

## 579d Aimd Studies of Atomic Oxygen Erosion on the Poss Materials

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One of the main challenges in designing space vehicles is to keep the structural integrity of the vehicles by preventing hazardous species from penetrating into the cabin to cause malfunction of the instrument or health issues to crew members. A variety of different polymers including polyamides, polyimides, polyterephthalate, and Kapton® have been used at the surface of space vehicles to provide electrostatic as well as thermal isolation<sup>1-4</sup>. These polymers, however, degrade severely in the low earth orbit (LEO) where abundant atomic oxygens continuously impact the vehicle surface at 4.5 eV of kinetic energy. Organic functionalized POSS polymers have been actively pursued as potential candidates for protective coatings because of their oxidative stability as silica, thermal insulation as polymers, the light weight nature compared to silica, and the ability to chemically incorporate into the organic polymer networks.

Recently, Gonzalez et al. probed the exposure of the POSS-polydimethylsiloxane copolymer films to hyperthermal atomic oxygen flux using the in-situ X-ray photoelectron spectroscopy<sup>5</sup>. Their results showed the decrease of mole percentage for carbon as well as the increase of mole percentage for silicon and oxygen, which ultimately reached a ratio of 1:2 for Si:O. They concluded their results as the abstraction of the hydrocarbon chains of the copolymer accompanied by the uptake of oxygen atoms, leaving the protective silica surface on top of the POSS-siloxane copolymer which prevents lower layers from further degradation. Nevertheless, the reaction mechanisms were never clearly illustrated.

Previous ab-initio studies on hydrocarbon dissociation by Gindulyte<sup>6</sup> and Troya<sup>7</sup> suggest that the activation barriers of C-C bond and C-H bond breaking are around 2 eV and 0.4 eV, respectively. The dynamic nature of the collision, however, was not included in their studies. Another missing link in their studies is the subsequent reaction paths that lead to the formation of CO<sub>2</sub> and water.

To probe various possibilities of reaction pathways, we employed ab-initio molecular dynamics (AIMD) using the VASP program. Based on density functional theory (DFT), AIMD has been applied for simple chemical reactions and shown satisfactory results. Our previous results<sup>8</sup> have shown that (1) an isolated POSS cube is stable under AO attack at kinetic energy 7 eV, (2) AO with 4 eV kinetic energy is capable of breaking Si-H and Si-C bonds, resulting in the increase of oxygen ratio which is consistent with the experimental data, and (3) POSS cages can undergo coalescence process via Si-O-Si bonds. In this follow up paper, we employ a more systematic approach to explore the angular and energy dependencies of the reaction pathways, intermediates, and the corresponding barriers.

We investigated the angular dependency of products from the first-step erosion reaction of isolated hydrido-POSS (H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub>) and ethyl-POSS ([C<sub>2</sub>H<sub>5</sub>]H<sub>7</sub>Si<sub>8</sub>O<sub>12</sub>) molecules with atomic oxygen of 4.5 eV kinetic energy. For the hydrido-POSS, despite different attacking angles, the atomic oxygen inserts in between Si and H atoms thereby forming the hydroxyl corner group. For the ethyl-POSS, the atomic oxygen erosion yields various different products depending on the inserting angles. These products include, but not limit to aldehydes, methane, alcohols, hydrocarbon radicals, hydroxyl radicals, and C atom insertion in between the Si-O bond of POSS cage. This is in consistent with the experimental results of Gonzalez. In addition, we vary the kinetic energy of the atomic oxygen for the same attacking angle to probe possible reaction paths. We will also investigate the subsequent reactions of the intermediates that may lead to the cage opening of POSS.

### References

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