

Modeling of PDMS - Silica Nanocomposites

J. S. Smith*, G. D. Smith** and O. Borodin***

Department of Materials Science and Engineering, University of Utah,
122 S. Central Campus Dr., Rm. 304,
Salt Lake City, UT USA, * jsmith@cluster2.mse.utah.edu,
** gsmith@gibbon.mse.utah.edu, *** borodin@eng.utah.edu

ABSTRACT

A hydrogen bonding pathway between polydimethylsiloxane (PDMS) and hydroxyl groups on a silica surface was studied using quantum chemistry calculations of disiloxane and hexamethyldisiloxane molecules with small silica clusters. A newly developed classical force field for PDMS was developed for atomistic molecular dynamics simulation studies of PDMS – silica nanocomposites to determine the effect of these interactions on the dynamics and structure of PDMS. A three nanometer silica particle (β -cristobalite) with (111) surface hydroxyl group density of 4.8 OH groups/nm² was simulated in a PDMS melt in the temperature range of 300 to 500K. The density and structure of PDMS chains near the silica surface were strongly influenced by the hydrogen bonding interaction which is not properly represented in other current force fields. Residence time correlation analysis confirmed that PDMS oxygen – silica surface hydrogen atom dynamics were consistent with polymer hydrogen bonding.

Keywords: nanocomposites, quantum chemistry, molecular dynamics, polymers, modeling

1 INTRODUCTION

There is an extensive and rapidly growing literature describing the properties of filled and nanocomposite polymer systems. In addition, there has been much effort to model the constitutive behavior of such systems, and PDMS – silicone systems have been perhaps the second most studied system next to rubber – carbon black. Recent simulations have investigated the effects of particle shape, interaction, and surface structure on various systems [1,2,3]. In order to correctly model these systems the underlying mechanisms of polymer – particle interaction must be investigated.

In the PDMS – silica system experiments have determined that the PDMS chains near the surface are constrained and their motions are much slower compared to bulk PDMS. Experiments suggest that this behavior is due to hydrogen bonding between the silica surface hydroxyl atoms and the PDMS chains, or covalent bonding of certain chains to the surface [4]. Recent quantum chemistry and simulations investigating PDMS – silica interfaces concluded that hydrogen bonding was not possible, but

failed to suggest an alternate explanation for the polymer dynamics [5]. We have undertaken an ab initio quantum chemistry investigation of likely hydrogen bonding geometries between PDMS oligomers and hydroxyl bearing silica clusters in order to develop a classical force field to correctly describe PDMS – silica interactions. Molecular dynamics simulations have been initiated to investigate the particle polymer interface, understand underlying mechanisms such as hydrogen bonding, and generate useful mechanical properties for use in constitutive models.

2 PDMS – SILICA INTERACTION

2.1 Quantum Chemistry

In order to investigate the intermolecular bonding between PDMS and silica surfaces with hydroxyl groups, the binding energies of representative molecules were calculated using the Gaussian 98 package [6]. The binding energy is defined as the difference in the energy of the complex and the sum of the energies of the isolated molecules. The smallest molecules were disiloxane (DS, SiH₃OSiH₃) and silanol (H₃SiOH) shown in their minimum energy geometry in Figure 1. While frozen in their minimum energy geometries, the molecules were moved closer together and farther apart along the bonding path and Hartree-Fock (HF) and Møller-Plesset second order perturbation theory (MP2) energies were calculated with 6-311G(2df), aug-cc-pvDz, and aug-cc-pvTz basis sets.

Additional calculations were done on a larger trisiloxysilanol cluster (TSS, (H₃SiO)₃SiOH, see Figure 2) at the aug-cc-pvDz level where the MP2 binding energy was found to be -5.18 kcal/mol, with a DS oxygen to silanol oxygen separation, $r_{OO} = 2.943$ angstroms (O-H distance ~2.0 angstroms). This binding energy is 3.2 to 4.2 kcals stronger than that reported in the literature [5]. The hexamethyldisiloxane molecule (HMDS, (CH₃)₃SiO-Si(CH₃)₃, see Figure 3) has a hydrogen bonding approach path with TSS which had a binding energy of -7.08 kcal/mol at the 6-31G(2d) level of theory.

This demonstrates the feasibility of hydrogen bonding even in the presence of additional methyl groups and suggests that the level of theory (basis set) is very important in determining the binding energy, although it limits the size of molecules that can be examined. The additional binding energy of ~1.8 kcal/mol is similar to the binding

energy of methyl groups to a silica surface found in the literature on much larger molecules [5]. The variations of binding energy with separation are shown in Figure 4.

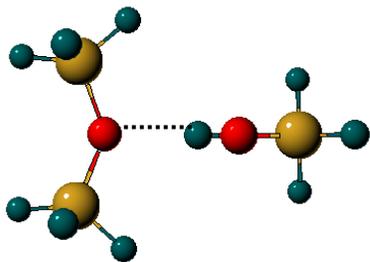


Figure 1: Hydrogen bonding paths between disiloxane and silanol.

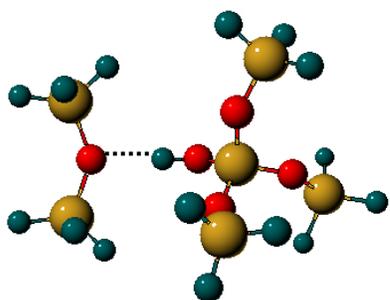


Figure 2: Hydrogen bonding path between disiloxane and the TSS cluster.

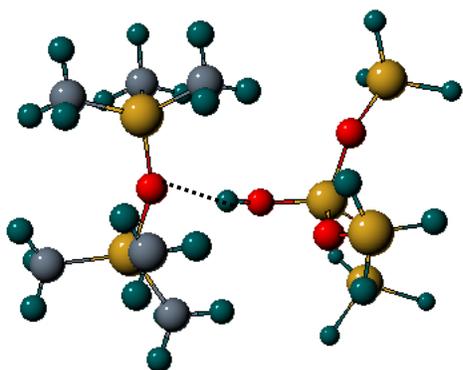


Figure 3: Hydrogen bonding path between hexamethyldisiloxane and a TSS cluster.

2.2 Force Field Methodology

The interaction between the particle surface and PDMS chains in this treatment is of a purely nonbonded nature. Parameters for the PDMS – PDMS and silica – silica atomic intra- and intermolecular interactions are published elsewhere [7,8]. The total binding energy, $U^{BIND}(\mathbf{r})$ of an ensemble of PDMS molecules and particles represented by coordinate vector \mathbf{r} , includes contributions from

electrostatic, van der Waals (VDW) and hydrogen bonding, U^{HB} , interactions.

$$U^{BIND}(r_{ij}) = \sum_{i < j} \frac{q_{\alpha} q_{\beta}}{4\pi\epsilon_0 r_{ij}} + A_{\alpha\beta} \exp(-B_{\alpha\beta} r_{ij}) - \frac{C_{\alpha\beta}}{r_{ij}^6} + U^{HB}(r_{ij}) \quad (1)$$

The electrostatic and VDW energies are represented by coulombic and Buckingham equations where r_{ij} is the distance between the i^{th} particle atom and j^{th} polymer atom of type α and β respectively. The equation for hydrogen bonding is presented in section 2.4. In order to correctly represent the PDMS – hydroxylated silica interaction the following methodology was carried out. First the partial charges, q , for the atom of each representative molecule were calculated. Second, it was determined that the Buckingham potential parameters, A , B and C from the newly parameterized PDMS force field would be used to represent the PDMS polymer – silica particle interactions [7]. Finally an appropriate hydrogen bonding function is parameterized which represents the both the relatively strong and short ranged nature of this interaction [9].

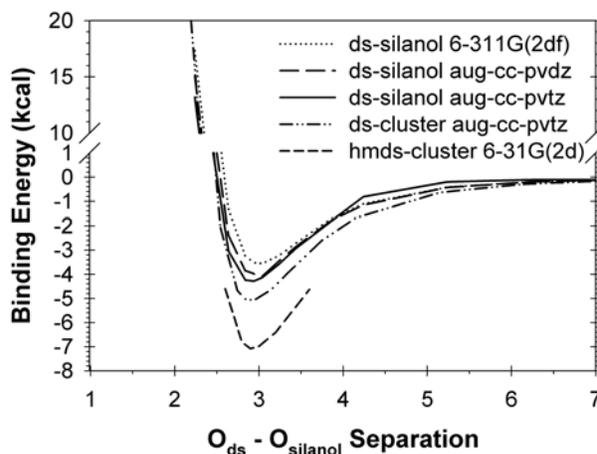


Figure 4: The variation of binding energy with molecular separation showing the effect of level of theory and molecular structure.

2.3 Charge Parameterization

Electrostatic charges were calculated from minimization of the $(\varphi_i^{QC} - \varphi_i^{FF})^2$ objective function for the DMTS molecule, where φ_i^{QC} and φ_i^{FF} are the electrostatic potentials on a grid point i from quantum chemistry calculations and from the force field respectively [10]. The grid points within one van der Waals (VDW) radius of each atom were excluded from the calculation because such separations are highly unlikely in MD simulations and points any farther than 4.0 Å from any atom were also excluded. The VDW radii were 2.0, 2.0, 2.5 and 1.8 angstroms, for Si, O, C, and H, respectively.

2.4 Hydrogen Bond

The excess binding energy between the disiloxane – silanol molecule was fit at the 6-311G(2df) level with a special attractive hydrogen bonding function [9]:

$$U^{HB}(r_{ij}) = \sum_{i < j} -A_{OH}^{HB} \exp(-B_{OH}^{HB} r_{ij}) \quad (2)$$

where r_{ij} is the atomic separation of the silica surface hydroxyl's hydrogen atom and PDMS' oxygen atom with hydrogen bonding parameters A_{OH}^{HB} and B_{OH}^{HB} . Equation 2 was fit using A and B parameters of 5942 and 3.649 respectively. These same parameters fit the higher level aug-cc-pvDz results for the DS – TSS energies as shown in Figure 5. Also shown in Figure 5 is the binding energy calculated using the consistent force field (CFF) parameters of Sun and Rigby [11] which does not capture the hydrogen bonding energy as reported recently in the literature [5].

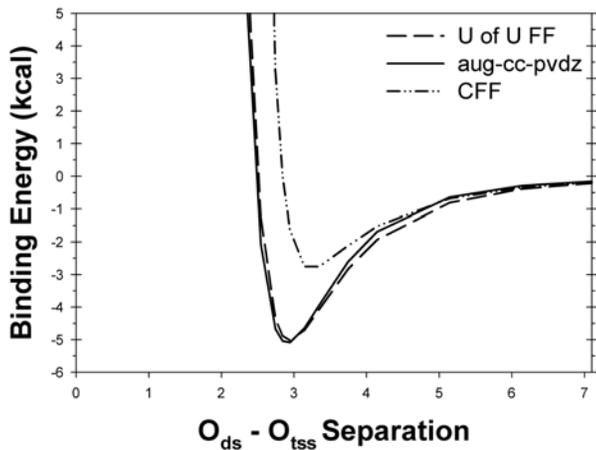


Figure 5: Fit of the binding energy between disiloxane and a TSS cluster using the current U of U force field and the CFF force field.

3 SIMULATIONS AND PROPERTIES

3.1 Simulation Methodology

MD Simulations of an ensemble of 40 PDMS molecules, MD₁₉M (20 repeat units each and 1571 g/mol), and a single silica nanoparticle were performed at 500 K. All simulations were carried out with the *Lucretius* [12] MD simulation package using a Nose-Hoover thermostat [13] and barostat [14] to control the temperature and pressure. The particle-mesh Ewald (PME) technique [15] was used to treat all electrostatic interactions. A multiple time step reversible reference system propagator algorithm [14] was employed with a time step of 0.5 fs for bond, bend and torsional motions, a 1.0 fs time step for all VDW and real electrostatic interactions within a sphere of radius 6.0

Å, and a 2.0 fs time step for nonbonded interactions in the shell between radii of 6.0 and 10.0 Å and for the reciprocal space PME calculations.

For the initial investigations, a force field potential was used which combined the newly derived nonbonded parameters and partial charges to describe PDMS and PDMS – silica interactions and the CFF internal parameters [11] to describe the bond, bend and dihedral energies of PDMS. This parameter combination will certainly affect the thermodynamic and dynamic behavior of the PDMS chains but should give a qualitative indication of the effect of the PDMS polymer interaction with a hydroxylated silica surface and a reasonable comparison with previous works using the unaltered CFF force field.

A freely rotating β -cristobalite crystal (approximately, 27.8, 24.7, and 29.6 angstroms thick) surrounded by PDMS melt was simulated at 500 K. This crystal was fully hydroxylated on the 111 surface to a density of 4.8 OH groups/nm². The intra- and inter-atomic interactions of only silica atoms were represented by a CFF type force field from the literature [8]. After box size equilibration in an NPT ensemble, NVT runs were then carried out for an additional 2.4 ns. The crystal was then fixed at the center of the box with faces parallel to the periodic boundaries so that the distance between crystal faces was approximately 20 to 25 angstroms and NVT production runs were carried out for an additional 1.9 ns.

3.2 PDMS – Silica Properties

Although qualitative, initial density profiles of PDMS layers near the hydroxylated (111) silica surfaces show increased structure closer to the hydroxyl atoms while the bare surfaces show simply a broad first layer peak with fewer undulations. The PDMS constituent atom arrangement next to the surface also shows that the surface hydroxyl groups induce strong ordering in the atom peaks and that the PDMS oxygen atom peak moves closer to the hydroxylated surface as it participates in hydrogen bonding whereas the bare surface is predominantly bordered by the PDMS methyl groups.

The first coordination shell of PDMS' oxygen atoms around the silica surface hydroxyl's hydrogen atoms is 2 angstroms according to the radial distribution function. Using this distance to define O-H hydrogen-bonding pairs we can calculate mean hydrogen bonding residence time correlation functions:

$$R_1(t) = \langle H(0) \bullet H(t) \rangle \quad (3)$$

$$R_2(t) = \langle \text{average time until Oxygen atom exits the hydroxyl's H atom coordination shell} \rangle \quad (4)$$

where $H(t) = 1$ if the oxygen atom is in the first coordination shell of the hydroxyl group's hydrogen atom and $H(t) = 0$ otherwise. The difference between the residence time correlation functions $R_1(t)$ and $R_2(t)$ is that

the $R_2(t)$ function probes the time that each oxygen atom spends in the hydroxyl group's hydrogen atoms coordination shell until it first exits regardless of any subsequent reentries, whereas the $R_1(t)$ function probes the total time the oxygen atom spends in a particular coordination shell no matter how many times it leaves and reenters. The difference between the residence time correlation functions suggest that hydrogen bonds form, break, and reform many times before the PDMS oxygen atom finally leaves the surface hydroxyl's hydrogen atom.

The mean squared displacement (MSD) of the PDMS backbone silicon and oxygen atoms were examined to see the effect of the additional hydrogen bonding near the hydroxyl covered silica surface. The MSD of the PDMS surface layer was an order of magnitude less after 800 ps when hydroxyl groups are present than for PDMS near bare silica surfaces. These results support the assertion that silica surfaces in the PDMS – silica nanocomposites slow down the PDMS chains by means of hydrogen bonding at surface hydroxyls. This mechanism certainly factors in to the mechanical behavior of these composites.

4 CONCLUSIONS

An ab initio quantum chemistry investigation of disiloxane or hexamethyldisiloxane with silanol or a larger silica cluster revealed hydrogen bonding configurations with a minimum binding energy of -5.2 kcal/mol at the MP2/aug-cc-pvDz level of theory. From this data a quantum chemistry based PDMS - silica force field has been developed that includes a hydrogen bonding function which shows transferability between levels of theory and to other polymer systems.

Molecular dynamics simulations of PDMS - silica systems at 500 K qualitatively showed increased density and structure near the hydroxyl covered (111) SiO₂ surface. PDMS oxygen atoms were drawn near to the surface to participate in hydrogen bonds contrary to previous simulation studies in the literature [5]. Residence time correlation analysis showed that hydrogen bonding atom pairs remained coordinated for some time forming, breaking and reforming hydrogen bonds. This hydrogen bonding model is also supported by an order of magnitude decrease in the mean squared displacement of PDMS backbone atoms next to a hydroxylated surface as compared with the same bare surface. Further studies are underway with the recently completed PDMS force field [7] and the results will be presented at the conference.

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