Material Properties and Modeling of Room Temperature Vulcanizing Silicone

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Overview

Room Temperature Vulcanizing Silicone (RTV) is a high temperature adhesive, commonly used as a gap-filler in tiled heatshields and as a bonding agent for instrumentation plugs onto the heatshield. While RTV is traditionally modeled as a non-porous, non-pyrolyzing material, experiments have shown that:

- There is significant pyrolysis in RTV which material response models currently do not include.
- A heating-rate dependent volume change of RTV occurs, causing either swelling (known as intumescence) or shrinkage, combined with a different recession than PICA, can cause roughness-induced boundary layer transition.
- Outgassing and surface oxide formation of RTV could be a source of contamination for heat shield sensors.

To understand phenomena of RTV ablation, dedicated experiments and modeling efforts have been conducted to study RTV pyrolysis, volume change, and recession in different environments. Based on the experimental data collected [1], a material response database was created in the Porous Material Analysis Toolbox based on OpenFOAM (PATO) [2]. A new intumescence model was developed for RTV based on experiments and implemented in PATO, that couples stress analysis with pyrolysis gas internal pressure build-up.

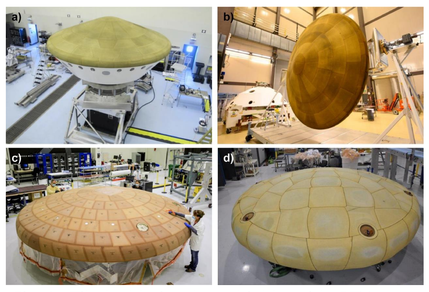

Fig 1. Tiled ablative heatshields with RTV gap-filler: (a) Mars Science Laboratory, (b) Mars2020 (c) Orion and (d) SpaceX Dragon [Credit: NASA]

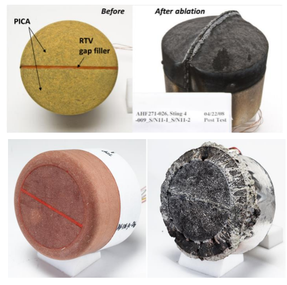

Fig 2. Differential recession between RTV and (a) PICA, (b) AVCOAT forming a *fence* [3,4].

RTV Material Properties

Pyrolysis Properties

Thermogravimetric Analysis (TGA) was performed in an inert environment, where RTV was heated to 1000°C and the mass loss as a function of temperature was measured.

- TGA showed that 55% of mass loss occurs in RTV.
- Four chemical reactions occur, with the main reaction at 550°C.
- PATO and DAKOTA were used for calibrating the pyrolysis coefficients, assuming Arrhenius-type reactions, given by.

$$\frac{d\chi_i}{dt} = \mathscr{A}_i \exp\left(\frac{-\epsilon_i}{RT}\right)(1-\chi_i) \qquad \rho(t) = \rho_0\left(1 - \sum_{i=1}^{N_{p_i}} \mathscr{F}_i \chi_i\right)$$

Table 1. Calibrated Linear Arrhenius coefficients

Reaction	$\mathcal{F}_i$ [-]	$\mathcal{A}_i$ [s^{-1}]	ϵ_i [kJ/mol]	m [-]
1	0.0253	3.327×10^7	86.60	2
2	0.9789	3.395×10^8	164.35	2
3	0.0212	9.629×10^8	212.57	1
4	0.0963	7.629×10^8	230	1

Pyrolysis Gas Chromatography and Mass Spectrometry (PyGCMS) was conducted, where RTV was heated instantaneously to 1000°C and the pyrolysis gases were analyzed.

- Results showed formation of heavy cyclic compounds known as Polydimethyl Siloxanes (PDMS) along with Benzene.
- Theory suggests that these PDMS further decompose into simpler compounds such as SiO_2, SiO, CH_4, H_2O.
- The elemental composition of the pyrolysis gases was calculated using the PDMS general chemical formula of $C_{2x}H_{6x}O_xSi_x$.
- Using the elemental composition and the theoretical compounds formed from PDMS, the gas properties of RTV were determined using PATO and Mutation++.

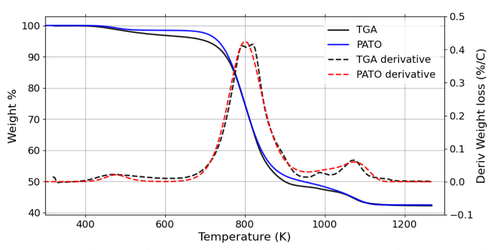

Fig 3. Mass loss of RTV and its derivative as a function of temperature obtained from TGA.

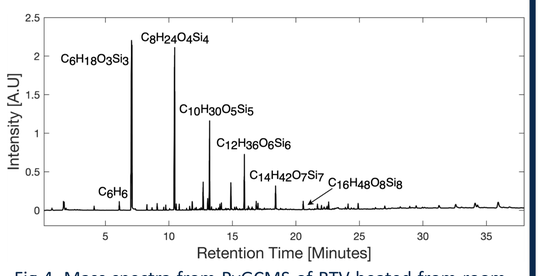

Fig 4. Mass spectra from PyGCMS of RTV heated from room temperature to 1000°C.

Microstructure

In-situ Scanning Electron Microscopy (SEM) was performed in vacuum to determine the variation in microstructure of RTV as it is heated. Test showed that:

- RTV is composed of two phases, whiskers and substrates.
- With the onset of pyrolysis, the substrate phase slowly starts decomposing
- The substrate is fully decomposed by the end of pyrolysis, resulting in a highly connected network of open-pores.
- Pores of size ranging from sub-micron scale to millimeter scale are formed due to pyrolysis.

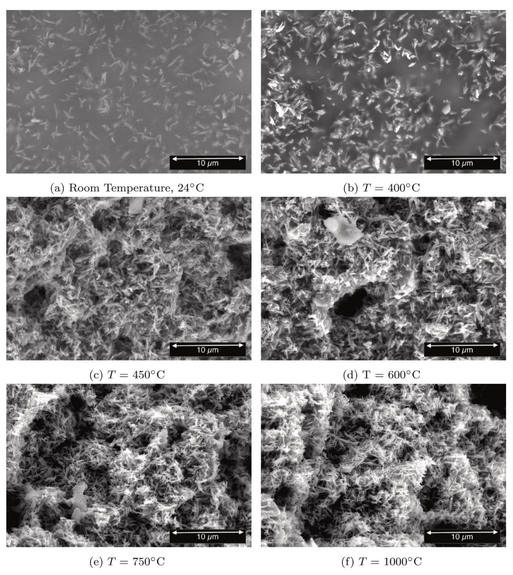

Fig 4. In-situ SEM of RTV heated to 1000°C at 50°C/min.

Porosity of Charred RTV

- Micro- to milli-meter scale porosity was characterized using X-ray Computed Micro-Tomography (μ-CT).
- Gas adsorption techniques such as Helium pycnometry (HeP) and Mercury intrusion porosimetry (MIP) and Nitrogen gas adsorption (BET) were used for quantifying sub-micron porosity..
- Solid and pore volume for a charred RTV sample were determined using HeP and MIP respectively.
- Porosity was calculated as 82% for the charred sample.

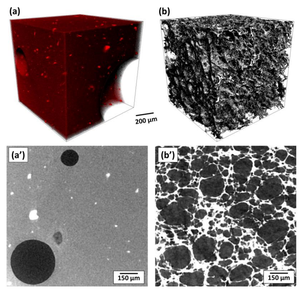

Fig 5. μ-CT renderings of (a) virgin and (b) charred RTV.

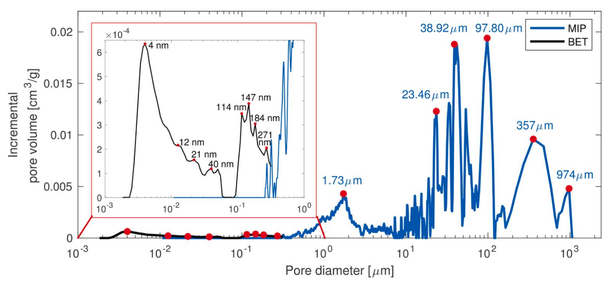

Fig 6. Pore size distribution of charred RTV from BET and MIP.

Thermal Conductivity and Specific Heat

- For accurately modeling RTV, the thermal properties such as thermal conductivity and specific heat as a function of temperature are required.
- These properties were taken from legacy data obtained during the Space Shuttle Program [5].
- Additionally, Young's Modulus, Bulk Modulus and Poisson ratio were also obtained from this material database.

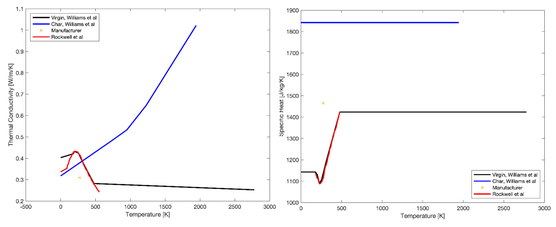

Fig 7. Thermal conductivity and specific heat for RTV [5].

Macrostructure

In-situ Computed Micro-Tomography (μ-CT) was performed at the Advanced Light Source (ALS) in Berkeley National Laboratory [6,7]. Full 3D tomographies of RTV were collected while it was being heated in an inert environment.

- Allowed to obtain total volume change as a function of temperature and heating rate.
- Showed that RTV intumescences is around 10%, followed by 60% shrinkage.
- Extent of intumescence was seen to be a function of heating rate.

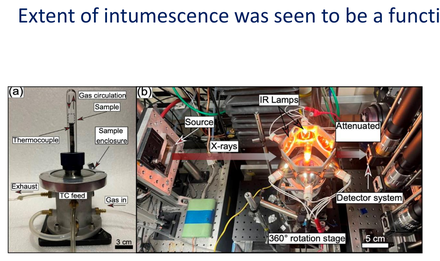

Fig 8. In-situ heating and μ-CT setup at ALS used for testing RTV.

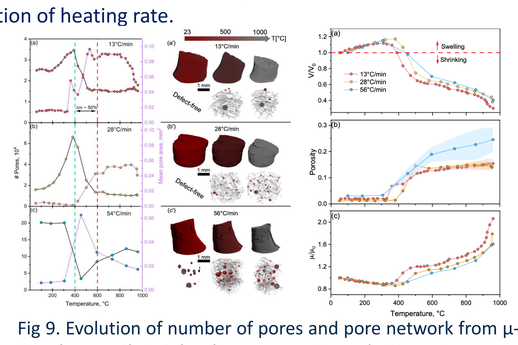

Fig 9. Evolution of number of pores and pore network from μ-CT, along with total volume, porosity and attenuation as a function of temperature.

Intumescence Modeling

Proposed model for intumescence

- There are trapped air bubbles formed while curing RTV. As a sample is heated, there is a pressure build-up in these air bubbles, causing the sample to swell volumetrically.
- With increase in temperature, the swelling is also accompanied by formation of pores due to pyrolysis, allowing the trapped gases to form a highly connected open-pore network.
- The high-pressure gases eventually connect to a surface air bubble that allows them to outgas into the atmosphere. This outgassing phenomenon can be seen as a burst air bubble.
- As the temperature further increases above 800°C, a glassy silicon oxycarbide layer is formed, with hardening of the remaining substrate.
- Due to these phenomena, the region of RTV exposed to the environment in heatshields forms a glassy char layer whereas RTV deeper in the heatshield intumesces due to lower temperatures.

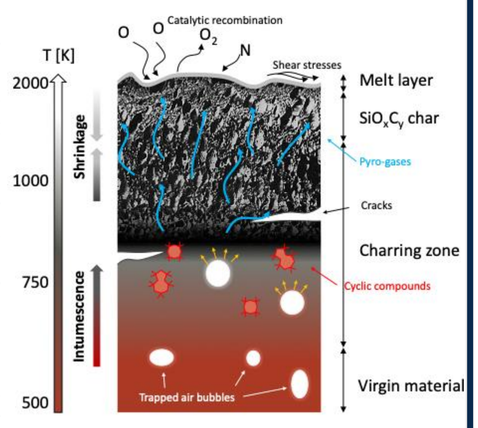

Fig 10. Illustration of the decomposition process for RTV at high temperatures.

Modeling in PATO

Using the stress analysis solver implemented in PATO, new models were created that account for volume change of a material not only due to thermal expansion but also pyrolysis shrinkage, and internal pressure build up. The stress/strain fields are obtained by solving the conservation of linear momentum in PATO:

$$\frac{\partial}{\partial t}\int_{\Omega_0} \rho \frac{\partial u}{\partial t}\, d\Omega_0 = \overbrace{\oint_{\Gamma_0} n_0 \cdot (K \cdot \nabla u)\, d\Gamma_0}^{\text{Implicit Term}} + \overbrace{\oint_{\Gamma_0} n_0 \cdot \sigma\, d\Gamma_0 - \oint_{\Gamma_0} n_0 \cdot (K \cdot \nabla u)\, d\Gamma_0}^{\text{Explicit Terms}} - \int_{\Omega_0} \nabla P\, d\Omega_0$$

The stress term, σ, contains the contributions from the thermal expansion and pyrolysis shrinkage, while the pressure build-up stress term is modeled by adding the gas pressure gradient across the material as a source term.

As inputs to the model, the Poisson ratio and Young's modulus are provided, which were gathered from literature. The coefficient of thermal expansion (CTE), obtained from a dilatometry experiment conducted by NASA, was also given as an input.

Verification testcase

To validate the code implementation, the dilatometry test case was recreated. In this case:

- A 6 mm cylinder of RTV is heated at 5°C/min in Argon,
- The cylinder intumesces due to thermal expansion and pressure build-up as it heats up,
- Further heating causes RTV to shrink and eventually melt, at temperatures above 1200°C.

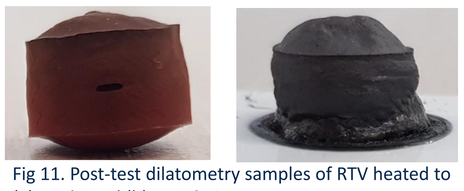

Fig 11. Post-test dilatometry samples of RTV heated to (a) 500°C and (b) 1350°C in Argon.

Results from simulation showed that the bulged shape of RTV could be well-captured using the pressure build-up approach. Using the dilatometry data as an input, the contribution of pure thermal expansion and pure pressure build-up were identified. It was seen that:

- The coefficient of thermal expansion does not vary with heating rate and is only a function of temperature.
- **Pressure build-up is a function of heating rate**, which causes intumescence to be higher for higher heating rates.

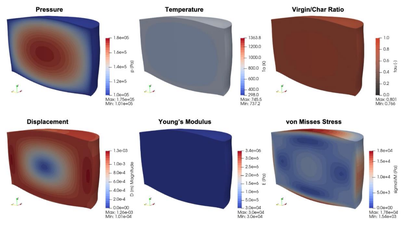

Fig 12. Contours obtained from simulation showing bulged shape of RTV.

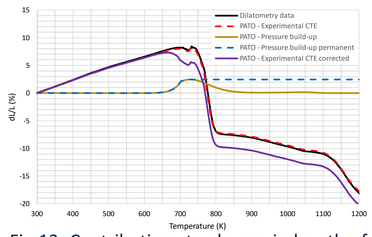

Fig 13. Contributions to change in length of RTV due to thermal expansion and pressure build-up.

Conclusion and Future Work

- **RTV** is widely used as a gap-filler on heatshields, and determining its aerothermal response is crucial for improving material response models and for assessing mission criticality.
- Experiments have shown that RTV undergoes unique micro- and macrostructural changes as it is heated, which causes pore formation, drastic volume change and formation of a glassy layer in some cases.
- Based on the experiments conducted, a model for intumescence was theorized, and implemented in PATO.
- Simulations in PATO showed that the intumescence of RTV is a combination of thermal expansion and pressure build-up, with the pressure build-up term being heating rate dependent.

Future Work

- Perform in-situ heating and μ-CT experiments at ALS of RTV confined in a tube allowing for expansion only in one direction, followed by in-situ heating of RTV confined in a cylinder of PICA.
- Conduct Plasmatron X high enthalpy tests of PICA with an RTV slot to characterize aerothermal response.

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