

Towards a chemical understanding of decomposition and molecular-weight growth in a non-thermal plasma operating in siloxane

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Abstract: In this contribution, we report molecular-beam mass spectrometry measurements of the decomposition and molecular-weight growth products during plasma reformation of siloxanes. The experiments used a tubular configuration of an atmospheric pressure dielectric barrier discharge (DBD). To provide chemical insights, a chemical kinetic model containing a simple four-step polymerization of dimethyloxosilane was constructed.

1. Introduction

Siloxanes constitute a group of low-molecular-weight volatile organosilicon polymers that are widely used in pharmaceutical, medical, cosmetic, and food production. Many siloxane-containing products are deposited in landfills, which is a source of landfill gas (LFG), an alternative energy resource. Because enhancing the use of LFG depends on the successful and economical removal of the siloxanes, plasma chemical reforming of these compounds is explored as a viable option.

In this work, we elucidate, through experiments and modeling, the thermodynamics and kinetics of the underlying mechanism of the chemical transformation of siloxane when exposed to atmospheric pressure non-equilibrium plasma.

2. Methods

We have studied the plasma reforming of two different linear siloxanes – hexamethyldisiloxane (HMDSO) and octamethyltrisiloxane (OMTSO) using a tubular configuration of an atmospheric pressure dielectric barrier discharge (DBD) followed by molecular-beam mass spectrometry. To this end, helium-siloxane gas mixtures were used with siloxane concentrations maintained at ~100 ppm. The experiments were conducted over a range of different plasma powers (~0.5-15 W) and residence times (0.5-4 s).

A chemical kinetic model was constructed to provide insight into the key reaction steps that drive the plasma reformation of siloxanes. In addition to the decomposition chemistry, the model also contains a simple four-step polymerization of dimethyloxosilane, $\text{Si}(\text{CH}_3)_2\text{O}$, extending to polydimethylsiloxanes (PDMS).

3. Results and Discussion

Figure 1 compares the mass spectra of HMDSO in the presence (upper frame) and in the absence (lower frame) of a plasma. Under plasma conditions, reactive intermediates are clearly visible, providing valuable insights into the chemistry of the plasma-assisted HMDSO reforming.

For HMDSO, measurements show that at higher power, higher mass species are formed in larger amounts; a repetitive sequence 73/74 mass units apart (most likely

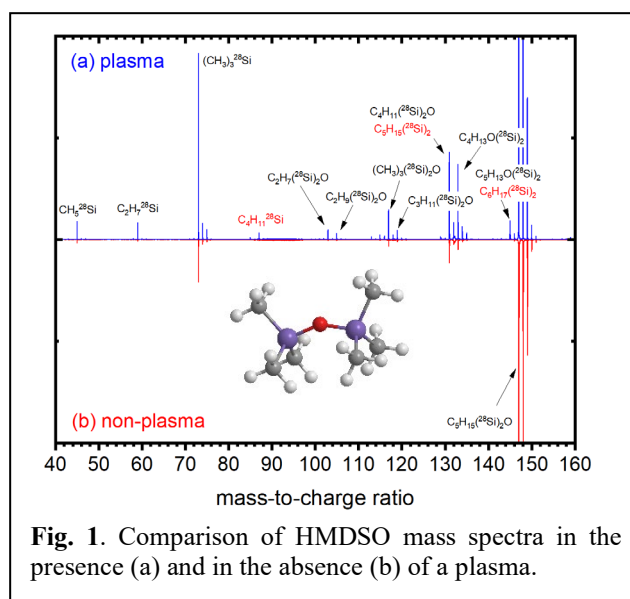


Fig. 1. Comparison of HMDSO mass spectra in the presence (a) and in the absence (b) of a plasma.

$\text{C}_2\text{H}_5\text{SiO}$ and/or $\text{C}_2\text{H}_6\text{SiO}$), which are the building blocks to form PDMS. Experiments also show significant deposition of PDMS on the reactor walls. At lower power, the mass growth is less significant.

4. Conclusion

A combined experimental and modeling study of siloxane decomposition in non-thermal plasma is underway. We used molecular-beam mass spectrometry to probe plasma-driven chemical decomposition and molecular-weight growth. A detailed chemical mechanism is being developed. The predicted species profiles are in qualitative agreement with the measurements, although the current model overpredicts conversion. All species concentrations show a non-linear response to the plasma power.

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