

Quantification of RTV Intumescence using X-ray Imaging

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1 TGA-MS

Fig 1 presents the thermogravimetric analysis (TGA) and corresponding mass spectrometry (MS) for heating rates of 20, 30, 100 and 230 °C/min. With increasing heating rate, a rightward shift in pyrolysis decomposition with temperature is observed. Production of similar chemical species is observed for all four heating rates. Table 1 presents the species identified from TGA-MS that were reported by Smith *et al.* [1]

Table 1: Identified ions in MS of silicones from Smith *et al.* [1].

m/z	Ion	Compounds	Origin
73	Me_3Si^+	Methyl-containing silicones	RTV substrate
147	$\text{Me}_5\text{Si}_2\text{O}^+$	Methyl-containing silicones	RTV substrate
149	$\text{C}_8\text{H}_5\text{O}_3^+$	Phthalates	Common plasticizer in silicones
207	$\text{Me}_5\text{Si}_3\text{O}_3^+$	$(\text{Me}_2\text{SiO})_3$	Thermal degradation of silicones
281	$\text{Me}_7\text{Si}_4\text{O}_4^+$	$(\text{Me}_2\text{SiO})_4$	Thermal degradation of silicones
355	$\text{Me}_9\text{Si}_5\text{O}_5^+$	$(\text{Me}_2\text{SiO})_5$	Thermal degradation of silicones

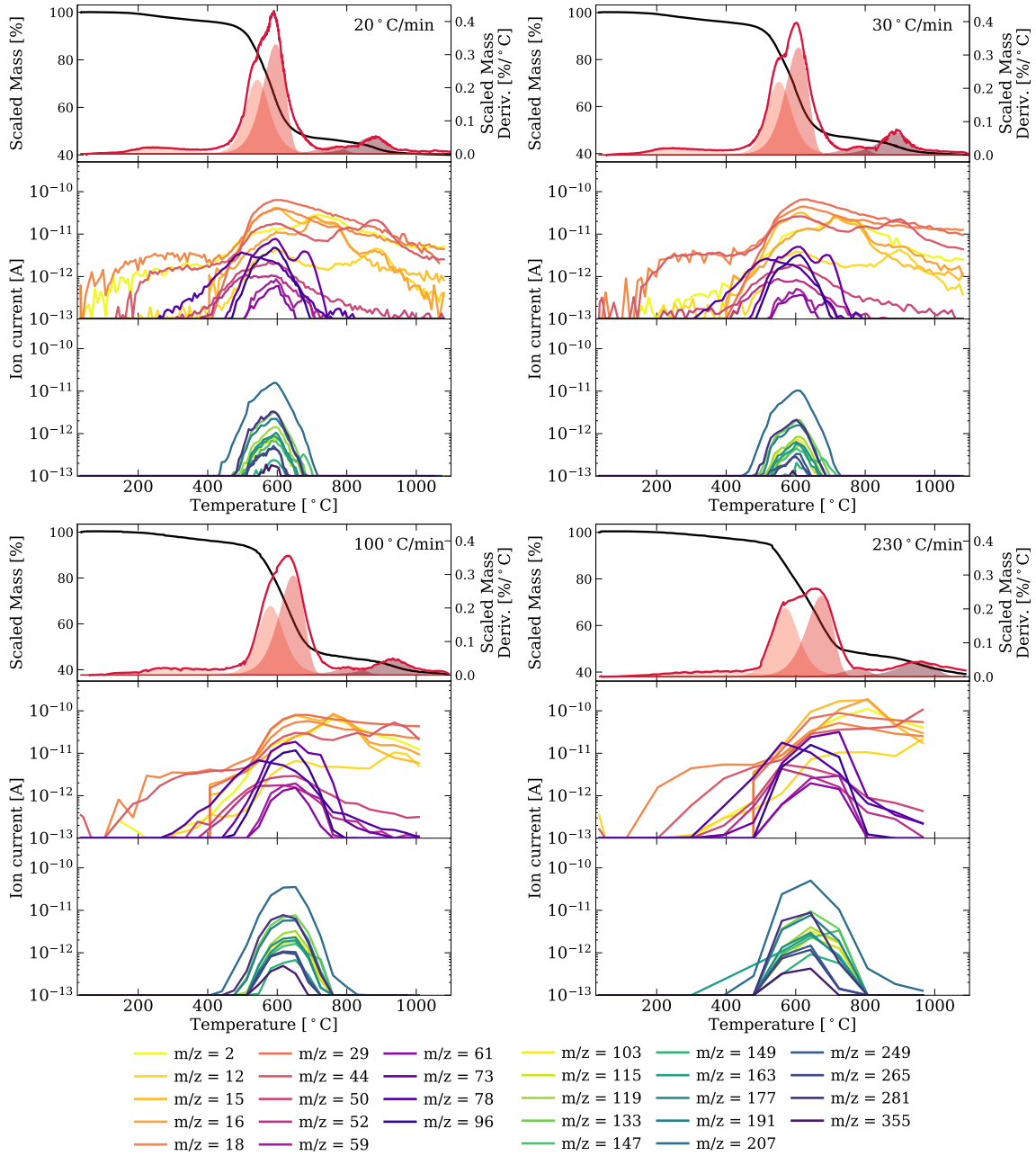


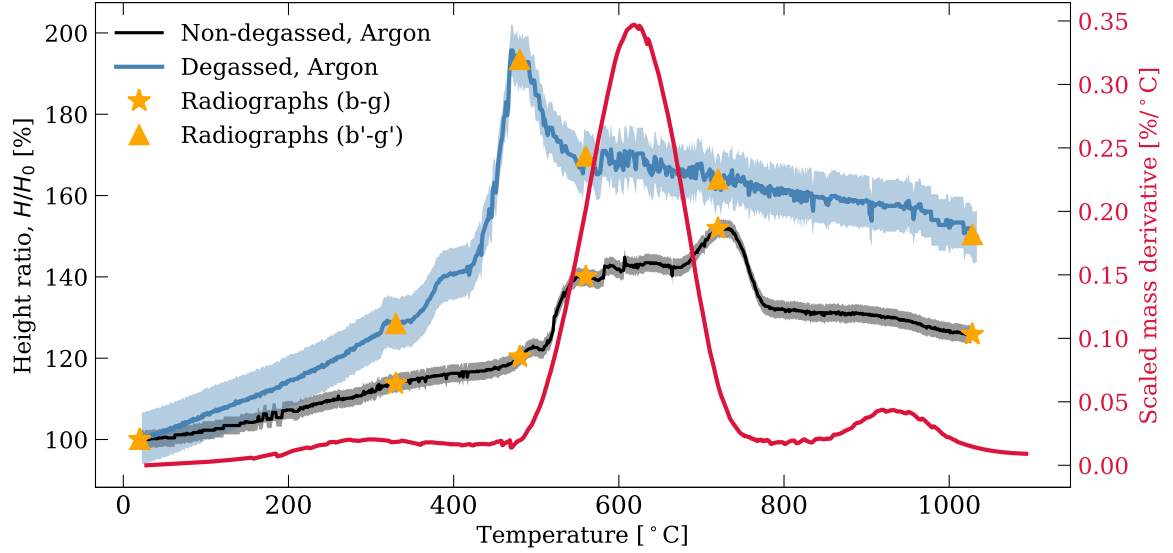
Fig. 1: TGA-MS curves at heating rates ranging from 20 to 230 °C/min.

2 Intumescence at 102 °C/min

Fig. 2a shows the percent swelling, expressed as height ratio ($= \text{height}/\text{initial height} \times 100$) as a function of temperature for RTV samples heated at 102 °C/min, co-plotted with the TGA derivative at 100 °C/min. Fig. 2(b-g) show the radiographs of the two samples at key temperatures. The behavior of non-degassed and degassed samples are separately discussed below.

Non-degassed RTV

The sample first expands at a quasi-linear rate due to thermal expansion at $T \leq 300$ °C (Fig. 2(b-c)), followed by non-uniform bulging and relaxation of the RTV at 300 °C $\leq T \leq 420$ °C due to the first pyrolysis reaction (Fig. 2(c-d)). The height ratio curve up to 420 °C is similar to those from the *in situ* μ -CT data showing $\approx 20\%$ height increase. At 420 °C, a steep rate of swelling is observed, which corresponds to the onset of the second pyrolysis reaction (Fig. 2(d-f)). Contrastingly, in the 30 °C/min μ -CT experiments, shrinkage of the RTV was observed with the onset of the second



(a) Height ratio of RTV heated at 102 °C/min along with the derivative from TGA collected at 100 °C/min (in red).

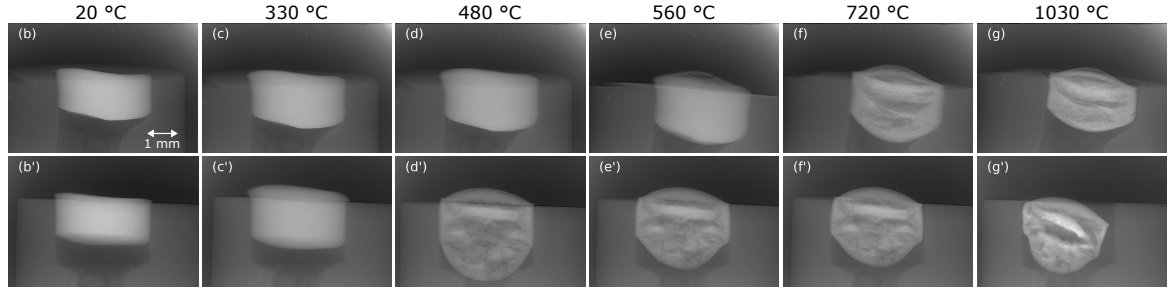


Fig. 2: Height ratio and radiographs of (b-g) non-degassed and (b'-g') degassed RTV at key temperatures when heated at 102 °C/min.

pyrolysis step. This discrepancy is attributed to the RTV being heated non-uniformly in the top-heating configuration, causing it to bulge and crack layer-by-layer in order to outgas. After the third pyrolysis reaction, the RTV outgasses and relieves its gas pressure, causing it to shrink. Finally, the fourth and fifth pyrolysis reaction causes further shrinkage of the RTV.

Degassed RTV

For degassed RTV, the height ratio shows an initially linear expansion with a slope (i.e., coefficient of thermal expansion) greater than that of the non-degassed sample. With the onset of the first pyrolysis reaction, the sample swells significantly as seen in Fig. 2(d'), due to presence of only closed porosity and absence of permeable, nano-scale pathways due to the degassing process. The RTV sample is seen to swell downward into the graphite holder until it contacts the graphite, after which it ruptures and relieves gas-pressure, followed by shrinkage as seen in Fig. 2(e'-g'). Overall, the extent of intumescence is much higher for the degassed RTV and the effect of pyrolysis onset was observed for the first reaction.

3 Post-test characterization

Fig. 3 presents the post-test electron micrographs of non-degassed samples tested in Argon and air at instantaneous heating (Sample Gr-ND5 and Gr-ND20, respectively), along with a sample heated in air at 1946 °C/min (Gr-ND12) at 34× and 800×, respectively. Weight percentage obtained at different points on the surface using EDS is tabulated in Table 2.

Gr-ND5 shows pores of various sizes on the outer surface along with cracking on the top due to outgassing. At 800×, macro-pores are observed throughout the sample. EDS spectra on the surface of Gr-ND5 is also similar to that of charred RTV noted in our previous studies [2].

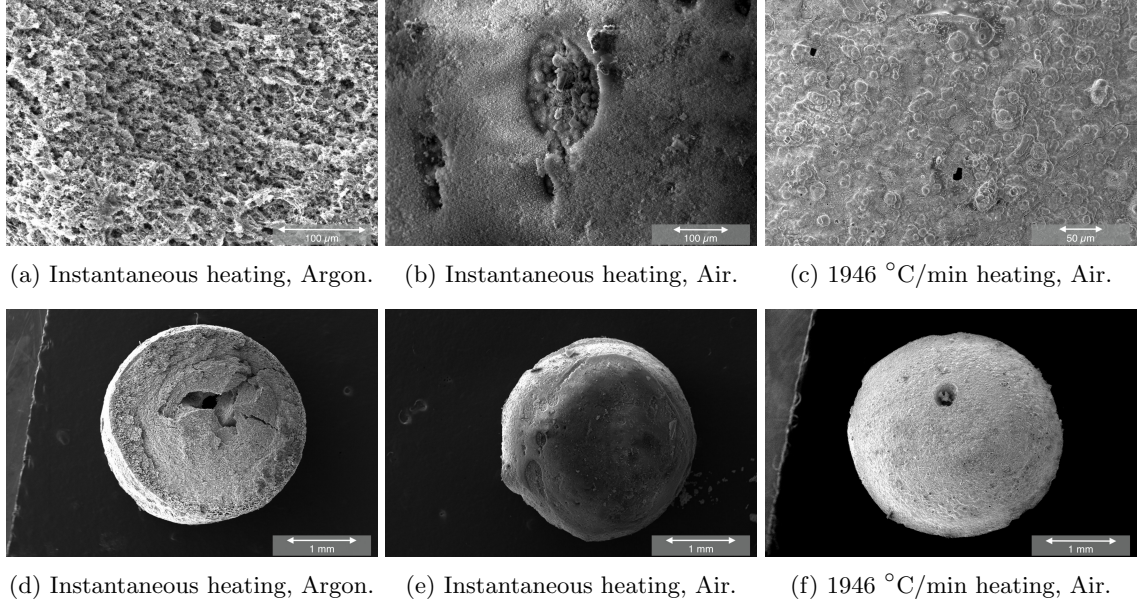


Fig. 3: Micrographs of post-test samples tested in (a, d) Argon, (b, e) air and sample holder (c, f) after air test.

In contrast, the samples tested in air (Gr-ND20 and Gr-ND12) show a cohesive coating, seemingly impermeable, formed on the surface. At higher magnifications, sparse porosities ($2\ \mu\text{m}$ - $10\ \mu\text{m}$) are observed. EDS of the post-test samples in air indicates a predominant presence of silicon and oxygen on the surface with significantly lesser amount of carbon and iron than in Gr-ND5. Therefore, a glassy silica surface is formed on the surface of the samples tested in air, indicating reaction of the RTV with ambient air.

The air-tested sample holders displayed a white coating on the graphite surface possibly due to the outgassed silicon-rich species reacting with the ambient air and depositing on the graphite surface. Micrographs of the coating are shown in Fig. 4 along with EDS maps of the holder. A distinct Si-O layer is observed on the carbon substrate, thereby confirming silica formation from RTV charring in an air environment.

Table 2: Elemental composition for the post-test charred RTV samples.

Sample Name	Weight%					
	C	O	Na	Al	Si	Fe
Gr-ND5	10	27.3	0.4	0.5	21.2	40.6
Gr-ND20	5.8	50.4	-	0.4	41.6	2.0
Gr-ND12	4.1	49.2	-	0.2	45.1	1.4
Gr-ND12 holder	33.3	40.1	-	-	26.6	-

Fig. 5 shows the post-test micrographs of FF-RTV and PICA-RTV after instantaneous heating. The FF-RTV sample shows large cracking on the surface, which occurs during pyrolysis and causes gas pressure relief. A non-porous, impermeable skin is observed on the surface of the sample, with a highly porous internal microstructure. As this sample was tested in Argon and a glass coating is not expected to form, this skin is expected to form due to adhesion while the liquid RTV cures in the FF holder. RTV-coated fibers are also observed at the wicking interface.

In the case of the PICA-RTV sample, similar microstructure is observed, with a non-porous skin on the surface and a porous, permeable internal volume. Propagation of the RTV crack into the PICA holder is observed, implying that RTV intumescence imparts stresses on the surrounding PICA holder that are capable of causing the PICA to crack. Furthermore, fibers of PICA near the crack interface show significant deposition of RTV pyrolysis products (Fig. 5g), whereas fibers away from the interface display conventional, charred PICA-fiber microstructure [3].

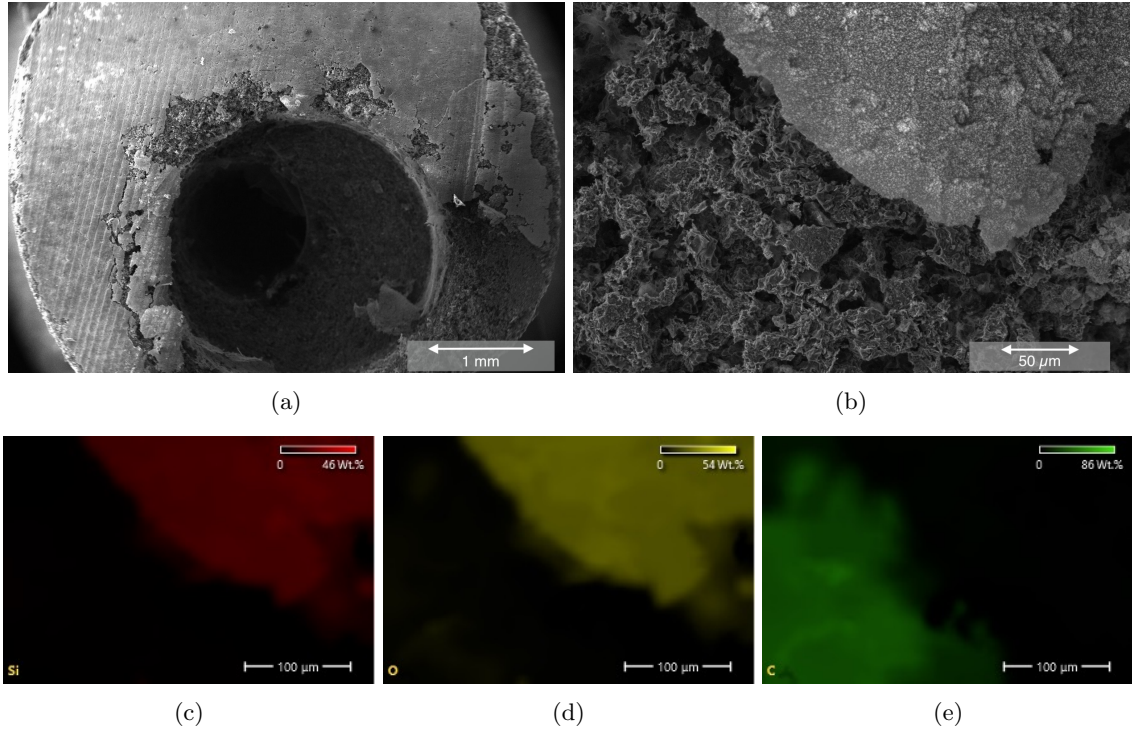
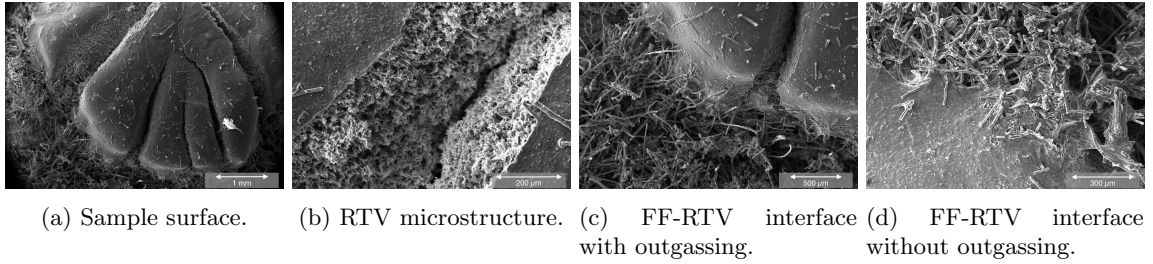


Fig. 4: Graphite holder used for 1946 °C/min heating in air, imaged at (a) 34× and (b) 600× magnification, and corresponding EDS maps of (c) silicon, (d) oxygen and (e) carbon.

FF-RTV instantaneous heating



PICA-RTV instantaneous heating

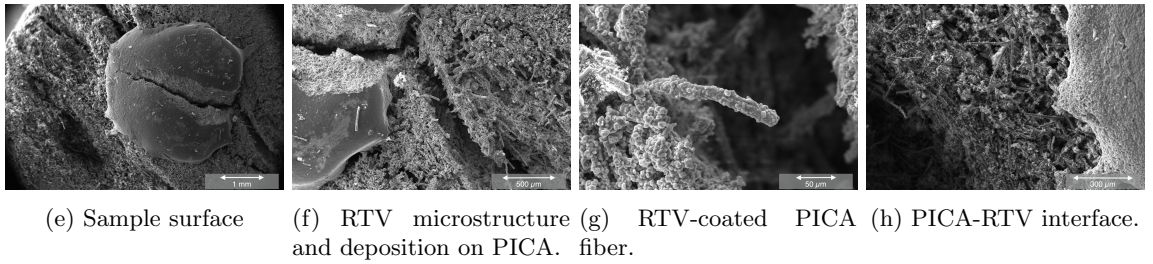


Fig. 5: Micrographs of post-test samples of RTV wicked into FF (a-d) and PICA (e-h).

References

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