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## **PUSHING THE BOUNDARIES: HIGH TEMPERATURE EVALUATIONS OF SILICONE PSAs**

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# **PUSHING THE BOUNDARIES: HIGH TEMPERATURE EVALUATIONS OF SILICONE PSAS**

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## **Introduction**

Silicones, also called polysiloxanes, are polymers with the chemical formula  $[R_2SiO]_n$ , where R may be an organic group, commonly found as methyl, phenyl, alkenyl, or hydrogen. These form long polymer chains with the backbone of the polymer forming a (...Si-O-Si-O-Si-O-Si-O-...) chain. Since their inception in the early 1940s, various uses have been found for this unique structure.

Silicone pressure sensitive adhesives utilize some of the unique characteristics of these silicone polymers to form high temperature tapes currently found on the market. For high temperature applications  $> 180^\circ\text{C}$  ( $356^\circ\text{F}$ ), silicones find uses in masking, bonding, or surface protection type applications. Some applications, for instance in masking tapes to mask gold finger attachment points on circuit boards during solder reflow operations, are pushing the needs of the tape to survive higher and higher temperatures. Traditional solder reflow temperatures might have traditionally been  $160\text{-}180^\circ\text{C}$  for 1-3 minutes while immersed in the molten solder. However, as the development of lead-free solder has taken over for lead-based solder usage in the electronics manufacturing arena, temperatures have increased up to  $230\text{-}260^\circ\text{C}$  for 1-3 minutes<sup>1</sup>.

To survive such high temperature exposures, recent studies exploring the upper boundaries of silicone pressure sensitive adhesives have been conducted. By identifying the physical property boundaries of existing silicone PSA chemistry, and exploring the chemical mechanisms of the chemical reactions happening at various temperatures, advancements in both the chemistry and the applications may be realized. New studies on temperature evaluations at various temperatures were conducted, examination of rheology curves as a function of temperature, and TGA/Stepped Isothermal Gravimetric Analysis (SIGA) were explored.

## **Chemistry and Properties of silicone PSA**

Silicone Building Blocks: Polymers and Resins

Conventional silicone PSAs are essentially a dispersion of silanol (-OH) or vinyl ( $\text{H}_2\text{-C}=\text{C-}$ ) functional silicone polymers blended with functional siloxane MQ resin in aromatic solvents. The solvent is most commonly toluene or xylene. Some silicone PSAs are solvent-free, but have the same basic composition of a silicone polymer and a silicone resin at a given ratio.

Silicone polymers provide many benefits. Their wide bond angles, ability to freely rotate and stretch, and spring-like behavior, as well as the high energy of the siloxy bond compared to

organic carbon-carbon bonds, allow them to be subjected to a number of different harsh environments and temperatures. Typical silicone polymers have a dimethylsiloxane polymer backbone, with reactive groups at the end of the chain, or along the chain at various intervals. Some silicone PSA systems utilize a diphenyl dimethyl copolymer system (referred hereafter as diphenyl) at low concentrations for some unique applications.

The theory behind the use of diphenyl dimethyl silicone copolymers within the silicone polymer backbone is to incorporate an electron withdrawing pendent group with an available pi cloud, which will allow additional stability within the polymer backbone, as well as to have a sacrificial pendent group that can absorb any free radicals that might be generated. This phenyl group will also break up the crystal like lattice structure that may form at low temperature.

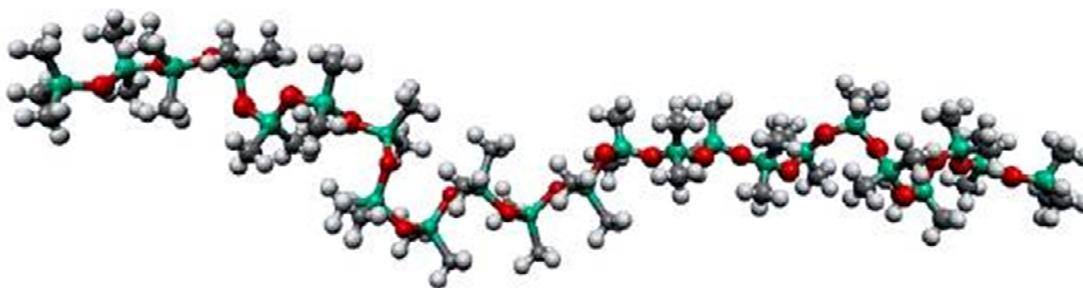


Figure 1. 3D Model of Silicone Polymer<sup>2</sup> (AV07577)

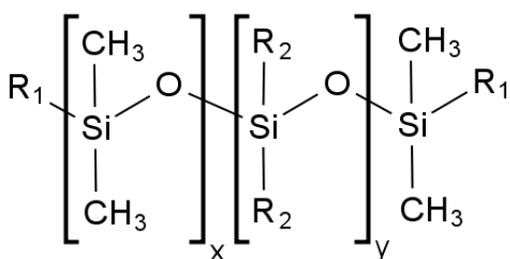


Figure 2. Silicone Polymer R<sub>1</sub>= (OH, vinyl, alkyl, phenyl, etc.), R<sub>2</sub>= (methyl, phenyl, alkyl, vinyl, etc.)<sup>2</sup>

The second main component in a silicone PSA is a silicone resin, typically pictured as a cage-like branched structure. This low molecular weight structure provides the adhesion component, while the polymer chain component provides more tackiness to the system.

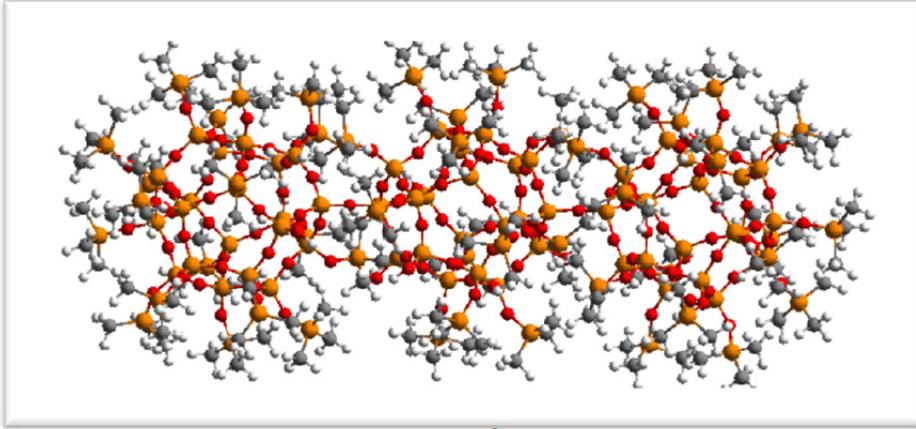


Figure 3. Silicone resin proposed structure<sup>2</sup>

The combination of high molecular weight silicone polymers with siloxane resins creates a silicone PSA with a wide range of flexibility over a wide temperature range, low surface tensions for easy wetting to surfaces, high thermal stability, chemical resistance, and excellent weathering resistance.<sup>2</sup>

Silicone PSAs are generally cured by one of two primary methods, either by a peroxide free radical mechanism, or a platinum catalyst induced addition cure mechanism. The primary focus for the work presented here will be on peroxide catalyzed PSAs.

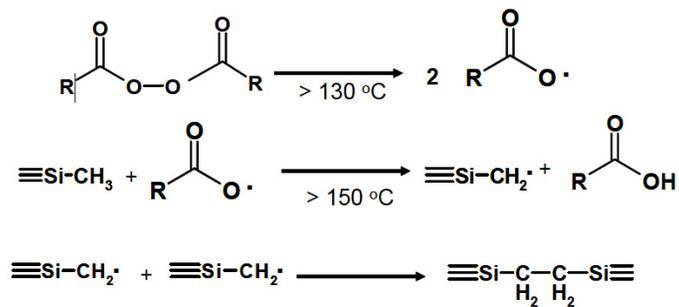


Figure 4. Peroxide induced free radical crosslinking of silicones<sup>2</sup>

Catalysts such as benzoyl peroxide (BPO) can be added at levels of 0.5-3wt%, depending on the application requirements. The resulting crosslinked structure is thought to be a multi-phase structure, consisting of resin-rich, gum rich, and hybrid blended phase zones.

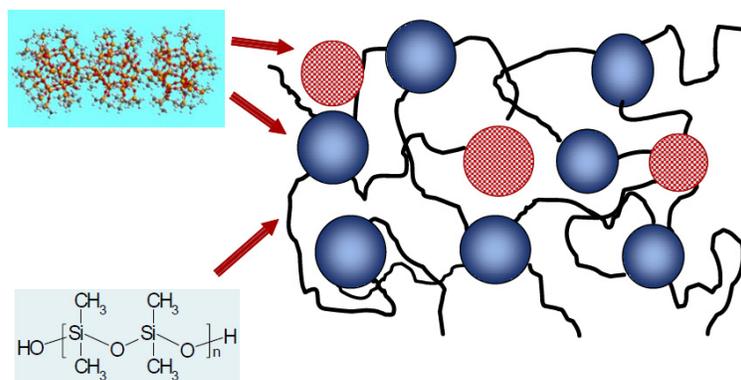


Figure 5. Proposed multi-phase structure for silicone PSAs, based on resin rich, gum rich, and hybrid zones.<sup>2</sup>

One of the benefits of a silicone PSA is its ability to withstand high temperature applications, over 200°C, while maintaining adhesion. It is the intent of this paper to explore the upper temperature boundary for silicone PSAs to identify what happens to various existing formulations as we approach 300°C, and to identify and explore formulation and chemical structure relationships to identify the impact that various chemical groups have on survivability at these challenging extreme conditions.

### Adhesive preparation and characterization

The adhesives evaluated were generally processed in a similar fashion, except where noted. A solvent solution of BPO was added to a base formulation (typically to yield 1 or 2% BPO per silicone solids), and diluted to reach 50% solids with additional xylene or toluene. A bird bar applicator was used to apply a coating onto the specified substrate to yield a 1.5-2.0 mil dry coat weight. PET samples were cured in a static oven at 80°C for 2 minutes to remove the solvent, followed by 180°C for 2 minutes to crosslink the system. DuPont™ Kapton® HN film samples were cured at 204°C for 2 minutes.

Adhesives were characterized by 180° peel adhesion per PSTC-101, probe tack, TGA and rheometry.

The products evaluated were as follows:

Silicone PSA Type A	Dimethyl silicone PSA.
Silicone PSA Type B	High temperature dimethyl silicone PSA with thermal stabilizer
Silicone PSA Type C	High adhesion dimethyl silicone PSA with thermal stabilizer
Silicone PSA Type D	High temperature diphenyl PSA with thermal stabilizer
Acrylic PSA Type I	Resin modified acrylic PSA
Acrylic PSA Type J	High temperature acrylic PSA

## High temperature analysis

PSA	Catalyst	Substrate	180° Peel Adhesion (g/in), 24 hr dwell	Probe Tack (g) (PT-1000)
Si Type A	1% BPO	2 mil PET	1787	775
Si Type A	2% BPO	2 mil PET	1633	591
Si Type B	1% BPO	2 mil PET	1522	584
Si Type B	2% BPO	2 mil PET	1384	510
Si Type C	1% BPO	2 mil PET	2327	1096
Si Type C	2% BPO	2 mil PET	1822	622
Ac Type I	N/A	2 mil PET	1607	500
Ac Type J	N/A	2 mil PET	1312	826

Table 1: Room Temperature, 24 hour data for 180° Peel Adhesion per PSTC 101 at 12 ipm, and Probe Tack using ChemInstruments PT-1000, 0.5 sec dwell. PSA on PET was cured 2 min 80°C, 2 min 180°C. Ave of 5 data points.

PSA	Catalyst	Substrate	180° Peel Adhesion (g/in), 24 hr dwell	Probe Tack (g) (PT-1000)
Si Type A	2% BPO	1 mil Kapton	585	361
Si Type B	2% BPO	1 mil Kapton	698	328
Si Type C	2% BPO	1 mil Kapton	837	322
Si Type D	2% BPO	1 mil Kapton	625	600
Ac Type I	N/A	1 mil Kapton	777	402
Ac Type J	N/A	1 mil Kapton	800	352

Table 2: Room Temperature, 24 hour data for 180° Peel Adhesion per PSTC 101 at 12 ipm, and Probe Tack using ChemInstruments PT-1000, 0.5 sec dwell. PSA on PI was cured 2 min 80°C, 2 min 204°C

The above tables provide a baseline peel adhesion and tack value for the systems evaluated, with the typical differences in adhesion and tack based on substrate thickness.

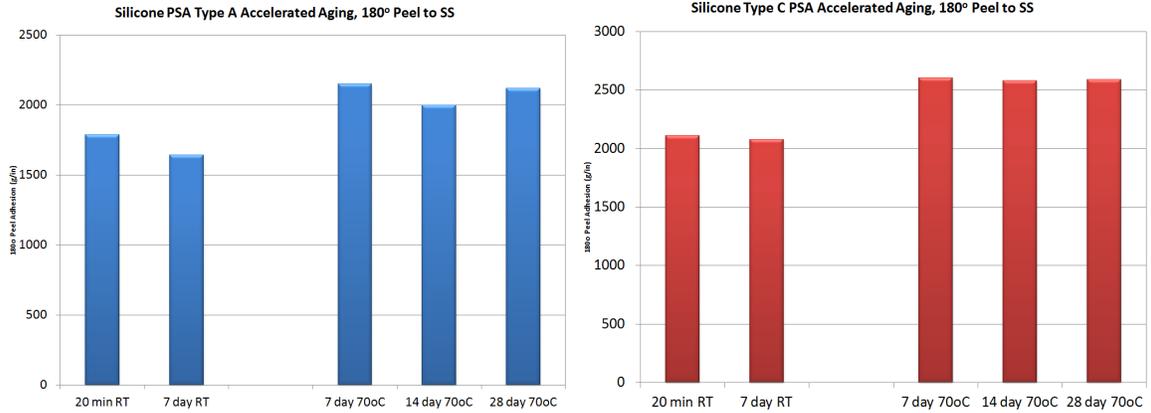


Figure 6: Accelerated aging adhesion results at room temperature (25 °C) and at 70 °C on 2 mil PET. (Left) Silicone Type A PSA and (right) Silicone Type C PSA.

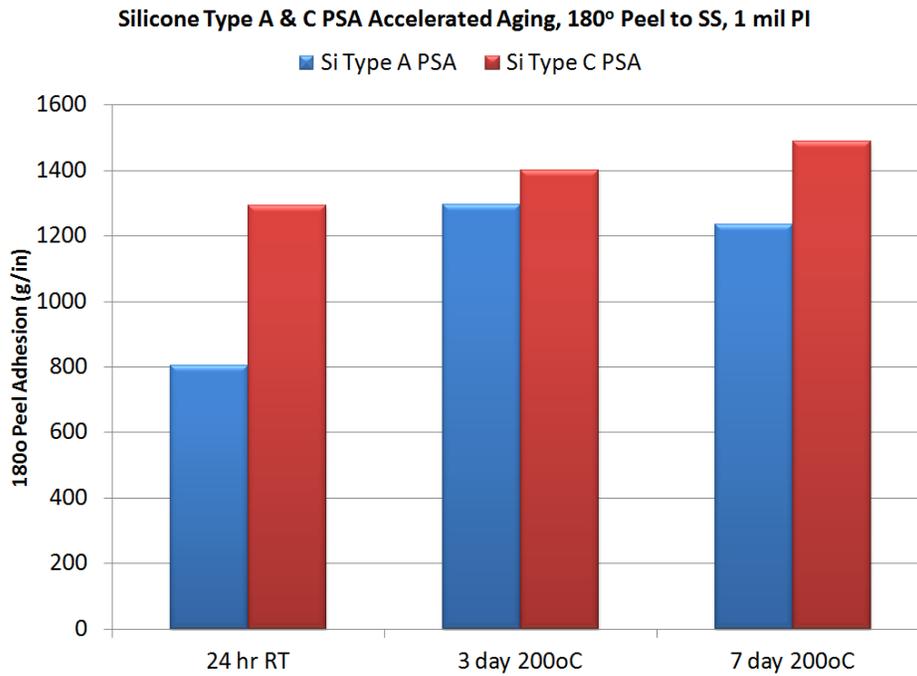


Figure 7: Accelerated aging adhesion results at room temperature and at 200°C on 1 mil Kapton

PSA	Initial Adhesion, RT, 24 hr (g/in)	Adhesion after 250oC, 24 hr (g/in)	Bubbles forming within interface
Si Type A	585	897	0%
Si Type B	698	998	0-2%
Si Type C	837	1017	50-60%
Si Type D	600	840	0%
Ac Type I	777	0	Charred
Ac Type J	800	0	Charred

Table 3: Adhesion results after exposure to 250°C for 24 hours, and then letting the sample return to RT prior to pulling.

An increase in adhesion after exposure to 250°C for 24 hours is typical, most likely from additional crosslinking that can improve both cohesion strength within the silicone PSA, as well as additional interaction with the surface.

### Hot Peel versus Cold Peel

Another method to analyze high temperature survivability is to evaluate by hot peel/cold peel, and look for residue remaining on the stainless steel panel. The most common test condition requested by customers is to expose the sample on a stainless steel panel to 270°C for 10 minutes, and pull the strip from the panel as it comes out of the oven (hot peel), followed by a few hours at room temperature and pull a second strip from the surface and record relative residue levels (cold peel). For this study, additional times and temperatures were added, namely 270°C for 30 minutes, and 300°C for 10 minutes. Residue was ranked from 5 (best) to 1 (worst). A ranking of 5 would be clean removal. A ranking of 4 would be slight ghosting, 3 would be tramlines, 2 would be some residue, and a 1 would be heavy residue.

This method is important to some applications where masking of a surface during a high temperature painting process is critical during the manufacturing operation, and the tape may be removed while still at high temperature.

PSA	Hot Peel 270°C, 10 min	Hot Peel, 270°C, 30 min	Hot Peel, 300°C, 10 min	Cold Peel, All conditions
Si Type A	5	3	1	5
Si Type B	5	4	1	5
Si Type C	5	4	1	4
Si Type D	5	4	4	5
Ac Type I	1	1	1	1
Ac Type J	1	1	1	1

Table 4: Results of hot peel and cold peel evaluations under different dwell times and temperatures.

## Rheometric Temperature Sweeps

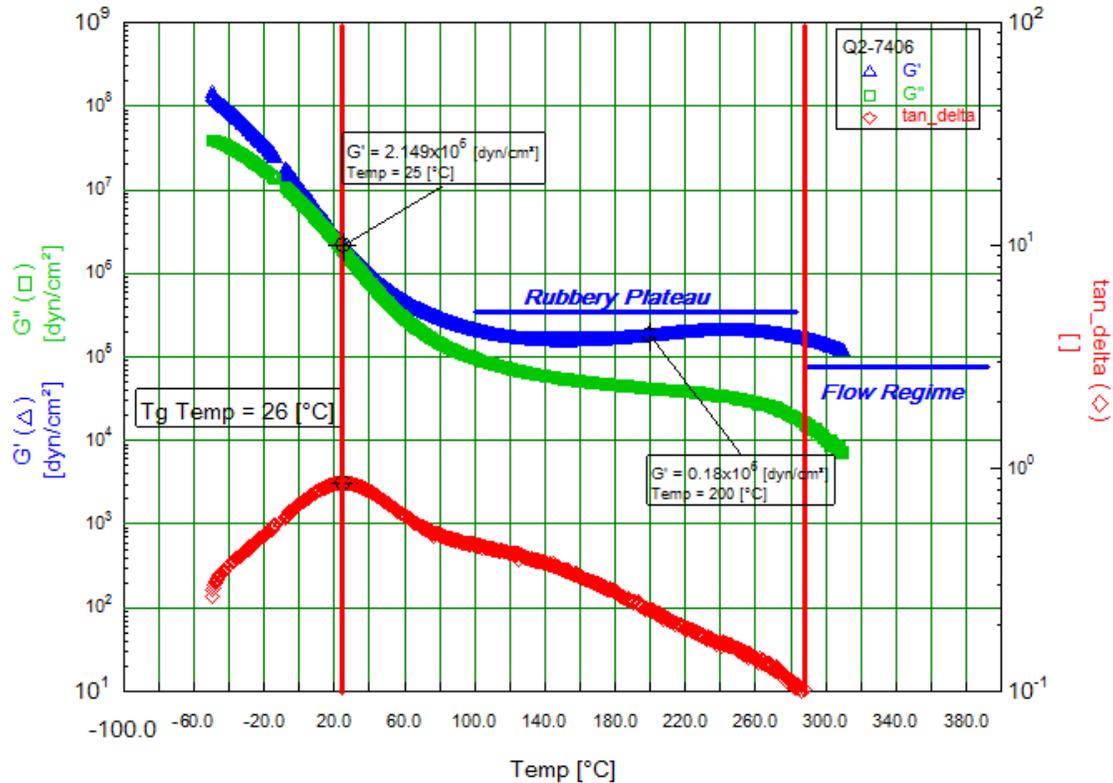


Figure 8: Si Type A dimethyl PSA temperature sweep at 1 Hz, from -50°C to 325°C. Cured with 2% BPO, 2 min 80°C, 2 min 180 °C cure

The rheometry curves for pressure sensitive adhesives can give indications of the glass transition temperature (Tg), and helps correlate to the relative tack of the pressure sensitive adhesive. Many acrylate and rubber based PSA's target a low Tg of 0°C or below in order to position the tack at room temperature well within the rubbery region of elastomers and plastics. A pressure sensitive adhesive with a low modulus at room temperature will feel tackier to customers.

The rheometry curve also indicates a rubbery plateau in the G' curve, or storage modulus, which indicates a consistent modulus over a wide temperature range. This tracks well with adhesion test results at varying temperature exposures, and can be an indicator for operating temperature ranges, depending on the length of time required.

The G'' curve, or loss modulus, should ideally track the G' curve, and approximate the same curve shape, with minimal changes over the operating temperature.

A few select curves are presented here. For ease of review, a summary table is presented below.

PSA	Catalyst	Tg	G' @ 25°C (dyn/cm <sup>2</sup> )	Onset of Rubbery Plateau	G' at 200°C (dyn/cm <sup>2</sup> )	Onset of Flow regime
Si Type A	2% BPO	26°C	2.15x10 <sup>6</sup>	100°C	0.18x10 <sup>6</sup>	>310°C
Si Type A	1% BPO	30°C	1.26 x10 <sup>6</sup>	140°C	0.02x10 <sup>6</sup>	318°C
Si Type B	2% BPO	23°C	2.01 x10 <sup>6</sup>	116°C	0.11x10 <sup>6</sup>	>330°C
Si Type C	2% BPO	39°C	5.73x10 <sup>6</sup>	119°C	0.12x10 <sup>6</sup>	280°C
Si Type C	1% BPO	46°C	6.20 x10 <sup>6</sup>	80°C	0.08x10 <sup>6</sup>	245°C
Si Type D	2% BPO	-10°C	0.33 x10 <sup>6</sup>	80°C	0.15x10 <sup>6</sup>	325°C
Ac Type I	-	-4°C	0.79 x10 <sup>6</sup>	50°C	0.08x10 <sup>6</sup>	255°C
Ac Type J	-	-9°C	0.52 x10 <sup>6</sup>	38°C	0.06x10 <sup>6</sup>	224°C

Table 5: Rheometry values for various PSAs, allowing for evaluation of Tg, G', and rubbery plateau region. Some samples were evaluated at both 1% and 2% BPO to evaluate the effects on Tg and flow regime onset.

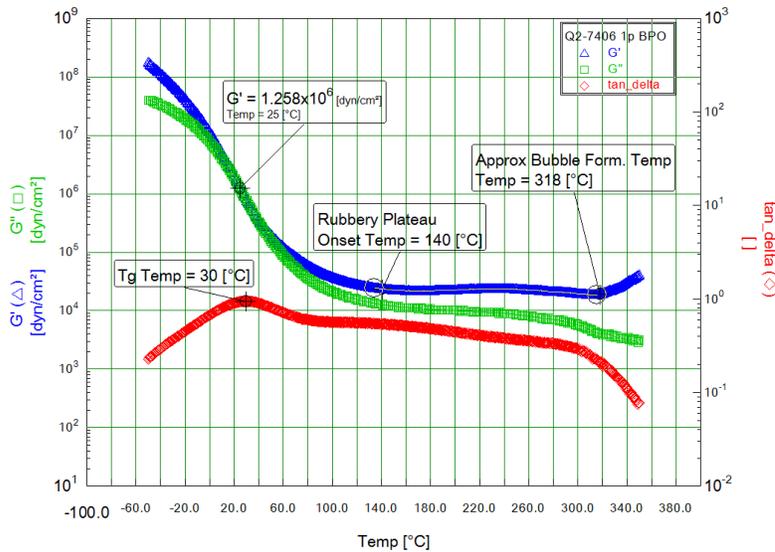


Figure 9: Si Type A Dimethyl PSA Temperature Sweep at 1 Hz, from -50°C to 325°C, when cured with 1% BPO, for 2 min 80°C, 2 min 180°C.

Higher levels of BPO will reduce tack slightly at room temperature, and increase the modulus slightly over the operating temperature, consistent with additional crosslinking occurring during the curing process. Generally, higher levels of BPO have been thought to

increase the chances of surviving very high temperature applications by forcing crosslinking into the system, and reducing the ability of the PSA to flow. Tapes manufactured with BPO levels up to 3% & 4% are not unheard of, but it depends on the PSA system and application.

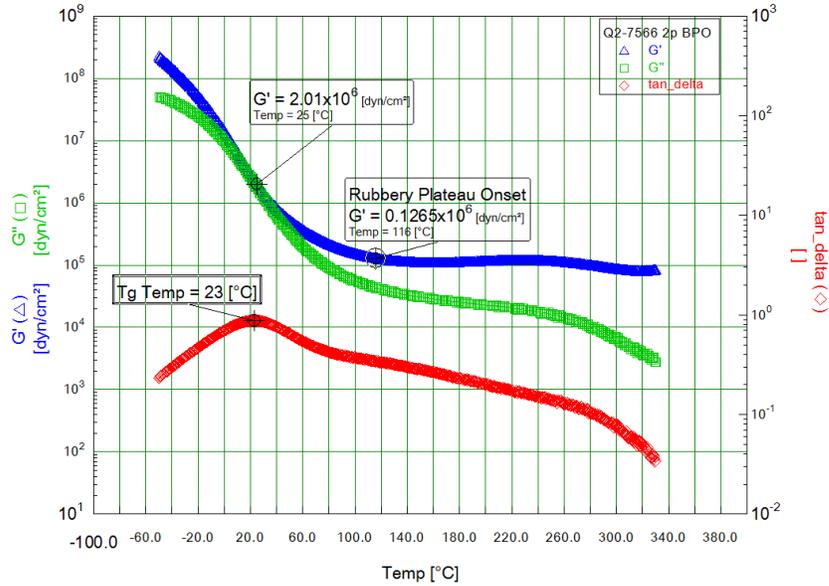


Figure 10: Si Type B Temperature Sweep at 1 Hz, from -50°C to 325°C. Cured with 2% BPO, 2 min 80°C, 2 min 180°C cure

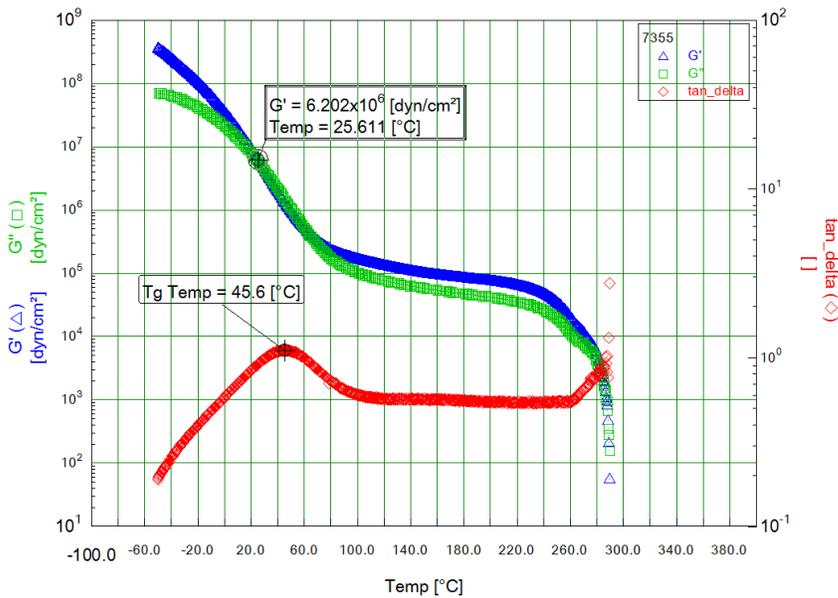


Figure 11: Si Type C Temperature Sweep at 1 Hz, from -50°C to 325°C. Cured with 1% BPO, 2 min 80°C, 2 min 180°C.

Some dimethyl PSAs have a very high  $T_g$ , as evident with Si Type C, with a  $T_g$  of  $+46^\circ\text{C}$ . This indicates that the PSA will have a low tack value. The minimal difference between  $G'$  and  $G''$  throughout the operating range suggests that this material will soften at the onset of the flow regime. When compared with the figure below of Si Type C cured with 2% BPO, the  $G'$  loss modulus behave consistently over a wider temperature range with little change to adhesion as the application gets warmer, with little slip or creep. This would indicate a good high temperature hold ability at higher temperatures of  $>550^\circ\text{F}$  ( $288^\circ\text{C}$ ).

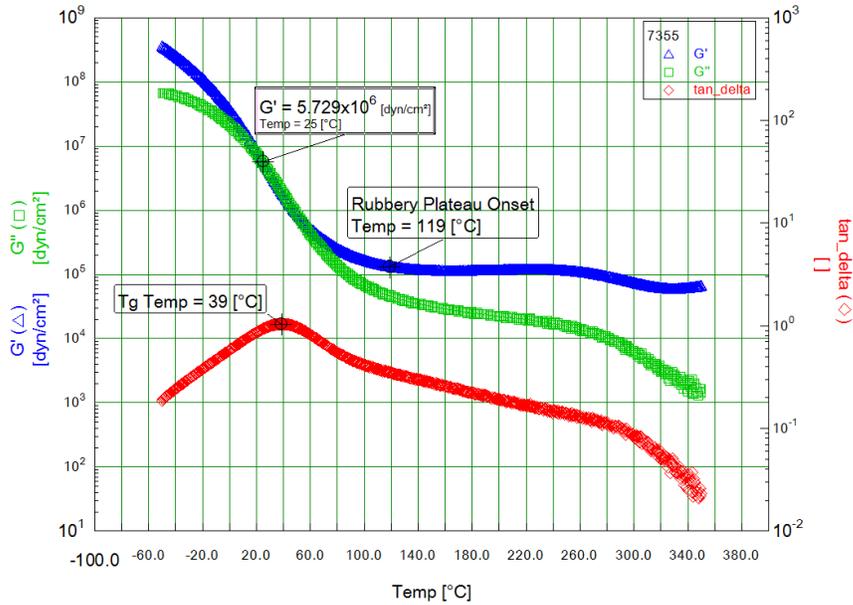


Figure 12: Si Type C Temperature Sweep at 1 Hz, from  $-50^\circ\text{C}$  to  $325^\circ\text{C}$ . Cured with 2% BPO, 2 min  $80^\circ\text{C}$ , 2 min  $180^\circ\text{C}$ .

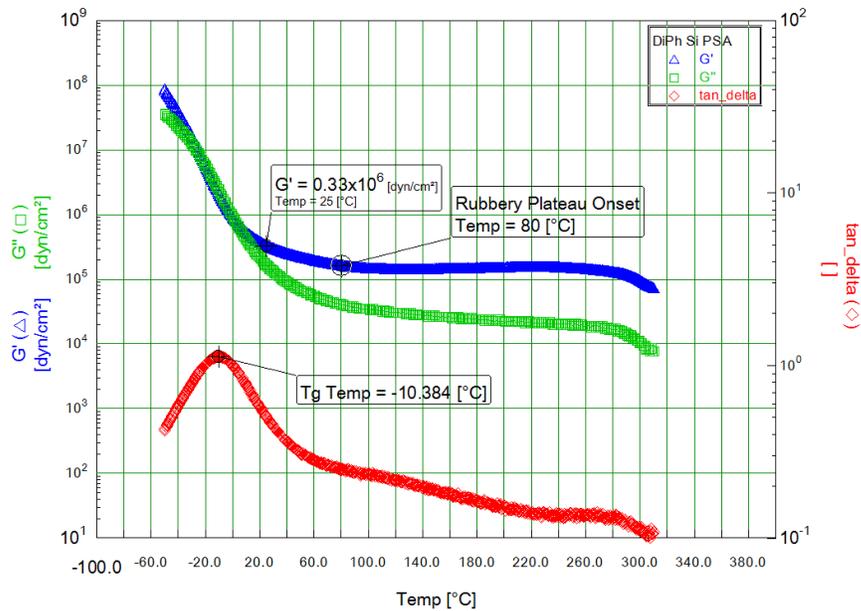


Figure 13: Si PSA Type D diphenyl PSA temperature sweep at 1 Hz, from  $-50^{\circ}\text{C}$  to  $325^{\circ}\text{C}$ . Tg identified as  $-10^{\circ}\text{C}$  based on tan-delta inflection point. The storage modulus  $G'$  shows a modulus of  $0.33 \times 10^6 \text{ dyn/cm}^2$  at  $25^{\circ}\text{C}$ . The storage modulus  $G'$  remains fairly stable until well over  $300^{\circ}\text{C}$  with minimal degradation effects. Cured with 2% BPO, 2 min  $80^{\circ}\text{C}$ , 2 min  $180^{\circ}\text{C}$ .

Advancements of diphenyl dimethyl copolymer based silicone PSAs highlight the ability to have a larger rubbery plateau, suggesting a larger operating temperature range. By reducing the Tg to  $-10^{\circ}\text{C}$ , the transition between a glassy state and a rubbery state occurs at lower temperatures, allowing for a greater range where the modulus stays consistent, and extends over  $300^{\circ}\text{C}$ . The low Tg also suggests a softer, gummier PSA at room temperature.

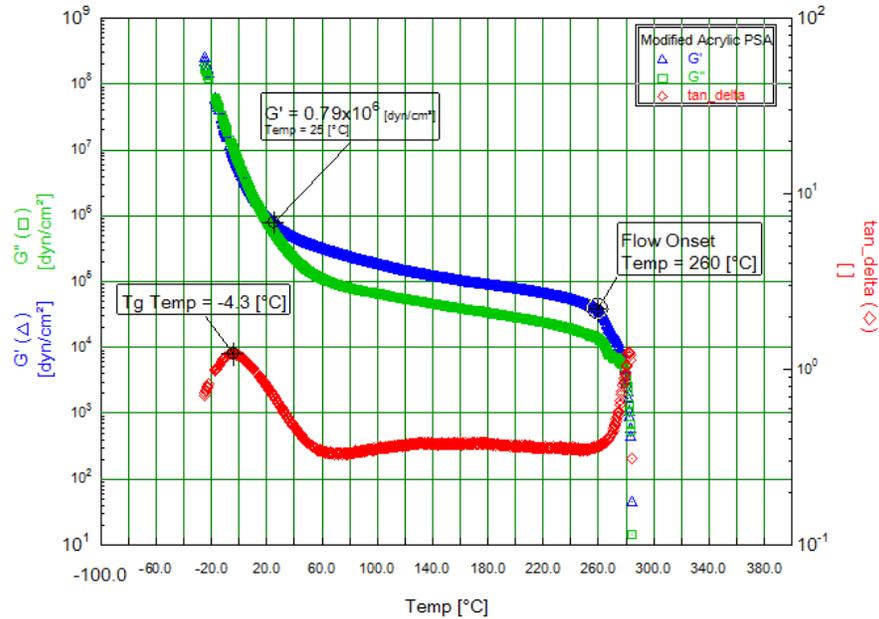


Figure 14: Ac Type I Temperature Sweep at 1 Hz, from -50°C to 325°C.

As a comparison, a resin modified acrylic, Ac Type I has a Tg identified as -4°C. The rubbery plateau shown in the figure above identify that the modulus decreases at a fairly constant rate over the operating temperature range, becoming softer as the material becomes warmer. Ultimately this material reaches an inflection point at approximately 260°C, at which point the modulus enters a flow regime where the PSA cannot maintain the physical properties, and may begin to creep or slide rapidly in a hanging weight type test. It should be noted in this rheometry test that the sample may be in an oxygen free environment due to the majority of the sample sandwiched between the 8 mm probes.

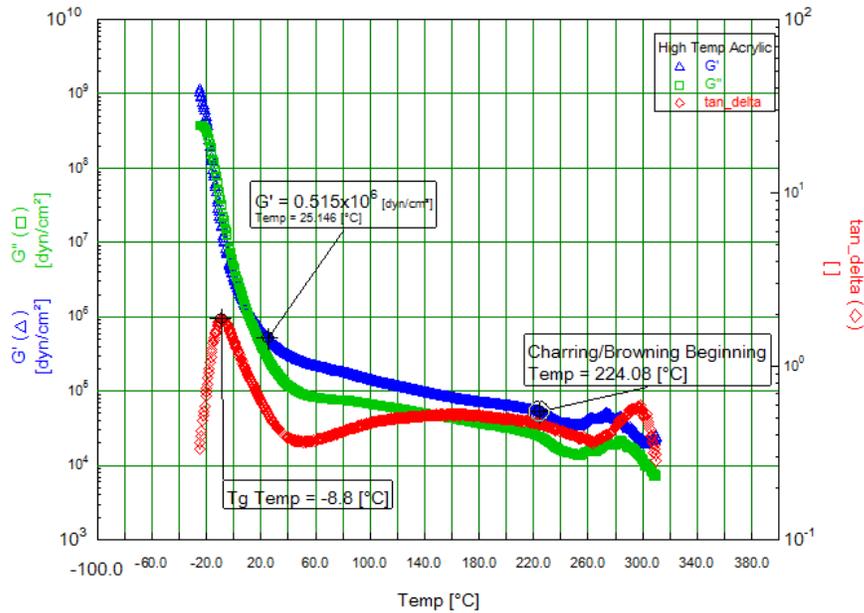


Figure 15: Ac Type J Temperature Sweep at 1 Hz, from -50°C to 325°C. Tg identified as -9°C. The storage modulus  $G'$  shows a modulus of  $0.5 \times 10^6$  dyn/cm<sup>2</sup> at 25°C, which can be correlated to high finger tack at room temperature. A color change was noted at a little over 220°C, with a dark amber/brown color appearing in the sample. The modulus may be misleading after this point, as the material did not soften but rather appeared to char and crosslinked further during a degradation step, and may be crosslinking internally as well as to the rheometer plates, forming more of an adhesive bond that may be masking the thermal decomposition of the organic PSA.

### TGA/Stepped Isothermal Gravimetric Analysis (SIGA)

Thermogravimetric analysis is a technique consisting of heating a couple of milligrams of PSA from room temperature to high temperatures (>800°C) at a constant rate and recording the weight loss occurring versus time/temperature. The resulting graph can indicate onset of degradation, and hence the beginning of weight loss. Experiments were conducted in both an inert atmosphere of nitrogen, as well as air, allowing for a differentiation of both decomposition due to energy, versus a decomposition due to oxidation. As most customer applications are evaluated in air, our discussion will focus mainly on the impact of air.

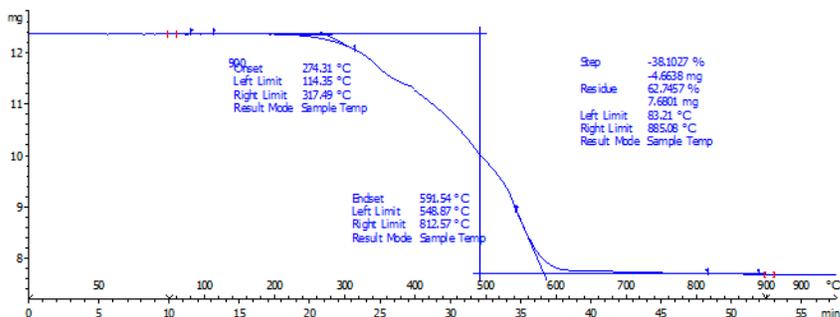


Figure 16. Thermo Gravimetric Analysis (TGA) of Si Type A in air. Si Type B, C, and G have similar profiles, differing slightly between 274-290°C.

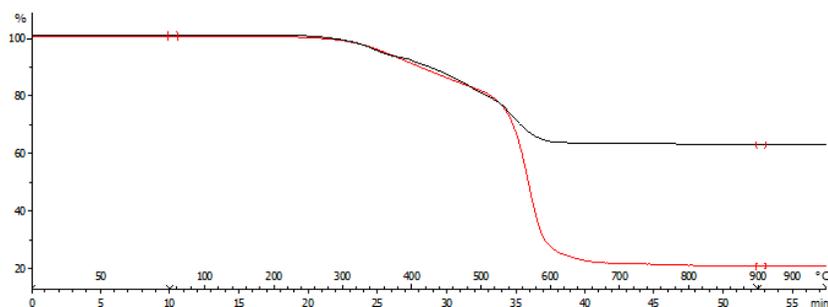


Figure 17. Overlay of Thermo Gravimetric Analysis (TGA) of Si Type A in Nitrogen (bottom) & Air (top).

### **Stepped Isothermal Gravimetric Analysis (SIGA)**

Differentiated from TGA, which used a typical ramp rate of 20°C/min, was thought to potentially confuse results if species elute at different rates at different temperatures. By holding at different temperatures within the key operating ranges, outgassing or migrating species are removed, allowing the system to reach an equilibrium/steady state until the next temperature level.

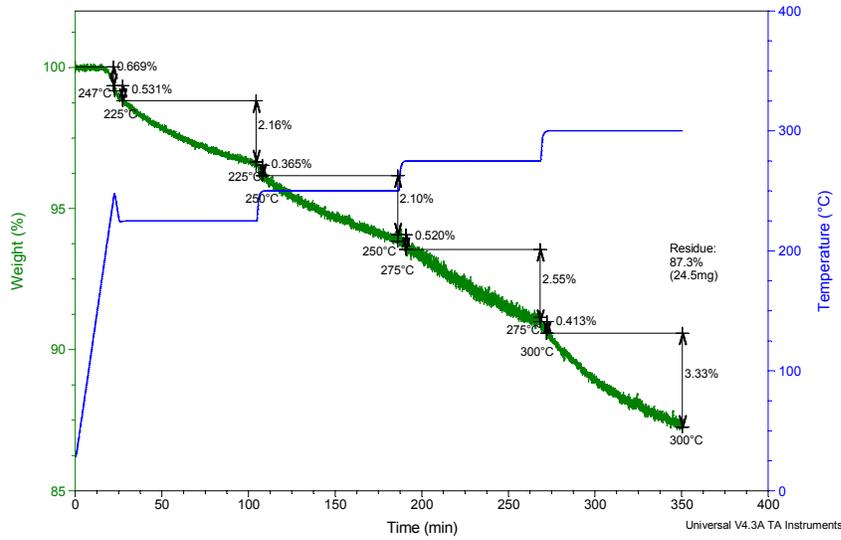


Figure 18: Stepped Isothermal Gravimetric Analysis (SIGA)- Thermogram of Si Type A showing weight loss as held at constant temperatures in steps up to 300°C over 80 minutes per step. Cured using 2% BPO.

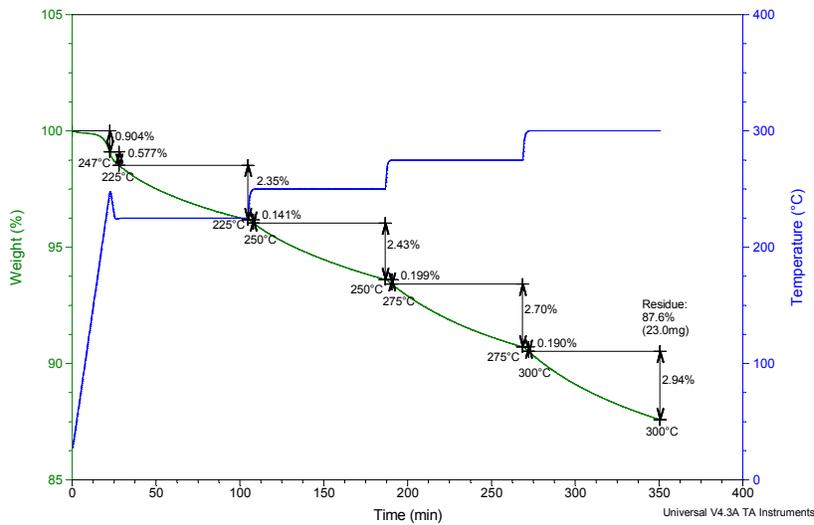


Figure 19: SIGA Thermogram of Si Type B. Cured using 2% BPO

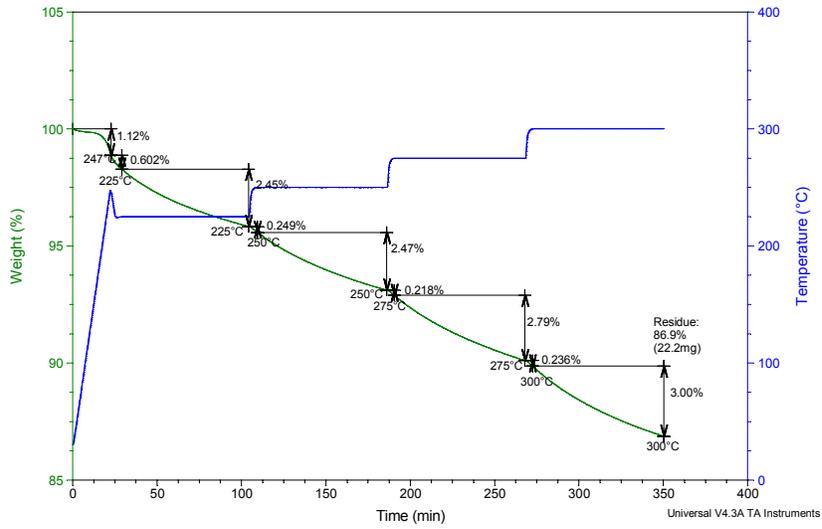


Figure 20: SIGA Thermogram of Si Type C. Cured using 2% BPO

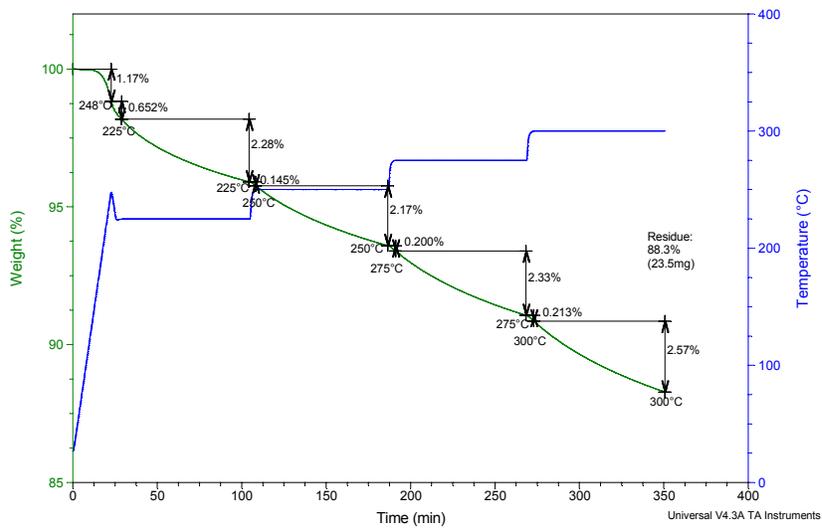


Figure 21: SIGA Thermogram of Si Type D variant. Cured using 2% BPO

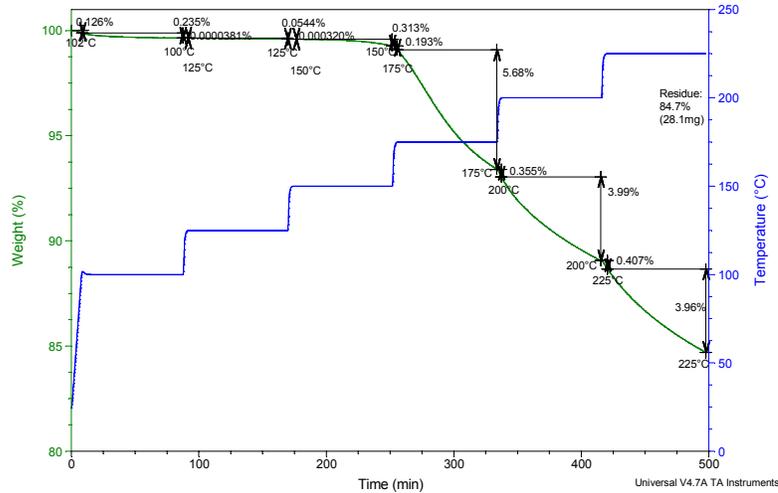


Figure 22. SIGA of Ac Type I. Starting at initial temperature of 100°C, holding for 80 minutes in air, with steps of 25°C to reach a maximum temperature of 225°C. 15.3% weight loss observed, primarily at temperatures > 150°C.

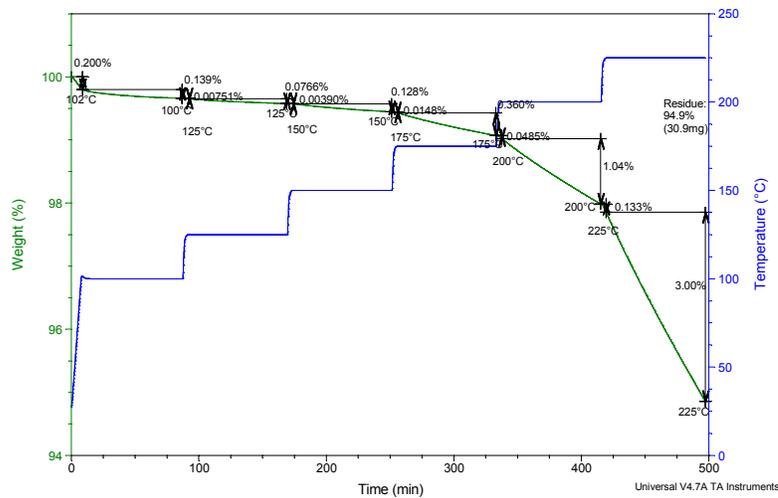


Figure 23. SIGA of AC Type J. Starting at initial temperature of 100°C, holding for 80 minutes in air, with steps of 25°C to reach a maximum temperature of 225°C. 5.1% weight loss observed, primarily at temperatures > 150 °C.

Evaluation of the stepped isothermal gravimetric analysis profiles identify the initiation of some weight loss event, occurring at 150-175°C for the acrylic systems analyzed here, and over 225°C for many of the silicone systems. A few percent weight loss over time/temperature, whether from the loss of small molecules entrapped in the system, or the breakdown of polymer chains in a degradation mechanism, may or may not have an impact on the actual bond line and usage of the tape. It depends on the application and intended usage, temperature, and time exposure to determine if there will be a loss in bond strength of the tape.

## Summary

Silicone PSAs are well known for their ability to survive harsh environments. Survival at both high and low temperatures is required for many applications, from electronics platters tape to high velocity oxygen fuel (HVOF/Plasma) masking tapes to permanent bonding for high altitude applications.

### Chemistry Set

- Silicone building blocks used to create Si PSAs can vary based on the polymers' pendent groups, yielding, for example, either dimethyl siloxane homopolymers or diphenyl dimethyl siloxane copolymers.
- Depending on the formulation, Mw, reactivity, and resin to polymer ratio, some Si PSA systems will have higher heat tolerance than others, and higher than most acrylic PSA systems when subject to over >200°C.
- Diphenyl silicone systems, when optimized properly, can survive a higher temperature hot peel test than even standard dimethyl silicone systems. This can be useful for masking operations that see extreme temperatures, such as masking or labels for lead free solder bath submersion.
- Diphenyl silicone systems can also lower the Tg of silicone systems.
- It should be noted that silicones have a lower surface energy than acrylic PSA systems, and can still wet to a substrate even with a higher Tg in the 20-40°C temperature range as compared to their acrylic brethren. This enables adhesion to develop over time as the silicone PSA wets to the surface. Tg for silicone PSA systems seems to only impact the various tack tests that tape users employ, from finger tack to probe tack to loop tack.

### Cure system

- In this paper, analysis of 1% and 2% benzoyl peroxide were evaluated to understand the impact on different testing criteria. General learnings were reaffirmed – higher peroxide levels will yield slightly lower 180° peel adhesion and tack values, but be able to sustain higher operating temperatures as seen in rheometry testing as an extension of the rubbery plateau.

Understanding the boundaries of a PSA is important to select the right adhesive system for the application. As each application has its own criteria for success or failure, it is often necessary to evaluate tapes in different manners, and to use different techniques to identify just where and how to push the boundary.

## REFERENCES

1. Houston, P., Lewis, B., Baldwin, D., Kazmierowicz, P., *Taking the Pain out of Pb-Free Reflow*, APEX 2003 Technical Conference, Anaheim, CA.  
<http://www.northtouch.com/documents/taking-the-pain-out.pdf>
2. Lin, S., Durfee, L., Knott, A., & Schalau, G. (2009). *Silicone Pressure Sensitive Adhesives* (Vol. Technology of Pressure Sensitive Adhesives and Products). (I. Benedek, & M. Feldstein, Eds.) Boca Raton, FL: CRC Press.
3. Hwang, J; Stiff, D; Melancon, K; Filiatrault, T, *Ultra High Temperature Pressure Sensitive Adhesive for Electronics Assembly*, SMTAI 2003 Technical Conference.
4. Czech, Z; Pelech, R; *Thermal degradation of acrylic pressure sensitive adhesives based on copolymers of 2-ethylhexyl acrylate and acrylic acid*, POLIMERY 2009, 54, nr 11-12, pp 828.
5. Noll, W; *Chemistry and Technology of Silicones*, 1968, Academic Press, London