

Original Article

**INTERACTION OF COMPONENTS OF EPOXY COMPOSITE CONTAINING
CARBON NANOTUBES AND GRAPHENE OXIDE MIXTURE**

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ABSTRACT

Mixtures of carbon nanotubes (CNTs) and graphene oxide (GO) in composite materials often exhibit synergistic effects with respect to mechanical and electrophysical properties. In this paper, the mechanisms of interaction between CNTs, GO and epoxydian resin macromolecules were discussed based on the results of molecular dynamics simulations. Calculations were performed in the MM3 force field at exposure times up to 100 ps. The influence of the CNT's graphene layers shape and the presence of oxygen-containing functional groups on the self-assembly process during the epoxy composite formation has been demonstrated. It is shown that graphene oxide sheets are arranged around cylindrical nanotubes and envelop them, while when using tapered nanotubes, the formation of alternating layers of CNTs and GO should be expected. The presence of oxygen-containing groups on the surface of cylindrical nanotubes promotes the penetration of epoxydian resin macromolecules into the space between CNTs and GO. The simulation results of the "cylindrical CNTs – GO" and the "conical CNTs – GO" hybrid particles were confirmed by scanning electron microscopy data.

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ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ КОМПОНЕНТОВ ЭПОКСИДНОГО КОМПОЗИТА, СОДЕРЖАЩЕГО СМЕСЬ УГЛЕРОДНЫХ НАНОТРУБОК И ОКСИДА ГРАФЕНА

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АННОТАЦИЯ

Смеси углеродных нанотрубок (УНТ) и оксида графена (ОГ) в составе композиционных материалов часто демонстрируют эффекты синергизма в отношении механических и электрофизических свойств. В статье рассмотрены механизмы взаимодействия УНТ, ОГ и макромолекул эпоксидно-диановой смолы между собой на основании результатов моделирования систем методами молекулярной динамики. Расчеты проводились в силовом поле ММ3 при времени экспозиции до 100 пс. Продемонстрировано влияние формы графеновых слоев УНТ и наличия на их поверхности кислородсодержащих функциональных групп на характер процесса самосборки в ходе формирования эпоксидного композита. Показано, что листы оксида графена располагаются вокруг цилиндрических нанотрубок и обволакивают их, в то время как при использовании конических нанотрубок следует ожидать образования чередующихся слоев из УНТ и ОГ. Наличие на поверхности цилиндрических нанотрубок кислородсодержащих групп способствует проникновению макромолекул эпоксидно-диановой смолы в пространство между УНТ и ОГ. Результаты расчетов при моделировании подтверждаются данными сканирующей электронной микроскопии гибридных частиц «цилиндрические УНТ-ОГ» и «конические УНТ-ОГ».

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Introduction

Hybrid modifiers based on different nanocarbon forms are attracting researchers as a polyfunctional additive to improve a number of properties of polymer matrix. In the review [1], it is shown that simultaneous introduction of carbon nanotubes (CNTs) and graphene into epoxy resin can improve physical and mechanical characteristics, thermal and electrical conductivity of nanocomposite. The influence of CNTs and graphene on composite properties often has a pronounced synergistic character.

The authors of some papers [2–3] believe that the synergistic effect is always present, and explain it by the formation of ordered structures arising from nanomodifier components in polymer volume. In [4], it is assumed that CNTs intercalate between individual graphene nanoplates (GNPs) preventing the aggregation of the latter. In [2, 4–5], the schematic representations of nanotube and graphene structures in composites are presented without considering the mechanisms of their formation.

New opportunities to study the interaction of carbon nanostructures with each other and with polymer macromolecules have emerged due to development of computational chemistry methods. The most popular modeling methods are based on quantum chemistry approaches [6] but they require considerable computational resources when considering systems with more than 80 atoms. To gain insight into the mechanisms of formation of composites containing macromolecules of polymers, CNTs and graphene, it is necessary to analyze the behaviour of the system consisting of 10^4 – 10^5 atoms.

In [7], to predict the percolation probability and piezoresistive sensitivity of a hybrid conductive nanocomposite, an one-step Monte-Carlo method teamed up with a percolation model is developed. The computational model calculates the separation distance of CNTs and GNPs by taking into account the dimensional properties of their state of dispersion.

In [8], the thermal conductivities of CNTs/graphene/epoxy composites are investigated by mesoscopic simulations using dissipative particle dynamics (DPD) and smoothed particle hydrodynamics (SPH). An analysis of the effect of the size and volume fraction of fillers on the thermal conductivity of CNTs and/or graphene-based epoxy resin composites are presented.

In [9], the molecular dynamics method is used to evaluate the influence of the hybrid graphene/CNTs filler on the tensile properties of epoxy resin. In our opinion, this method can also be used to consider the self-assembly mechanisms of the components during the composite formation.

The aim of this work was to simulate the evolution of systems comprising of graphene oxide, carbon nanotubes with conical and cylindrical shapes of graphene layers, and epoxy resin macromolecules to determine the factors affecting structural features of composite.

Experiment

The potential energy fields of a molecular system are determined by the sum of paired interatomic interactions, depending on the type of atoms and the distance between them [10–11]. The state of a system consisting of N atoms at time τ is determined by the velocities (impulses) $\vec{V}_{n,m}(\tau)$ and coordinates of all particles $\vec{r}_{n,m}(\tau) = \{x_n, y_n, z_n\}$ in a vector form, where $n = 1..N_a$; $m = 1,2,3$. The main problem is to find the state of the molecular system at an arbitrary instant of time τ , if the state of the system is known at the initial time (at $\tau = 0$). In classical mechanics, this problem is solved by calculating the trajectory of motion, which is determined by solving the Newton equation. Hence, we can write:

$$m_n \frac{d^2 x_n(\tau)}{d\tau^2} = -\frac{\partial U(x)}{\partial x_n}, \quad (1)$$

$$m_n \frac{d^2 y_n(\tau)}{d\tau^2} = -\frac{\partial U(y)}{\partial y_n}, \quad (2)$$

$$m_n \frac{d^2 z_n(\tau)}{d\tau^2} = -\frac{\partial U(z)}{\partial z_n}, \quad (3)$$

initial conditions:

$$x_n = x_{0n}; y_n = y_{0n}; z_n = z_{0n}; \quad (4)$$

$$\frac{dx_n(\tau)}{d\tau} = V_{0x}; \frac{dy_n(\tau)}{d\tau} = V_{0y}; \frac{dz_n(\tau)}{d\tau} = V_{0z} \quad (5)$$

where $n = 1..N_a$; N_a – number of atoms in the system; m_n – atomic mass, x, y, z – spatial coordinates; $U(r)$ – potential energy depending on the mutual arrangement of all particles of the system.

The potential energy of the particles is considered as the sum of the following components:

$$U = U_b + U_v + U_\phi + U_f + U_q + U_{LJ} + U_{hb}, \quad (6)$$

where the items correspond to the following types of

interaction: U_b – chemical bonds; U_v – valence angles; U_φ – torsion angles; U_f – flat groups and pseudo-torsion angles; U_{LJ} – Van der Waals forces; U_q – electrostatic interactions; U_{hb} – hydrogen bonds.

The vibration energies of valence angles and the energy of valence interactions of particles in molecular system are described by parabolic potentials. The potential energy for torsion and pseudo-torsion angles of chemical bond is given by the Fourier series [12]. Similarly, the potential energy of planar groups is determined. Using the Lennard-Jones potential, the interaction of atoms not bound by a covalent bond but interacting via van der Waals forces and hydrogen bonds is described [13]. According to the Coulomb law, the potential energy of interaction of charged particles is characterized by the magnitude of electrostatic potential.

The mathematical formulation of the problem of calculating the coordinates of the atoms of a molecular system including carbon nanotube, graphene oxide sheet and epoxide resin macromolecule is being formed as follows:

$$\{\bar{r}_{n,m}\}; n = 1 \dots N_a; m = 1 \dots 3; \quad (7)$$

$$\vec{l} = f_l(\{\bar{r}_{n,m}\}); \quad \vec{\alpha} = f_\alpha(\{\bar{r}_{n,m}\}); \quad \vec{\varphi} = f_\varphi(\{\bar{r}_{n,m}\}); \quad (8)$$

$$\vec{l} \in \Omega_l; \quad \vec{\alpha} \in \Omega_\alpha; \quad \vec{\varphi} \in \Omega_\varphi,$$

where \bar{r} is the matrix of coordinates of N_a atoms in three-dimensional space; \vec{l} – vector of chemical bonds length values; $\vec{\alpha}$ – vector of angles of chemical bonds values; $\vec{\varphi}$ – vector of torsional angles of chemical bonds values; $\Omega_l, \Omega_\alpha, \Omega_\varphi$ are the region of acceptable values.

According to (5) and (6), the atom potential energy can be calculated as follows:

$$U = U_b(\vec{l}) + U_v(\vec{\alpha}) + U_\varphi(\vec{\varphi}) + U_f(\vec{\varphi}) + U_q(\vec{r}) + U_{LJ}(\vec{r}) + U_{hb}(\vec{r}), \quad (9)$$

$$U_b(\vec{l}) = \frac{1}{2} \sum_{t=1}^T K_{b,t} (l_t - l_{0t})^2, \quad (10)$$

where $K_{b,t}$ – is the effective rigidity of valence bond; l_{0t} – the equilibrium length of chemical bond.

$$U_v(\vec{\alpha}) = \frac{1}{2} \sum_{h=1}^H K_{v,h} (\alpha_h - \alpha_{0h})^2, \quad (11)$$

where $K_{v,h}$ – effective elasticity of valence angle; α_{0h} – the equilibrium value of chemical bond angle.

$$U_\varphi(\vec{\varphi}) = \frac{1}{2} \sum_{g=1}^G \sum_{s=1}^S K_{\varphi,g,s} [V_{g,s} \cos(s\varphi_g - \delta) + 1], \quad (12)$$

$$U_f(\vec{\varphi}) = \frac{1}{2} \sum_{g=1}^G \sum_{s=1}^S K_{f,g,s} [V_{g,s} \cos(s\varphi_g - \delta) + 1], \quad (13)$$

where $K_{\varphi,g,s}, K_{f,g,s}$ are constants determining the heights of potential barriers of dihedral angles, $V_{g,s}$ is the contribution of the harmonic to the torsion angle potential ($-1 < V_{g,s} < 1$), $s_{g,s}$ is the multiplicity of torsional barrier, δ is phase shift, s is harmonic number, S is the number of harmonics.

$$U_q(\vec{r}) = \sum_{i=1}^{N_a-1} \sum_{j=i+1}^{N_a} \left[\frac{q_i q_j}{\varepsilon W_{i,j}} \right], \quad (14)$$

where q_i, q_j – partial charges on atoms, ε – dielectric permittivity of the medium (water in our case), $W_{i,j}$ – the distance between the i and j atoms, $W_{i,j} = |\vec{r}_i - \vec{r}_j|$.

$$U_{LJ}(\vec{r}) = \sum_{i=1}^{N_a-1} \sum_{j=i+1}^{N_a} \left[\frac{A_{i,j}}{W_{i,j}^{12}} - \frac{B_{i,j}}{W_{i,j}^6} \right], \quad (15)$$

$$U_{hb}(\vec{r}) = \sum_{i=1}^{N_a-1} \sum_{j=i+1}^{N_a} \left[\frac{A'_{i,j}}{W_{i,j}^{12}} - \frac{B'_{i,j}}{W_{i,j}^{10}} \right], \quad (16)$$

where $A_{i,j}, B_{i,j}, A'_{i,j}, B'_{i,j}$ – constants that determine the depth of potential wells depending on the types of atoms (i and j) involved in the interaction.

Evolution of molecular system at 298 K and exposure time up to 100 ps was investigated using Gromacs software. Coordinates of atoms were determined by solving problem (1) – (16) using the grid method with a calculation step equal to 0.002 ps. The calculation model of force fields MM3 was used.

Molecular systems included diglycidyl polyether diphenylolpropane macromolecules (ED-20 epoxy resin), fragments of initial or oxidised CNTs, and graphene oxide sheets. The model cylindrical nanotube was a 5 nm long consisting of three graphene layers. A model conical nanotube with cup-stacked morphology was a 7.1 nm long with a taper angle of 60°. Its outer and inner diameters were 5.7 and 4.1 nm, respectively. The size of graphene oxide sheet was 6×6 nm. The initial and oxidized CNTs as well as graphene oxide models included defects due to the presence on the surface of C-H bonds, oxygen-containing groups and -SO₃H groups. The degree of functionalization of oxidized CNTs was 0.2 mmol/g.

To assess the adequacy of the calculation results, the morphology of the hybrid particles "GO-conical CNTs" and "GO-cylindrical CNTs" was

studied. Cylindrical CNTs “Taunit-M” ($d = 8 \div 15$ nm, length $l \geq 2$ μm , specific surface area ≥ 300 m^2/g), conical CNTs “Taunit” ($d = 20 \div 70$ nm, length ≥ 2 μm , specific surface area = 120–140 m^2/g) and graphene oxide (1 wt. % aqueous suspension) produced by “NanoTechCenter” Ltd. (Tambov, Russia) were used herein. The mixture of graphene oxide suspension (100 ml) with CNT (1 g) was prepared by treatment with ultrasound for 30 minutes and then it was dried in a Scientz-10N lyophilizer. SEM images of hybrid particles were obtained using a JSM-6390LA JEOL scanning electron microscope.

Results and Discussions

Evolution of the "cylindrical CNT – GO – ER" system

According to molecular dynamics calculations, the GO is initially approaching the surface of nanotube. At the same time, the surface of the GO sheets begins to curve. The ER macromolecules also cluster near the CNT surface. At an exposure time of 80 ps the GO sheets take their final shape by enveloping the CNT surface. Then ER macromolecules start approaching the outer surface of the GO. A view of the system at an exposure time of 120 ps is shown in Fig. 1, a. It can be seen that the interaction between the components is predominantly due to Van der Waals forces. Hydrogen bonds between the oxygen-containing groups of GO and ER macromolecules are not formed.

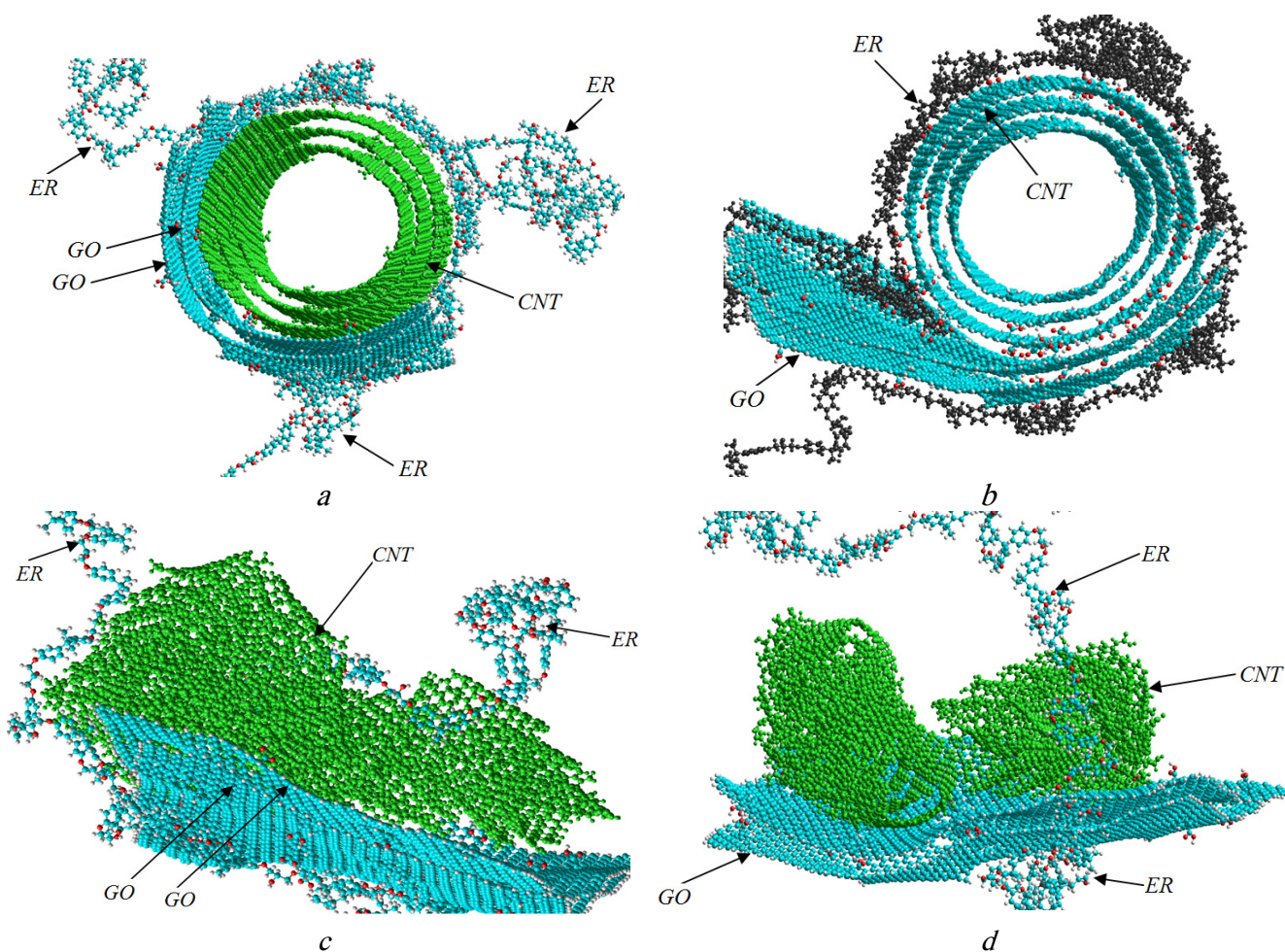


Fig. 1. States of the systems: "cylindrical CNT – GO – ER" (a), "oxidized cylindrical CNT – GO – ER" (b), "conical CNT – GO – ER" (c), and "oxidized conical CNT – GO – ER" (d) at 120 ps exposure time according to molecular dynamics simulations

Evolution of the "oxidized cylindrical CNT – GO – ER" system

In this case, the epoxy resin macromolecules approach the surface of nanotube faster than graphene oxide sheets. The oxygen-containing groups have an orienting effect on the arrangement of epoxy macromolecules due to electrostatic forces. The change in graphene sheets shape is slower due to the fact that a part of nanotube surface is coated with epoxy resin. The graphene sheets change their shape more slowly because the surface of nanotube is already partially coated with epoxy resin. As a result, the epoxy macromolecules end up in the space between CNT and GO (Fig. 1, b).

Evolution of the "conical CNT – GO – ER" and "oxidized conical CNT – GO – ER" system

Graphene oxide sheets do not change their shape. Nanotubes are located on their surface. The most active interaction centers with the epoxy resin

are the edges of tapered CNTs (Fig. 1, c). The system with oxidized tapered nanotubes looks similar (Fig. 1, d). In this case, the oxygen-containing groups do not affect the arrangement of epoxy macromolecules. Such systems can be expected to form a composite of alternating layers consisting of nanotubes, linearly spaced graphene sheets and epoxy resin.

Morphology of experimental samples of hybrid particles "cylindrical CNT – GO" and "conical CNT – GO"

On SEM images of the "cylindrical CNT – GO" hybrid particles, individual nanotubes are not visualized (Fig. 2). Apparently, GO sheets are indeed located around nanotubes, completely enclosing them. There is no sharp curvature of the graphene sheets surface because their planar dimensions are noticeably larger than the diameter of nanotubes in comparison with the model calculation.

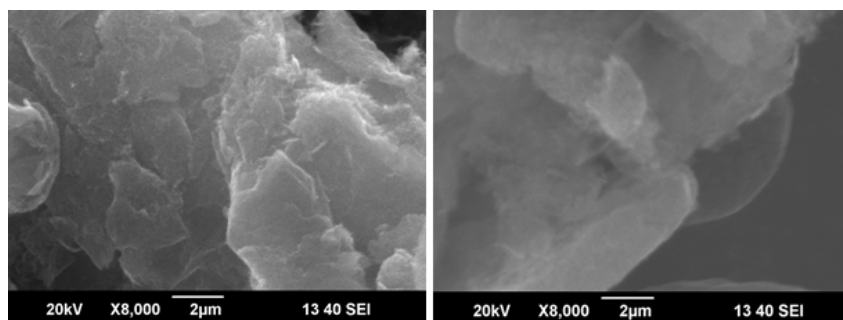


Fig. 2. SEM images of the "cylindrical CNT – GO" hybrid particles

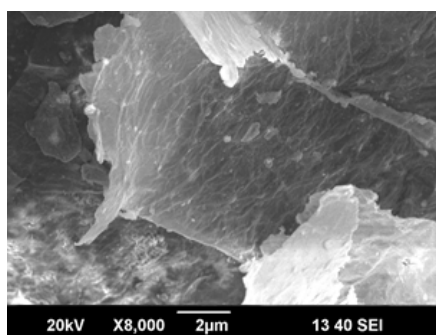


Fig. 3. SEM image of the "conical CNT – GO" hybrid particles

SEM images of hybrid particles obtained by combining conical nanotubes with graphene oxide look different. A network of carbon nanotubes is clearly visualized on almost straight sheets of graphene oxide (Fig. 3). Thus, it can be assumed that

SEM data satisfactorily correlate with the molecular dynamics calculations.

Conclusions

In this work, the evolution of the systems consisting of epoxy resin and mixtures of graphene oxide and different shape carbon nanotubes have been simulated by the methods of molecular dynamics. It is shown that the carbon components interact with each other and form structures of different morphology depending on the type of nanotubes.

In systems with cylindrical CNTs, the composite formation regularities are also influenced by the presence of oxygen-containing functional groups on nanotube surface. The correctness of performed calculations is confirmed by the data of scanning electron microscopy of the hybrid particles

obtained by combining conical and cylindrical CNTs with graphene oxide.

In the future, it is planned to investigate the mechanical and electrophysical properties of epoxy composites containing hybrid fillers with different structures, which will explain the nature of synergistic effects observed using together different carbon nanomaterials as fillers.

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