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Stretching siloxanes: An ab initio molecular dynamics study

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Abstract

We present an ab initio molecular dynamics study of siloxane elastomers placed under tensile stress for comparison with single molecule AFM experiments. Of particular interest is stress-induced chemical bond breaking in the high force regime, where a description of the molecular electronic structure is essential to determine the rupture mechanism. We predict an ionic mechanism for the bond breaking process with a rupture force of 4.4 nN for an isolated siloxane decamer pulled at a rate of 27.3 m/s and indicate lower values at experimental polymer lengths and pulling rates.

1. Introduction

The advent of single molecule atomic force microscopy (AFM) has made the measurement of the strength of a single chemical bond possible [1,2]. Until now, this technique has been principally of interest for studying the mechanical properties of biopolymers [3,4], but can also be applied to synthetic polymers used in high performance materials. Polydimethylsiloxane (PDMS), $Si(CH_3)_3[OSi(CH_3)_2]_nOSi(CH_3)_3$, is used as an adhesive under extreme conditions because of its exceptional physical and chemical stability. However, low resistance to crack propagation in the bulk polymer in the absence of silica filler particles is not well understood. In order to inhibit this macroscopic process, a characterisation of its microscopic origins in terms of the breaking of chemical bonds is necessary. The relevant property is the strength of the bond in terms of the force required for rupture caused by an applied tensile stress under specified experimental conditions. This can be investigated using single molecule AFM in conjunction with computer simulations to identify the breaking bond. Siloxanes provide an interesting system for a single molecule AFM investigation as only a silicon–oxygen bond in either the chain or in the attachment can rupture. This can be accurately characterised and avoids the problems associated with analysing complex systems. In order to clarify the bond breaking process in the siloxane backbone, we apply first principles molecular dynamics calculations, where an ab initio electronic structure calculation is performed for each step of a molecular dynamics trajectory to PDMS chains containing up to ten silicon atoms. This enables us to follow the evolution of the electronic structure during the bond breaking process.

The strength of chemical attachments, as measured by the force required to break them in single molecule AFM experiments, is dependent on factors such as solvent, temperature and pulling velocity [5–7]. The strength of a covalent attachment has been measured by Grandbois et al. [8] to be 2.0 ± 0.3 nN. This was predicted to be associated with an Si–C bond located in the

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attachment between amylose and a siloxane surface functionalised with amino groups by comparison with DFT calculations [8,9]. However, these calculations did not take factors such as temperature, interactions with solvent molecules or the dynamics of the system into account, all of which can influence the bond breaking mechanism and consequently the rupture force.In the ongoing AFM experiments, a chain consisting of Si–O bonds only is stretched in the non-protic solvent hexamethyldisiloxane (HMDS). This greatly simplifies the system and gives a good starting point for a theoretical investigation.

The application of CPMD calculations involves an 'on the fly' determination of the potential surface: by constantly increasing the distance between the terminal silicon atoms the molecule can be pulled apart at a specified rate. Instead of building a potential for a model we determine the potential directly as the molecule is stretched. This approach has previously been successfully applied to examine factors which influence bond rupture [6,7,10,11]. In this study, we determine the rupture force of siloxane oligomers of different lengths and at different pulling rates.

2. Method

In order to simulate the chemical process of bond breaking under the conditions of a single molecule AFM experiment, the electronic structure of the system must be accurately determined at each stage of the reaction. We apply Car–Parrinello Molecular Dynamics [12] with the CPMD code [13] using density functional theory [14,15] to describe the electrons. We simulate a polymer chain under tensile stress by calculating isolated PDMS chains with up to 10 silicon atoms in the backbone at 300 K. We fix one terminal silicon atom and move the other terminal silicon atom at a predefined rate along the long molecular axis to cause stretching of the molecule until one of the bonds in the backbone breaks. This gives the total energy as a function of the extension of the molecule from which the rupture force can be determined.

We expand the Kohn–Sham wavefunctions [15] using a plane wave basis set with a kinetic energy cutoff of 70 Ry. The pseudopotentials of Troullier–Martins [16] are used to describe the core electrons and the BLYP functional [17,18] accounts for the electron exchange–correlation energy.

We investigate only the part of the force spectrum where bond breaking occurs. To make our calculations tractable we start with a slightly stretched siloxane chain and equilibrate the geometry for a fixed distance between the terminal silicon atoms clearly before the rupture point for 200 fs. The dynamics of PDMS chains containing 2, 3, 6 and 10 silicon atoms in the backbone (siloxane dimer, trimer, hexamer and decamer, respectively) was simulated at pulling rates ranging from 273 to 27.3 m/s using a timestep of 0.1 fs in the molecular dynamics runs. The rupture forces resulting from the simulations are collected in Table 1. The supercell dimensions were $12.7 \times 7.4 \times 7.4$ Å for the dimer and trimer, $25.4 \times 7.9 \times 6.9$ Å for the hexamer and $34.9 \times 7.9 \times 6.9$ Å for the decamer. This allows us to determine the influence of molecular length and pulling rate on the rupture force.

Table 1
The rupture forces for different siloxane lengths and pulling rates as determined from the gradient of energy/extension plots

Molecule	Pulling rate (m/s)	Rupture force (nN)
Dimer	55	6.6
Trimer	273	6.0
	137	5.4
	55	5.2
Hexamer	55	4.6
Decamer	55	4.4
	27.3	4.4

For comparison we have performed a series of static calculations with the semi-empirical AM1 Hamiltonian and with the B3LYP functional using a 6-31G** basis set from GAUSSIAN98 [20]. In these calculations, the molecular structures were optimized for fixed distances between the terminal silicon atoms.

3. Results and discussion

3.1. Stress-induced deformation and bond rupture mechanism

The deformation of the molecule during stretching is characterised by the elongation of the Si–O bonds and an increase in the magnitude of the O–Si–O and Si–O–Si bond angles. Figs. 1 and 2 show how flexible the bond lengths and angles are: the range over which the Si–O bond lengths oscillate increases and the O–Si–O bond angles increase simultaneously, the Si–O–Si bond angles continuously oscillate between 130° and 180°.

The siloxane molecules are stretched until one of the bonds in the backbone is broken which, apart from the dimer obviously, is never observed to be a terminal bond in contrast to the static calculations presented in [19]. We determine a rupture mechanism for the dimer and trimer where a Si–O bond ruptures to give two charged species followed by the transfer of a proton atom to the terminal oxygen atom which neutralises the products. This reaction scheme is shown with a plot of the localised molecular orbitals associated with the electrons in the siloxane backbone in Fig. 3. The electrons are initially delocalised over the Si–O–Si bond but as a tensile stress is applied polarisation