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Influence of surface modification of halloysite nanotubes on their dispersion in epoxy matrix: Mesoscopic DPD simulation

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ABSTRACT

The problems of constructing of a meso-scale model of composites based on polymers and aluminosilicate nanotubes for prediction of the filler's spatial distribution at early stages of material formation have been considered. As a test system for the polymer matrix, the mixture of 3,4-epoxycyclohexylmethyl-3,4epoxycyclohexanecarboxylate as epoxy resin monomers and 4-methylhexahydrophthalic anhydride as curing agent has been used. It is shown that the structure of a mixture of uncured epoxy resin and nanotubes is (mainly) determined by the surface functionalization of nanotubes. The results indicate that only nanotubes with maximum functionalization can preserve a uniform distribution in space.

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1. Introduction

Halloysite is a natural nano material consisting of multilayer aluminosilicate nanotubes [1-3] (NT). In the literature, halloysite nanoparticles having thread-like, spherical, flat, disk-shaped, and other shapes have been also reported [3]. Halloysite is contained in kaolinite clay, which is formed in the Earth's crust by the weathering of geological materials formed under high pressure in the layers of silicon dioxide and aluminum oxide. The cost of obtaining of halloysite nanotubes (HNT) is lower than that of carbon nanotubes because of the high prevalence of kaolinite deposits.

The chemical composition of halloysite, $Al_2Si_2O_5(OH)_4nH_2O$ (n = 0, 2), is close to that of kaolinite, dickite and nacrite. The morphology of the halloysite nanotube can be seen as a kaolin layer (having a thickness of about 0.7 nm) folded to a "roll", see Fig. 1. The HNT length is ranging from 0.5 µm to 1.2 µm and diameter is <100 nm. The outer and inner surface of kaolin layer are formed by silica and alumina tetrahedra, respectively. The hydrated halloysite can contain between the kaolin layers a layer of water molecules of thickness of about 1 nm which is weakly bound to the surfaces of kaolin. Dehydrated HNT consist of about 15–20 layers packed with period 0.72 nm and with the interior diameter of about 15 nm (see Ref. [2]).

HNT can be used as "ready-made" nanocontainers [2]. When added in polymer matrices, HNT may serve a dual function: to increase the strength of the material due to bonding with the poly-

* Corresponding author. E-mail address: markina@polly.phys.msu.ru (A. Markina). mer matrix and to provide a variety of additives contained in their inner cavity, this leading to many varieties of applications [4]. The surface properties of halloysite nanotubes have a significant impact on physical properties of polymer nanocomposites. Due to the high surface energy HNT readily form aggregates, and this decreases the mechanical strength of nanocomposites. To increase the degree of dispersion, HNT surface is preliminarily subjected to an appropriate modification, e.g. covalent functionalization using cationic surfactants, polycations [2] (due to the negative charge of HNT surface), organosilanes [5-7,9], other modifiers [8,10], or non-covalent functionalization [7]. Also, HNT surface may be modified by grafting of different polymer chains, which may act as a coating agent or a binder. In the first case, the modifier's role is to prevent the aggregation of nanoparticles (NPs), while the second case is used to fix the modifier in the matrix, by involving modifier molecules in polymerization reactions. To increase the degree of NT dispersion, it is highly desirable to use modifiers possessing a high degree of compatibility with monomers of the matrix, otherwise the incompatibility of the modifier and the polymer matrix may induce a phase separation in the system [11].

Despite the large number of computer simulation studies of nanocomposites, to the best of our knowledge there are no data in the literature on the large-scale atomistic modeling of polymer matrix filled with halloysite nanotubes. This is partly explained by the chemical structure of such materials – it includes some atoms for which there is no parameterization in the valence force fields (FF), used in the methods of atomistic simulations. In addition, the characteristic size of HNT (outer diameter about 100 nm, length about 0.5–1.2 μ m) does not allow to use such







Fig. 1. (a) Schematic representation of the structure of a kaolin layer and halloysite nanotube. (b) Structure of talc. (c) The simplified structure to simulate the outer surface of halloysite. Here the symbols correspond to the names of chemical elements.

objects in direct atomistic modeling because simulation box should necessarily have a volume $\sim 1 \ \mu m^3$ and contain about 1 billion atoms, which lies far outside performance capabilities of modern supercomputers. In such cases, coarse-grained models [12,13] should be used that allow for simulation of large volumes of a material on long time scales. To calculate the interaction parameters between structural units in a coarse-grained model, atomistic simulation or other modeling techniques can be employed. Calculation schemes based on the using of several methods on different length and time scales, are called hybrid or multiscale modeling methods [14,15].

In this paper we have developed a hybrid model for mesoscopic computer simulations of polymer/HNT composite systems. Our first interest was to study the influence of functionalization of HNT surface on the dispersion of HNTs in polymer matrix at the early stages of formation of a nanocomposite material. Our paper is organized as follows. In Section 2 we discuss our model and the simulation approach, Section 3 presents the results of our simulations and Section 4 contains a summary and conclusions.

2. Model and simulation technique

We have studied the behavior of halloysite nanotubes in a polymer precursor, i.e., at early stages of a nanocomposite preparation before a polymerization reaction starts. As precursor of a polymer matrix, the mixture of epoxy monomers 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate and the anhydride of 4-methylhexahydrophthalic acid as a hardener (curing agent) was examined. Halloysite nanotubes with modified and unmodified surface have been considered. As a surface modifier we have considered the anhydride of 3-(triethoxysilyl)-propyl-succinic acid, which is similar in chemical structure to the curing agent and is often used for crosslinking with the epoxy matrix [16,17].

In order to study large-scale structures of a nanocomposite in a coarse-grained representation, we have chosen the dissipative particle dynamics (DPD) method [18–21]. Currently, DPD method is widely used for modeling various polymer nanosystems [22,23]. As a software implementation of the DPD method, we have used an improved program code developed by the authors of Ref. [23]. The calculation of interaction parameters between coarse-grained particles in DPD model was performed using the extended Flory–Huggins model [24,25]. To verify the parameterization, we have calculated by means of atomistic molecular dynamics method the relative adhesion energy of ultra-thin layers of a mixture of epoxy resin and hardener monomers placed at the modified and unmodified halloysite nanotube surface. For calculations by means of the extended Flory–Huggins model and atomistic molecular dynamics we have used PCFF force field [26].

The obvious way to simplify the model of HNT is to use enclosed nanotubes with diameters chosen in accordance with the frequency of alternation of layers of kaolin. As noted above, the halloysite nanotube is a rolled-up layer of kaolin having the structure shown in Fig. 1, the outer side consisting of silica and inner side consisting of alumina. Although the structure of kaolin (Fig. 1a) can serve as a basis for building nanotubes and surfaces of halloysite, the presence of aluminum atoms makes atomistic simulations of these structures impossible, because popular valence force fields (for example, PCFF) do not contain the necessary force constants. Direct modeling of such structures can be realized only within the framework of quantum–mechanical methods [27].

Since only atoms of silica in the outer layer directly interact with the polymer matrix, substances with surface structure similar to that of kaolin can be used as a surface model of kaolin. For example, talc meets partly these requirements, see Fig. 1b. Although force filed parameters for all atoms contained in talc are available in PCFF, to simplify the simulation, we removed the magnesium ions and converted the oxygen atoms with free valences to OH groups. The resulting layer having two silica surfaces with inwardly facing hydroxyl groups is shown in Fig. 1c. Such simplified model of the kaolin surface (SMKS) can be used to construct models of halloysite nanotubes as well as external surfaces of kaolin in problems when it is important to take into account only the properties of outer surface of HNT.

Following the DPD methodology [22], the coarse-grained model of the matrix precursor with HNT was built. It consists of identical spherical particles of diameter σ (unit of length) and mass *m*. The main components of the model on the atomistic level, and the principles of their conversion to DPD coarse-grained particles are shown in Fig. 2. The total number of subsystems is equal to 5, namely C (epoxy resin molecule fragment, see Fig. 2a), O (hardener molecule, see Fig. 2b), H (fragment of hydroxylated silica surface, see Fig. 2c), S (fragment of SiO₂ surface, see Fig. 2c) and P (fragment of modified SiO₂ surface, see Fig. 2c). Hereinafter DPD notation for particles used names of chemical elements. It should be noted that these conditional notations are used to facilitate the visualization of the process simulation results by using standard tools of molecular graphics.

In DPD method, the conservative forces of intermolecular interaction can be expressed through the Flory–Huggins parameters [20–23], χ_{ii} , which provide the relationship between the physical



Fig. 2. Mapping of atomistic structures on coarse-grained representation for models: (a) an epoxy resin monomer 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, (b) a hardener 4-methylhexahydrophthalic acid anhydride, and (c) halloysite nanotube modified by anhydride of 3-(triethoxysilyl)-propyl-succinic acid. Here the symbols in the circles correspond to the names of subsystems (coarse-grained particles) of the model.

and chemical properties of the prototype DPD-particles and characteristics of their interaction.

The hardener monomers (particle type O) were chosen as the smallest particles in the system. Epoxy monomers in the coarsegrained representation are represented by two C-type particles, bound by a covalent bond, and its deformation is described by Hooke's law

$$\mathbf{F}_{ij}^{spr} = k|r_{ij} - \sigma|\mathbf{r}_{ij}',\tag{1}$$

where *k* is the stiffness coefficient equal to $4k_BT$ (k_B – Boltzmann constant, *T* – absolute temperature), r_{ij} is the distance between particles *i* and *j*, \mathbf{r}'_{ij} is the unit vector along the direction connecting these two particles. It should be noted that in the DPD method it is assumed that $\sigma = 1$, m = 1, $k_BT = 1$.

Coarse-grained HNT model was built based on two enclosed carbon nanotubes. To assign to the HNT model additional rigidity between the particles spaced by distances $\leq 2\sigma$, additional chemical bonds between DPD particles from nearest enclosed nanotubes have been introduced. The resulting structure is shown in Fig. 2c. The inner surface of nanotubes was constructed from particles of type H, and the outer surface – from S- and P-type particles. S particles correspond to the silica surface, P – to the grafted modifier molecules.

To define the interaction parameters a_{ij} between coarse-grained particles it is necessary to calculate the Flory–Huggins parameters. For this purpose we used the extended Flory–Huggins theory. In this case, the value χ_{ii} (*i*,*j* denote DPD particle types) is given by:

$$\chi_{ii} = E_{mix,ij}/RT, \qquad (2$$

where $E_{mix,ij}$ is the mixing energy, *T* is the absolute temperature, and *R* is the gas constant. If $\chi \gg 1/2$, mixture of components is not energetically favorable [28,29]. Mixing energy $E_{mix,ij}$ corresponds to the difference in the energy of mixed and unmixed systems. In classical Flory–Huggins theory, each single component of the system occupies one lattice site, and in this case the mixing energy is defined as:

$$E_{mix,ij} = \frac{1}{2} \left(Z_{ij} \langle E_{ij} \rangle_T + Z_{ji} \langle E_{ji} \rangle_T - Z_{ii} \langle E_{ii} \rangle_T - Z_{jj} \langle E_{jj} \rangle_T \right), \tag{3}$$

here $\langle E_{ij} \rangle$ is the averaged energy of interaction between the components *i* and *j*, Z_{ij} is the coordination number, i.e. the number of molecules *j*, which can be placed around a molecule *i*. Mixing energy $E_{mix,ij}$ can be calculated by generating molecular configurations by means of Monte Carlo method (MC), followed by calculation of E_{ij} (using the PCFF force field) and Z_{ij} , and then averaging over the ensemble at a given temperature:

$$\langle E_{ij} \rangle_T = \frac{\sum_N E_{ij} e^{-E_{ij}/RT}}{\sum_N e^{-E_{ij}/RT}},\tag{4}$$

where \sum_{N} means the sum over all generated configurations (microstates), while their number *N* should be reasonably large.

The geometry of the generated configuration for a found Z_{ij} can be optimized as well as a part of the MC design scheme by changing the mutual arrangement of molecules and the calculation of the interaction energy.

To carry out these calculations of χ_{ij} , the following models of molecules and nanoparticles have been used: (1) 3,4-epoxycyclo-hexylmethyl-3,4-epoxycyclohexanecarboxylate (EP), (2) 4-methyl-hexahydrophthalic acid anhydride (curing agent, CA), (3) silica nanoparticles (SNP) with diameter 1.5 nm, (4) modified silica nanoparticles (MSNP) with diameter of 1.5 nm and grafted molecules of anhydride of 3-(triethoxysilyl)-propyl-succinic acid, see Figs. 2a and 3b, and (5) water molecules (H₂O) which are used to model the interaction of the internal surface of hydroxylated nanotubes with other system components. The parameters of the

Tabla	1
Table	

Values χ_{ij} calculated using PCFF.

	EP	CA	H_2O	SNP	MSNP
EP CA H ₂ O SNP	0 - - -	-0.2 ± 0.3 0 -	$\begin{array}{c} 1.5 \pm 0.3 \\ 1.2 \pm 0.2 \\ 0 \\ - \end{array}$	$\begin{array}{c} 37 \pm 10 \\ 46 \pm 10 \\ 87 \pm 14 \\ 0 \end{array}$	$\begin{array}{c} -31 \pm 16 \\ -9 \pm 5 \\ -13 \pm 10 \\ -0.7 \pm 1.0 \end{array}$
MSNP	-	-	-	-	0

Table 2Values χ_{ij} selected for DPD calculations.

С	0	S	Р	Н
0.0	0.0	37	0.0	1.5
-	0.0	45	0.0	1.2
-	-	0.0	0.0	87.3
-	-	-	0.0	0.0
-	-	-	-	0.0
	C 0.0 - - - -	C O 0.0 0.0 - 0.0 - - - - - - - - - -	C O S 0.0 0.0 37 - 0.0 45 - - 0.0 - - 0.0 - - 0.0 - - 0.0 - - - - - -	C O S P 0.0 0.0 37 0.0 - 0.0 45 0.0 - - 0.0 0.0 - - 0.0 0.0 - - 0.0 0.0 - - - 0.0



Fig. 3. Additional molecular systems selected for calculations of χ_{ij} parameters for the model: (a) simplified models of unmodified and modified surface of the halloysite, (b) models of unmodified and modified silica nanoparticles of diameter 1.5 nm. Here the symbols corresponded to the names of chemical elements.

calculations were the number of generated configurations *N* and the number *n* of MC steps used to optimize the geometry of generated configurations.

3. Results and discussion

Calculation of χ_{ij} parameters was performed using the PCFF foce field for $N \sim 10,000-500,000$ generated molecular configurations followed by geometry optimization during $n \sim 1000-100,000$ MC steps. The obtained results are summarized in Table 1. Negative values of χ_{ij} indicate a strong affinity of these subsystems to each other. In this case, to calculate the DPD conservative force parameters a_{ij} , the corresponding values of χ_{ij} should be set to zero [30]. On this basis, we have chosen the following values χ_{ij} collected in Table 2.

To verify the obtained values χ_{CS} , χ_{CP} , χ_{OS} , χ_{OP} , additional calculations were performed for the averaged adhesion energy density E_{ij} between ultrathin layers formed of epoxy matrix monomers and modified and unmodified surfaces of SMKS model (Fig. 3a). For $\langle E_{ij} \rangle$ we have used the formula:

Table 3 Calculated values $\langle E_{ii} \rangle$.

())	
System	E _{ij} (kcal/mol)
EP/SMKS	-0.197
EP/modif. SMKS	-0.253
CA/SMKS	-0.202
CA/modif. SMKS	-0.292

$$\langle E_{ij} \rangle = \langle (E_{ij,total} - E_i - E_j)/2S \rangle_{\rm TP}, \tag{5}$$

where $E_{ij,total}$ is the total energy of the system, E_i and E_j are the energies of subsystems, S is the cross-section area of the simulation cell. Design and simulation of nanosystems by means of the atomistic molecular dynamics (under normal conditions), was performed using the principles described in Refs. [11,31]. For calculation of $\langle E_{ij} \rangle$ we have used productive run of the length of 0.25 ns.

The results are collected in Table 3 and show that the adhesion energy density between the polymeric matrix and the surface of the halloysite nanotube has larger absolute values in the case of modified nanotubes. This result confirms that the modified HNT have better compatibility with polymer matrix precursor.

The initial states for the mixture of the precursor epoxy matrix models (prior to the polymerization reaction) and aluminosilicate nanotubes have been generated by specifying the coordinates of all components of the system randomly. The values of volume fractions of EP and CA monomers were chosen equal to 0.32 and 0.63, the volume fraction of nanotubes was equal to 0.05. The ratio of monomers EP: CA = 1:2 corresponds to the stereochemical ratio when a matrix having the largest density is obtained [16,32]. Simulation cell size was chosen to be $(24\sigma)^3$. To test the suggested DPD model, nanotubes were constructed with the overall surface functionalization 0–100%. Two variants of the initial distribution of the nanotubes have been generated – ordered (all nanotubes are oriented along the axis *OX*) and unordered (arbitrary initial orientation). Selected parameters allow to evaluate the



Fig. 5. The phase diagram of the internal state of a mixture of epoxy monomers and HNT. The maximum simulation time was 1,000,000 DPD steps.

functionalization impact on the final features of the distribution of the nanotubes prior to the reaction of epoxy resin curing.

An example of simulation cell for a system with 50% surface modification is shown in Fig. 4. Usually, the aggregation of nanotubes with the surface modification of less than 80% occurs during 100,000–150,000 DPD steps. The maximal simulation time for those systems where no aggregation has been observed was equal to 1,000,000 DPD steps. According to the results of computer simulation, the phase diagram of morphologies (internal states) of the model mixture (at fixed values of several model parameters, as indicated above) was composed in dependence on the degree of surface functionalization and on the initial (starting) configuration, see Fig. 5. As can be seen, only at very large values of degree of surface functionalization the halloysite nanotubes do not aggregate in the final state. In all cases, the initial distribution of nanotubes does not significantly affect the final state of nanosystems.



Fig. 4. An example of the internal state of the simulation cell for the system with the initial ordering (parallel orientation) of NNT: (a) snapshots showing all the components of the system and showing only HNT, (b) state of the system after 1000 DPD steps, (c) 10,000 DPD steps, (d) 100,000 DPD steps, (e) 150,000 DPD steps. Surface modification is 50%. Coloring of DPD subsystems corresponds to Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Density pair correlation function (a) and static structure factor (b) for systems with different degree of HNT surface functionalization.

We have confirmed our visual analysis by calculation of the density pair correlation function g(r) and the static structure factor I(q) (Fig. 6). One can see from these plots, that upon increasing the degree of surface modification the contribution of the smaller distances $r \leq 5\sigma$, i.e. larger $q \geq 0.2/\sigma$, decreases while the contribution of the larger distances $r \sim 10\sigma$, i.e. smaller $q \sim 0.1/\sigma$, increases – note a small broad peak at $r \sim 10\sigma$ on g(r) for surface functionalization 95% and corresponding peak at $q/2\pi \sim 0.1/\sigma$ on I(q). Taking into account that our simulation cell has the linear size $\sim 20\sigma$, the occurrence of a characteristic length scale $\sim 10\sigma$ at largest values of the degree of functionalization means the uniform distribution of nanotubes in the simulation cell.

4. Conclusions

In summary, we have developed a coarse-grained DPD model, which can be used for mesoscale computer simulations of polymer systems containing aluminosilicate nanotubes. As test calculations, we have estimated the impact of a given initial distribution of HNTs in epoxy matrix precursor (before the polymerization reaction starts, which corresponds to the initial stage of the synthesis of a nanocomposite) and degree of their surface functionalization on the aggregation of aluminosilicate nanotubes. It has been shown that the structure of the mixture of epoxy resin monomers and nanotubes is mainly determined by the surface functionalization of HNT. The results indicate that only for nanotubes with maximal degree of functionalization their uniform distribution in space has been retained.

The resulting model can be also used to study polymer precursors and nanocomposites with embedded aluminosilicate nanotubes. It should be noted that this model can be used to construct nanocomposites with polymeric matrices having different degree of crosslinking, while the nanoparticles (due to the surface modification) can also form intermolecular bonds with the monomers of the matrix.

There are several experimental studies in the literature where the role of surface functionalization of the HNT surface for the improvement of their dispersion has been studied [6-8,4,9,10]. Actually, it is quite difficult to explicitly control in the experiment the degree of functionalization of HNT surface as the fraction of the surface covered by the modifier groups or molecules. However, it is possible to control this parameter implicitly by changing the pH of the solvent [6] or using different modifiers [7]. The only exception which we know is probably Ref. [10] where the time of modification was the control parameter. Therefore, we can compare our results with the experimental ones only quantitatively, and we really observe such an agreement because all experimental evidences support the conclusion that the increasing the HNT surface modification leads to improvement of HNT dispersion, i.e., our model is able to catch this important feature of polymer/HNT composites.

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