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Molecular Dynamics Simulations of Poly(dimethylsiloxane) Properties

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Models of poly(dimethylsiloxane) (PDMS) oligomers differing in topology are defined and structure and mechanical properties of these analysed by three different theoretical approaches: the Bicerano graph method, atomistic molecular dynamics simulations and mesoscale dissipative particle dynamics. The calculations are performed within the simulation software environment Materials Studio (Accelrys Software Inc.). The obtained values of the Young and bulk modulus are juxtaposed to experimental data available for real PDMS materials and quality of the agreement discussed in relation to the theory level and simulation method applied.

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1. Introduction

Poly(dimethylsiloxane) belongs into group of non-toxic, relatively inert and highly elastic polymers (elastomers) with very low glass transition temperature $T_{\mathrm{g}} \approx$ 148 K [1]. Consequently, it is in amorphous state under normal room conditions. In addition, this material is easy to fabricate and has favourable optical and mechanical properties, so it is widely used in industrial and scientific applications, such as electronics, telecommunications, packing industry, chromatography, optical fibre technologies, smart actuators and imprinting techniques used for optical gratings and microfluidic devices fabrication [2–4].

In many of the applications, mechanic and thermal behaviour of PDMS as well as its permeability to various gases and liquids is of high practical importance. (Noticeably, despite of its high hydrophobicity, PDMS still exhibits some low but nonzero level of sorption and diffusion of water molecules [2].)

The simulations presented in this paper are stimulated by our recent effort to get a closer insight into the structural background of physical properties of PDMS resin [5, 6]. Three different simulation techniques are used and tested in their ability to correctly reflect the expected relationship between the cross-linking level of PDMS network and the basic elasticity measures of bulk material. (Let us notice that the known dependence of elastic parameters on polymer layer thickness, as referred e.g. in [3], is not regarded here.)

The calculated results are juxtaposed to known experimental data with aim to verify (and optionally upgrade) the applied models. Moreover, evaluation of some properties that still have not been experimentally characterized is performed with aid of the simulated data. All calculations were performed within Materials Studio (MS, Accelrys Software Inc.) environment [7].

2. Simulation methods

Mechanical and thermal characteristics of PDMS are simulated using three different approaches. The first method, derived by Bicerano and others ([8]; further reported as BM) is based on transformation of the sequence of polymer repeat units to a graph model defining connectivity indices and taking in account element valences, atomic numbers and bonding rates. Polymer characteristics, such as the repeat unit volume, T_{g}, bulk (K) or the Young (E) modulus can be then readily calculated using semi-empirical formulae varying according to the polymer type and applicable for materials containing any combination of carbon, hydrogen, nitrogen, oxygen, silicon, sulphur, fluorine, chlorine and bromine [7, 8].

The calculations were performed with the MS module Synthia on three different types of topologies shown in Fig. 1. The model structures follow the PDMS cross-linking mechanism described in [9]. The structures combine two types of components, linear DMS oligomers (chains of 50 monomer units are used, marked as PDMS(50)) and four-functional tetrakis(dimethylsiloxy)silane (TDMSOS), into the (i) "linear" model (PDMS(50) molecules only), (ii) the cross-linked model "A" (longer linear chains, the two para-oriented functional groups of the cross-linker are connected to the linear chains) and (iii) the cross-linked model "B" (cross-like branched chains, all four functional groups of the cross-linker are connected to the liner chains). Before the production runs, geometrical optimization of PDMS repeat unit was performed by means of molecular mechanics (MM, module MS Forcite Plus). The second approach consisted in molecular dynamics (MD) simulations realized with the module MS

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Forcite Plus. *Ab initio* force field (FF) MS Compass was used to evaluate interatomic forces and energies for MM and MD calculations. Atomistic models of linear and cross-linked PDMS oligomers were designed using the random-walk method (MS Amorphous Cell) and let to relax using the procedure consisting of geometrical optimization, annealing and NPT/NVT MD simulations [10].

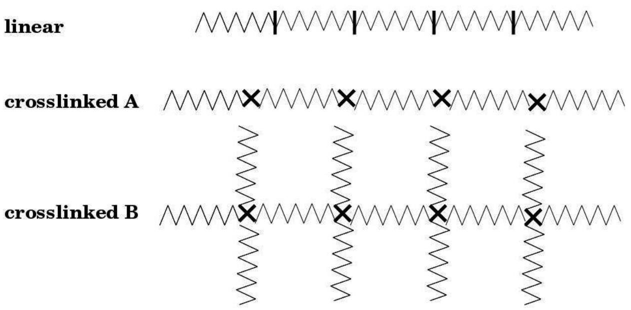

Fig. 1. Three types of structures used in BM calculations. All polymers contain PDMS(50) oligomer chains. Small crosses denote the positions of TDMSOS cross-linkers.

Our previous simulations [5] dealing with dependence of mass density (ρ) on the monomer units number (n) and calculations of diffusion coefficient (D) of small gas molecules (O_2, NH_3) in PDMS matrix showed that the mentioned procedure results in PDMS models providing a good level of agreement with the corresponding ρ and D experimental data. In order to characterize elastic properties, MD trajectories evolved at NPT conditions ($T = 298$ K, time step 1 fs, P set gradually as 0.1, 0.4, 0.8 and 1.0 GPa) were calculated. Finally, mesoscale models were constructed and tested by dissipative particle dynamics (DPD) method. Single DMS unit was used as the bead in the applied coarse-grained (CG) PDMS models. Two types of CG models were tested: the ensembles containing (i) linear chains formed by 50 beads and (ii) cross-linked CG chains analogical to the topology marked as "cross-linked B" in Fig. 1. Values of the K-modulus were determined from NPT trajectories according to the formula $K = \rho_0(\mathrm{d}P/\mathrm{d}\rho)_{\rho_0}$, where ρ_0 is the experimental density at the given T and n. Analogical formula was used in case of the MD data, too. For overview of atomistic MM and MD methods and mesoscale DPD approaches see e.g. the review [11].

3. Results and discussion

The simulated values of the K and E modulus calculated by all three methods are summarized in the Table. The obtained values can be compared with the experimental values of K and E modulus of PDMS reported in [12] for the commercial resin Sylgard 184 (Dow Corning) cured under low (20 °C) or high (200 °C) curing temperature. Values 186.9/117.8 MPa (K) and 1.32/2.97 MPa (E) were obtained for the low/high curing temperature, respectively. The observed enhancement of experimental K and E values reflects the increase in the cross-links density of the polymer resin with the rising curing temperature. For the BM approach, $K \approx 530$ MPa is obtained for all the tested structure types. Such structural independence follows very likely from the small overall molecular mass of the macromolecule involved in the models. The result clearly emphasizes that widely-extended networks must be included into the tested PDMS models in order to make simulations of the cross-linked PDMS more realistic. In case of E modulus, the BM values obtained for the tested systems differ, being similar and fairy close to experimental values for the linear and cross-linked A model ($E \approx 0.8$–0.9 MPa) and showing significantly lower value for the cross-linked B model ($E \approx 0.2$ MPa). Such simulated trend is opposite to those following from the experiment.

TABLE

Elastic parameters K and E calculated by BM, MD and DPD approach, respectively (see the text for details).

PDMS form	n	K^{BM} [MPa]	E^{BM} [MPa]	K^{MD} [MPa]	K^{DPD} [MPa]
linear	10	(535±80)	(0.87±0.15)	–	–
linear	50	(535±80)	(0.9±0.2)	1.44	742
cross A	10	(530±80)	(0.8±0.1)	–	–
cross A	50	(530±80)	(0.9±0.2)	–	–
cross B	10	(535±80)	(0.21±0.04)	–	–
cross B	50	(535±80)	(0.21±0.04)	1.08	766

The results of mesoscale simulations also overestimate the K values, the reasons being likely similar as in the BM case. Finally, the K-values obtained from MD simulations are strongly underestimated; however, at least the structural trend is conformal with the experimental data. All the simulated models seem to be "softer" than the real material. Thus, the ensembles used in MD simulations suits well to description of diffusion processes, but are apparently not sufficient for description of mechanical properties. Further research is planned to search for improved PDMS models applicable in conjunction with the tested simulation methods.

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