a property that is manifested due to the presence of a high content of fluorine and does not contain hydrogen atoms in its composition. However, it slightly swells in halocarbon compounds, ethers, esters, and aromatic compounds [21].

PCTFE can be molded under pressure and extruded, while these methods are not suitable for PTFE [22]. This compound finds most of its applications due to its main properties: hydrophilicity, chemical stability and high electrical resistance. PCTFE films are used as a protective layer against moisture in pharmaceutical blister packaging, as well as a vapor barrier to protect phosphor coatings in electroluminescent lamps (phosphors are sensitive to moisture), protection of moisture-sensitive liquid crystal displays, cryogenic seals and components [23]. Due to its chemical stability, PTFE-3 acts as a protective barrier against chemicals and is used as a coating (ready liner for chemical applications), for laminating other polymers such as PVC, polypropylene, *etc*. It is also used in transparent glasses, tubes, valves, liners of chemical tanks, sealing rings, seals and gaskets [24]. Its other uses include flexible printed circuits and insulation of wires and cables [25].

The interaction organic polymers with graphene-like planes (GLP) and properties of related composites are successfully studied by computer modeling methods [26–29]. The results of studying the properties of graphene-polymer nanocomposites, in particular, those of polychlorotrifluoroethylene [30], showed that the use of graphene to fill polymer matrices significantly changed their physicochemical properties compared to the original polymers. However, the influence of graphene on the properties of the obtained nanocomposites at a molecular level has not been definitively clarified. The purpose of this work was to determine the effect of the interaction between graphene-like planes and oligomers of polychlorotrifluoroethylene on the thermal stability of the formed nanocomposites due to modeling by means of quantum chemistry methods.

OBJECTS AND METHODS OF EXAMINATION

Within the frameworks of the density functional theory (DFT) with B3LYP functional [31–32] and 6-31G(d,p) basis set, simulations of intermolecular complexes formed by graphene-

like planes with oligomers containing one, two, and three elementary links were carried out (hereinafter monomer, dimer, and trimer) of polychlorotrifluoroethylene polymer. The GAMESS program (US) [33] was used for calculations.

To take into account the dispersion effects of binding [34] due to formation of noncovalent intermolecular complexes, the Grimme D3 dispersion correction [35, 36] was used in the calculations of the intermolecular interaction energy (ΔE_{react}). In addition, the second order Møller-Plesset perturbation theory method MP2 [37] was used for comparison.

A graphene-like plane consisting of 40 carbon atoms (Fig. 1 *a*) was chosen as a graphene model, as proposed in [38]. At the same time, the distance between the outermost carbon atoms in this graphene-like cluster is 1.2 nm. Therefore, in order to level the uncompensated valences and preserve sp^2 hybridization on carbon atoms, 16 hydrogen atoms were added to the peripheral atoms, one to each carbon atom (see Fig. 1 *a*). In addition, to take into account the dimensional effect of the graphene-like plane on the interaction energy, in addition to the one described above, two larger models with the general formula $C_{54}H_{18}$ and $C_{96}H_{24}$ were used (Fig. 1 *b*, *c*).
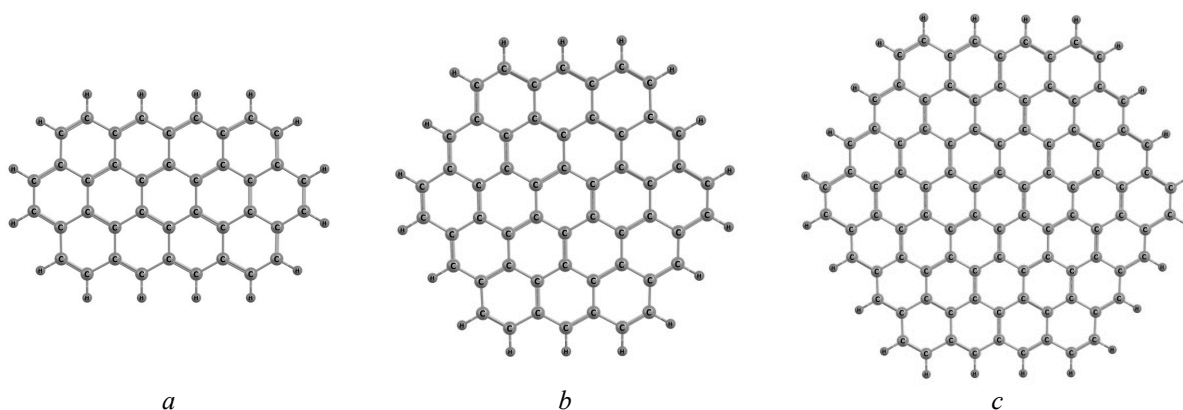

a b c

Fig. 1. Models for a fragment of the outer surface of a multilayer carbon nanotube with a gross composition: a – $C_{40}H_{16}$, b – $C_{54}H_{18}$, c – $C_{96}H_{24}$

The equilibrium spatial structures of reactant molecules and reaction products were found by minimizing the gradient norm to 0.0001 Hartree. The stationarity of energy minima of relative structures is proven by the absence of negative eigenvalues of Hessian matrices (force constant matrices) [39].

To study the interaction energy of PCTFE oligomers with each other, the reaction of the formation of an intermolecular complex (PCTFE ⋯ PCTFE) from two PCTFE oligomers of the same size was considered:

$$PCTFE + PCTFE = PCTFE \cdots PCTFE . \quad (1)$$

The energy effects of the reaction (ΔE_{react}) were calculated at the temperature of 0 K without taking into account the energy of zero oscillations (ZPE), according to the scheme (1), according to the following formula (2):

$$\Delta E_{react} = E_{tot}(PCTFE \cdots PCTFE) + 2\, E_{tot}(PCTFE), \quad (2)$$

where $E_{tot}(PCTFE \cdots PCTFE)$ is the total energy of the intermolecular complex formed from two identical polychlorotrifluoroethylene oligomers, $E_{tot}(PCTFE)$ is the total energy of the polychlorotrifluoroethylene oligomer.

To study the interaction energy of a graphene-like plane (GLP) with a polychlorotrifluoroethylene (PCTFE) oligomer, the reaction of the formation of an intermolecular complex (GLP ⋯ PCTFE) with a polychlorotrifluoroethylene (PCTFE) oligomer was considered, it can be represented schematically:

$$GLP + PCTFE = GLP \cdots PCTFE. \quad (3)$$

The energy effect of the reaction (3) was calculated according to formula (4):

$$\Delta E_{react} = E_{tot}(GLP \cdots PCTFE) +$$

$$+ (E_{tot}(GLP) + E_{tot}(PCTFE)), \quad (4)$$

where E_{tot}(GLP $\cdots$ PCTFE) is the total energy of the intermolecular interaction complex of a graphene-like plane (GLP) with a polychlorotrifluoroethylene (PCTFE) oligomer, E_{tot}(GLP) is the total energy of a graphene-like plane, E_{tot}(PCTFE) is the total energy of a polychlorotrifluoroethylene oligomer.

To take into account the effect of temperature on thermodynamic parameters, the values of the Gibbs free energy (ΔG_{react}) of the interaction of PCTFE oligomers with each other were calculated, the reaction of the formation of an intermolecular complex (PCTFE $\cdots$ PCTFE) from two PCTFE oligomers of the same size (5) was considered, as well as the ΔG_{react} value of the interaction of a graphene-like plane (GLP) with a chlorotrifluoroethylene (PCTFE) oligomer considered as well as that of the formation of an intermolecular complex (GLP $\cdots$ PCTFE) with a polychlorotrifluoroethylene (PCTFE) oligomer (6), in the temperature range from 50 to 600 K:

$$\Delta G_{react} = G^T(\text{PCTFE} \cdots \text{PCTFE}) +$$
$$+ 2\, G^T(\text{PCTFE}), \qquad (5)$$

$$\Delta G_{react} = G^T(\text{GLP} \cdots \text{PCTFE}) - (G^T(\text{GLP}) +$$
$$+ G^T(\text{PCTFE})), \qquad (6)$$

where $G^T = E_{tot} + \text{ZPE} + G^T_{corr}$, E_{tot} is the total energy of the corresponding optimized structure, ZPE (zero point vibrational energy) is the energy of zero vibrations of the optimized structure, G^T_{corr} is the thermodynamic correction to the Gibbs free energy.

RESULTS AND DISCUSSION

Research on the interaction of chlorotrifluoroethylene oligomers with each other. It is known from the literature [28, 40, 41] that for thermoplastic polymers, the intermolecular binding energy between their structural units correlates with the melting temperature of the corresponding polymer. When studying the energy of intermolecular interactions (ΔE_{react}) due to binding the surface of GLP with PCTFE oligomers of different sizes, it is necessary firstly to find the energy of intermolecular interactions of PCTFE oligomers among themselves according to reaction (1).

Fig. 2 shows the most likely optimal intermolecular complexes. From this figure, it can be seen that the distance between the carbon atoms of neighboring oligomers is greater for those molecules in which there is a covalent bond with a chlorine atom, compared to carbon atoms that are bound only to fluorine atoms, regardless of the size of these oligomers. It should be noted that in localized intermolecular complexes, the distance between oligomers is greater when calculated by the MP2/6-31G(d,p) method rather than by the B3LYP-D3/6-31G(d,p) method. This can be explained by the fact that relatively small components of dispersion interactions are not fully taken into account in the MP2 method [42, 43].

The results of the analysis of calculations by the B3LYP-D3/6-31G(d,p) method indicate that the energy effect of the interaction of two single-chain PCTFE oligomers with each other with the formation of an intermolecular complex (Fig. 2 *a*), calculated according to formula (2), is -35.7 kJ/mol (see Table). They have the smallest distance (3.9 Å) between the carbon atoms of the interacting PCTFE monomers. An increase in the size of oligomers by one unit leads to an increase in the energy of intermolecular interaction by 20.5 kJ/mol and is -56.2 kJ/mol. This intermolecular complex is characterized by an increase in the distance between the carbon atoms of two PCTFE dimers, and its smallest value is 4.8 Å (Fig. 2 *b*). The energy effect for the intermolecular complex formed from two three-membered PCTFE oligomers is even greater in absolute value and amounts to -79.5 kJ/mol (see Table). However, as can be seen from Fig. 2 *c*, the distance between the carbon atoms of two interacting trimers is slightly smaller and has a value of 4.6 Å.

Using the MP2/6-31G(d,p) method to calculate the energy effect according to formula (2) leads to significantly smaller numerical values of ΔE_{react} compared to the B3LYP-D3/6-31G(d,p) method discussed above. In particular, when two PCTFE monomers interact with each other, the interaction energy is -7.1 kJ/mol. The distance between carbon atoms of adjacent monomers that formed an intermolecular complex is 4.9 Å (for those carbon atoms that are chemically bonded to fluorine atoms) and 5.0 Å for similar carbon atoms that are bonded to both fluorine and chlorine atoms (Fig. 2 *d*). As can be seen from Fig. 2 *d* and Fig. 2 *a*, the distance between the carbon atoms of the monomers is greater by approximately 1 Å compared to the corresponding value calculated by the B3LYP-D3/6-31G(d,p) method.

Due to interaction of two PCTFE dimers, almost the same amount of energy is released (-7.3 kJ/mol according to the results of calculations by the MP2/6-31G(d,p) method)

(see Table). The distance between the two dimers in this case is slightly larger compared to the complex consisting of monomers (Fig. 2 *d*) and is 5 Å (Fig. 2 *e*).
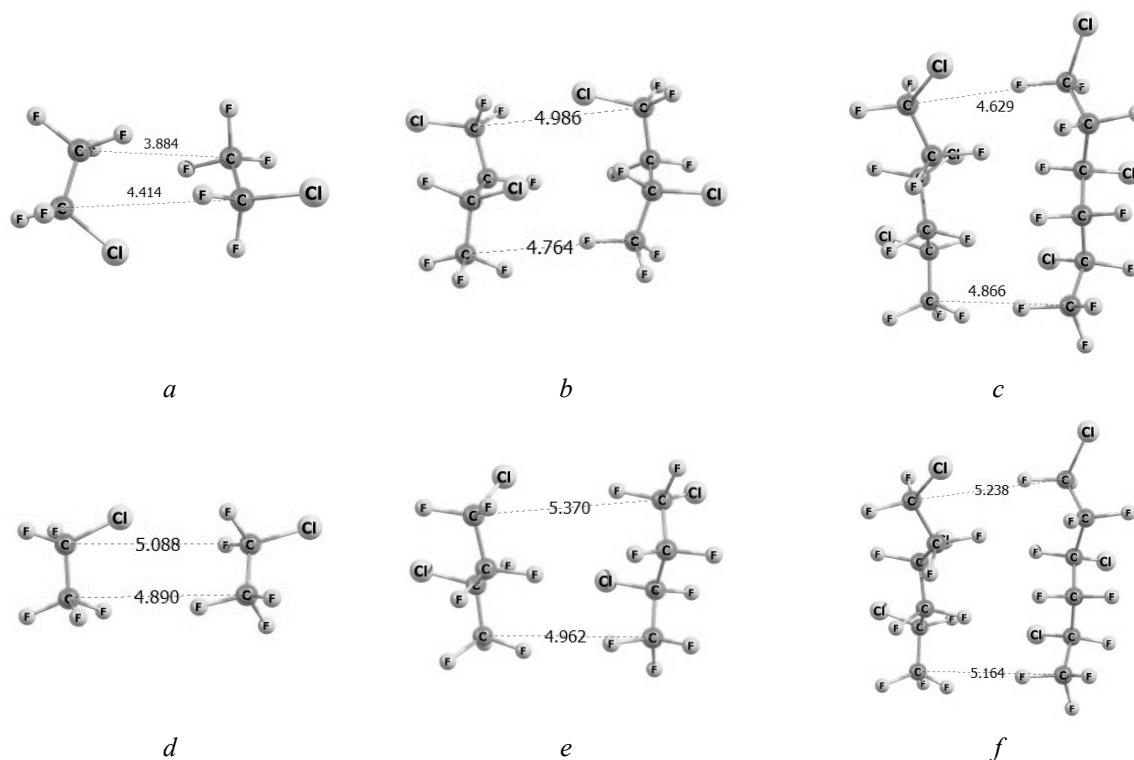

Fig. 2. Equilibrium distances (Å) between carbon atoms in intermolecular complexes of polychlorotrifluoroethylene oligomers obtained by the B3LYP-D3/6-31G(d,p) (*a, b, c*) and MP2/6-31G(d,p) (*d, e, f*)

The energetic effect of the interaction of two trimers, calculated by the MP2/6-31G(d,p) method, is 2.3 kJ/mol greater than the ΔE_{react} for a complex of two dimers and is 9.6 kJ/mol. The distance between carbon atoms in this intermolecular complex is slightly larger and is 5.2 Å (Fig. 2 *f*) compared to the B3LYP-D3/6-31G(d,p) method (4.6 Å) (Fig. 2 *c*).

Interaction of polychlorotrifluoroethylene oligomers with graphene-like planes. When PCTFE monomer interacts with GLP of the smallest size, which has the composition $C_{40}H_{16}$, by the B3LYP-D3/6-31G(d,p) method, an intermolecular complex is formed, shown in Fig. 3 *a*, where the PCTFE monomer is 3.5 Å away from GLP. This is closer than in the case of interaction between two monomers, where the distance was 3.8 Å (Fig. 2 *a*). The energy effect of this process (3), calculated according to formula (4), is 13.1 kJ/mol greater than the similar value for the interaction of two

monomers with each other and has a value of -48.8 kJ/mol, which correlates with a decrease in the distance between the interacting components in the case use of GLP.

The interaction of PCTFE monomer with GLP of larger size, gross composition $C_{54}H_{18}$, forms a complex (Fig. 3 *b*), for which the intermolecular distance between the oligomer and the graphene-like plane is 3.6 Å. The value of ΔE_{react}, calculated by formula (4), in this case, despite the increase in the intermolecular distance between the monomer and GLP, has a larger absolute value, which is -54.9 kJ/mol (see Table). This can be explained by the fact that the size of the GLP with the composition $C_{40}H_{16}$ is insufficient for simulating the interaction of the PCTFE monomer with the graphene-like plane, and when using a larger GLP, it leads to an increase in the energy effect of the interaction.

When using GLP of an even larger size ($C_{96}H_{24}$), an intermolecular complex is formed

when simulating the interaction with the PCTFE monomer, shown in Fig. 3 c, in which the distance between the carbon atoms of the interacting molecules is smaller (3.5 Å) compared to the complex in which the PCTFE monomer interacts with GLP of smaller size, gross composition $C_{54}H_{18}$, which is characterized by a distance of 3.6 Å between carbon atoms

neighboring molecules. At the same time, the energy effect of the reaction does not differ significantly and is -54.1 kJ/mol. This indicates that the size of GLP ($C_{96}H_{24}$) is sufficient to simulate the interaction with the PCTFE monomer, and further increase in the size of GLP will not lead to an increase in the energetic effect of the reaction.
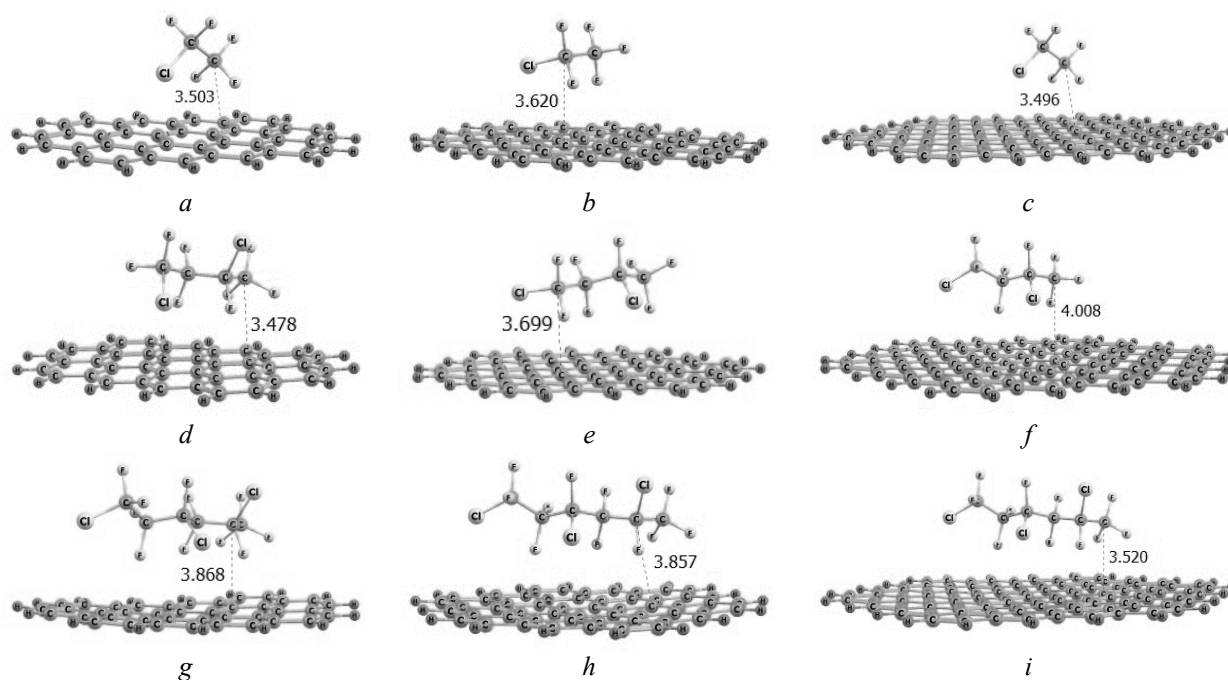

Fig. 3. The structure of intermolecular complexes of polychlorotrifluoroethylene oligomers with graphene-like clusters $C_{40}H_{16}$ (*a, d, g*), $C_{54}H_{18}$ (*b, e, h*) and $C_{96}H_{24}$ (*c, f, i*), calculated by the B3LYP-D3/6-31(d,p) method

When PCTFE dimer interacts with GLP of the smallest size, which has a gross composition of $C_{40}H_{16}$, by the same B3LYP-D3/6-31G(d,p) method, it forms an intermolecular complex shown in Fig. 3 *d*, which shows that the PCTFE dimer is located near GLP at the distance of 3.5 Å. This is much closer than in the case of two dimers interacting with each other, where the distance is 4.8 Å (Fig. 2 *b*). The energy effect of this process (ΔE_{react}), calculated by formula (4) is 12.5 kJ/mol greater in absolute value than the equivalent value of the interaction of two dimers with each other and has a value of -68.7 kJ/mol, which, as in the previous case with monomer, correlates with a decrease in the distance between the interacting components in the case of using GLP (see Table).

The interaction of the PCTFE dimer with GLP, the gross composition of $C_{54}H_{18}$, forms a complex (Fig. 3 *e*), for which the intermolecular

distance between the oligomer and the graphene-like plane is 3.7 Å. The value of ΔE_{react}, calculated by formula (4), in this case, despite the increase in the intermolecular distance between the dimer and GLP, has a larger absolute value of -76.3 kJ/mol (see Table).

When using GLP of the maximum size ($C_{96}H_{24}$) to simulate the interaction with the PCTFE dimer, an intermolecular complex is formed, shown in Fig. 3 *f*, in which the distance between the carbon atoms of the interacting molecules is larger (4.0 Å) compared to the complex where the PCTFE dimer interacts with the smaller GLP ($C_{54}H_{18}$), which is characterized by a distance of 3.7 Å between the carbon atoms of neighboring molecules. At the same time, the energy effect of the reaction, as in the previous case with the PCTFE monomer, does not differ significantly and is a slightly smaller value of -75.2 kJ/mol (see Table). This indicates that the

size of the GLP ($C_{54}H_{18}$) is sufficient to model the interaction with both the monomer and the PCTFE dimer, and further increase in the size of the GLP will not lead to an increase in the reaction energy effect of the interaction of the graphene-like plane with the PCTFE dimer.

Investigating the interaction of the PCTFE trimer with GLP using the same method (B3LYP-D3/6-31G(d,p)), as in the previous cases, the formation of an intermolecular complex with a graphene-like plane of the smallest size ($C_{40}H_{16}$) was first considered. It is characterized by an intermolecular distance of 3.87 Å (Fig. 3 *g*). This is the largest value of all considered cases for intermolecular complexes using $C_{40}H_{16}$ (see Fig. 3 *a, d, g*). The energetic effect of the reaction in this case is more important compared to the previous cases and is 102.0 kJ/mol (see Table), which indicates the correlation of the length of the oligomer with the energy of dispersion interactions.

When the PCTFE trimer interacts with the following GLP, gross composition $C_{54}H_{18}$, a complex is formed (Fig. 3 *h*), for which the intermolecular distance between the oligomer and the graphene-like plane is 3.86 Å. The value of ΔE_{react}, calculated by formula (4), in this case has a slightly larger absolute value (-105.9 kJ/mol) (see Table). This, as in the previous cases, can be explained by the fact that the size of the GLP composed of $C_{40}H_{16}$ is insufficient for simulating the interaction of the PCTFE trimer with the graphene-like plane, and using a larger GLP leads to an increase in the energy effect of the interaction.

When using GLP of the largest size ($C_{96}H_{24}$) to simulate the interaction with the PCTFE trimer, an intermolecular complex is formed, shown in Fig. 3 *i*, in which the distance between the carbon atoms of the interacting molecules is smaller (3.52 Å) compared to the complex in which the PCTFE trimer interacts with graphene-like planes of smaller size $C_{40}H_{16}$ and $C_{54}H_{18}$, which are characterized by a distance of 3.87 and 3.86 Å between atoms carbon of neighboring molecules (see Fig. 3 *g, h, i*). The energy effect of the reaction for the PCTFE trimer and $C_{96}H_{24}$, compared to the previous cases, has a much larger value (-117.5 kJ/mol) (see Table), which indicates that the size of GLP ($C_{54}H_{18}$) is also not sufficient to model the interaction as with the PCTFE trimer.

When PCTFE monomer interacts with GLP of the smallest size, which has the composition $C_{40}H_{16}$, an intermolecular complex is formed shown in Fig. 4, *a*, from which it can be seen that the PCTFE monomer is located to GLP at the distance of 5.55 Å (MP2/6-31G(d,p) method). The energy effect of this process, calculated according to formula (4), is 8.6 kJ/mol greater than the similar value for the interaction of two monomers with each other (-15.7 kJ/mol), which correlates with a decrease in the distance between the interacting components in the case of using GLP. This is significantly smaller compared to the similar value for the interaction of PCTFE monomer with GLP of the smallest size obtained by the B3LYP-D3/6-31G(d,p) method (-48.8 kJ/mol).

When the PCTFE monomer interacts with a larger GLP, gross composition $C_{54}H_{18}$, calculated by the MP2/6-31G(d,p) method, a complex is formed (Fig. 4 *b*), for which the intermolecular distance between the oligomer and the graphene-like plane is 4.42 Å. The value of ΔE_{react}, calculated by formula (4), in this case, despite the increase in the intermolecular distance between the monomer and GLP, has a larger absolute value (-22.9 kJ/mol) (see Table). As in the previous cases, this regularity can be explained by the fact that the size of GLP with the composition $C_{40}H_{16}$ is insufficient for modeling the interaction of the PCTFE monomer with the graphene-like plane.

When using GLP of the largest size ($C_{96}H_{24}$) to simulate the interaction with the PCTFE monomer, the same method forms the intermolecular complex shown in Fig. 4 *c*, in which the distance between the carbon atoms of the interacting molecules is 4.62 Å. The energetic effect of the reaction for PCTFE monomer and $C_{96}H_{24}$, in comparison with the previous cases, has a slightly larger value (-25.2 kJ/mol) (see Table). This indicates that the size of GLP ($C_{54}H_{18}$) is sufficient for modeling the interaction with PCTFE monomer.

The interaction of PCTFE dimer with GLP of the smallest size, gross formula $C_{40}H_{16}$, leads to the formation of an intermolecular complex, shown in Fig. 4 *d*, which shows that the PCTFE dimer is located near GLP at the distance of 5.31 Å (MP2/6-31G(d,p)). This is somewhat closer than in the case of the interaction of the monomer with GLP, where the distance is 5.55 Å (Fig. 4 *a*). The energy effect of this

process (ΔE_{react}), calculated according to formula (4), is 12.2 kJ/mol greater in absolute value than the analogous value of the interaction of two dimers with each other (-19.5 kJ mol), which, as in the previous case with the monomer, correlates with a decrease in the distance between interacting components in the case of using GLP (see Table).
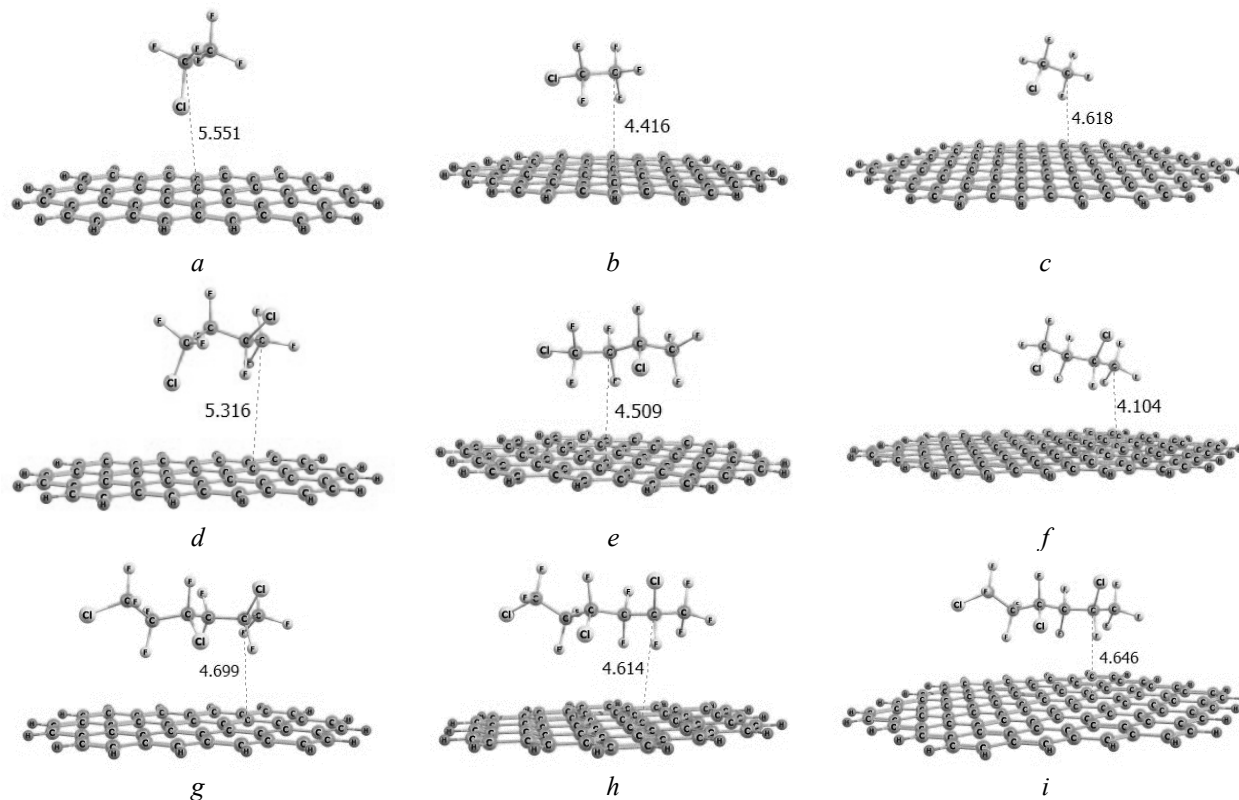

Fig. 4. The structure of intermolecular complexes of polychlorotrifluoroethylene oligomers of different lengths with graphene-like clusters of different sizes, calculated by the MP2/6-31(d,p) method ($C_{40}H_{16}$ (*a, d, g*), $C_{54}H_{18}$ (*b, e, h*) and $C_{96}H_{24}$ (*c, f, i*))

When the PCTFE dimer interacts with the following GLP, the gross formula of $C_{54}H_{18}$, a complex is formed (Fig. 4 *e*), for which the intermolecular distance between the oligomer and the graphene-like plane is 4.5 Å compared to the similar value with the intermolecular complex discussed above (Fig. 4 *d*). The calculated value of ΔE_{react}, in this case, has a slightly larger absolute value (-24.1 kJ/mol) (see Table).

Next, the interaction of PCTFE dimer with GLP of the largest size $C_{96}H_{24}$ was investigated by the MP2/6-31G(d,p) method. As a result, an intermolecular complex is formed, shown in Fig. 4 *f*, in which the distance between the carbon atoms of the interacting molecules is 4.10 Å. The energetic effect of the reaction for the PCTFE dimer and $C_{96}H_{24}$, in comparison with the previous calculations, has a larger value (-31.1 kJ/mol) (see Table).

Investigating the interaction of the PCTFE trimer with GLP, within the same method (MP2/6-31G(d,p)), the formation of an intermolecular complex with a graphene-like plane of the smallest size ($C_{40}H_{16}$) was first considered. It is characterized by an intermolecular distance of 4.70 Å (Fig. 4 *g*). This is the smallest value of all considered models for intermolecular complexes using $C_{40}H_{16}$. The energetic effect of the reaction in this case is more important in comparison with the cases of using a monomer and a dimer with this GLP (27.2 kJ/mol).

The interaction of the PCTFE trimer with GLP, in which the gross composition was $C_{54}H_{18}$, forms a complex (Fig. 4 *h*), for which the intermolecular distance between the oligomer and the graphene-like plane, with an increase in the size of the GLP, is somewhat smaller compared to the previous case (Fig. 4 *g*) (is

4.61 Å). The value of ΔE_{react} in this case has a slightly larger absolute value (-31.7 kJ/mol) (see Table).

When using GLP of the largest size with the composition $C_{96}H_{24}$ to simulate the interaction with the PCTFE trimer, an intermolecular complex is formed, shown in Fig. 4 *i*, in which the distance between the carbon atoms of the interacting molecules is 4.65 Å compared to the complex in which the PCTFE trimer interacts with the graphene-like plane of smaller size $C_{54}H_{18}$, which is characterized by a distance of 4.61 Å between the carbon atoms of neighboring molecules (see Fig. 4 *h*). The energetic effect of the reaction for the PCTFE trimer and $C_{96}H_{24}$ has a much larger value (is -43.4 kJ/mol) (see Table). This indicates that the size of GLP ($C_{54}H_{18}$), as in the previous cases, is also not sufficient to model the interaction, as with the PCTFE trimer.

The summary table shows the numerical values of the intermolecular binding energy between two identical PCTFE oligomers of different sizes, as well as for their complexes with graphene-like planes of different sizes. Comparing the results of calculation of intermolecular complexes of PCTFE oligomers with GLP by the B3LYP-D3/6-31G(d,p) and MP2/6-31G(d,p) methods (Figs. 3 and 4), it can be seen that for the second order Møller-Plesset method is characterized by a larger intermolecular distance and a lower energy of intermolecular interactions compared to the density functional theory method with the Grimme dispersion correction (see Table). This can be explained, as in the case of interactions between oligomers (Fig. 2), by the fact that relatively small components of dispersion interactions are not fully taken into account in the MP2 method.

Table. Intermolecular binding energies for pure polychlorotrifluoroethylene and polychlorotrifluoroethylene nanocomposites with graphene-like planes (kJ/mol)

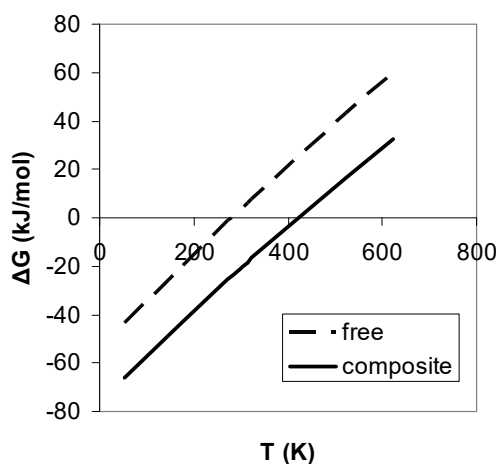| Number of links in the oligomer	Pure polymers		Nanocomposites					
	B3LYP-D3/ 6-31G(d,p)	MP2/ 6-31G(d,p)	B3LYP-D3/6-31G(d,p)			MP2/6-31G(d,p)		
			$C_{40}H_{16}$	$C_{54}H_{18}$	$C_{96}H_{24}$	$C_{40}H_{16}$	$C_{54}H_{18}$	$C_{96}H_{24}$
1	-35.7	-7.1	-48.8	-54.9	-54.1	-15.7	-22.0	-25.2
2	-56.2	-7.3	-68.7	-76.3	-75.2	-19.5	-24.1	-31.1
3	-79.5	-9.6	-102.0	-105.9	-117.5	-27.2	-31.7	-43.4

Fig. 5. Temperature dependence of the Gibbs energy of the interaction of polychlorotrifluoroethylene dimers with each other (free) and polychlorotrifluoroethylene dimer with a graphene-like plane (composite)

Comparing these values in the Table, we can see that, regardless of the size of the graphene-like clusters, the intermolecular interaction between the graphene-like planes and oligomers of polychlorotrifluoroethylene is greater than that for two oligomers of this polymer between themselves.

In our recent work [44] it is shown that the introduction of graphene or other carbon materials containing graphene-like planes into

the PCTFE polymer matrix increases the strength and melting point of the obtained nanocomposites compared to pure polymers, by analogy with other thermoplastic polymers, as was shown in our theoretical works [28, 29].

Also, using the B3LYP-D3/6-31G(d,p) method, the dependence of the change in the Gibbs free energy of the reaction on temperature was examined for the process of formation of two PCTFE dimers and the formation of the intermolecular complex $C_{54}H_{18} \cdots$ PCTFE dimer (Fig. 5). It can be seen from the graph that the zero value of ΔG_{react} for the reaction of the interaction of two dimers with each other is characteristic at 270 K, and the similar value of the interaction of the PCTFE dimer with GLP is at a much higher temperature (420 K). This fact reflects the growth in thermostability of nanocomposites as compared to the polymer itself.

CONCLUSIONS

According to the simulation results, oligomers of chlorotrifluoroethylene with a graphene-like plane form intermolecular complexes that are not covalently bound and are held by the forces of intermolecular dispersion interaction. Oligomers of chlorotrifluoroethylene and graphene-like planes in the formed nanocomposites are located closer to each other than individual polymer links to each other.

Comparing the results of calculations by the B3LYP-D3/6-31G(d,p) and MP2/6-31G(d,p) methods in the case of interactions between polychlorotrifluoroethylene fragments and intermolecular complexes of polychlorotrifluoro-ethylene fragments and graphene-like planes, it has been found that that the second order Møller-Plesset method is characterized by a larger intermolecular distance and a lower energy of intermolecular interactions compared to the method of the density functional theory with the Grimme dispersion correction, which is explained by the fact that the MP2 method does not fully take into account the relatively small components of dispersion interactions.

It has been found that the addition of graphene-like planes to the polychlorotrifluoro-ethylene increases the intermolecular interaction energy regardless of the size of polychlorotrifluoroethylene fragments and graphene-like planes. This may indicate greater strength and thermal stability of the nanocomposite based on graphene-like planes with chlorotrifluoroethylene oligomers.

It has been found that the methods used give similar results of calculations of the interaction between PCTFE fragments and graphene-like planes.

The results of the calculations indicate greater strength and thermal stability of nanocomposites based on graphene-like planes with polychlorotrifluoroethylene in comparison with pure PCTFE. This is explained by the higher energy of intermolecular interaction of graphene-like planes with polychlorotrifluoro-ethylene.

Теоретичне дослідження взаємодії фрагментів поліхлортрифторетилену з графеноподібними площинами

Ю.В. Гребельна, Є.М. Дем'яненко, М.І. Тереть, А.Г. Гребенюк, Ю.І. Семенцов, Н.В. Сігарьова, С.М. Махно, М.Т. Картель

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України вул. Генерала Наумова, 17, Київ, 03164, Україна, teretsmariya@gmail.com Китайсько-український інститут промислових технологій нових матеріалів буд. Кечуанг, 777, Жонгуан роад, Ніньбо, 315211, Китай

Методами квантової хімії досліджувалась взаємодія графену з фрагментами поліхлортрифторетилену. В межах теорії функціоналу густини з обмінно-кореляційним функціоналом B3LYP, базисним набором 6-31G(d,p) і дисперсійною поправкою Грімме та методом теорії збурень Меллера-Плесета другого порядку (MP2) розраховані величини енергії взаємодії графену з олігомерами поліхлортрифторетилену і оптимізовані найбільш ймовірні структури їхніх міжмолекулярних комплексів. За модель графену було обрано графеноподібні площини різного розміру, а саме: $C_{40}H_{16}$, $C_{54}H_{18}$ та $C_{96}H_{24}$.

Олігомери поліхлортрифторетилену і графеноподібних площин у сформованих нанокомпозитах розташовані ближче один до одного, ніж окремі полімерні ланки між собою.

Порівнюючи результати розрахунку методами B3LYP-D3/6-31G(d,p) і MP2/6-31G(d,p) як у випадку взаємодій олігомерів поліхлортрифторетилену між собою, так і міжмолекулярних комплексів олігомерів поліхлортрифторетилену і графеноподібних площин, з'ясовано, що для методу Меллера-Плесета другого порядку характерна більша міжмолекулярна відстань і менша енергія міжмолекулярних взаємодій в порівнянні з методом теорії функціонала густини з дисперсійною поправкою Грімме, що пояснюється тим, що в методі MP2 не повністю враховані відносно малі складові дисперсійних взаємодій.

Аналіз результатів розрахунку методами квантової хімії свідчить про те, що додавання графеноподібних площин до полімера поліхлортрифторетилену веде до збільшення енергії міжмолекулярної взаємодії незалежно від використаного методу розрахунку і розмірів олігомерів поліхлортрифторетилену та графеноподібних площин. Це може свідчити про більшу міцність і термічну стабільність нанокомпозиту на основі графеноподібних площин з олігомерами поліхлортрифторетилену.

Нульове значення вільної енергії Гіббса (ΔG_{react}) для взаємодії двох димерів один з одним характерне при 270 К, а аналогічне значення взаємодії димера ПХТФЕ з GLP – при значно вищій температурі (420 К). Цей факт відображає зростання термостабільності нанокомпозитів порівняно з самим полімером.

Ключові слова: *нанокомпозит, графен, графеноподібна площина, поліхллортрифторетилен, метод теорії функціоналу густини, кластерне наближення*

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