



# The adsorption modeling of bisphenol A derivatives on the surface of carbon materials

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A carbon nanotube and a graphene surface with bisphenol A derivatives have been simulated in the DFT framework using periodic boundary conditions. Such compounds are components of epoxy diene resins, which are important composite materials for aircraft structures. The simulation results allow one to state that the use of the specialized exchange-correlation functional Berland and Hyldgaard developed to account for weak Van der Waals interactions is preferable to DFT-D2 method. We observed that the energy of complexes formation depends on the orientation of the functional groups of diglycidyl ether of bisphenol A and determines by whether the surface of the carbon material is flat, like graphene, or curved, like nanotubes. It was found that the strongest binding is observed for nanotubes with a diameter of 1 nm, for which the energy of complex formation is 65% lower than for the complex of diglycidyl ether of bisphenol A on graphene with the same orientation of functional groups relative to the surface. On the curved outer surface of the nanotubes, the ester derivatives form a greater variety of non-covalent interactions in accordance with the QTAIM analysis of electron density and the energy of complexes formation is lower.

**Keywords:** bisphenol A diglycidyl ether, graphene, carbon nanotube, periodic boundary conditions, electron density.

## 1. Introduction

Composite materials consisting of a matrix based on epoxy resins and various carbon materials are promising materials for the aerospace industry. Due to the low density of carbon nanomaterials, the density of the composite does not increase compared to the original matrix, even for epoxy-based components. Graphene and nanotubes are carbon materials with a very simple atomic structure and an extraordinary range of useful and desired physical and chemical properties. The combination of high strength and large allowable deformations makes it is possible to use the carbon materials as reinforcing elements of various composites [1–3], creation of thermally- and electrically-conductive composites [4,5]. The strengthening effect of the composite material is commonly reduced due to the inertness of graphene and carbon nanotubes: they do not bind strongly enough to the polymer matrix.

To find the optimal way to enhance the binding of carbon reinforcing elements to the matrix, it is necessary to study in detail the features of non-covalent interactions of the structural elements of the polymer matrix with the plane of carbon atoms. For this purpose, the development of reliable structural models taking into account the features of weak non-covalent binding of bisphenol derivatives to atoms and functional groups on the carbon surface is of prime importance. The selected methods are to provide correct assessment of the characteristic features of composite materials and the interaction energy of their components. Such models make it possible to predict properties and develop recommendations for the design of a material

composition to improve the required functional properties. Advances in digital technology allow structural models of functional materials constructed *in silico* to coexist with their physical twins [6]. Materials digital twin concept includes virtual representation of real objects and leads to effectiveness of the material choice in industry.

The adsorption of bisphenol A by graphene and carbon nanotubes was studied both experimentally and theoretically relative to the development of effective sorbents for water purification [7,8]. The experiment showed a monolayer coating of graphene oxide [9] and carbon nanotubes [10] with bisphenol A molecules. The enthalpy of bisphenol A adsorption was approximately  $-10.8$  kcal/mol, which is the average of the estimates given in several sources:  $-10.39$  kcal/mol [10] and  $-11.19$  kcal/mol [11] on multilayer carbon nanotubes and  $-8.2$  kcal/mol [12] on graphene oxide.

Despite the rapid development of methods for multiscale modeling of functional materials, there are very few theoretical studies of the structural aspects of the interactions of epoxy resins or their fragments with a carbon surface [13,14]. The main observations are focused on the estimates of the adsorption energy or the energy of interaction of the carbon surface with molecules containing epoxy groups.

It was shown in [13] that bisphenol A could exist near graphene in one of several metastable configurations. The configuration in which bisphenol A adhered to the graphene surface as tightly as possible had the lowest adsorption energy ( $-14.69$  kcal/mol). The configuration in which the phenolic groups were directed toward the surface and the methyl group of this molecule was directed away from the surface had a lower adsorption energy ( $-13.66$  kcal/mol). The configuration

in which one of the phenyl rings was almost parallel to the graphene plane was even less favorable ( $-12.21$  kcal/mol). In [14], the results of modeling the interaction of bisphenol A with the finite fragments of a carbon nanotube and graphene, which form isolated gas-phase complexes, were presented. The adsorption energy was  $-26.2$  kcal/mol and  $-34.1$  kcal/mol for the nanotube and graphene, respectively. These are to some extent overestimated results, compared to the above experimental data [10–12].

On the one hand, it should be noted that any experimental data depend on the effects of the solvent in which the adsorption was studied. On the other hand, the approaches described above for modeling the adsorption of bisphenol A on a carbon surface had a significant drawback: they modeled relatively small fragments of the carbon surface, often without using periodic boundary conditions. The lack of rationale for choosing the size of the structural model prevented from evaluating the influence of boundary effects on the results obtained. Thus, the accumulated data indicate that the conclusions about the preferred adsorption of bisphenol A on graphene and on the surface of nanotubes are ambiguous. Nevertheless, close values of the adsorption energy point to the dependence of these characteristics on the structural features of the constructed models.

In addition, the modeling of structural features affecting the interaction energy of bisphenol A derivatives with various carbon surfaces is focused on the finding out the ways to enhance the adhesion of epoxy resins on the non-oxidized surface of carbon materials. This step is important for developing the practical recommendations.

To study the properties of non-covalent bonds at the level of electron density properties, the most reasonable is the use of the quantum theory of atoms in molecules (QTAIM) [15]. There were examples [16–19] where an analysis of the topological characteristics of the electron density made it possible to classify the types of interactions in systems with carbon materials similar to ours. Such an analysis provided a more complete insight into understanding of the nature of non-covalent bonds between atoms than effective charges calculated by one of the possible methods.

## 2. Model and computational procedure

When building the structural models, the molecules of bisphenol A (BPA) and diglycidyl ether of bisphenol A (DEBA) were used. Graphene and carbon nanotubes (5, 5), (6, 6), (7, 7), (8, 8) and (9, 9) were used as models of the carbon surface. The choice of these modeling objects makes it possible to evaluate the effect of surface curvature on the adsorption properties in relation to bisphenol A derivatives.

When studying the adsorption of molecules on a nanotube, the computational cell (supercell) was a parallelepiped with dimensions  $a \times b \times c = 4 \times 5 \times c$  nm, where parameter  $c$  was determined for each of the nanotubes independently, but was approximately 2 nm. The larger cell parameter  $b$  was chosen because the adsorbed molecule was located in this direction. The tube was placed along a short edge of the parallelepiped. When studying the adsorption of molecules on a graphene the computational cell was a parallelepiped with dimensions  $a \times b \times c = 4.3 \times 1.5 \times 5$  nm. The graphene was located in the

$xy$  plane. With this choice of supercells, the minimum distance between periodic images of adsorbed molecules was about 1 nm.

Modeling was carried out within the framework of the electron density functional theory implemented in the SIESTA package [20]. This package uses the pseudopotential formalism and an atomic-like basis set. In the study, we used the double-zeta polarized (DZP) basis set. The search for the optimal geometry was carried out using the conjugate gradient method. The convergence criterion for the force acting on an atom (MaxForceTol) was set equal to 0.4 eV/nm.

Two exchange-correlation functionals were used for comparison: PBE (Perdew, Burke and Ernzerhof) [21] based on the generalized density gradients approximation with taking into account the Grimme DFT-D2 [22] empirical correction and the BH (Berland and Hyldgaard) [23] functional developed to account for weak van der Waals interactions. The use of the empirical Grimme correction is a common practice in modeling intermolecular interactions [13, 24]. This is due to the fact that the popular PBE functional does not describe weak Van der Waals interactions well. The Monkhorst-Pack grids of  $1 \times 1 \times 16$  and  $4 \times 8 \times 1$  were used when modeling nanotubes and graphene, respectively. A mesh cut-offs of 350 Ry were used for calculations.

Pseudopotentials were taken from the FHI pseudodatabase [29]. In work [25] it was shown that these pseudopotentials make it possible to obtain reliable results for carbon models.

The energy of formation of all compounds, or so-called energy of interaction between the adsorbable molecule and graphene or a nanotube was estimated by the formula:

$$\Delta E_{\text{form}} = E_{\text{carb+bisp}} - (E_{\text{carb}} + E_{\text{bisp}}) - E_{\text{CP}}$$

where  $E_{\text{carb}}$  is the energy of graphene or a carbon nanotube,  $E_{\text{bisp}}$  is the energy of bisphenol derivative,  $E_{\text{carb+bisp}}$  is the energy of a model which contains graphene or carbon nanotube and bisphenol derivative,  $E_{\text{CP}}$  is the correction that takes into account the error of the basis set superposition. This correction was calculated according to the Boys and Bernardi scheme [26]. In the SIESTA package, the calculation of this correction is not implemented, but it is possible to introduce “ghost atoms” into the system. For such atoms, the necessary orbitals are added to the calculation, but electrons are not added.  $E_{\text{CP}}$  was calculated based on the results of four additional calculations for fixed positions of atoms:

$$E_{\text{CP}} = E_{\text{carb}} - E_{\text{carb-ghost}} + E_{\text{bisp}} - E_{\text{ghost-bisp}}$$

where  $E_{\text{carb}}$  and  $E_{\text{bisp}}$  are the energies of graphene or a carbon nanotube and bisphenol, calculated in the basis of their atoms and  $E_{\text{carb-ghost}}$  and  $E_{\text{ghost-bisp}}$  are the corresponding energies in the basis of the complex.

The use of a wider basis set (triple-zeta polarized, TZP), a larger carbon surface to increase the distance between molecules, or a larger number of k-points did not lead to an error in the energy of formation  $\Delta E_{\text{form}}$  of more than 0.5 kcal/mol.

All QTAIM results presented in this paper were obtained using the Critic2 program [27], the input data for which were obtained in the SIESTA program.

The visualization of the atomic structure of the models, bond paths and bonds critical points was carried out using the GUI4DFT program [28].

### 3. Results and discussion

Let us start with discussion of the methodology and the level of calculations selected for modelling the bisphenol A molecule adsorption on different carbon surfaces. We tested our approach by comparing the energy of different structural models of the bisphenol A molecule adsorbed on the graphene surface (Fig. 1). When using the DFT-D2, the energy was equal to  $-15.0$  kcal/mol. This result is quantitatively consistent with the result of [13] ( $-14.7$  kcal/mol), where the DFT-D3 (PBE-D3) approximation was used for the exchange-correlation functional, but for the gas-phase calculation. In both cases, the structure of BPA-GN-3 shown in Fig. 1c corresponded to the lowest energy. This result was not confirmed when using a specialized exchange-correlation functional BH to take into account the specifics of van der Waals interactions, which were decisive in the structures under consideration during the adsorption of bisphenol A on graphene. In this more accurate model, the strongest interaction was found for the BPA-GN-1 structure shown in Fig. 1a ( $-15.7$  kcal/mol versus  $-15.3$  kcal/mol for the model in Fig. 1c). Thus, our results were close to the literature data. Small discrepancies fit into the errors of the modeling approaches used.

A complex of BPA and a carbon nanotube, potentially possessing the highest BPA-SWNT (7,7) energy of formation,  $\Delta E_{\text{form}}$ , was considered (Fig. 1d). The value of  $\Delta E_{\text{form}}$  when using the BH exchange-correlation functional was  $-13.1$  kcal/mol, which indicated a weaker interaction of BPA with the nanotube than with graphene. This agrees with the results of [14]. Meanwhile, the use of the DFT-D2 functional leads to a twofold overestimation of the interaction energy of the BPA molecule with the nanotube, compared with the experimental results [11]. This can be interpreted as an erroneous choice of the DFT-D2 approximation. It should be noted that the atomic structure represented by these functionals is predicted to be close to the experimental data (Table S1, supplementary material). Bond length in Bisphenol A molecules adsorbed on carbon surface are presented in Table S2 (supplementary material).

Thus, we decided upon using the BH functional to search for an equilibrium structure and estimate the energy of formation,  $E_{\text{form}}$ , (Table 1) for adsorbed fragments of epoxy-diane resins on the surface of carbon materials. Unfortunately, this approach is significantly more demanding on computing resources. Therefore, only some calculations were repeated for the DFT-D2 approach (Table S3, supplementary material).

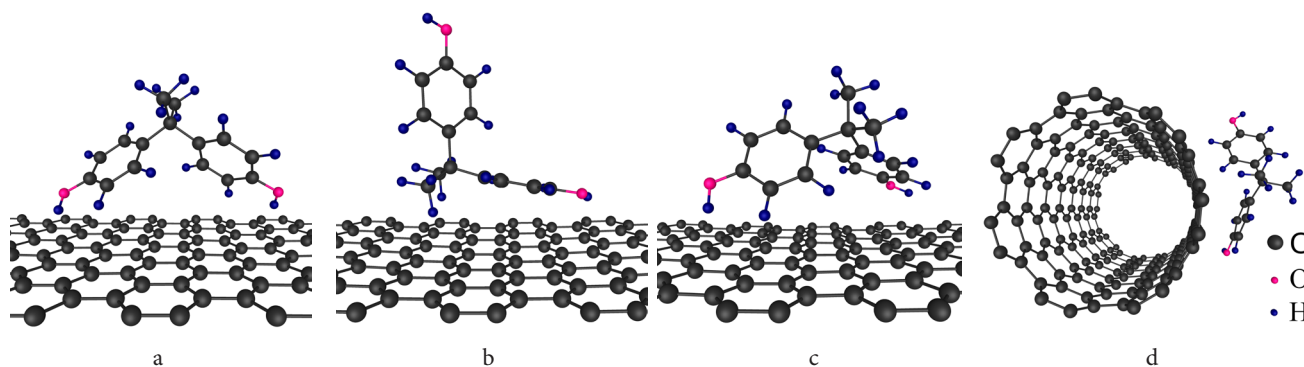
**Table 1.** Energy of formation,  $\Delta E_{\text{form}}$ , number of bond paths for non-covalent interactions,  $N$ , and sum of values of electron density at BCPs of non-covalent interactions,  $\Sigma\rho$ , for bisphenol A derivatives adsorbed on the carbon surface for the different equilibrium configurations.

Model	$\Delta E_{\text{form}}$ , kcal/mol	$N$	$\Sigma\rho$ , a.u.
BPA-GN-1	-15.7	4	0.043
BPA-GN-2	-14.6	8	0.056
BPA-GN-3	-15.3	5	0.042
BPA-SWNT(7,7)	-13.1	6	0.074
DEBA-SWNT(5,5)	-11.3	9	0.123
DEBA-SWNT(6,6)	-13.4	11	0.142
DEBA-SWNT(7,7)	-17.7	11	0.136
DEBA-SWNT(8,8)	-18.9	9	0.105
DEBA-SWNT(9,9)	-18.7	11	0.136
DEBA-GN	-11.4	4	0.029

At the next stage of the research, we modeled the interaction of graphene and carbon nanotube with diglycidyl ether of bisphenol A (DEBA) as a typical fragment of epoxy resin. We studied the adsorption of DEBA on carbon nanotubes with diameters from 6.8 to 10.9 Å to evaluate the effect of surface curvature of the carbon backbone on the energy of interaction with DEBA. At the same time, we did not aim to determine the most favorable mutual orientation of the DEBA relative to graphene. It was important for us to consider systems with the same orientation of the molecule to the surface. For this reason, configurations similar to BPA-GN-1 and BPA-SWNT(7,7) were chosen as starting configurations for the cases of DEBA adsorption on a graphene and nanotube, respectively. Equilibrium atomic structures and the interaction energies corresponding to them are shown in Fig. 2.

The case of adsorption on a flat surface corresponds to the  $\Delta E_{\text{form}} = -11.4$  kcal/mol. Approximately the same energy ( $-11.3$  kcal/mol) was obtained for adsorption on the thinnest of the considered nanotubes SWNT(5,5). As the diameter of SWNTs increases, the energy of complexes formation with DEBA decreases and stops at the case of DEBA-SWNT(8,8). Then, for DEBA-SWNT(9,9), a slightly higher  $\Delta E_{\text{form}}$  is observed. Therefore, it was interesting to analyze the structural features and non-covalent interactions that can be associated with stabilization of DEBA adsorption at a certain curvature of the nanotube surface.

The orientation of DEBA on the surface of nanotubes of different diameters did not fundamentally change. The

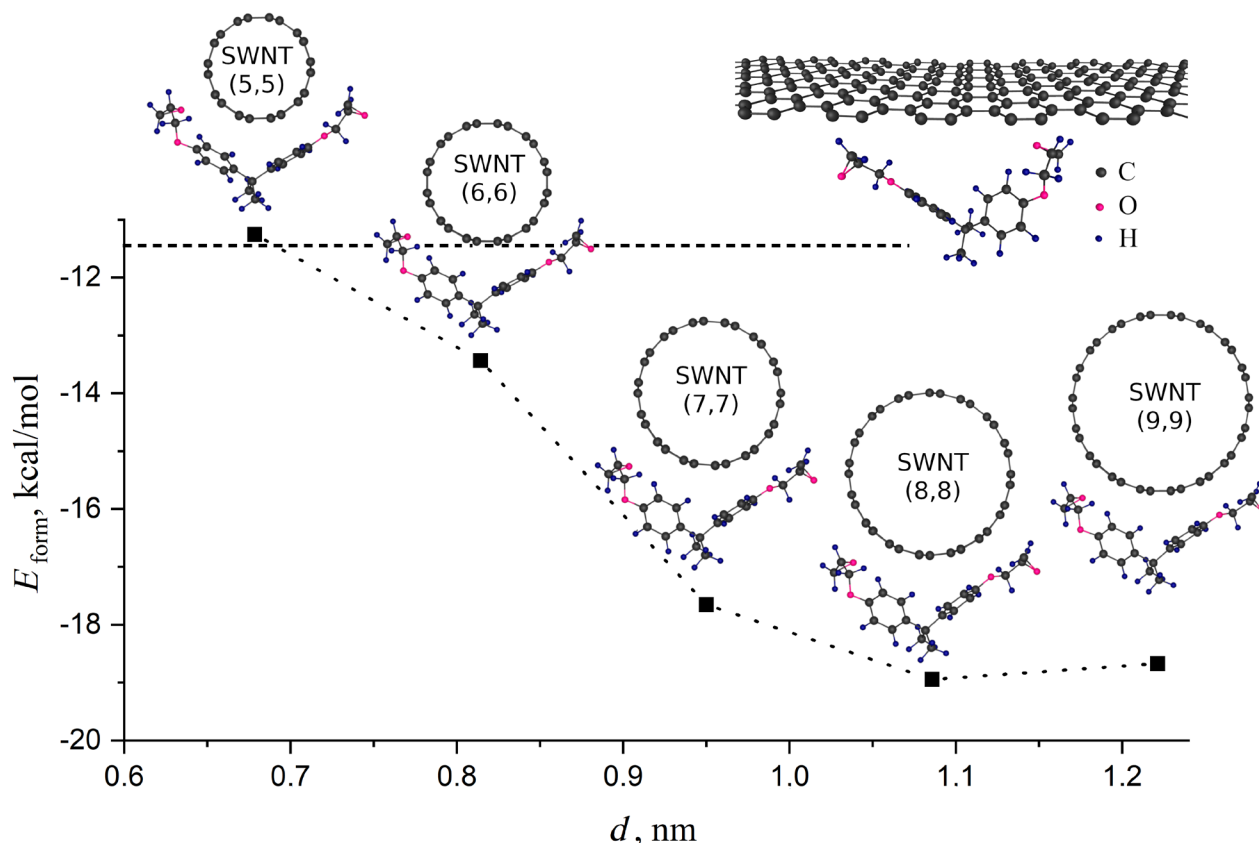


**Fig. 1.** (Color online) Structure models of bisphenol A on graphene: BPA-GN-1 (a), BPA-GN-2 (b), BPA-GN-3 (c) and nanotube BPA-SWNT(7,7) (d).

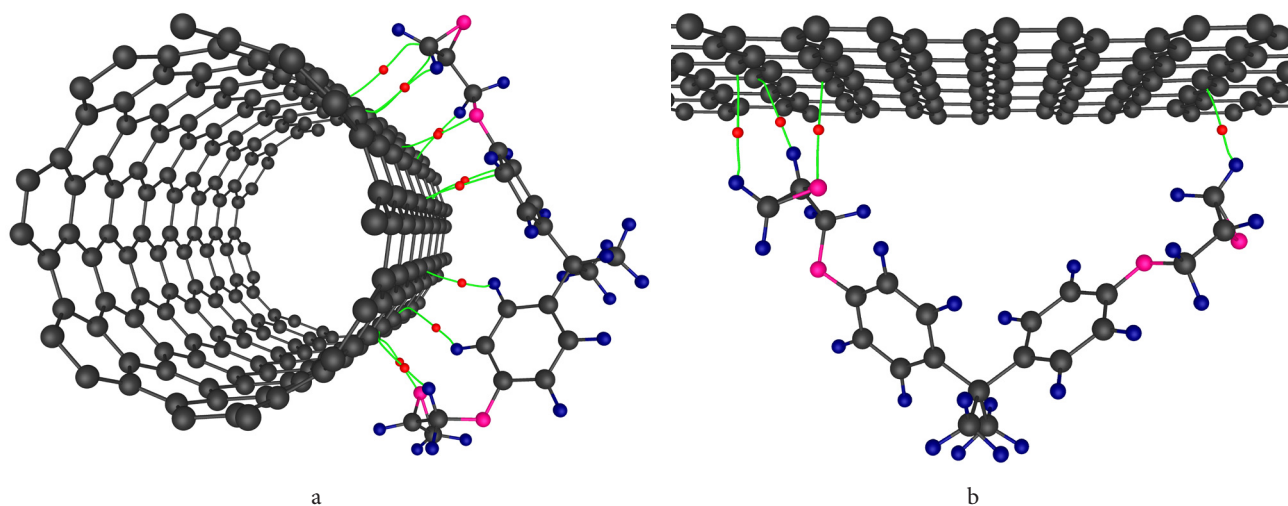
tetrahedral carbon at the center of DEBA molecule was approximately in the same position relative to the atoms of the nanotube. The greatest differences were in the phenyl and epoxy cycles. According to QTAIM (Table S4, supplementary material), the total number of the bond critical points (BCP) of electron density corresponding to non-covalent interactions between DEBA and carbon atoms of nanotubes remains approximately the same (9–11), nevertheless this number is about twice higher than for DEBA or BPA molecules adsorbed on graphene (Fig. 3).

Generally, three types of such interactions are formed. The most numerous are the Cg...H interactions, among which

there are bond paths formed by H atoms of phenyl groups. The electron density at the BCP of such bonds is relatively low  $\rho(r_{\text{bcp}})=0.008 \div 0.014$  a.u. As a rule, one of etheric oxygens and one oxygen epoxy group necessarily form a bond paths with carbon atoms of a nanotube. In terms of electron density, the interactions Cg...O and Cg...C compete with each other. Note that they have the values of  $\rho(r_{\text{bcp}})=0.017 \div 0.020$  a.u., which are higher for the surface of SWNTs with smaller diameter. In this case, the electron density at the rest interactions is lower. However, as the SWNT diameter increases, the maximal values of  $\rho(r_{\text{bcp}})$  no longer exceed  $\rho(r_{\text{bcp}})=0.017$  a.u.; the curvature of bond paths increases and the bifurcated interactions appear.



**Fig. 2.** (Color online) Dependence of energy of formation,  $\Delta E_{\text{form}}$ , for DEBA adsorption on nanotube diameter. The horizontal line shows the  $\Delta E_{\text{form}}$  for DEBA on graphene.



**Fig. 3.** (Color online) Bond critical points (red balloons) and bond paths (green lines) for cases of DEBA adsorption on carbon nanotube (7,7) (a) and graphene (b).

#### 4. Conclusions

We have created a reliable model of the adsorption of single bisphenol A and its diglycidyl ether (DEBA) on the carbon surfaces of graphene and nanotubes using periodic boundary conditions. Among other things, a suitable exchange-correlation functional, grid detailing in direct and reciprocal spaces were selected.

It has been established that the energy of  $\Delta E_{\text{form}}$  formation for DEBA on the SWNT surface rapidly increases in absolute value in the diameter range from 0.65 to 0.95 nm. The most preferred nanotube radius was 1.1 nm.

Thus, the curved surface of SWNT(5,5)-SWNT(9,9) allows the formation of approximately twice as many bond paths between the atoms of DEBA molecule and carbon atoms of SWNT as compared to the flat surface of graphene. In addition, the diversity of such non-covalent interactions is increasing. At least two Cg...O bond paths are formed per one complex. Moreover, the Cg...C interactions are necessarily formed. The curvature of bond paths in these cases is high. Nevertheless, the electron density at the bond critical points for interactions of DEBA with the surface of nanotubes is significantly higher than for analogous bonds with the surface of graphene. The interaction of the carbon surface with pure bisphenol A largely depends on whether relatively strong C...H-O hydrogen bonds are formed.

The simulation results show that to enhance the interaction of the epoxy resin with the surface, the carbon material should be enriched with components that carry fragments of twisted surfaces, and nanotubes of the optimal diameter should be used.

Therefore, the modeling task focused on finding ways to enhance adhesion on the non-oxidized surface of carbon materials can be considered completed.

**Supplementary material.** *The online version of this paper contains supplementary material available free of charge at the journal's Web site (lettersonmaterials.com).*

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