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THEORETICAL STUDY ON THE EFFECT OF CARBON GRAPHENOUS NANOCLUSTERS ON THE STABILITY AND CAPACITY OF POLYAMIDE IN A NANOCOMPOSITE

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By the density functional theory method with the exchange-correlation functional B3LYP, the basis set 6-31G(d,p) and Grimme dispersion corrections, the energy values has been calculated of intermolecular interaction between adjacent polyamide fragments, and the effect of graphene-like nanoclusters on the similar values for intermolecular complexes of polyamide fragments with graphene-like nanoclusters has been evaluated. The effect of carbon materials on the energy magnitudes of covalent bonds in the polymer matrix of polyamide has been also examined.

Comparison of the energy values of intermolecular interaction between two monomers (-86.0 kJ/mol, two hydrogen bonds) and two dimers (-302.0 kJ/mol, three hydrogen bonds) indicates that the energy of interaction between two components consists of that of hydrogen bonds and the energy contribution of dispersive forces.

The energy of intermolecular interaction between two dimers with the graphene matrix (C₁₁₀H₂₆) is approximately 40 kJ/mol higher (-346.2 kJ/mol) compared to respective value for two monomers. The less value of the interaction energy (-325.0 kJ/mol) for the nanocomposite with C₉₆H₂₄ species is due to the insufficient size of the selected model for the graphene matrix.

The analysis of the hydrogen bond lengths between the oxygen atom of carbonyl group and hydrogen one of amino group indicates that, regardless of length of linkage of the polymeric chain of polyamide (monomer and dimer) and the size of the graphene-like matrix (C₉₆H₂₄ and C₁₁₀H₂₆) in the nanocomposite, the hydrogen bond in composites is shorter in comparison with a those values in complexes without a carbon matrix. This indicates a greater strength of the bond, that is, the presence of a carbon matrix increases the strength of the formed nanocomposite, that explains the increase in the melting point compared with that of the original polymer. In the nanocomposite formed polyamide - a carbon matrix for all the models studied, the energy of intermolecular interaction in the nanocomposite increases significantly compared to respective value between two fragments of pure polyamide, so indicating an increase in the thermal stability of this nanocomposite what is confirmed by experimental data.

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

INTRODUCTION

Novadays one of the perspective and actual directions of development of modern applied science is obtaining polymeric nanocomposites possessing unique properties [1]. Their creation with predetermined properties is based on fundamental researches of physical and chemical processes of formation of materials and of their structure at the atomic level. In [2, 3] we described the efficiency of using nanosized compounds of different chemical nature, as modifiers of polymer matrices, in particular such polymers as polyethylene, polypropylene, polyamide, and so on.

As a filler, carbonaceous materials are often used, in particular thermo-exfoliated graphite [4], graphene [5] and carbon nanotubes (CNT)

[6, 7]. These carbon materials are considered to be the best reinforcing materials for polymers [3], which change the physical and mechanical properties of the resulting nanocomposite. In particular, it has been found that the addition of a very small amount (up to 5 % by weight) of CNT to thermoplastic polymers increases the material modulus of elasticity and strength by 50 % [8]. In addition, the inclusion of CNT in the polyamide matrix in small amounts (up to 5 % by weight) leads to a nonmonotonic change in the degree of crystallinity of the matrix, which affects the electrophysical and thermodynamic properties of the resulting nanocomposites [9–10]. However, the effect of CNT on the properties of nanocomposites obtained on the basis of polyamide at the atomic level has not yet

been fully elucidated. This can be done by computer simulation methods, since the interaction and properties of the composites of organic polymers with nanotubes are successfully investigated by methods of quantum chemistry [11–14]. In particular, [14] describes the interaction of graphene-like clusters as models for the external surface of nanoscale particles with polyethylene and polypropylene fragments. It is shown that the energy of the intermolecular interaction of the fragments of these polymers with graphene-like clusters is greater than that in the case of mutual interaction of polymer fragments, what is explained by an increase in the tensile strength and thermal stability of the formed nanocomposites compared with the initial polymers [15, 16].

It is known [17] that for thermoplastic polymers (including polyamide), the intermolecular binding energy between their structural units correlates with the melting temperature of the corresponding polymer. Therefore, in order to determine the influence of the addition of carbon materials on the stability and strength of the resulting polyamide-containing nanocomposites, the interaction energy (ΔE) of neighboring polyamide fragments was calculated in this work and in as well as respective ΔE values for the intermolecular

complexes of polyamide fragments with graphene nanoclusters. The effect of carbon materials on the energy values of covalent bonds in the polymer matrix of polyamide is also examined.

OBJECTS AND METHODS OF EXAMINATION

The density functional theory (DFT) method with the functional B3LYP [18, 19], taking into account the dispersion correction Grimme D3 [20, 21]. and the basis set 6-31G(d,p), using the GAMESS (US) program [22], was used to calculate the energy of interaction (ΔE) between adjacent polyamide fragments (two fragments of polyamide consisting of single elementary link are used, see Fig. 1 *a*), as well as that of the interaction between two larger fragments, each of which consists of two elementary units, see Fig. 1 *b* (hereinafter referred to as monomers and dimers).

As a fragment of carbon material, the graphene-like cluster (GC) of the gross formula of $C_{96}H_{24}$ was selected (Fig. 2 *a*). In order to take into account the size effect on the investigated parameters, the graphene-like clusters of carbon polyaromatic molecules of a larger size, namely those with the $C_{110}H_{26}$ composition, were used (Fig. 2 *b*).

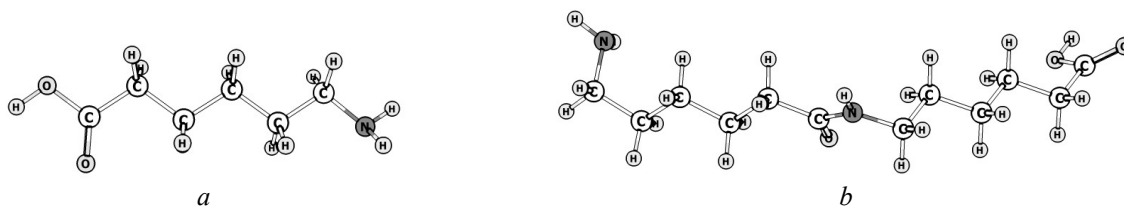


Fig. 1. Models for fragments of polyamide, consisting of: *a* – monomer, *b* – dimer

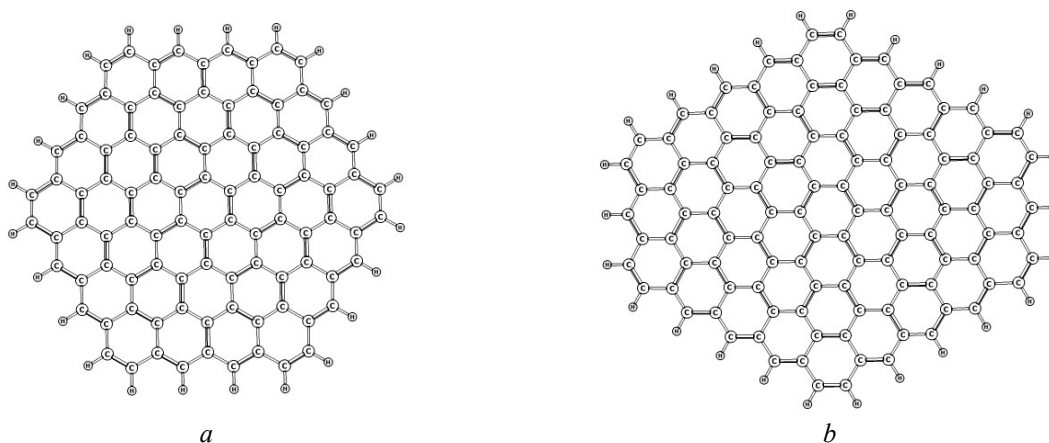


Fig. 2. Models for fragments of graphene-like clusters of gross formula: *a* – $C_{96}H_{24}$, *b* – $C_{110}H_{26}$

The energy of the intermolecular interaction (ΔE) between the two polyamide fragments was calculated by the formula (1):

$$\Delta E = E_{tot}(AB) - 2*(E_{tot}(A)) \quad (1)$$

where $E_{tot}(A)$ – the total energy of the monomer or dimer of amide, $E_{tot}(AB)$ is the total energy of the intermolecular complex of fragments polyamide.

The energy of intermolecular interaction (ΔE) between one polyamide fragment (monomer or dimer) and GC were calculated by the formula (2):

$$\Delta E = E_{tot}(AB) - ((E_{tot}(A)+E_{tot}(B))) \quad (2)$$

where $E_{tot}(A)$ is the total energy of the polyamide fragment, $E_{tot}(B)$ is the total energy of the GC, $E_{tot}(AB)$ is the total energy of the intermolecular complex of a fragment of polyamide with a graphene-like cluster.

The energy of intermolecular interaction (ΔE) between a graphene-like cluster and a complex consisting of two monomers or dimers was calculated by the formula (3):

$$\Delta E = (E_{tot}(ABC) - (E_{tot}(AB)+E_{tot}(C))) \quad (3)$$

where $E_{tot}(AB)$ is the total energy of the intermolecular complex consisting of polyamide fragments, $E_{tot}(C)$ is that of the graphene-like cluster, $E_{tot}(ABC)$ is the total energy of the intermolecular complex of polyamide with a graphene-like cluster.

The energy of the intermolecular interaction (ΔE) between the two polyamide fragments, taking into account the graphene-like plane, was calculated by the formula (4):

$$\Delta E = (E_{tot}(ABC) - (E_{tot}(A)+E_{tot}(BC))) \quad (4)$$

where $E_{tot}(A)$ – is the total energy of a polyamide fragment, $E_{tot}(BC)$ is the total energy of an intermolecular complex containing one fragment of polyamide and a graphene-like cluster, $E_{tot}(ABC)$ is the total energy of an intermolecular complex consisting of two identical fragments of polyamide and a graphene-like cluster.

RESULTS AND DISCUSSION

Intermolecular interaction between polyamide fragments. Due to formation of an intermolecular complex between two amide monomers, there are two hydrogen bonds because each of these monomers has carboxyl and amino groups. When the intermolecular complex is localized, several intermolecular complexes can be formed (Fig. 3). The results of comparison of the total energies for these intermolecular complexes evaluate a thermodynamically more stable complex *b* (Fig. 3). This is due to the fact that their mutual orientation makes it possible to form two hydrogen bonds of the length of 2.08 Å between the hydrogen atoms of amino groups and oxygen atoms of carbonyl groups, what in turn reduces the total energy for this complex.

The energy of intermolecular interaction, calculated by formula (1) for the complex *a*, is -42.4 kJ/mol, and for the complex *b* is -86.0 kJ/mol, respectively (Fig. 3).

The simulation of intermolecular complexes of larger polyamides, two dimers, as well as in the previous case, may result in several mutual orientations of the dimers (Fig. 4).

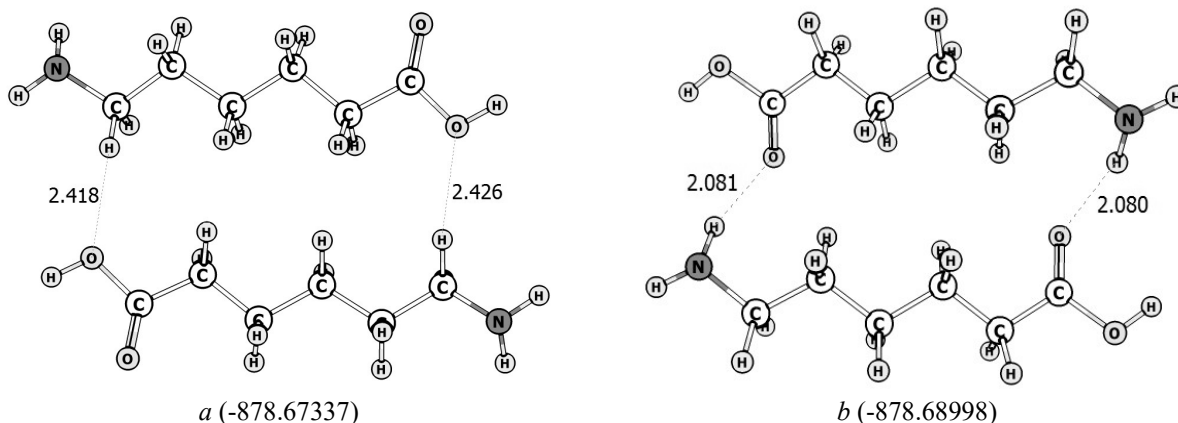


Fig. 3. The most probable intermolecular complexes formed from two monomers of amide (*a*) and (*b*) (here and further the distances between atoms in Å, and the total energy of the complexes in Hartree)

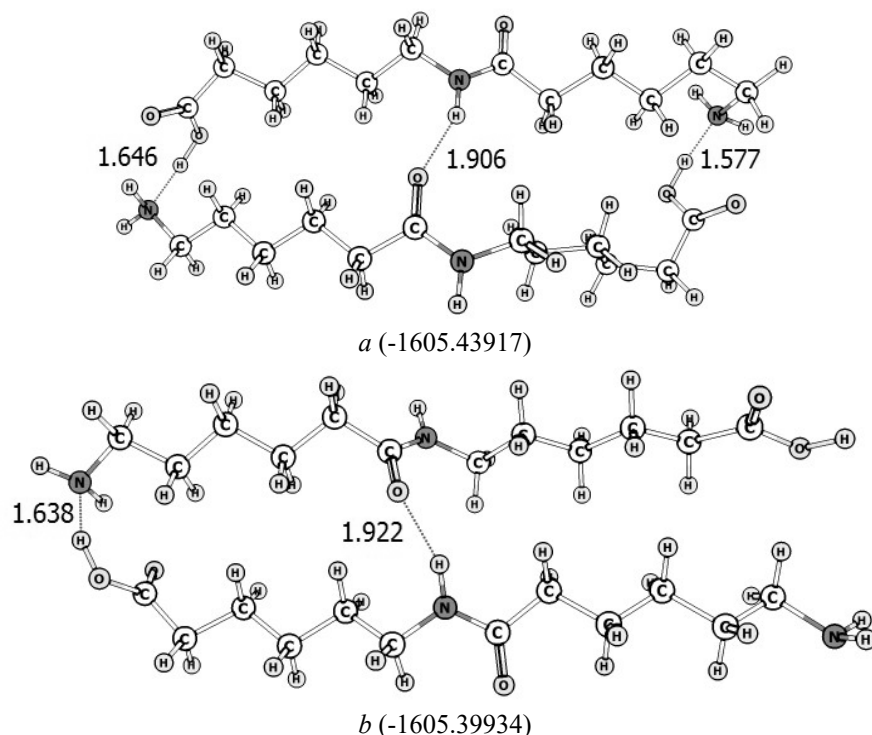


Fig. 4. Possible intermolecular complexes formed of two dimers of amide

Fig. 4 shows that in the structure *a*, dimers form three intermolecular hydrogen bonds, in contrast to the complex *b*, where dimers are bound only by two hydrogen bonds, which may indicate a lower thermodynamic stability of this complex in comparison with that indicated above. In contrast to the complexes discussed above (Fig. 3), in this complex (Fig. 4), there is also a hydrogen bond with the length of 1.9 Å, which is formed when two polymeric parts of the polyamide are bonded between the oxygen atom of the amide group of one dimer and the hydrogen atom of the analogous groups of another dimer. This bond is weaker compared to those between the terminal amino and carboxyl groups, which are shorter (about 1.6 Å).

The results of the analysis of total energies for these intermolecular complexes confirm that the complex *a* is for 104.5 kJ/mol more stable compared to the complex *b* (Fig. 4). The ΔE values for these structures are -302.2 kJ/mol (for the complex shown in Fig. 4 *a*) and -197.7 kJ/mol, (Fig. 4 *b*) respectively. Besides, when comparing the values of the total energy of these two complexes, that of complex *a* appears to be lower than this value for the complex *b*, so confirming that the first complex is

thermodynamically more stable, therefore, it was used in further calculations.

Intermolecular interaction between polyamide fragments and graphene-like planes.

Firstly, the interaction of single monomer with fragments of a graphene-like plane of different size with composition of C_9H_{24} and $C_{110}H_{26}$ was considered. As can be seen from Fig. 5, in the formation of these intermolecular complexes, regardless of the size of the GC, the distance between the carbon atoms of the monomer and the carbon atom of the graphene-like plane is almost the same as that between the nitrogen atom of the monomer and that of the graphene-like plane, and is approximately 3 Å. This is much greater than those in the above cases for intermolecular complexes consisting of polyamide monomers and dimers (Figs. 3 and 4), what is clear, since there is no specific group in the pure carbon graphene cluster that can form hydrogen bonds. An analysis of the results of calculations of the ΔE value, calculated according to formula (2), shows that irrespective of the size of the graphene-like cluster, the magnitudes of the intermolecular interaction energy are almost identical (-117.4 kJ/mol for the complex *a* and -121.2 kJ/mol for the

complex *b*, respectively, Fig. 5). These values are significantly greater in comparison with the analogous values for an intermolecular complex consisting of two monomers (-86.0 kJ/mol), although there is no hydrogen bond formed between the monomer and the graphene-like plane, what indicates the main role of the dispersion term in the interaction energy.

When considering the interaction of a complex containing two monomers connected by two hydrogen bonds (Fig. 3 *b*) with fragments of a graphene-like plane of various sizes, it was found that the hydrogen bonds between monomers were found to be slightly shortened from 2.08 Å to 2.065 Å in the case of using the C₉₆H₂₄ GC (Fig. 6 *a*) and up to 2.027 Å in the complex with the cluster C₁₁₀H₂₆ (Fig. 6 *b*). An analysis of the results of calculations of the ΔE value by the formula (3) found that when using a cluster of composition C₉₆H₂₄, it is -219.0 kJ/mol, with increased cluster this value increases by 9.1 kJ/mol to -228.1 kJ/mol. These values are much greater than those in the complexes of graphene-like clusters with single monomer. To find out the influence of the GC on the formation of hydrogen bonds between the monomers, an

adequate comparison of these interaction energy quantities is necessary. To do so, these values were divided into two, to determine how much the interaction energy was per monomer: $219.0/2 = 109.5$ kJ/mol, $-228.1/2 = 114.03$ kJ/mol. This is slightly less than the ΔE for monomers with GC, for 7.9 kJ/mol, with the smaller GC size and for 7.2 kJ/mol in the case of using the larger graphene cluster.

In order to find out how the presence of a graphene-like cluster affects the interaction energy of two monomers, calculations were made by formula (4) for the complexes including, together with two monomers, the GC of different sizes (C₉₆H₂₄ and C₁₁₀H₂₆). An analysis of calculations shows that, when two monomers interact with a GC, regardless of the size of the latter, there is an increase in the energy of the intermolecular interaction between these monomers: from 85.6 kJ/mol for two monomers, to 187.6 kJ/mol for a complex with the C₉₆H₂₄ GC and up to 192.8 kJ/mol for the C₁₁₀H₂₆ complex. This correlates with the decrease in the hydrogen bond lengths between monomers in the presence of graphene-like planes.

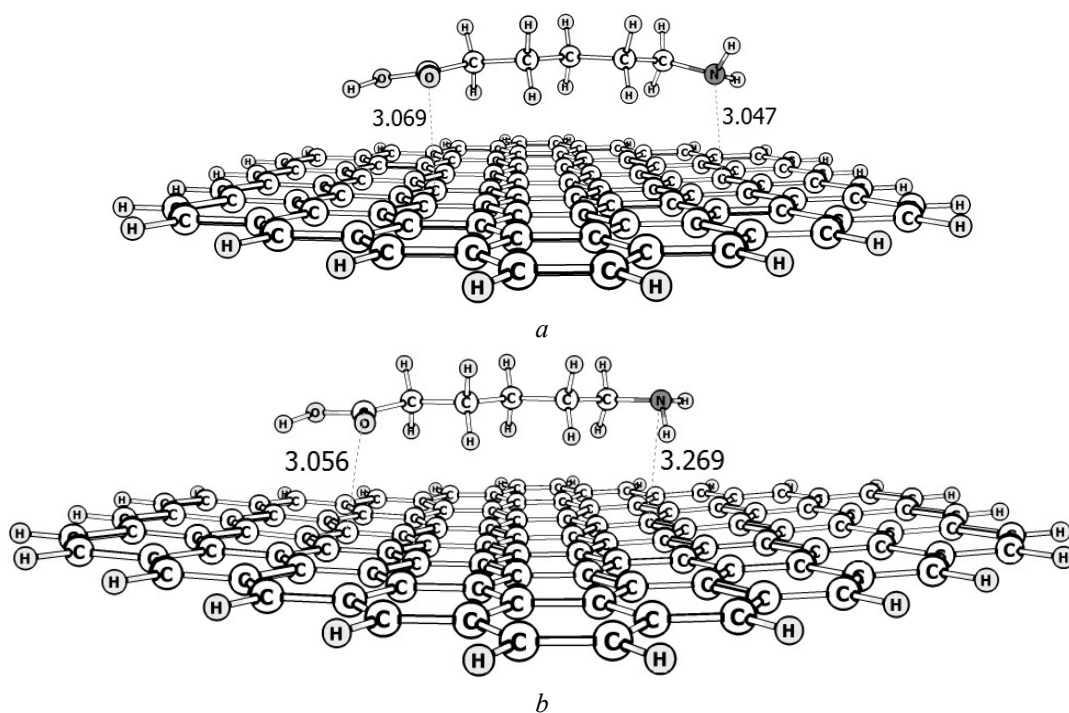


Fig. 5. Possible intermolecular complexes formed from amide monomer and graphene-like clusters of different sizes: *a* – C₉₆H₂₄, *b* – C₁₁₀H₂₆

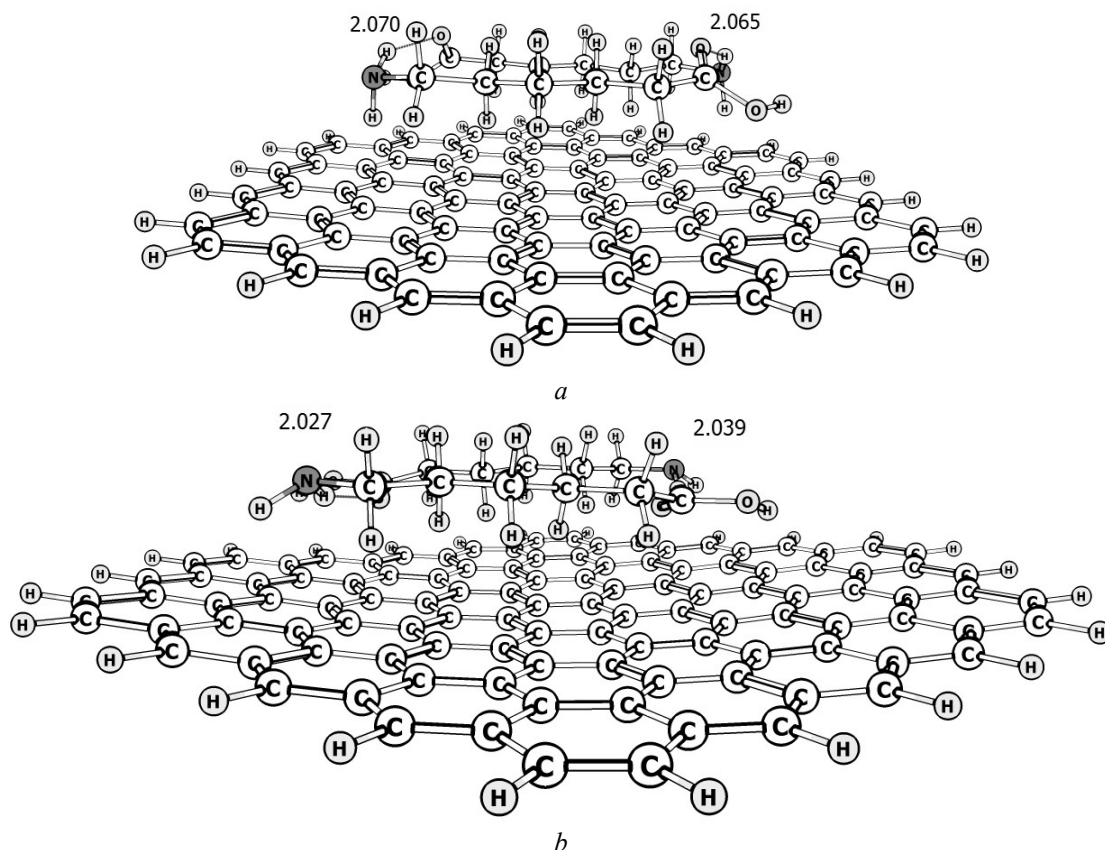


Fig. 6. Equilibrium geometry of intermolecular complexes formed of two monomers of amide and graphene-like clusters of different sizes: *a* – $C_{96}H_{24}$. *b* – $C_{110}H_{26}$

With an increase in the size of the fragment of the polyamide to the dimer in the complex with the GC, the distance between the molecules, as in the preceding case (Fig. 5), is close to 3 Å (Fig. 7). The energy of the intermolecular interaction calculated by the formula (2), due to the fact that the size of the polyamide fragment is 2 times larger than the previously considered monomers, and is equal, using the $C_{96}H_{24}$ GC to 180.5 kJ/mol, and with the participation of a larger GC, this ΔE value increases to 188.0 kJ/mol. This slight increase in the absolute value of the energy of intermolecular interaction is due to the fact that the size of a smaller graphene-like cluster is not optimal (Fig. 7 *a*).

In intermolecular complexes built from two dimers and graphene-like clusters (Fig. 8), the hydrogen bond lengths decrease in comparison with those in complexes formed from two dimers (Fig. 4). The reduction of the lengths of hydrogen bonds is similar to the case of the complex of two monomers with a GC, compared to intermolecular complexes with monomers. This indicates that the presence of a carbon

matrix (regardless of the GC size) in complexes with polyamide (regardless of the sizes of its fragments) strengthens the hydrogen bonds in the latter (Fig. 6).

An analysis of the energy values calculated in accordance with formula (3), the interaction of a graphene-like fragment with a complex consisting of two dimers of amide is, in the case of using the $C_{96}H_{24}$ GC, -461.7 kJ/mol, and -459.7 kJ/mol, when using the $C_{110}H_{26}$ cluster. Calculations by the formula (4) showed that the GC influences the interaction energy between two polyamide fragments, which is -346.2 kJ/mol for a smaller GC, and -145.6 kJ/mol for a larger fragment of the graphene-like plane. This is greater than the absolute value compared to a similar value between the two dimers (-302.2 kJ/mol), which also confirms the strengthening of the water-bound matrix of polyamide fragments in the presence of GC.

Comparison of the energy values of the intermolecular interaction of two monomers (86.0 kJ/mol, two hydrogen bonds) and two

dimers (-302.0 kJ/mol, three hydrogen bonds) indicates that the interaction energy of the two components consists of the energy of hydrogen

bonds and the energy contribution of the dispersion forces (see Table).

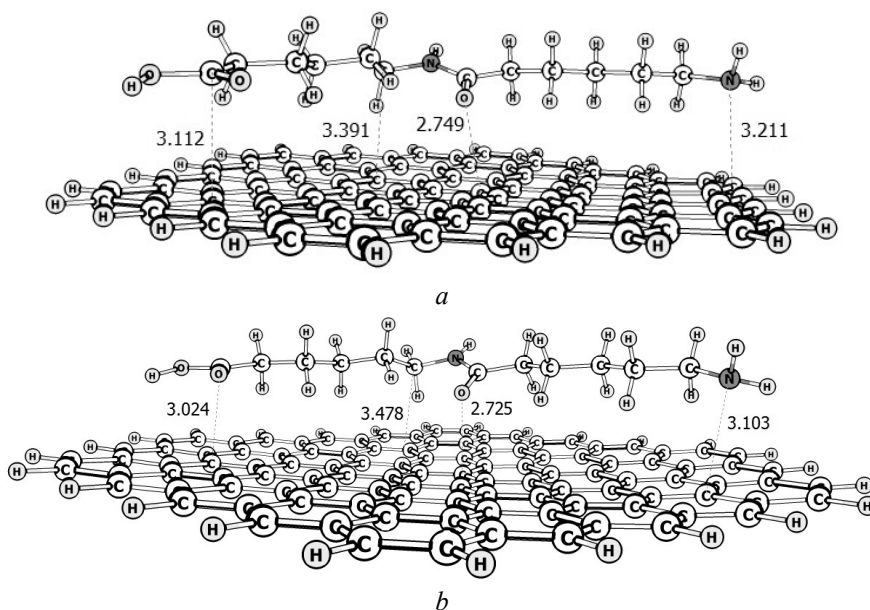


Fig. 7. Possible intermolecular complexes formed of dimer amide and graphene-like clusters of different sizes: *a* - $C_{96}H_{24}$. *b* - $C_{110}H_{26}$

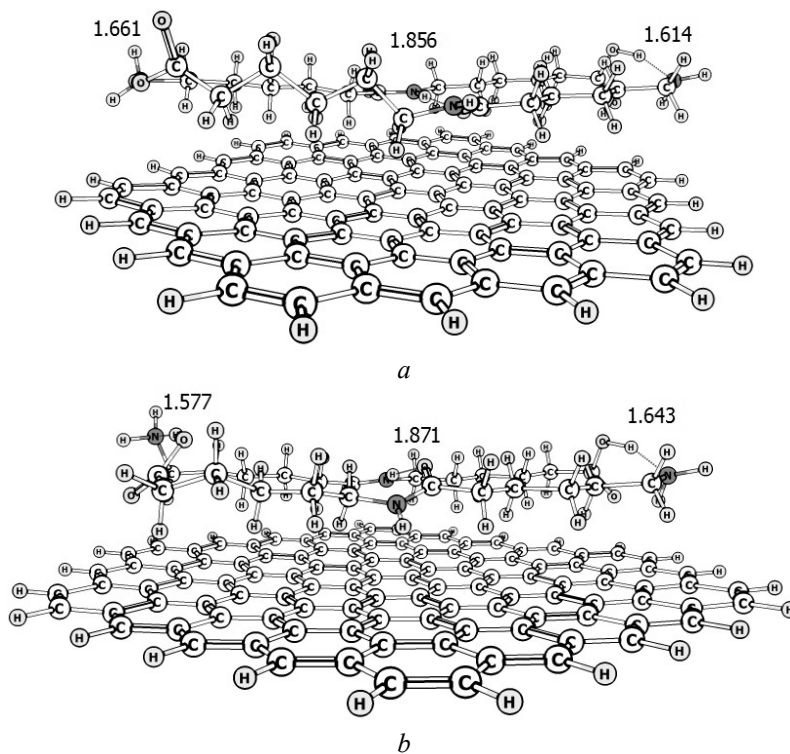


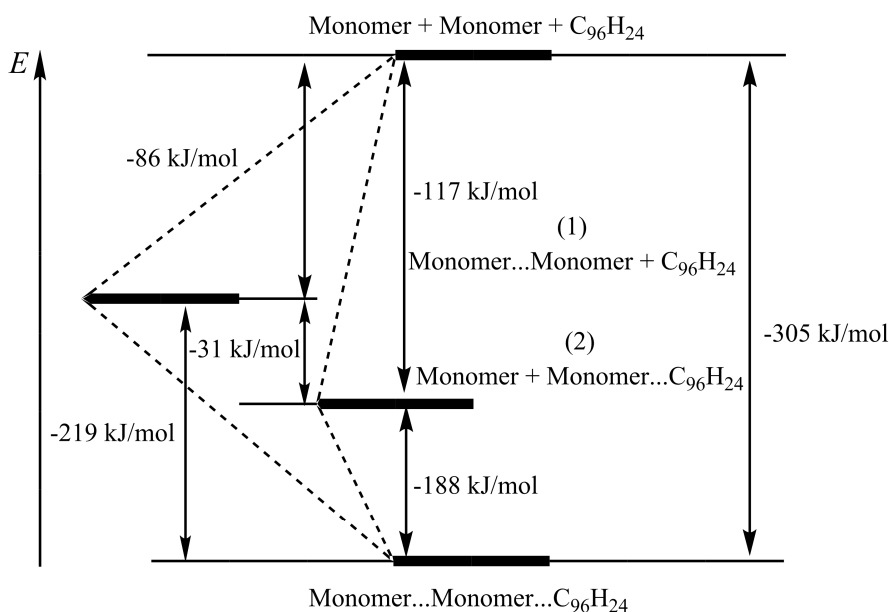
Fig. 8. The most probable intermolecular complexes formed of two dimers of amide and graphene-shaped planes of different sizes: $C_{96}H_{24}$ (*a*) and $C_{110}H_{26}$ (*b*)

Table. Hydrogen bonds lengths of between polyamide fragments and the intermolecular interaction energy for the corresponding complexes

Complex	$l(\text{N-H} \cdots \text{O}=\text{C}), \text{ \AA}$	$\Delta E, \text{ kJ/mol}$
Monomer \cdots monomer	2.08	-86.0
Dimer \cdots dimer	1.91	-302.2
Monomer \cdots C ₉₆ H ₂₄	-	-117.4
Monomer \cdots C ₁₁₀ H ₂₆	-	-121.2
2 Monomer \cdots C ₉₆ H ₂₄	2.06	-219.0
2 Monomer \cdots C ₁₁₀ H ₂₆	2.03	-228.1
Monomer \cdots monomer - C ₉₆ H ₂₄	2.06	-187.6
Monomer \cdots monomer - C ₁₁₀ H ₂₆	2.03	-192.0
Dimer \cdots C ₉₆ H ₂₄	-	-180.5
Dimer \cdots C ₁₁₀ H ₂₆	-	-188.4
2 Dimer \cdots C ₉₆ H ₂₄	1.86	-346.2
2 Dimer \cdots C ₁₁₀ H ₂₆	1.87	-345.6
Dimer \cdots dimer - C ₉₆ H ₂₄	1.86	-461.8
Dimer \cdots dimer - C ₁₁₀ H ₂₆	1.87	-459.7

As can be seen from the Table, the energy of the intermolecular interaction of two dimers with a graphene matrix (C₁₁₀H₂₆) is approximately for 40 kJ/mol (-346.2 kJ/mol) greater compared to the similar value for two dimers (-302.2 kJ/mol). The lesser ΔE value (-325.0 kJ/mol) for the C₉₆H₂₄ nanocomposite is due to the insufficient size of the selected model for the graphene matrix.

An intermolecular complex consisting of two monomers and a GC C₉₆H₂₄ species (Monomer...Monomer...C₉₆H₂₄) with the energy effect of -305 kJ/mol can be formed in two ways (Fig. 9). The first of these involves the formation of an intermolecular complex between two monomers, which further interacts with GC C₉₆H₂₄:

**Fig. 9.** Energy diagram of the interaction of two monomers with a C₉₆H₂₄ graphene cluster

As can be seen from Fig. 9, when adding the energy effect of the formation of the Monomer... Monomer complex (reaction *a*) with a similar magnitude of the interaction of the Monomer...Monomer complex and GC (reaction *b*), the same value -305 kJ/mol is obtained (-86 + (-219)), as in full energy



The sum of the energy effects of these two reactions (-117 + (-188)) is also -305 kJ/mol. This means that regardless of the path of formation of the intermolecular Monomer ... Monomer ... C₉₆H₂₄ complex, the magnitudes of the total energy effect are the same, which confirms the correctness of our calculations. It should be noted that this pattern is similar to the Hess law in thermochemistry, if we assume that the energy effect of the reaction at 0 K corresponds to the enthalpy of the reaction.

Similar dependences can be obtained for the systems with dimers and C₁₁₀H₂₆. It should be noted that Fig. 9 shows that the sum of the total energies (1) of the complex of two monomers and the graphene plane is for 31 kJ/mol higher than that (2) of the monomer and intermolecular complex (monomer...C₉₆H₂₄). This indicates that the interaction energy of GC with the monomer is greater than that of two monomers.

An analysis of the hydrogen bond lengths between the oxygen atom of the carbonyl group and the hydrogen atom of the amino group indicates that, regardless of the length of the linkage of the polymeric chain of polyamide (monomer and dimer) and the size of the graphene-like matrix (C₉₆H₂₄ and C₁₁₀H₂₆) in the nanocomposite (Fig. 8), the hydrogen bond is

shorter in comparison with similar findings in the complexes without a carbon matrix. This indicates a greater strength of the bond, that is, the presence of a carbon matrix increases the strength of the formed nanocomposite, what explains the increase in the melting point compared with that for the original polymer.

difference: E_{tot} (Monomer... Monomer...C₉₆H₂₄) and two E_{tot} (Monomer) and E_{tot} (C₉₆H₂₄).

According to the second path, the first interaction of one monomer with GC C₉₆H₂₄ (reaction *c*), and then the addition of another monomer (reaction *d*):

shorter in comparison with similar findings in the complexes without a carbon matrix. This indicates a greater strength of the bond, that is, the presence of a carbon matrix increases the strength of the formed nanocomposite, what explains the increase in the melting point compared with that for the original polymer.

CONCLUSIONS

Thus, in the nanocomposite polyamide – carbon matrix for all the models studied, the intermolecular interaction energy increases significantly compared to a similar value between two fragments of pure polyamide, indicating an increase in the thermal stability of the matter.

The presence of a carbon matrix (regardless of the size of the graphene cluster) in complexes with polyamide (regardless of the size of its fragments) strengthens the hydrogen bonds in the latter.

In the nanocomposite polyamide – a fragment of carbon nanotube, the energy of all investigated covalent bonds significantly increases compared to those in pure polyamide, what indicates an increase in the thermal stability of this nanocomposite. The indicated results of calculations are confirmed by experimental data [6].

Теоретичне дослідження впливу вуглецевого графеноподібного нанокластера на стабільність і міцність поліаміду у нанокompозиті

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Методом теорії функціоналу густини з обмінно-кореляційним функціоналом $V3LYP$, базисним набором $6-31G(d,p)$ і дисперсійною поправкою Грімме розраховані величини енергії міжмолекулярної взаємодії між сусідніми фрагментами поліаміду та встановлено вплив графеноподібних нанокластерів на аналогічні величини для міжмолекулярних комплексів фрагментів поліаміду з графеноподібними нанокластерами. Також досліджено вплив вуглецевих матеріалів на величини енергії ковалентних зв'язків в полімерній матриці поліаміду.

Порівняння величин енергії міжмолекулярної взаємодії двох мономерів (-86.0 кДж/моль, два водневих зв'язки) і двох димерів (-302.0 кДж/моль, три водневих зв'язки) вказує, що величина енергії взаємодії двох ланок складається з енергії водневих зв'язків та внеску енергії дисперсійних сил взаємодії.

Енергія міжмолекулярної взаємодії двох димерів з графеноподібною матрицею ($C_{110}H_{26}$), приблизно на 40 кДж/моль більша (-346.2 кДж/моль) в порівнянні з аналогічною величиною для двох димерів. Менше значення енергії взаємодії (-325.0 кДж/моль) для нанокompозиту з матрицею C_9H_{24} обумовлене недостатнім розміром вибраної моделі графеноподібною матриці.

Аналіз довжин водневого зв'язку між атомом Оксигену карбонільної групи і атомом Гідрогену аміногрупи свідчить, що незалежно від довжини ланки полімерного ланцюга поліаміду (мономер і димер) та розміру графеноподібною матриці (C_9H_{24} і $C_{110}H_{26}$) в нанокompозиті, водневий зв'язок коротший в порівнянні з аналогічною величиною в комплексах без вуглецевої матриці. Це свідчить про більшу міцність даного зв'язку, тобто наявність вуглецевої матриці збільшує міцність утвореного нанокompозиту, що і пояснює підвищення температури плавлення в порівнянні з вихідним полімером. В утвореному нанокompозиті поліамід – вуглецева матриця для всіх досліджених моделей енергія міжмолекулярної взаємодії в нанокompозиті значно збільшується у порівнянні з аналогічною величиною між двома фрагментами чистого поліаміду, що свідчить про підвищення термічної стійкості даного нанокompозиту та підтверджується експериментальними даними.

Ключові слова: поліамід, нанокompозит, графеноподібна площина, метод теорії функціоналу густини, кластерне наближення

Теоретическое исследование влияния углеродного графеноподобного нанокластера на стабильность и прочность полиамида в нанокompозите

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Методом теории функционала плотности с обменно-корреляционным функционалом $V3LYP$, базисным набором $6-31G(d,p)$ и дисперсионной поправкой Грімме рассчитаны величины энергии межмолекулярного взаимодействия между соседними фрагментами полиамида и установлено влияние графеноподобных нанокластеров на аналогичные величины межмолекулярных комплексов фрагментов полиамида с графеноподобными нанокластерами. Также исследовано влияние углеродных материалов на прочность ковалентных связей в полимерной матрице полиамида.

Сравнение величин энергии межмолекулярного взаимодействия двух мономеров (-86.0 кДж/моль, две водородные связи) и двух димеров (-302.0 кДж/моль, три водородные связи) указывает, что величина энергии взаимодействия двух звеньев состоит из энергии водородных связей и вклада энергии дисперсионных сил взаимодействия.

Энергия межмолекулярного взаимодействия двух димеров с графеноподобной матрицей ($C_{110}H_{26}$) примерно на 40 кДж/моль больше (-346.2 кДж/моль) по сравнению с аналогичной величиной для двух

димеров. Меньшее значение энергии взаимодействия (-325.0 кДж/моль) для нанокompозита с $C_{96}H_{24}$ обусловлено недостаточным размером выбранной модели графеноподобной матрицы.

Анализ длин водородных связей между атомом кислорода карбонильной группы и атомом водорода аминогруппы свидетельствует, что независимо от длины звена полимерной цепи полиамида (мономер и димер) и размера графеноподобной матрицы ($C_{96}H_{24}$ и $C_{110}H_{26}$) в нанокompозитах, водородная связь короче по сравнению с аналогичной величиной в комплексах без углеродной матрицы. Это свидетельствует о большей прочности данной связи, то есть, наличие углеродной матрицы увеличивает прочность образованного нанокompозита, что и объясняет повышение температуры плавления по сравнению с исходным полимером. В образованном нанокompозите полиамид - углеродная матрица для всех исследованных моделей энергия межмолекулярного взаимодействия в нанокompозитах значительно увеличивается по сравнению с аналогичной величиной между двумя фрагментами чистого полиамида, что свидетельствует о повышении термической устойчивости данного нанокompозита и подтверждается экспериментальными данными.

Ключевые слова: полиамид, нанокompозит, графеноподобная плоскость, метод теории функционала плотности, кластерное приближение

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