

# Construction of self-healing PDMS materials models by supercomputer MD simulations\*

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To investigate self-healing and another properties of PDMS based materials we elaborated a computational procedure to obtain a three-dimensional atom-level structure of these multicomponent polymer materials. We obtained several condensed material structures from gas phase mixtures of the required components using the MD simulation performed on the “Tornado” supercomputer. In the obtained structures, we reproducibly observed a formation of ionic aggregates which are the prominent nature of ionomers, but in the case of PDMS materials, they were found to have a more complex structure with inner and outer surrounding layers.

*Keywords:* MD simulation, supercomputer, self-healing materials, PDMS.

## 1. Introduction

Self-healing materials with their capability to heal emergent mechanical defects are of increasing interest as a component of the sustainable development concept due to their increased durability and service life with reduced material waste [1]. They are expected to be widely used in different areas and devices [2]. Materials on the basis of polydimethylsiloxanes (PDMS) have demonstrated a high self-healing efficiency and a wide range of mechanical properties, thus being a very perspective class of such kind of materials [3]. The properties of known PDMS materials are described to be sensible to qualitative and quantitative composition of a pre-polymerization mixture, and this dependence is not always incremental and obvious. Thus, any further directed material development would require a reliable model of a structure-properties relationship for these polymers. The first stage of such a model would be an atomistic three-dimensional structure of this type of materials. However, irregular structure of polymer materials make them inexpedient objects for diffractional and other experimental methods.

In this research we aimed to adjust the MD simulations protocol in order to provide reliable structures for this class of self-healing materials and shed some light on the nature of self-healing mechanisms. Noteworthy, the starting structure for the simulation is a crucial point for the reliability of the molecular dynamic model. The available proprietary software for initial polymer cell construction rely on different probabilistic algorithms which, in fact, arbitrary mix the building blocks. This approach does not take into account chemical interactions that guide the self-organisation of a modelled material, which could play the crucial role in a mutual arrangement of polymer chains and other system components. So, it is critically important to start the MD simulations from the structure that was found as a minimum on a potential energy surface via virtual sliding on it guided by intermolecular interactions between the polymer system components. To carry out this, we elaborated an MD simulation protocol that in basic principles resembles some kind of the simulated annealing protocol [4], but heating and the temperature value here is a real kinetic energy that provides overcoming potential energy barriers and movement of the system towards the most optimal structure. Upon this protocol, the system was first heated to a high temperature and then slowly cooled down to the ambient temperature, during which molecules and ions aggregated according to intermolecular interactions modelled by a force field.

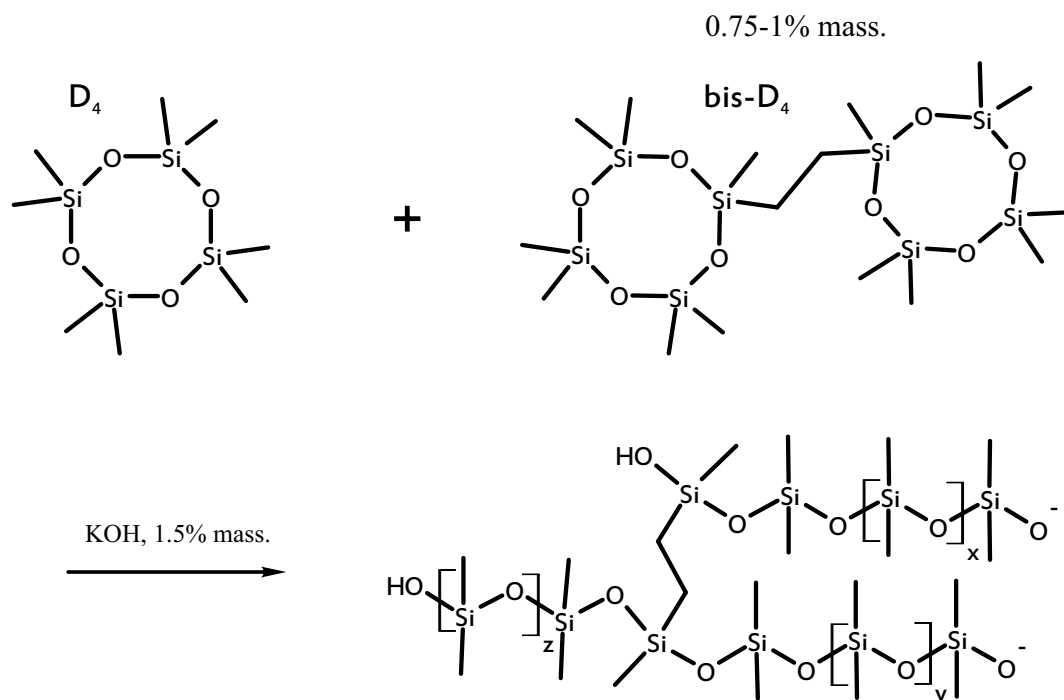
The first materials which were aprobed in our protocol were so-called examples of the

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“siloxane equilibration” rubber. It is obtained by anionic polymerization of octamethylcyclotrisiloxane molecules D4 with slight admixture of bis-D4, a product of a radical recombination of two D4 molecules with a C-C bond formation, that provides ethylene crosslinks in the resulting material (Fig. 1). The “siloxane equilibration” material also demonstrated a significant self-healing ability depending on the bis-D4 proportion [5, 6].

Our approach enabled to observe aggregation of positively charged counterions and self-organisation of charged and polar groups and molecules around these aggregates. These structures assembled reproducibly in different cells with varying composition and in different MD recalculation with randomly distributed components owing to the thermal interfusion.



**Figure 1.** Polymerisation reaction for one of the “siloxane equilibration” material with bis-D4 admixture

## 2. Methods

### 2.1. System construction

The pre-condensation structures were constructed on the basis of mass ratio between D4, bis-D4 and initiator (KOH). Average chain lengths were calculated from the monomer/initiator ratio for every system. The chains were generated in the system with lengths distributed according to the Poisson distribution, and positioned in the cubic cell at a steady pace from each other in every three dimensions.

To obtain a reliable three-dimensional structure *in silico*, the cell had to contain enough polymer molecules to create a phase volume where all the chains had enough space to unfold and intertwist without artificial restrictions by borders of the cell (i.e. in a cell with insufficient amount of molecules, the polymer chains would be restricted and forced to adopt a globule-like conformation, which would be an artifact and distort the model). Thus, there could not be less than 2 molecules in every dimension in the initial cell before condensation, and space adopted by any molecule in the final condensed phase should be no more than half of the edge of the final

condensed cell. The molecules should be evenly distributed in the cubic cell for further isotropic condensation. Therefore, after several preliminary attempts of system construction, every cell contained 216 polymer chains, among which only 11 had an ethylene crosslink originated from the bis-D4 reagent. They were distributed in the cell dimensions as  $2 \times 6 \times 18$ . The number of chains in every dimension of the cell and in total were selected in order to reproduce the required D4/bis-D4 ratio. The typical init cell size was around 38 nm.

The configuration around the ethylene crosslink from bis-D4 molecule may be di-substituted (as it is usually depicted on typical chemical formulas of the “siloxane equilibration”, when every Si atom neighbouring to the crosslink is connected to one PDMS chain and one -OH group; so, the crosslink is substituted by 2 PDMS chains), tri-substituted (with only one -OH group, as it is depicted on Fig. 1) and tetra-substituted (without -OH groups in the crosslink surroundings). Though in our program di:tri:tetra ratio is tunable, we made it 1:1:1 for all the systems to observe the behavior of every variant of the crosslink configuration.

All these procedures were carried out by the Python script applying the *cmd* module.

After that, randomly distributed ions and water molecules were added to the cell using *gmx genion* and *gmx solvate* instruments of GROMACS software, respectively. In total, the systems contained from 112.9 to 115.6 thousands of atoms.

## 2.2. MD simulations

The molecular mechanical models were prepared using the General Amber force field [7]. The missing covalent force field parameters for the “siloxane equilibration” monomers were extracted from DFT calculations with M06-2X/6-311++G\*\* basis, along with organosilicon compounds parameters from [8]. Partial charges for these residues were assessed using the RESP model [9].

The MD simulations were carried out by GROMACS software [10,11], version 2019.4. The integration time step was 2 fs with writing coordinates to the XTC trajectory file every 10 thousand steps. The LINCS algorithm controlled all the bonds lengths during the simulations [12]. The velocity rescaling thermostat with additional stochastic correction [13] was applied for the temperature control, while Berendsen barostat [14] maintained pressure in NPT simulations. Long-range electrostatic interactions were treated by Ewald particle mesh method with the sixth order of interpolation and a 0.1 nm grid step [15].

Every MD simulation was preceded by a geometry optimisation using the Broyden-Fletcher-Goldfarb-Shanno method [16]. The general protocol of molecular modeling is described in (Table 1).

## 2.3. Details of supercomputer calculations

The size of the system cells (113-116 thousands of atoms) and the required lengths of MD trajectories (from 20 to 500 ns) required significant computational sources with deep parallelisation. So, all the MD simulations of this work were performed using the “Tornado” supercomputer [17] on 24 CPU nodes (Intel Xeon 5680X, 6 cores, 3.33 GHz) for every single simulations. The performance in every trajectory calculation is given in Table 2. The NVT dynamics proceeded a bit slower due to a high load imbalance (up to 60%), but these were the shortest simulations in all the protocols. This could be explained by an intensive particle exchange between the domains, into which the cell is divided for the parallel calculation, so changing of particle assignment to a node occurred in larger quantities. The domain decomposition of the cell volume between the nodes was  $2 \times 3 \times 4$  in all the cases.

**Table 1.** MD simulation protocol applied for the “siloxane equilibration” materials structure obtaining. All the simulations and energy optimizations are described sequentially

| № | Time                | Temperature     | Pressure |
|---|---------------------|-----------------|----------|
| 1 | L-BFGS optimization |                 |          |
| 2 | 20 ns               | 1073 K          | NVT      |
| 3 | L-BFGS optimization |                 |          |
| 4 | 3 ns                | 1073 K          | 30 bar   |
| 5 | 50 ns               | 1073 K to 298 K | 30 bar   |
| 6 | 50 ns               | 298 K           | 30 bar   |
| 7 | L-BFGS optimization |                 |          |
| 8 | 500 ns              | 298 K           | 1 bar    |

**Table 2.** Performance of the MD simulations of the PDMS-bases systems on the “Tornado” supercomputer, ns per day. “WC” denotes water content in mass. %. *NVT* denotes the first simulation at a constant volume and 1073 K, *NPT cond.* – the second one with the temperature decrease, *NPT final* – the final 500 ns one under ambient conditions

| Trajectory | WC, 0% | WC, 0.47% | WC, 1.4% |
|------------|--------|-----------|----------|
| NVT        | 30.8   | 31.3      | 31.1     |
| NPT cond.  | 40.4   | 42.1      | 42.2     |
| NPT final  | 42.2   | 41.9      | 42.2     |

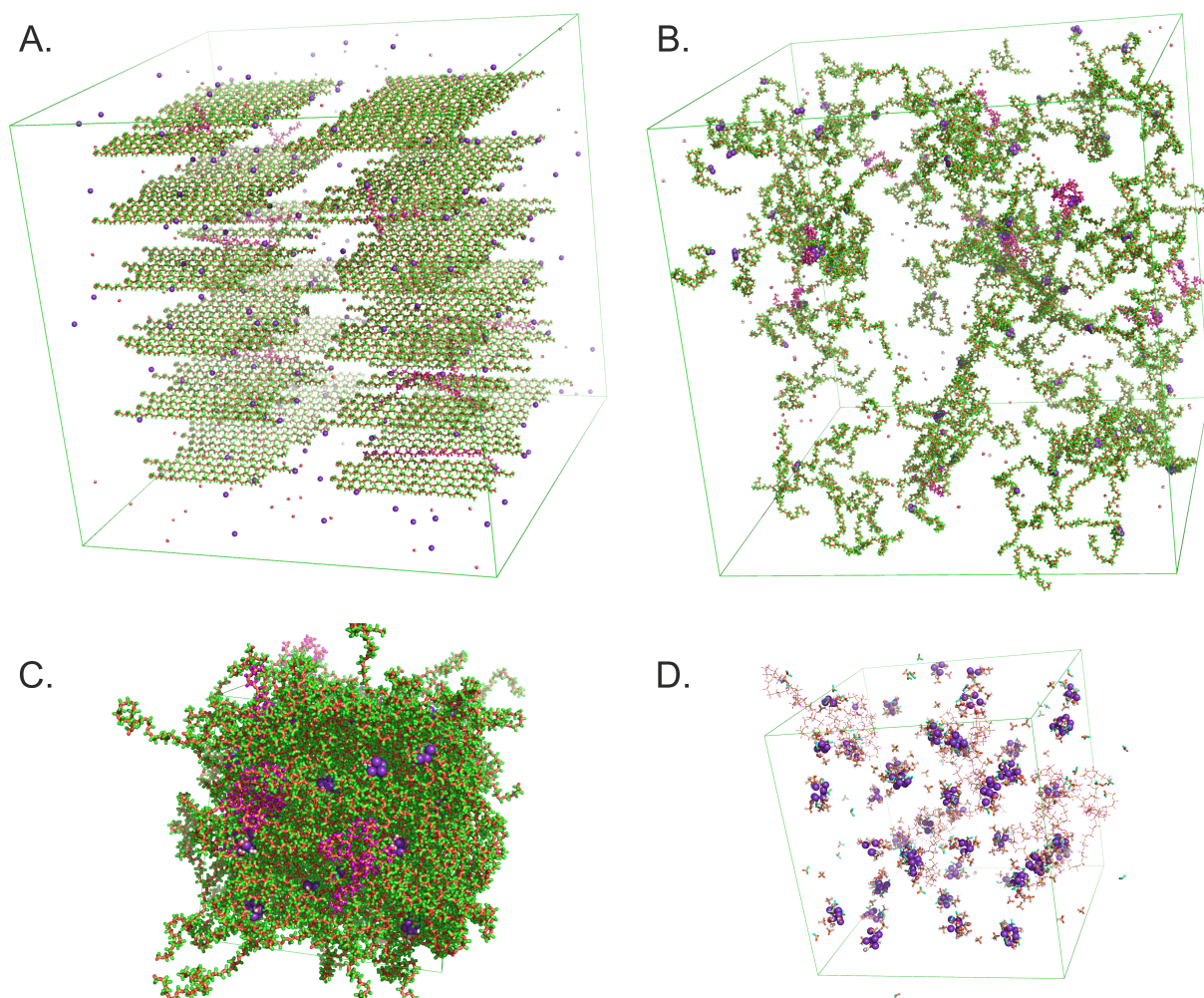
### 3. Results and discussion

#### 3.1. Development of a system preparation protocol

The composition of the “siloxane equilibration” mixture was reconstructed from mass ratios of the initial components: D4, bis-D4 and the polymerization initiator. As a starting point, ratios of the sample, obtained by R.M. Islamova and co. at the Institute of Chemistry of the Petersburg State University, exactly 0.75% mass. bis-D4 and 1.5% mass. KOH, was applied. Every effective initiator molecule was considered to start one uniq polymer chain, taking into account that every crosslink region of the bis-D4 fragment consumes two anions of the initiator, thus every ethylene crosslink connects two polymer chains. After calculation of a number of polymer molecules and their average length, the chains were generated with lengths distributed according to the Poisson distrubution and uniformly spread in the cubic cell (Fig. 2A). The counterions, unconsumed initiator ions were added to the cell further.

Also, polysiloxanes can absorb some amount of water. Therefore, we created 3 equivalent systems and added 0.47% or 1.4% mass. of water molecules to the second and the third systems





**Figure 2.** Condensation of the PDMS material upon the MD simulations protocol. The linear PDMS chains are shown in green, while those ones with ethylene crosslinks – in magenta. The  $K^+$  ions are depicted as purple spheres, while water molecules – as red-and-white spheres. **A.** The initially constructed system. **B.** The system after 20 ns of the NVT simulation at 1073 K. **C.** The system after the NPT condensation. **D.** The system after the NPT condensation in details. The most of PDMS chains are hidden except carrying crosslinks (magenta), their negatively charged terminal residues (cyan) and polar initial chain residues (pink)

according to the thermogravimetric experiment (with 0.47% or 1.4% mass loss upon heating up to 100 and 200°C, respectively) carried out with a material sample in our laboratory.

To reconstruct the three-dimensional organisation of the material, a stepwise interfusion and condensation molecular dynamics protocol was applied (Table 1). At the first step, the 20 ns NVT dynamics at 1073K was calculated. Upon this simulation, the polymer chains and other components interfused intensively remaining spread all over the cell without significant condensation. Upon this dynamics,  $K^+$  counterions retained close to the anionic groups. Some of them formed aggregates of several molecules, which, however, were not complete stable upon this simulation and underwent ion exchanges with each other. The example of resulting structures of these simulations is shown on Fig. 2B.

After that, NPT simulation with gradual temperature decrease was performed. The temperature first was retained at 1073 K for 3 ns, then linearly declined down to the ambient 298 K temperature during next 50 ns, and this value was maintained during the last 50 ns. At the normal pressure (1 bar) and standart cell compressibility the cell sizes almost didn't react on

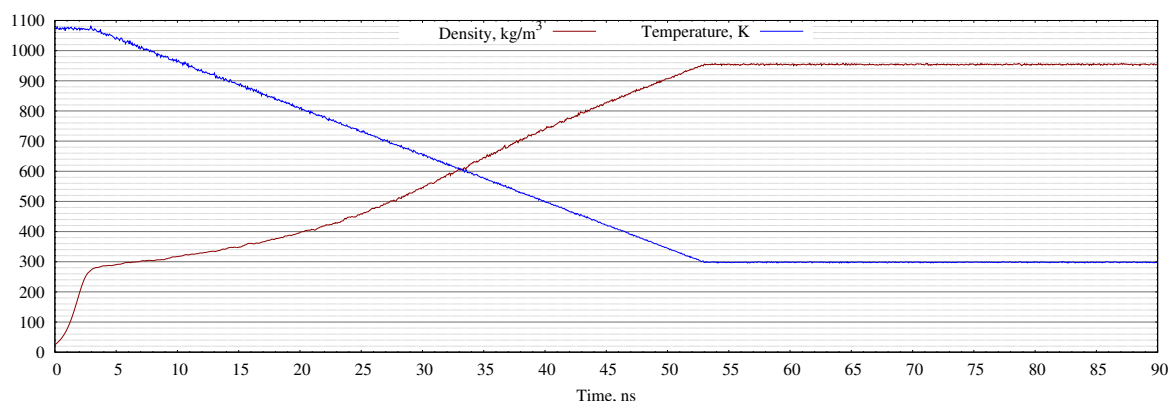
the temperature decrease (i.e. system condensation was too slow). So, we had to increase the pressure up to 20–30 bar and the cell compressibility up to  $10^{-4}$  bar $^{-1}$ , and this was just enough high to provide steady but smooth compression of the system upon condensation and without urging the LINCS algorithm to interrupt the simulation. With these parameters, the system smoothly compressed into the condensed phase with final density around 0.954 (Fig. 3), which fell within the 0.91–1.00 diapason for such kind of PDMS materials [18].

### 3.2. Ion aggregation in PDMS materials during the MD simulations

Upon the condensation in the MD simulations, the cationic aggregates enlarged up to 5–6 cations in average (Fig. 2C). All the water molecules and the unconsumed initiator ions diffused to the cationic aggregates, therefore, the space between the aggregates was filled with low-polarity PDMS chains only. The molecular basis of the ionic aggregates formation was provided by both electrostatic and van-der-Vaals interactions reproduced in the model by the forcefield. Electrostatic attraction between the anionic PDMS tails and the cations in combination with hydrophobic expulsion of all charged and polar groups (including water) gathered all them together into compact aggregates, where the terminal anionic groups connected the  $K^+$  ions at a 4–5 Å distance, which is significantly lesser then in solid crystals, but still is a rather close distance. The polymer chains remained rather extended upon the phase condensation due to connections of all its terminal and initial residues to the ionic aggregates and absence of any solvent in the non-polar medium of the PDMS chains, so the system did not undergo any kind of a coil-globule phase transition during the *in silico* condensation.

The final trajectories of 500 ns length were obtained at 298 K and 1 bar from resulting structures of the previously described condensation simulations. Upon the pressure change, a very slight decrease of density (around  $3/10^{-3}$ ) was detected. The cationic aggregates retained stable upon all the simulations, no ion exchange between them were detected. Such the aggregates are typical for polymers with charged groups neutralized by corresponding counterions, called ionomers [19]. In the case of PDMS materials these aggregates appeared to have a more complex structure: anionic terminal groups intercalated inside the cationic aggregates between the very  $K^+$  ions, while water molecules and relatively polar initial chain groups were found to form the outer layers of the aggregates. Another feature of the siloxane polymer was that every chain has one or, in the case of chains carrying an ethylene crosslink, two negatively charged terminal groups, every of which is connected to the cationic aggregate. Thus, every polymer molecule is involved in the so-called “restricted mobility region” (RMR) in the ionomer, and several polymer molecules may form a connection between different aggregates (see Fig. 2D). Though some ionomer materials also demonstrated self-healing abilities [20–22], PDMS materials are known to demonstrate a high effectiveness in uninduced self-healing under ambient conditions, while most of the ionomers require heating or another kind of activation for significant self-healing effectiveness. The role of the structural features in the PDMS self-healing ability is a subject of a further deeper investigation.

Thus, the condensation of the polymer mixture upon the MD simulations provided formation of extremely stable ionic aggregates within the PDMS materials which are described for another polymers with a moderate content of ionic groups and their counterions. The structure, distribution and organisation of polysiloxane chains around the detected aggregates is expected to be the key to the connection between the structure and the properties of the PDMS materials. A further investigation is expected to establish the role of the size and the structure of the aggregates and their surroundings in the self-healing capability. The elaborated method can be easily applied to another materials with different ratios of components, ion and initiator specificity, or with additional copolymer blocks.



**Figure 3.** Temperature decrease and density increase upon the PDMS material condensation in the NPT MD simulation

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