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Thermal Properties and Topology of Epoxy Networks: A Multiscale Simulation Methodology

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ABSTRACT: We present a novel hierarchical multiscale methodology aimed at generating the atomistic structure of epoxy networks and predicting their properties and topology. Our approach combines several computational techniques and consists of four separate procedures: (1) mapping of the polymerizing monomers onto a coarse-grained representation using the method of neural-gas networks, (2) cross-linking the coarse-grained monomers at mesoscale by applying dissipative particle dynamics and a probabilistic reaction scheme, (3) reverse mapping of the coarse-grained polymer network to a fully atomistic representation, and (4) simulation of the atomistic model by means of molecular dynamics technique. As a case study, we simulate DGEBA + DETDA epoxy network formation and analyze the thermal properties and the network topology. It was found that the parameters used for generating the atomistic structures (degree of coarse graining in our case) can significantly influence the network topology and properties. Moreover, we show that rather big simulation boxes are necessary to obtain the proper local structure of an epoxy resin.
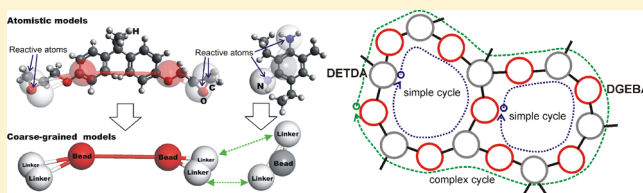
I. INTRODUCTION

Epoxy resins are thermosetting polymers with a very complex three-dimensional structure; they are obtained from reaction between epoxy monomers and hardeners. Since both epoxy and hardener molecules usually have multiple functionalities, the resulting structure is, in fact, a giant hyperbranched molecule. Epoxy resins are important industrial material due to their outstanding thermal, chemical, electrical, and mechanical properties.[1] Also, they are often used as matrixes for composite materials. While the properties of these systems have been studied experimentally rather extensively, there are still many open questions due to the fact that the experimental studies do not always lead to unambiguous conclusions. Computer simulation can be helpful in overcoming this problem, because it allows one to fine-tune the conditions under which the system is studied.

A major challenge in the simulation of epoxy resins and epoxy-based composites is to generate a reliable structure of a highly cross-linked polymer network. It should be stressed that an irregular polymer network is one of the most complex molecular objects. This is because cross-linked polymers produced both industrially and in laboratories are a typical "black box", since their structure and topology are unknown. This circumstance makes it very important to work out verifiable models, specific simulation methods, and efficient software capable of analyzing and monitoring network formation processes and network structure. Molecular processes occurring in these systems may theoretically only

be rigorously followed by direct molecular level simulations, e.g., atomistic molecular dynamics (MD).

In the majority of the simulation schemes used for obtaining cross-linked epoxies, the cross-linking process occurs at atomistic scale. For example, in an early work by Yarovsky and Evans all the cross-links were created simultaneously ("static approach").[2] Such an approach works very fast; however, the resulting network has unrealistically high internal stresses. Wu and Xu proposed a method in which only one cross-link per step is created, and the structure is equilibrated between the cross-linking steps.[3] Heine et al. used a method in which covalent bonds between polymerizing monomers are formed dynamically during MD simulation,[4] and a single bond can occur when two reactive atoms approach each other at a certain distance. A soft relaxation bond potential was used in order to shorten the newly formed bonds to their equilibrium length. One can also mention a number of other publications which address similar simulation models and schemes (see refs 5−11 and references therein).

There are some features of polymer networks and network-based composites that make them extremely difficult to simulate at the atomistic level of detail. Real cross-linked polymer materials relax very slowly relative to the time scales accessible by molecular simulations. As a result, a serious problem is associated with the achievement of the equilibrium

state for sufficiently large systems at realistic densities and without unrealistically strong internal stresses. Another difficulty is related to the simulation of irreversible cross-linking process: it is rather problematic to achieve a high degree of cross-linking for a realistic network model. In general, one can say that atomistic simulations of sufficiently large cross-linked systems for long times remain currently an uphill fight within the framework of a single simulation method. In order to overcome the mentioned problems, a multiscale modeling strategy, which combines complementary computational techniques, has to be utilized correspondingly.

In their pioneer work, Komarov et al. developed a four-stage multiscale approach, which combines mapping/reverse mapping schemes, a network building method based on Monte Carlo simulation, and atomistic molecular dynamics.[12] In this work, the concept of "mesoscale chemistry" was applied for the first time for generating complex network-like structures at the atomistic level of detail, combining molecular and coarse-grained simulations. A similar simulation scheme was used by Liu et al.[13] Importantly, multiscale simulations allow one to achieve practically any desirable conversion degree relatively easily. Furthermore, the resulting network is not stressed due to its fast relaxation at mesoscale. However, the multiscale methods mentioned above suffer from complexity of their implementation as well as the problems associated with universality: if one wants to change the system (for example, by changing the monomers or by adding some filler particles), it is necessary to adjust the coarse-grained model by hand, which sometimes is a nontrivial task.

It should also be noted that while a number of works on atomistic simulations of epoxy resins have been published, there was no attempt to investigate the network topology more or less thoroughly. At the same time, this issue seems to be rather important: even networks without internal stresses can have incorrect topology (compared to that obtained in real experiments), which could manifest itself in incorrect properties of the model resin.

Therefore, the first goal of this work is to develop a universal multiscale simulation scheme that would allow one to generate the cross-linked structure for a wide variety of systems made from multifunctional monomers. The second goal is to use the developed methodology for studying the network topology and the effect of the parameters used to generate the atomistic structure on the topology and thermal properties of highly cross-linked resins.

II. SYSTEM DESCRIPTION

As a case study, we simulated epoxy resins composed of the epoxy monomer DGEBA (diglycidyl ether of bisphenol A also known as EPON 828) and the hardener DETDA (diethylenetoluenediamine). DGEBA can be cross-linked in the presence of curing agent to yield one of the frequently used epoxy polymers; Figure 1 shows the corresponding structures and reaction scheme. Since this system is an important engineering matrix material, it has been extensively studied experimentally[14−18] and by means of computer simulations.[19]

The ratio between DGEBA and DETDA in all the samples studied here was always stoichiometric: two DGEBA molecules per one DETDA molecule.
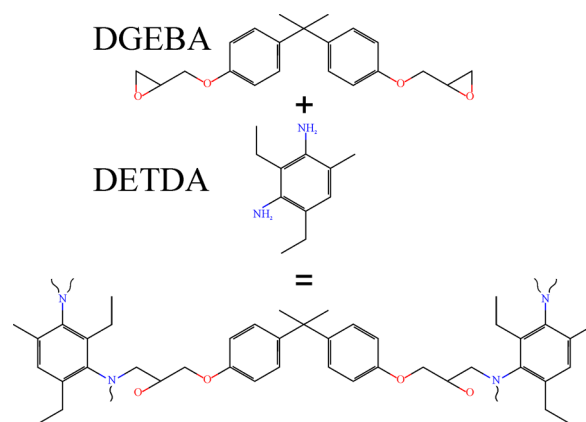
Figure 1. Polymerizing monomers and the scheme illustrating reaction between them.

III. MULTISCALE SIMULATION

The multiscale simulation scheme used in this work is somewhat similar to that proposed by Komarov et al.[12] It combines information-theoretic methods, coarse-grained (dissipative particle dynamics, DPD) and fully atomistic models and provides coupling of different length scales of simulation together.

A. Automatic Coarse-Graining: Neural-Gas Algorithm. One of the most important parts of our multiscale simulation strategy is the construction of a coarse-grained system. To do this adequately, we have developed an automatic approach based on the method of neural-gas (NG) networks, the so-called topology-generating network. As a starting point, we used the scheme described in ref 20, which was successfully applied for construction of the coarse-grained structures of complex biomacromolecules.[21] The method can be summarized as follows: (1) Atomic mass distribution serves as a target probability distribution. (2) Neural-gas algorithm and competitive Hebbian learning rules are employed to optimize the positions of coarse-grained (CG) sites. (3) Connectivity of the CG sites is described by a connectivity matrix $\mathbf{C}(i,j)$. (4) The number of CG sites is defined by the ratio $N_{CG} = (R/R_{min})^b$, where R denotes the gyration radii of molecules, R_{min} is the minimal gyration radius among all the gyration radii of the molecules in the system, and b is a coarse-graining parameter that defines coarse-graining level (spatial resolution).

The method of NG networks is a kind of adaptation iterative algorithm in which the neighborhood of a set of points ("neurons") is changed each adaptation step according to the given input (atomic mass distribution in our case). The process imitated by this method has a physical analogy of a gas spreading in a closed space. NG networks combine two specific learning paradigms—own NG learning and competitive Hebbian learning. For more details, see ref 20.

To simulate chemical reactions at mesoscale, we have developed a concept of *composite DPD particles*. To this end, we introduce two different types of CG sites: *beads* and *linkers*. Beads are normal CG particles; they participate in all site−site interactions. On the other hand, linkers are *semivirtual sites*; they participate in intramolecular interactions only (namely, in bond stretching and valence angle bending interactions) but can form covalent bonds; that is, they can react. The NG-based algorithm described above is applied to define the position of the CG sites (beads) only, while the positions of the linkers coincide with the positions of the reactive sites of molecule.

Since our system contains two types of polymerizing molecules, DGEBA and DETDA, and the DETDA molecule is the smallest one, it is always represented by one bead and two linkers. The linker positions coincide with the positions of the corresponding nitrogen atoms (Figure 1). With the coarse-graining level being a free parameter of the model, the DGEBA molecule can be represented by a different number of beads N_{CG}, depending on the b value. In this study, we set $N_{CG} = 1, 2, 3,$ and 8. The number of linker particles was always equal to 4 for each DGEBA molecule (since both carbon and oxygen atoms from an epoxy cycle are reactive). The coarse-grained structures for $N_{CG} = 2$ are shown as an example in Figure 2.
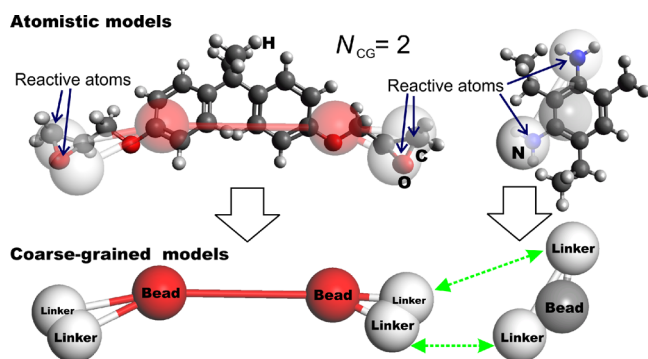
Figure 2. Coarse-grained structures of DGEBA and DETDA for N_{CG} = 2.

Note that, in principle, any molecule or even discrete particles used as filler in composite materials can be coarse-grained with this technique; therefore, properties of polymer nanocomposites can be studied. Also, since the algorithm of coarse-graining is fully automatic, the results do not depend on any by hand modifications, which improves the reproducibility.

B. Network Building Procedure. We used the DPD method to simulate chemical reactions at mesoscale and equilibrate the structure of networks. DPD is a version of the coarse-grained molecular dynamics adapted to polymers and mapped onto the classical lattice Flory–Huggins (FH) theory.[22−25] This is a well-known computational technique, which has been used to simulate various types of polymer systems, including epoxy resins.[13] We therefore do not give here more detailed description of it; more detail can be found elsewhere.[25]

Coarse-grained structures of the polymerizing molecules were used to generate the polymer network at mesoscale. The CG molecules were initially placed randomly into the simulation box. The box size was taken so that the corresponding atomistic structure at any of the studied coarse-grained levels would have the size of $100 \times 100 \times 100$ Å^3 (if other not indicated) at a density of 1 g/cm^3. The number density of DPD beads was fixed at 3. Having these quantities, one can easily calculate the scale factor between DPD length unit and real length unit, which varied from 6.5 to 10.5 Å, depending on the coarse-graining level (the coarser the model, the more angstroms are represented by one DPD length unit).

The FH binary interaction parameters χ and the corresponding DPD interaction parameters $a_{\alpha\beta}$ are directly related to the Hildebrand single-component solubility parameters δ_α and δ_β, which are 20.3 and 21.8 (J/cm^3)$^{1/2}$ for DGEBA and DETDA, respectively (we used the Askadskii method[26] to estimate these

parameters). Using the reference molar volumes V_m of the DGEBA and DETDA molecules, we obtain $\chi = 0.208$. Such a small value of χ means that the DGEBA/DETDA system may be considered as an athermal blend (no heat of mixing). Therefore, for simplicity, we set $a = 25$ ($\chi = 0$) for all the intermolecular conservative interactions.

After that the chemical reactions between monomers were simulated. In our model, which is based on the concept of "mesoscale chemistry", reactions are probabilistic; the polymerization procedure was similar to that described in our previous works.[27−32] At regular intervals, the distance between reactive sites (linkers) is calculated and compared to a capture radius R_c. Pairs of reactive sites within the capture radius form a bond with some reaction probability, which is defined by reaction rate constants and adjusted to keep quasi-equilibrium conditions. Only the linker particles associated with the nitrogen atoms in DETDA and the oxygen atoms in the epoxy cycles of DGEBA were capable of forming bonds between each other and each of the nitrogen-associated linkers could form bonds with two oxygen atoms. The systems were being cross-linked until the desired conversion degree (CD) of 98% was reached (i.e., 98% of all possible bonds were formed). After that the system was additionally equilibrated for 1 million DPD steps to ensure there were no stressed bonds and/or angles. Because of the fact that the relaxation takes place at mesoscale and soft DPD potentials are used, such a nonstressed structure can easily be reached, while for MD-based cross-linking methods it is a problem to achieve a fully relaxed state.
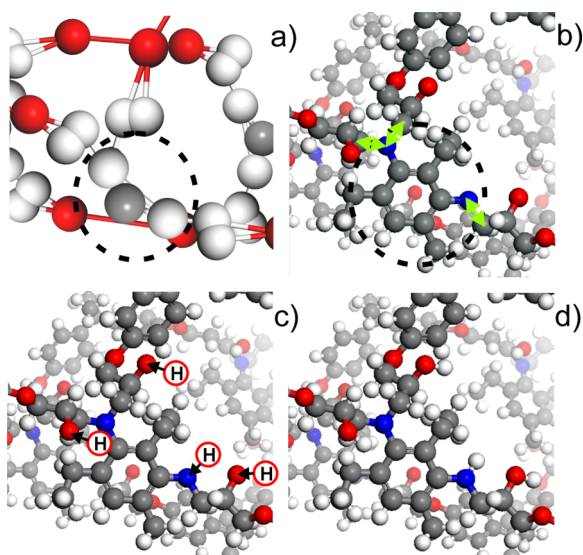
C. Reverse Mapping and "Chemical Cleaning". For the coarse-grained network structures generated and relaxed as described above, we carried out a reverse mapping procedure and another specific procedure, which we call "chemical cleaning". Because the positions of the CG sites were defined in correspondence with the atom positions of the polymerizing molecules, the reverse mapping is relatively straightforward. It is based on the least-squares best superposition of two coordinate sets (monomer-by-monomer) via the quaternion method. Chemical cleaning is a cascade of bond redistributions; in particular, structural changes in molecular geometry occur when epoxy cycles open. Chemical cleaning includes also recalculation of the partial charges, setting the correct force field types for atoms depending on their surroundings, adding hydrogen atoms, etc. (see Figure 3). Local stresses and close contacts between atoms as well as too long/short chemical bonds connecting monomers and bond/dihedral angles are left to relax out by standard atomistic MD simulations.

In order to start normal MD simulations, we should do the following: (1) identify force field types for the atoms taking into account their surroundings, (2) recognize all internal coordinates (bonds, angles, dihedral angles, out-of-plane elements, etc.), and (3) select the corresponding force field parameters from an existing database. It should be stressed that our program code can automatically do all these manipulations, both "chemical cleaning" and force field typing.

For the MD calculations, we used the class II consistent force field PCFF (polymer consistent force field).[33] As a member of consistent force fields family, it was parametrized against a wide range of organic compounds. PCFF is applicable for many synthetic polymers, melamine resins, polysaccharides, lipids, nucleic acids, etc.

D. MD Simulations. The properties of the obtained atomistic systems were studied by MD simulations using the LAMMPS package.[34] In particular, the specific volume as a

Figure 3. An example showing the stages of the reverse mapping and chemical cleaning procedures. (a) Coarse-grained model of a cross-linked network. DETDA monomer is marked with a dashed circle. (b) Reverse-mapping procedure with subsequent recovering of formed cross-links at the atomistic scale (green arrows). (c) Free valences of nitrogen and oxygen atoms are filled up with hydrogen atoms, shown by red circles. (d) Resulting atomistic model.

function of temperature, the coefficient of volume thermal expansion, and the glass transition temperature were calculated.

The network samples obtained at different N_{CG} were first well equilibrated. After that, productive MD runs under *NPT* conditions with a Nosé–Hoover thermostat/barostat were performed. The systems were gradually cooled from 900 to 150 K at $P = 10^5$ Pa during 15 ns. The high temperature interval between 900 and 800 K was used for additional relaxation of local elastic strains. In this study, we focus on the temperature dependence of the system density.

IV. PREDICTED PROPERTIES

Having the temperature dependence of the inverse system density (i.e., the specific volume) ρ^{-1}, the coefficients of volume thermal expansion (CVTE) and the glass transition temperature T_g can be easily calculated. From the slope of a plot of ρ^{-1} vs T it is possible to determine quite clearly two CVTEs: for the high-temperature region ($T > 600$ K) and the low-temperature region ($T < 300$ K). The intercept of the best-fit lines to the simulated data in these regions gives an estimate of T_g. The values of CVTEs and T_g obtained at different N_{CG} are summarized in Table 1. The system densities predicted at 300 K for all the network samples were the same within statistical error, and therefore they are not included in Table 1. To test the reproducibility of the results, two additional systems with

Table 1. Predicted Properties of the Systems for Different N_{CG}

| N_{CG}	CVTE, 1/K ($T > 600$ K)	CVTE, 1/K ($T < 300$ K)	T_g, K
1	3.1×10^{-4}	1.37×10^{-4}	435
2	2.8×10^{-4}	1.33×10^{-4}	410
3	3.1×10^{-4}	1.37×10^{-4}	443
8	3.8×10^{-4}	1.42×10^{-4}	475
experiment	5×10^{-4} [14]	2.4×10^{-4} [14]	441–476 [14,17,18]

N_{CG} = 2 and 8 were generated, starting from different initial random distributions of reactive species. The difference between obtained values was as small as 1–2%.

In general, we find a more or less satisfactory agreement with experimental data for T_g but significant differences for CVTEs. It is known that atomistic simulations typically give higher T_g and lower CVTE compared to experimental data due to very high cooling rates used in simulations. [19,35,36] Table 1 shows that the T_g values obtained in our multiscale modeling for N_{CG} = 1–3 are even lower than those measured experimentally. Without dwelling on other details responsible for the differences between simulation and experiment, we focus on the fact that the predicted values of CVTE and T_g depend quite strongly on the degree of coarsening adopted for polymerizing molecules. Since the average potential energies per atom were found to be nearly the same for all the systems and the force field used in our simulations was always the same, we incline to attribute this fact to topological differences of the generated networks.

V. NETWORK TOPOLOGY

A polymer network can be treated as a graph. Specific methods for analyzing network topology using graph theory were applied in this study. A graph is a mathematical object involving points (vertices) and connections (edges). [37] For an epoxy network it is convenient to treat each molecule as a vertex and each cross-link between them as an edge. While vertices associated with DGEBA and DETDA have different maximum number of incident edges (i.e., an edge which has a given vertex as one or both of the end-vertices), four edges for DETDA and two edges for DGEBA, we will not distinguish between them in network topology analysis. Therefore, the epoxy networks are represented by graphs with one type of edges and one type of vertices. The total number of vertices for the systems of size $100 \times 100 \times 100$ Å^3 is typically about 2000.

The simplest characteristic that can be studied is the number of multiple edges (an edge is multiple if there is another edge with the same end-vertices). Such situation occurs when a DGEBA molecule reacts with a single DETDA molecule with both of its epoxy cycles (Figure 4). We found that such structure is stable: no stressed bonds, bond angles, dihedral angles and out-of-plane elements were detected. It means that this structure can arise during curing.
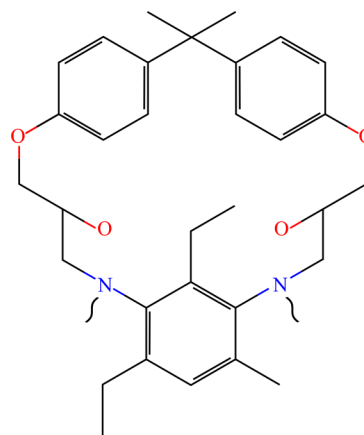
Figure 4. Atomistic representation of the multiple edge situation: a DGEBA molecule has reacted with a single DETDA molecule with both of its epoxy cycles.

Analysis of such structures showed that depending on N_{CG}, the number of multiple edges significantly differs: while for N_{CG} = 2 the number of such edges is relatively low, <0.1%, for N_{CG} = 8 their content in the system is much larger and is close to 5%. At N_{CG} = 1 and 3, their amount is about 0.2−0.3%. It should be noted that such edges (i.e., cross-links) are basically "dead ends"—they do not participate in the polymer network connectivity.

If we consider a polymer network as a complex graph, it is reasonable to extract from this graph different subgraphs (molecular fragment), for example, such subgraphs as simple chains, cycles, trees, etc. To this end, it is necessary to construct a matrix of topological distances between all possible pairs of vertices (the distance between two vertices is the length of the shortest walk between them).[37] The most important element in a graph with a large number of edges is a cycle. Cycles are dominant structural elements in a highly cross-linked network. A cycle is by definition a walk of length at least 1 such that no edge occurs more than once, no internal vertex is repeated, and the initial vertex is also the final vertex.[37] We will focus on the so-called *simple cycles*. We define them as cycles in which the lengths of the walks between any two vertices along the cycle are equal to the topological distances between those vertices. In other words, they are cycles for which no shorter walk between its vertices compared to that along the cycle can be found in the graph. Such structures seem to be more informative than "*complex cycles*" because they have more transparent meaning: they are the shortest cycles that can characterize the network structure. An example of the difference between "simple" and "complex" cycles is shown in Figure 5.
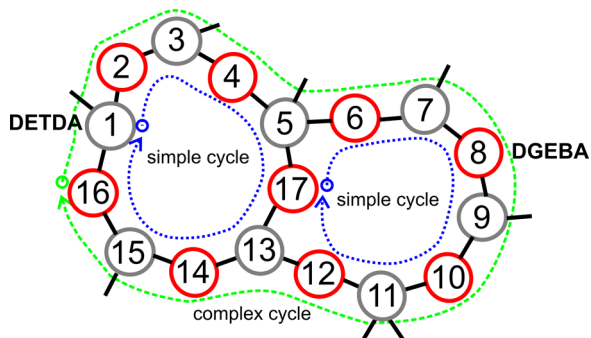
Figure 5. An illustration of simple and complex cycles. The big cycle is not simple because the shortest walk between vertices 5 and 13 is not a part of it.

First, we studied the effect of the system size on the distribution of simple cycle lengths. To do that, we additionally generated three coarse-grained systems in the simulation boxes of size 150^3, 200^3, and 250^3 Å³ at N_{CG} = 2 and CD = 98% and analyzed their topology in comparison with the smaller system (100^3 Å³). The simple cycle length distributions are presented in Figure 6.

The results reveal an interesting feature: while for the smallest system of the size 100^3 Å³ the distribution is unimodal, an increase in the system size leads to a pronounced bimodality. Starting from the box size of 150^3 Å³, the main peak located at smaller cycle lengths does not change its position and height, while the second peak moves toward bigger cycles. This can be explained by the fact that the first peak corresponds to the local network structure, while the second one is related to the presence of periodic boundary conditions. The latter peak
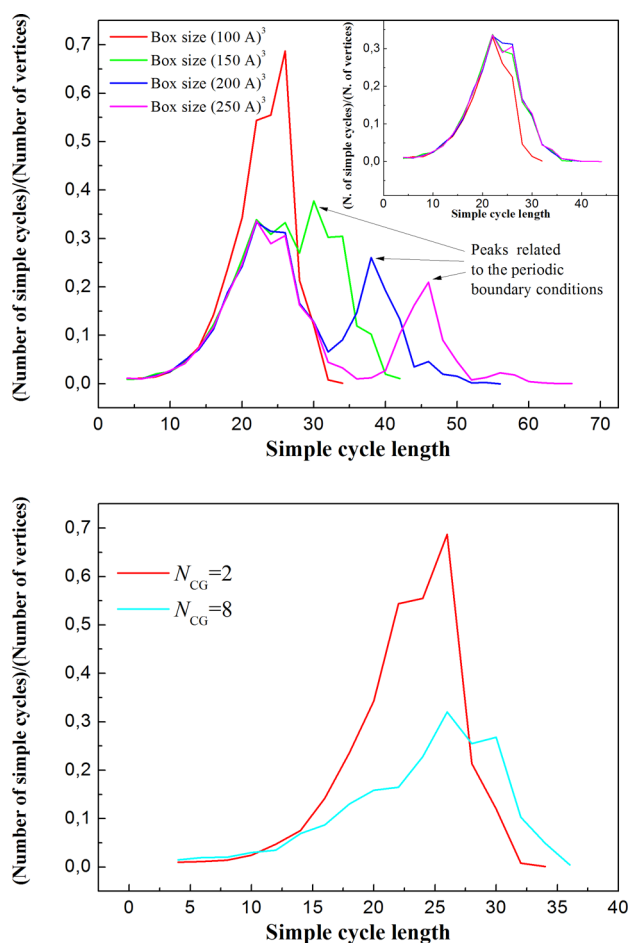
Figure 6. Distributions of simple cycles lengths for (top) different system sizes for N_{CG} = 2 and conversion degree 98.0% (inset: the same distributions but without the cycles which pass through periodic boundary conditions) and (bottom) the system of size 100^3 Å³, at N_{CG} = 2 and 8. In all cases, conversion degree is equal to 98%.

contains only the cycles which pass through periodic boundary conditions, and therefore, their length depends on the box size—the bigger the box, the longer a cycle needs to be to pass through the whole box. The position of this peak is proportional to the box size L, the behavior which is clearly seen in Figure 6. Indeed, the peak is not observed in the smallest system because the simulation box is too small and the peaks are simply overlap, resulting in a single peak of increased height.

In order to test if this is the case, we removed from the distribution all the cycles which pass through periodic boundary conditions—if we start to walk along such cycle starting from a vertex, we will return to that vertex not in the system image we started in. The result is shown in the inset of Figure 6 (top). It is seen that for the boxes of sizes from 150^3 to 250^3 Å³ the distributions practically coincide. However, the smallest system is clearly insufficient to reproduce the local topology just because it is too small for proper number of long cycles to exist. Therefore, one should use rather big systems in order to get the proper local topological structure of epoxy resins. In this regard, we would like to emphasize that in the majority of simulation works on epoxy resins the system size was too small, significantly smaller than 100^3 Å³. Apparently, there might be some exceptions, i.e., the properties which mainly depend on the local structure of polymer network, and one of such

exceptions is the thermal properties. Indeed, we observed no significant differences between the values of CVTE calculated for boxes of 100^3 and 150^3 Å^3.

Finally, we analyzed the effect of the degree of coarsening on the system topology. Figure 6 shows the distribution over simple cycle lengths calculated at N_{CG} = 2 and 8. The values of N_{CG} = 2 and 8 were chosen because they lead to the most pronounced differences in the thermal properties (see Table 1). It is apparent from Figure 6 that the network topology of these systems is also very different: the number of simple cycles at N_{CG} = 2 is almost twice larger than that for N_{CG} = 8, while the system with N_{CG} = 8 contains slightly more long cycles. One of the possible explanations for that may be hidden in the fact that there are much more multiple edges in the system with N_{CG} = 8, which results in an effectively less cross-linked system.

Overall, we conclude that the parameters used for generating the atomistic structures (degree of coarse graining in our case) can play a dramatic role in the formation of network structure. One should also note that this study was not focused on describing how to find a proper coarse-graining degree (because it could depend on the used coarse-graining model, for example) but in the first place tried to shed some light on the underlying problem of the changes in the calculated properties—the topology of the matrix, which can be influenced by the cross-linking procedure in an unpredictable manner.

VI. CONCLUSIONS

We have developed a new multiscale simulation methodology for generating of atomistic structures of highly cross-linked epoxy resins and predicting their properties. Our approach consists of the following stages: (1) Using the proposed concept of composite particles, atomistic structures of the molecules under consideration are approximated by mesoscopic particles composed of nonreactive beads and reactive linkers. To this end, a "direct projection" scheme based on the neural network method (growing neural gas algorithm) is employed. The procedure has a free parameter: the coarse-graining level that defines the number of beads N_{CG} in big molecules with respect to the smallest molecule. (2) Mesoscopic monomers react with each other and form a polymer network until the desired conversion degree is reached. The DPD method is used to simulate this process. (3) After an equilibration at mesoscale, an automatic reverse mapping is applied to recover the atomistic structure of the system. (4) A fully atomistic MD simulation is performed for predicting the materials properties. One of the central ideas evolved in the present work is related to the concept of "mesoscale chemistry". We stress that in many cases the only way to construct a cross-linked polymer material is to imitate the polymerization of appropriate monomers at mesoscale. This methodology can be used to simulate a wide variety of materials, including polymer nanocomposites.

Using the developed computational technique, we have studied the thermophysical and structural properties of highly cross-linked epoxy systems composed of diglycidyl ether of bisphenol A (DGEBA) as resin and diethylenetoluenediamine (DETDA) as curing agent. It was found that usage of different parameters of cross-linking (namely, the number of beads which represent each DGEBA molecule) can lead to significantly different properties, such as the coefficients of volume thermal expansion and glass transition temperature.

In order to explain the differences, the epoxy network was treated as a three-dimensional graph and its topological properties were analyzed. It was shown that the graphs generated at different N_{CG} contain different numbers of multiple edges, i.e., events when a DGEBA molecule reacts with a single DETDA molecule with both of its epoxy cycles. For studying more complex topological elements, we proposed to analyze so-called simple cycles, that is, cycles in which the lengths of the walks between any two vertices along the cycle are equal to the distances between those vertices. It turned out that the cycle length distributions are significantly different depending on N_{CG}: the number of cycles at N_{CG} = 2 is almost twice larger than that for N_{CG} = 8, while the system with N_{CG} = 8 contains slightly more long cycles.

We have also studied the effect of the system size on the distribution of simple cycle lengths. It was shown that there are two types of cycles: the first type describes the local structure of the resin, while the second one is related to the presence of periodic boundary conditions. If the system is not large enough (less than about 150^3 Å^3 for the studied resin), the periodic boundary conditions can dramatically affect the local network topology.

Therefore, the following conclusions can be drawn:

(1) Cross-linking algorithm (i.e., a set of rules and parameters which is applied in order to generate bonds in the system) has a significant influence on the network topology and, as a result, on the materials properties. It should be true for every cross-linking algorithm, including those based on MD simulations, as the rules of bond formation used in such algorithms are always artificial. This problem is overlooked in the existing literature.

(2) In order to get the proper local structure of an epoxy resin, it is necessary to use rather big simulation boxes (no less than ≈150 × 150 × 150 Å^3 for the studied resin), while in the majority of works on epoxy resins simulation the system size is likely too small. It should be noted, however, that for the thermal properties studied here we did not observe significant changes upon increasing the system size. Nevertheless, it may well be that other materials properties or other cross-linked systems would be much more sensitive to the system size.

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The authors declare no competing financial interest.

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