Exploring the High Temperature Reliability Limits for Silicone Adhesives

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ABSTRACT

The thermal stability of silicone polymers, fluids and resins has been well documented and studied extensively. The high temperature performance of silicone adhesives and sealants used for electronics applications has only moderately been investigated. This report documents the effects of very high temperature exposures to electronics-grade silicone adhesives and sealants for such properties as tensile strength, elongation, tensile modulus, weight loss, shrinkage, durometer, and lap shear adhesion. The goal of the work is to determine application "life expectancies" of the products as well as an extrapolated estimate of the Underwriter's Laboratories' "continuous use" temperature rating – the highest temperature at which a product is expected to lose no more than 50% of its original value for whatever key property degrades the fastest

Four different formulations of silicone adhesives and sealants were evaluated for high temperature stability. For these products, elongation was found to be the fastest degrading property among those tested. The data was found to fit a power curve of exposure temperature vs. time to reach a 50% loss of initial tensile strength and elongation to an R-squared value of 0.99 and to a linear fit in an Arrhenius plot to the same very strong fit. These plots could be used to closely estimate the effects of heat aging on the material over a wide range of temperatures.

INTRODUCTION

Silicone is the generic name used for many to identify a family of products based on the polydimethyl siloxane (PDMS) molecule with unique characteristics. For electronics applications silicones can be used as adhesives, encapsulants, gels, protective coatings, thermal management materials, even device packaging materials and wafer-level coatings.

Silicones have a combination of properties which contribute to provide a proven long term reliability and performance in electronics applications. These features include: unmatched thermal stability, flexibility, moisture resistance, adhesion to many common substrates used in electronics, low ionic impurity and compatibility with common processing techniques. Among all these characteristics that are shared by the majority of silicones, one property is recognized as one of the most useful in electronics applications and that is their consistent performance over a very wide temperature range. The lower and upper operating temperature limits for silicones are not very well defined. Some approaches have placed these limits in the range from -40 to 150 °C. Others, less conservative, have placed the limits between -50 and 200 °C. Both approaches are correct; however, the applicability of each will depend much on the product used. Operating temperatures for silicones have a great dependency on the formulation, filler type and content, additives, functionality of silicone polymer, etc. Silicone products can be formulated in different ways to provide higher thermal stability or lower temperature flexibility. There are silicone products that can be exposed for long periods of time to temperatures as high as 250 °C or as low as -80 °C. These would be considered, within the product line, as especial materials. For general purpose adhesives/sealants, within the scope of this paper, the operating temperature limits will be defined as -45 to 200 °C.

The performance of silicone adhesive/sealants, such as the ones under the scope of this paper, when exposed to temperatures around 200 ºC has been very well documented and evaluated. However, there is very little relevant data detailing the performance of these products when working above the operating limits (200 ºC) for long term exposures or even short term periods. This missing data acquires great relevance for today's electronics applications, where electronic modules may be exposed to extreme high temperatures for short or long periods of time; identifying as extreme high temperatures any temperature above the limit exposed here, which is 200 ºC. It is the goal of this paper to review the performance of four different formulations of silicone adhesives/sealants when exposed to temperatures above 200 °C as a way to provide valuable guidance in the proper selection of these kinds of products for an electronics application.

HIGH TEMPERATURE REQUIREMENTS

Nowadays a large number of industries require materials to be exposed to high temperatures, usually for rather short time durations but sometimes for extended periods that could go from a couple of months to several years. In electronics, the upper temperature limits are most frequently determined by the end use application. For some applications, such as automotive electronics, electronic parts may be exposed up to 175 ºC for extended periods of time or even higher temperatures for short durations. Likewise, the time duration used to determine thermal stability is extremely dependant on the specific requirements of each application. Solder reflow ovens may only subject the materials to a few seconds or minutes of high temperature – and materials are not expected to significantly change in performance even though the exposure temperatures may be very high.

Many applications may have transient temperature "spikes" that considerably exceed their standard operating temperatures. These spikes could have durations ranging from a few seconds to a few minutes or even an hour or more. While it may be assumed that a few seconds at relatively high temperature may have insignificant consequences on material properties, it is unrealistic to not recognize that even a few minutes at very high temperatures may change certain material characteristics. For example, for thermoplastics such changes may be readily apparent if the material begins to melt and lose dimensional stability. For thermoset products however, degradation may not be as easy to observe.

Table 1 Typical Application Temperatures and Durations

Application	**Max Temp**	**Duration**
Solder reflow ovens	225-260C	10-90 seconds
Automotive on-engine modules (extended warranty)	175C 150C 150C	5 min. 1000 hrs 3000 hrs
Industrial power devices	250C 200C 175C	hours months years

Silicone adhesives and sealants are widely used to bond, seal and sometimes protect electronic components or modules for high temperature applications. The stability of silicone adhesives and sealants to high temperature in the order of 200 ºC is well accepted, and typically is higher than most other polymeric materials used in electronics. However, there is very little relevant data detailing long term high temperature exposure (> 200 ºC) or even short term to the temperatures experienced in today's electronic applications (see Table 1).

Test Methodology

Determining the thermal stability of a material is not always a straightforward task. There are many important properties of a given material, and many or most will change with heat induced degradation. All important properties should be evaluated with a test methodology that ideally enables short, mid and long term durability estimates to be made.

Thermogravimetric analysis (TGA) has been extensively used to determine the thermal stability/degradation of different materials. The basic principle involved in TGA is simply to weigh a sample of the material under study in a controlled atmosphere while the temperature of the sample is varied in a known manner. Thermal degradation is related then to the weight loss of the sample. This method has proven poor efficacy in determining the thermal degradation of silicone products as silicones when exposed to high temperatures undergo several transformations by a variety of processes, including oxidation, siloxane rearrangement and hydrolysis. Siloxane rearrangement occurs without the formation of volatiles where extensive depolymerization may take place before fragments small enough to evaporate without further decomposition can be produced. This rearrangement will lead to the loss of physical properties, not precisely linked to weight loss. At the same time, the degradation of silicones at high temperature by oxidation slowly transforms the material into more quartz-like properties. Thus the electrical insulation properties of the product remain almost unchanged or even improve with such exposures. Under these bases, it is easy to understand that the thermal stability of silicones adhesives and sealants under the scope of this paper needs to be linked to the degradation of physical properties, such as: tensile strength, elongation, etc.

UL Standard 746B10 offers a methodology that can be used to estimate a ten year "life expectancy" or "half-life" of polymeric materials. It proposes the useful life of a material to be defined as the time required to lose no more than 50% of any application-important property. The highest temperature at which 10 years of continuous exposure will retain 50% of the most sensitive important property is referred to as the Relative Temperature Index, or RTI. This standardized method works quite well to study high temperature exposures for silicon adhesives and sealants as there are quantifiable properties such as tensile strength or hardness that can be easily measure to verify the performance of the material.

The UL RTI type of standard gives a means of quantitative comparison between materials for long term exposures, and the data can also readily provide short term exposure expectations as well. However, it is important to remark that sensitive applications may require additional validation with specific performance and exposure time parameters. UL RTI values are ten year exposure estimates. To obtain data for this length of aging is of course not practical. Instead data is typically collected at a minimum of four high temperatures. The time to lose 50% of original properties is then plotted vs. temperature to obtain predictive graphs. Ten year life estimates are then extrapolated from these plots. For this study, five exposure temperatures were used: 200, 225, 250, 275 and 300 ºC.

The performance and life expectancy of the silicone adhesives studied here when exposed to temperature higher than 200 ºC will then be expressed in a more useful way following the guidelines mentioned above.

Proposed Products and Tests

The group of products used for this study is formed by a one-part moisture cure silicone sealant and two heat cure adhesives (self-leveling and thixotropic). These products will be evaluated for thermal stability by measuring properties such as tensile strength, elongation, modulus of elasticity, durometer and lap shear adhesion (to unprimed aluminum) after exposure to the 5 different temperatures indicated above for up to 1000 hours or less, depending on the time to lose no more than 50% of original value for the property measured.

The typical properties for the products included in this study are shown in the following chart (Table 2).

Table 2 Typical Properties for the Products used for this study

Silicone Adhesive	1	2	3
Description	1-part het cure (self- leveling)	1-part heat cure (thixotropic)	1-part moisture cure (thixotropic)
Hardness, Shore A	65	65	40
Tensile Strength, psi	870	750	1150
Modulus, psi	600	660	200
Elongation, %	200	120	500
Lap Shear, psi	700	600	500

Cured sheets of 2 mm nominal thickness were prepared and standard tensile dog bone samples were die cut from listed products. These samples were laid onto trays and placed in convection ovens for set time durations and then removed, cooled to room temperature and tested. Lap shear adhesion was evaluated onto bare aluminum.

Results and Discussion

Samples prepared as described in the previous section of this report were aged in convection ovens at five temperatures. Since one of the purposes of the study was to find a much faster means to predict 10 years of heat aging, very high temperatures were used to obtain fast degradation rates.

At the very high temperatures the degradation of the silicone adhesive occurred very quickly. This led to a problem in how to account for the time the samples required to reach the oven set temperature. It was found that in nearly all cases the small dog-bone samples required approximately 6 minutes to reach 95% of the oven set point temperature. These 6 minutes were discounted for the purposes of this study. Therefore a time recording of 0.1 hours would in actuality refer to 6 minutes of residence time at the specified temperature plus an additional 6 minutes to reach the oven temperature. While this method has its drawbacks especially at the highest exposure temperature, it was a practical and expedient method that appeared to fall within the experimental error of the data.

For reporting purposes, the following experimental data presented in detail through next sections of this report will describe the performance of the adhesive 1 (one-part, self-leveling, heat cure adhesive) when exposed to high temperature as representative of the other two adhesives/sealants tested.

Table 3 Initial properties for Adhesive 1
(one-part, self-leveling heat cure)

Property	**Value**
Durometer, Shore A	64
Tensile Strength, PSI	874
Elongation, %	216
Tensile Modulus, PSI	622
Lap Shear Adhesion, PSI	674

Thermal degradation is often not catastrophic but instead a process of steady property loss. Determining a suitable endpoint can therefore be somewhat subjective. One line of reasoning would say that when any property exceeds specification limits it has degraded past the part design and qualification standards for which it was chosen.

However, many material specification limits are based on a standard set of properties that are more specific to identifying the main characteristics of the material vs. actual application-use requirements.

For a highly elastomeric material like silicone, an interesting point is elongation. Note that the typical elongation of the adhesive 3 (Table 1) is 500%. It is unlikely that for actual applications the adhesive is stressed close to its property capability, stretching the adhesive up to 500% its original size. Using the UL RTI type of test criteria where the end-of-life set point of any property is the loss of half of its original value, one would conclude that when the elongation of this material had dropped to 250% it is degraded to an end-of-life set point. However, a material retaining 250% elongation is still highly elastomeric and this property is likely still more than adequate for a great number of applications.

Another line of reasoning would say that an end-of-life set point should be determined as when a material reaches some certain minimum value for a given important property. In the material example above the criteria might be retention of an absolute value of 50-100% elongation. Of course, these criteria would be very application specific and would require a great deal of testing for any given application, considering operating conditions and geometric dimensions of the sealed part.

Table 4 show the % change in each property measured for sample 1 when exposed to 300 ºC at different times. Elongation and adhesion were found to be the most rapidly changing property during thermal aging. This is something typically observed in silicone products. High temperature degradation promotes polymer rearrangement and oxidation (as discussed earlier) that creates additional chemical bonds between polymers, forming a stiffer structure. As the new bonds are formed, it is common for silicones to become physically stronger exhibiting a higher tensile strength (figure 2), higher durometer (figure 3), and higher modulus (figure 4). However, tensile strength eventually will begin to decrease as the material continues aging at high temperature becoming somewhat brittle. As the new polymeric structure loses some of its flexibility, which is clearly shown in figure 1, elongation is dramatically reduced by thermal aging.

Table 4 Thermal Aging for Adhesive 1 @ 300 ºC

	% Change				
Time, hr	**Durometer, points**	**Tensile**	**Elongation**	**Modulus**	**Adhesion**
0	0	0	0	0	0
0.1	-1	76	52	101	60
0.2	-1	70	42	109	40
0.4	-3	60	34	117	26
1	0	53	29	114	17
2	1	46	22	140	12
4	4	42	19	160	6
8	10	50	16	201	8
24	21	62	12	348	4

For adhesive 1, the original elongation for the product reduces to 50% after an effective exposure of approximately 6 minutes at 300 ºC, marking this point the life expectancy limit at this temperature following the guidelines of UL Standard 746B10 previously mentioned. Similar behavior is observed when the adhesive is exposed to the other temperatures (fig. 1). A summary of results for the other properties (durometer, tensile strength, lap shear adhesion and modulus) are presented in the following figures.

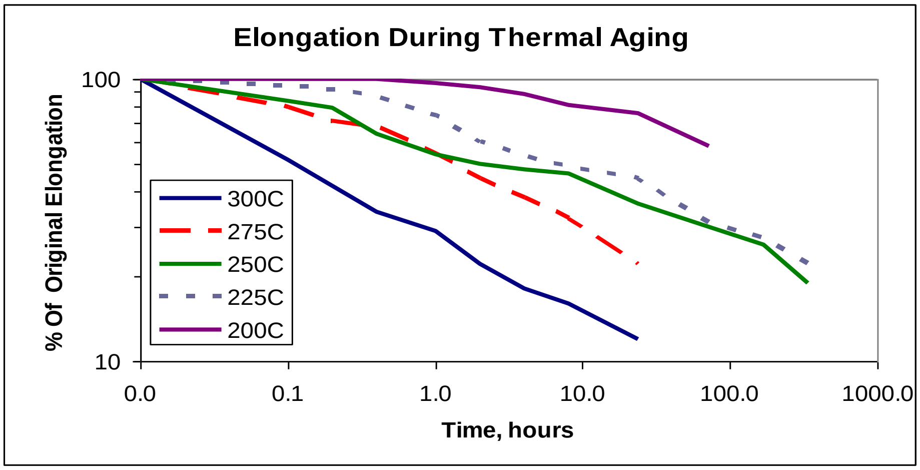

Fig. 1 Change in Elongation During Thermal Aging

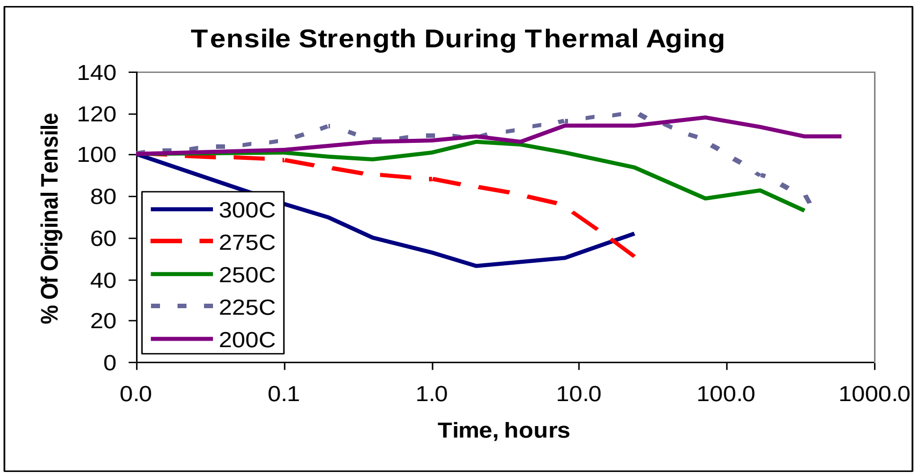

Fig. 2 Change in Tensile Strength During Thermal Aging

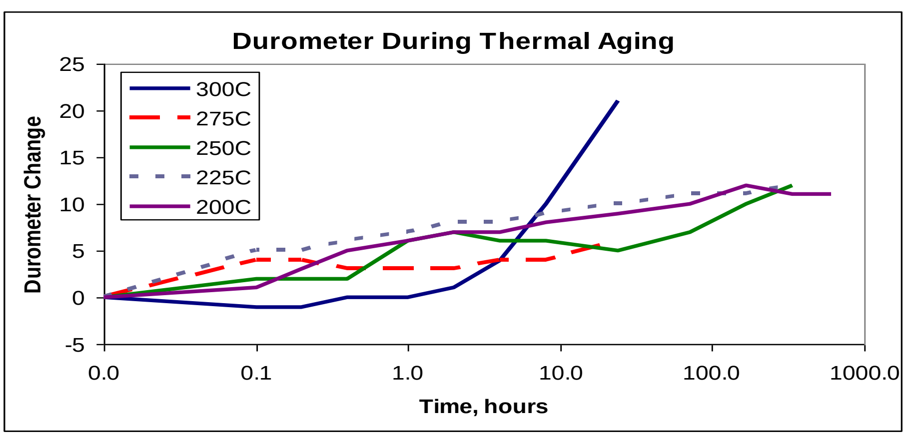

Fig. 3 Change in Durometer During Thermal Aging

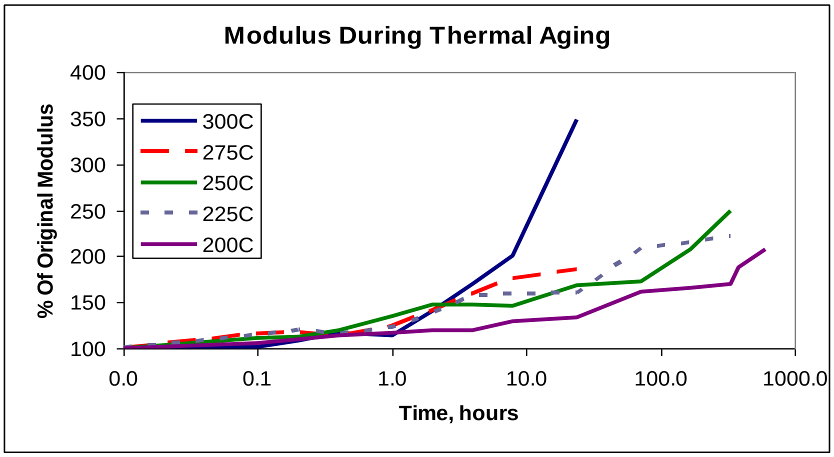

Fig. 4 Elastic Modulus During Thermal Aging

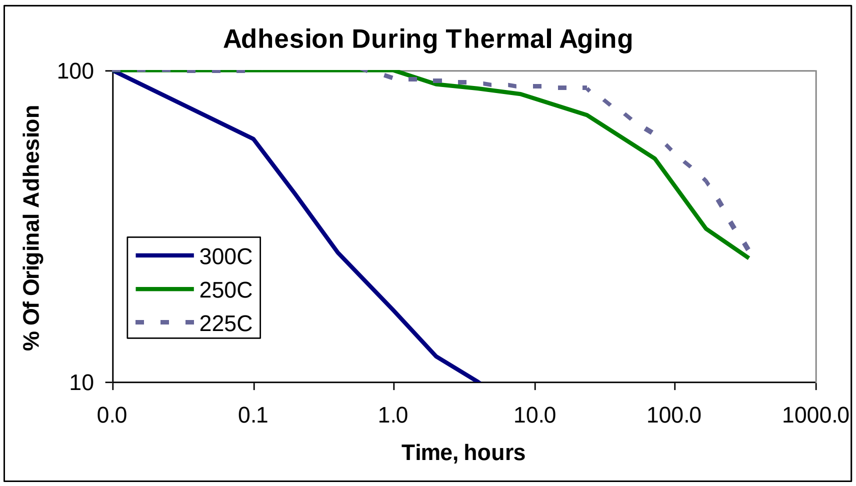

Fig. 5 Lap Shear Adhesion During Thermal Aging

The test procedures used in this study allows to obtain data in a period of weeks to a couple of months at very high exposure temperatures that could be used to confidently predict longer term property degradation at much lower temperatures. The 10 year life expectancy to lose no more than 50% of its initial elongation was predicted to be 149ºC for adhesive 1 (one-part, self leveling heat cure adhesive).

For this study working with silicone adhesives, elongation was probably the best property to track since it was found to degrade the fastest and had by far the most consistent results. Tensile strength generally lowered also over exposure time, but there was more scatter in the data and it is entirely possible that at early points in a given high temperature aging process the tensile strength may increase and durometers may decrease for a short period before going in the directions most normally observed in thermal oxidative degradation mechanisms. At the beginning of the work there was concern that lap shear adhesion may be the property to degrade the fastest. The data showed that while adhesion did indeed deteriorate with high temperature exposure, it did not change as fast as elongation.

Since elongation was the fastest degrading property, this was used to generate a predictive plot of time to lose 50% of the original value.

Using the same procedure and method as indicated for the adhesive 1 (one-part, self-leveling, heat cure adhesive), the estimated highest temperature exposure for the other 2 adhesives/sealants evaluated here is shown below (Table 5).

Table 5 Time to Lose 50% of Original Elongation for Silicone Adhesives

Silicone Adhesive	1	2	3
Description	1-part heat cure (self-leveling)	1-part heat cure (Thixotropic)	1-part moisture cure
10 yrs	149C	136C	158C
1000 hrs	188C	178C	254C
1 hr	265C	266C	321C
1 minute	325C	335C	340C

Conclusions

When silicone adhesives/sealants are exposed to temperatures above 200 °C, and in some cases above150 °C (depending on the silicone formulation), some chemical degradation starts impacting some of the physical properties of these products. This chemical degradation is promoted by a variety of processes, including oxidation, siloxane rearrangement and hydrolysis. The property that shows the highest and fastest degree of degradation is the elongation. Elongation was used then to predict the temperature limits exposure for the adhesives/sealants evaluated under the scope of this paper, following the guidelines offered by the UL Standard 746B10. In this way, the limits indicated here were determined by the time required for the adhesive/sealant to lose no more than 50% of its original elongation when exposed to different temperatures. It is important to remark that for some silicone adhesives/sealants with initial elongation values in the range of 400 or 500%, losing 50% of its original value leave them with an elongation in the range of 200 or 250%. A material retaining 250% elongation is still highly elastomeric and this property may still be more than adequate for a great number of applications. Therefore, the data reported in this paper should be used only as a guideline to establish general temperature exposure limits. Any specific application will require extensive testing and evaluations to determine the durability and maximum temperature exposure for the silicone, taking into consideration operating conditions and environmental factors.

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  Application Development Manager

- The thermal stability of silicone polymers, fluids and resins has been well documented and studied extensively.

- The high temperature (> 200 ºC) performance of silicone adhesives and sealants used for electronics applications has only moderately been investigated.

Goals:

- Explore the performance of silicone sealants/adhesives when exposed to temperature above 200 ºC
- Determine application “life expectancies” : the highest temperature at which a product is expected to lose no more than 50% of its original value for whatever key property degrades the fastest (UL 746B10).

Si Adhesives/Sealants Thermal Stability

The lower and upper operating temperature limits for silicones adhesives/sealants are not very well defined.

- Some approaches point out to: -45 to 200 °C
- Less Conservative approach: -65 to 260 °C

Both approaches are correct; however, the applicability of each will depend much on the product used.

Table 1 Typical Application Temperatures and Durations

High Temperature Requirements

Application	Max Temp	Duration
Solder reflow ovens	225-260C	10-90 seconds
Automotive on-engine modules (extended warranty)	175C 150C 150C	5 min. 1000 hrs 3000 hrs
Industrial power devices	250C 200C 175C	hours months years

Thermal Degradation of Silicones

Silicones when exposed to high temperatures (> 200 ^{o}C) undergo several transformations by a variety of processes:

- Oxidation
- Siloxane Rearrangement
- Hydrolysis

Thermal Degradation of Silicones

- Siloxane rearrangement occurs without the formation of volatiles.
- Extensive depolymerization may take place before fragments small enough to evaporate without further decomposition can be produced.
- This rearrangement will lead to the loss of physical properties, not precisely linked to weight loss.

Thermogravimetric analysis (TGA)

- (TGA) has been extensively used to determine the thermal stability/degradation of different materials.
- This method has proven poor efficacy in determining the thermal degradation of silicone products.

High Temperature Stability

Thermal stability of silicones needs to be linked to the degradation of physical properties:

- Tensile Strength
- Elongation
- Modulus of Elasticity
- Durometer

Experimental work

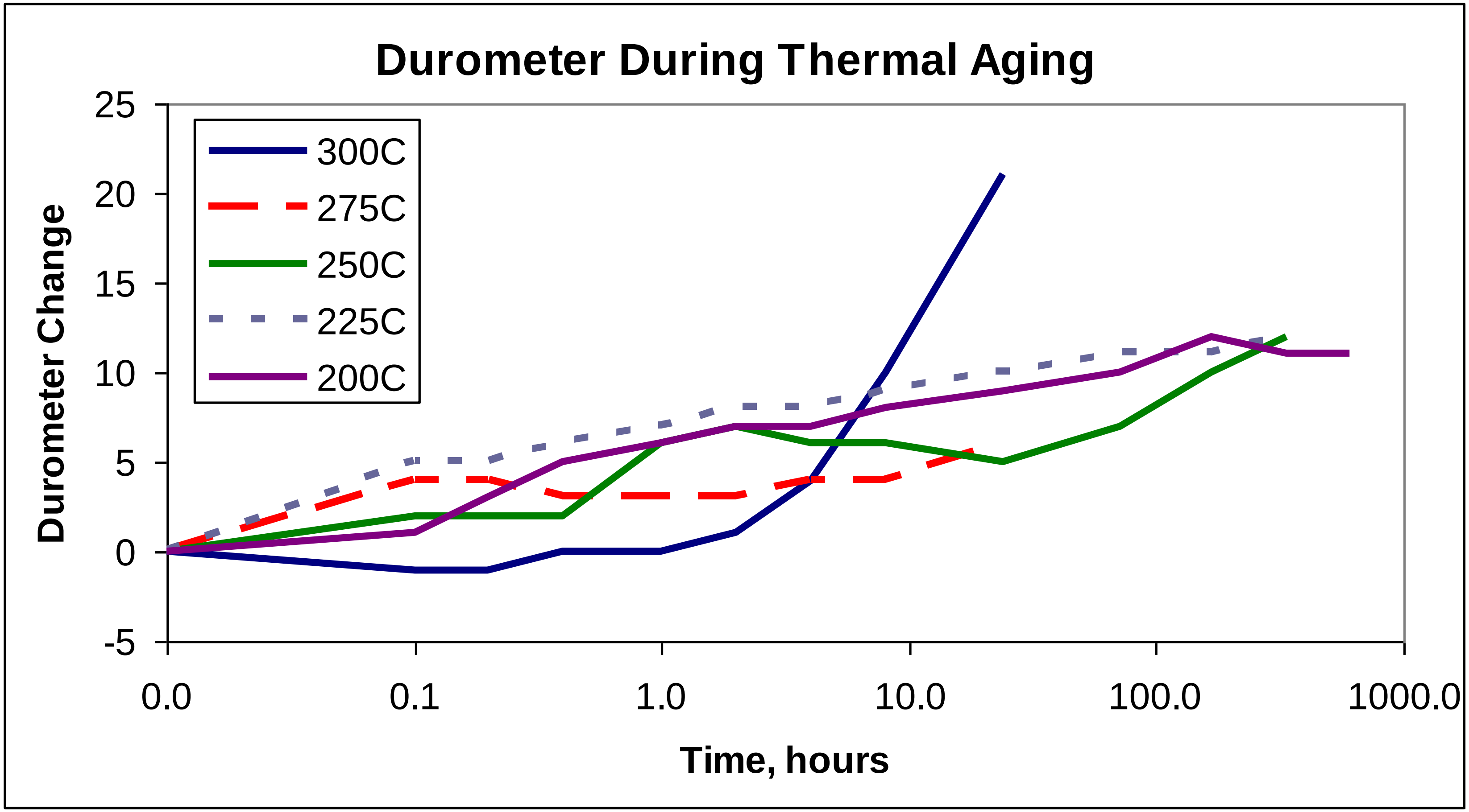
- One-part moisture cure silicone sealant (RTV)
- One-part heat cure adhesive (self-leveling and non-flow).
- Evaluated for thermal stability @ 300, 275, 250, 225 and 200 ^{o}C for 1000 hrs.
- Measuring properties: tensile strength, elongation, modulus of elasticity, durometer and lap shear adhesion (to unprimed aluminum).

- Cured sheets of 2 mm nominal thickness were prepared
- Standard tensile dog bone samples were die cut.
- Samples were laid onto trays and placed in convection ovens for set time durations and then removed, cooled to room temperature and tested.
- Lap shear adhesion was evaluated onto bare unprimed aluminum

Typical Properties for the Products used for this study

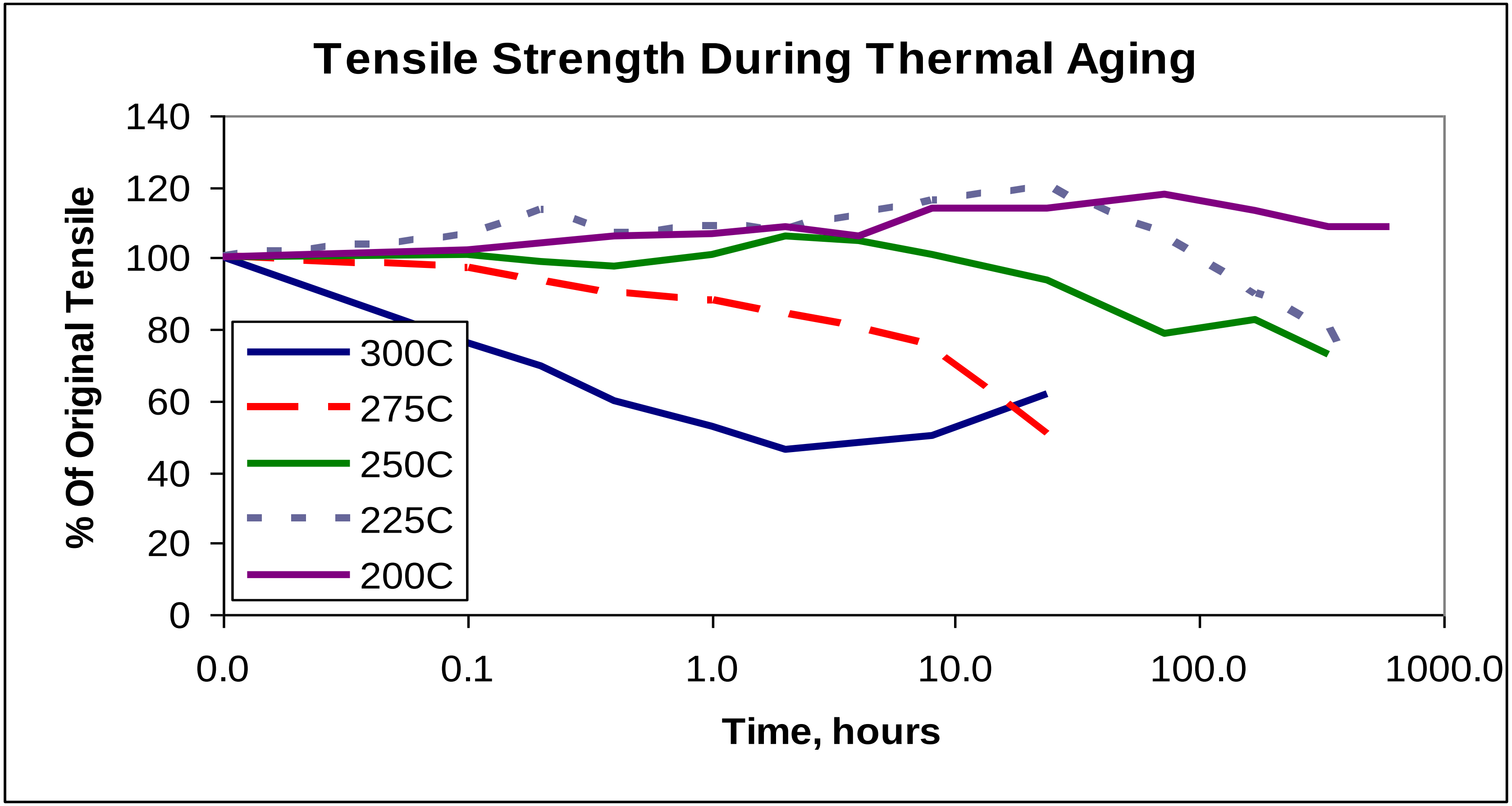
Silicone Adhesive	1	2	3
Description	1-part het cure (self- leveling)	1-part heat cure (non-flow)	1-part moisture cure (non-flow)
Hardness, Shore A	65	65	40
Tensile Strength, psi	870	750	1150
Modulus, psi	600	660	200
Elongation, %	200	120	500
Lap Shear, psi	700	600	500

Summary of Results



Adhesive 1 (one-part, self-leveling heat cure adhesive)

Summary of Results



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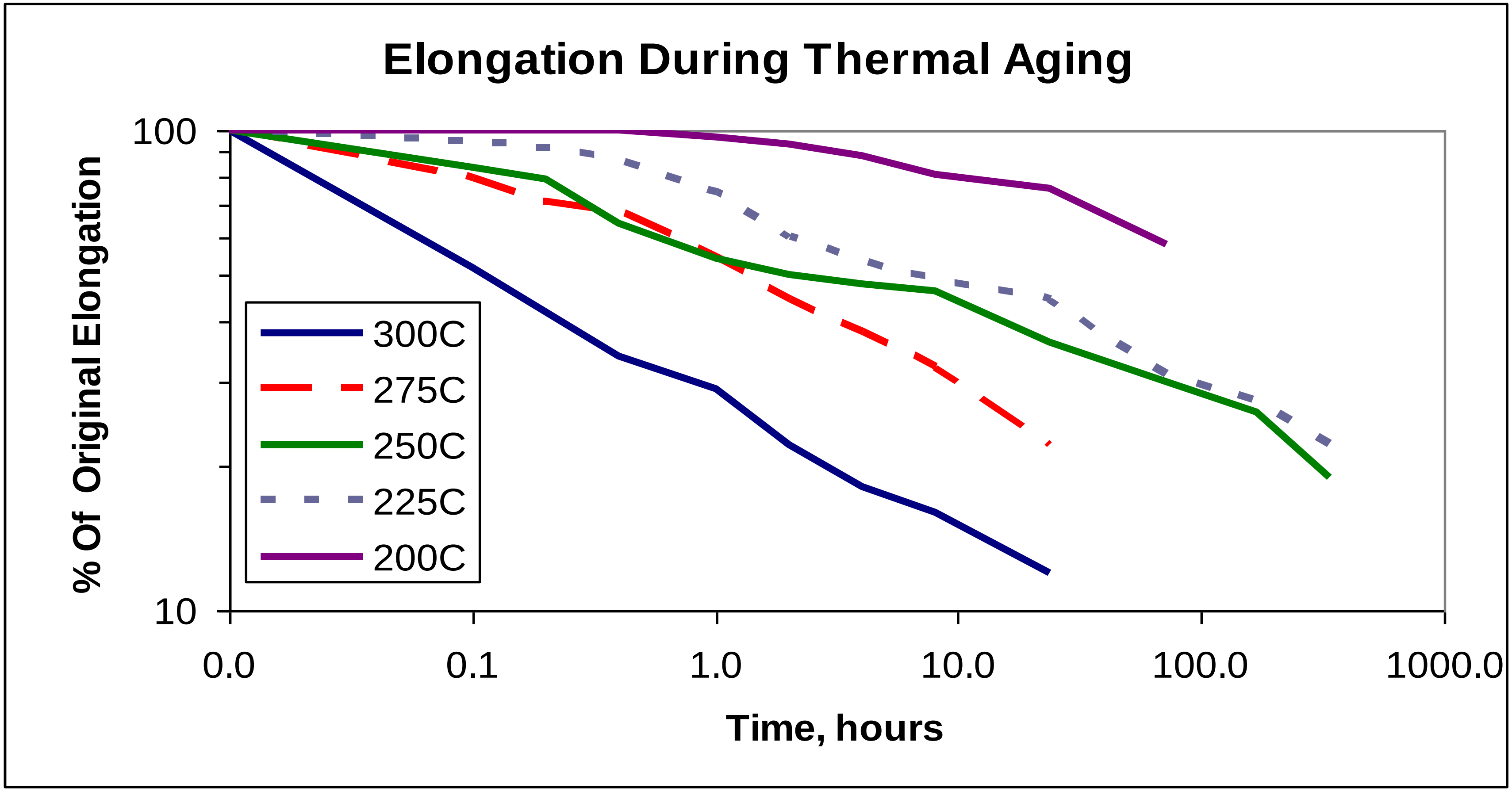

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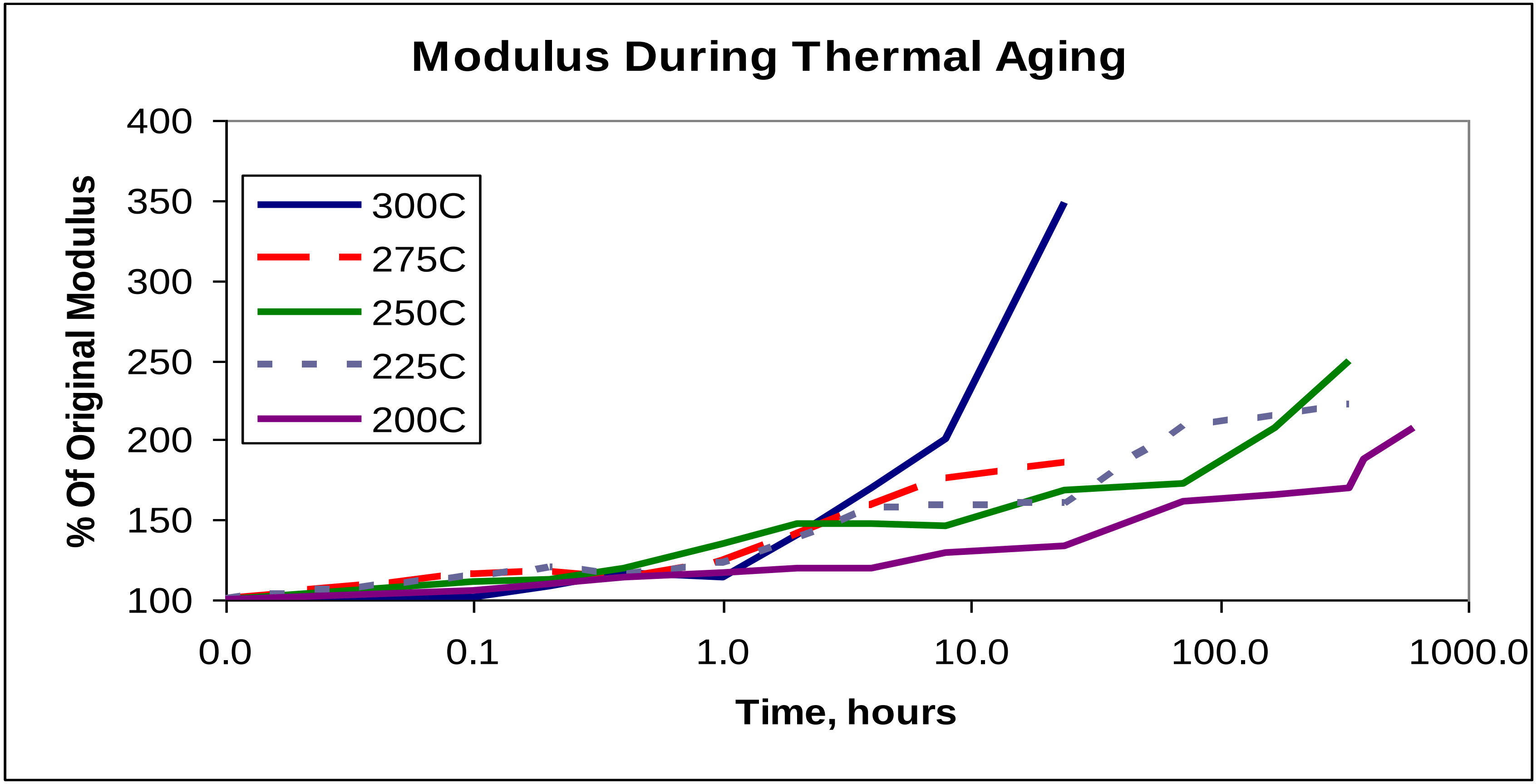

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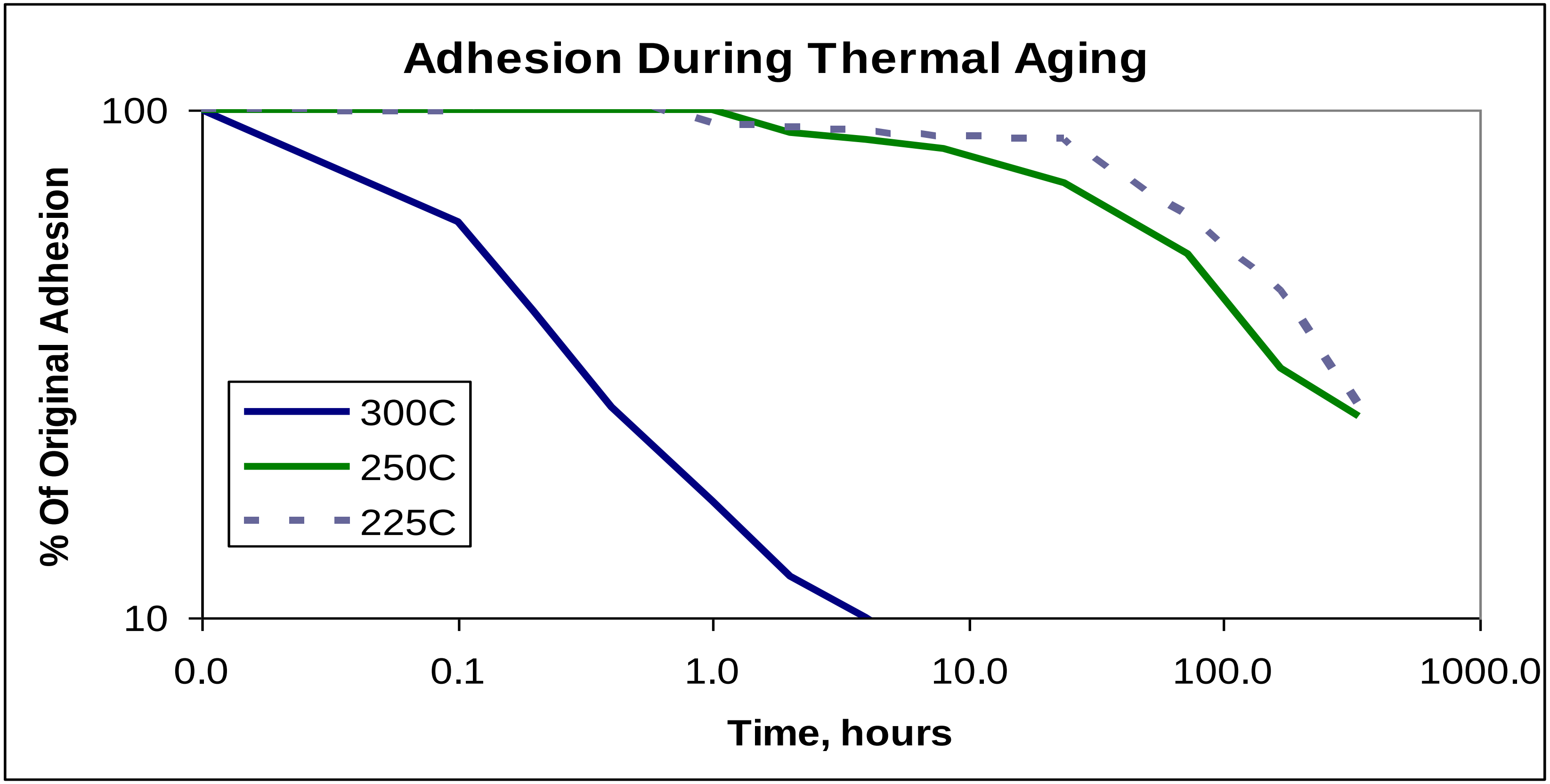


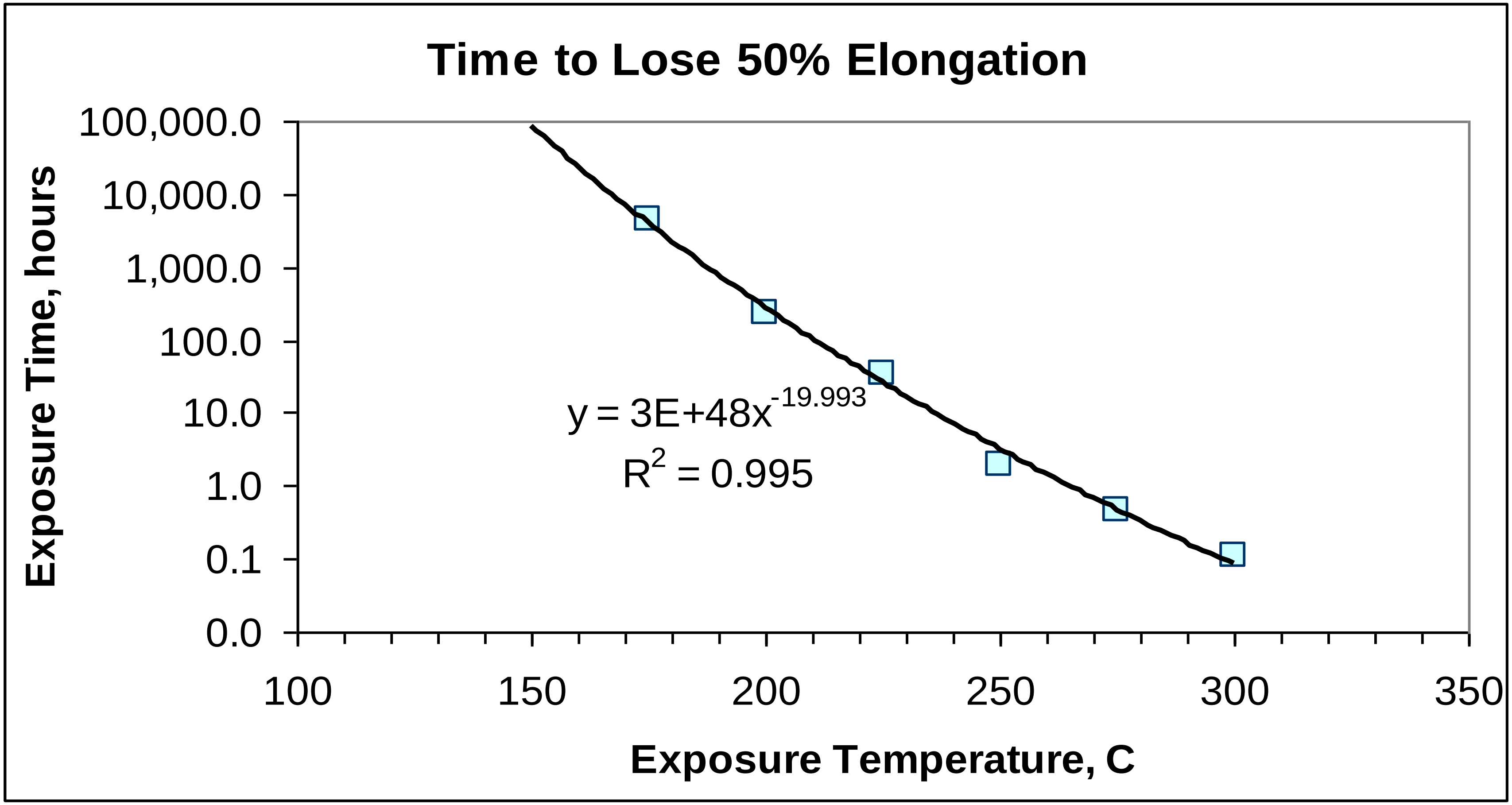
Adhesive 1 (one-part, self-leveling heat cure adhesive)

Thermal Aging for Adhesive 1 @ 300 °C

	% Change				
Time, hr	**Durometer, points**	**Tensile**	**Elongation**	**Modulus**	**Adhesion**
0	0	0	0	0	0
0.1	-1	76	52	101	60
0.2	-1	70	42	109	40
0.4	-3	60	34	117	26
1	0	53	29	114	17
2	1	46	22	140	12
4	4	42	19	160	6
8	10	50	16	201	8
24	21	62	12	348	4

- For the products evaluated, elongation was found to be the most rapidly changing property during thermal aging.

- Elongation will be the property used to determine end-of-life expectancy parameters (based on UL 746B10 guidelines).



Adhesive 1 (one-part, self-leveling heat cure adhesive)

Time to Lose 50% of Original Elongation for Silicone Adhesives/Sealants

Silicone Adhesive	1	2	3
Description	1-part heat cure (self-leveling)	1-part heat cure (non-flow)	1-part moisture cure (non-flow)
10 yrs	149C	136C	158C
1000 hrs	188C	178C	254C
1 hr	265C	266C	321C
1 minute	325C	335C	340C

Conclusions

- When silicone adhesives/sealants are exposed to temperatures above 200 °C some chemical degradation starts impacting some of the physical properties of these products.
- This chemical degradation is promoted by a variety of processes, including oxidation, siloxane rearrangement and hydrolysis.
- The property that showed the highest and fastest degree of degradation was the elongation.
- Elongation was used then to predict the temperature limits exposure for the adhesives/sealants evaluated under the scope of this paper, following the guidelines offered by the UL Standard 746B10.

Conclusions

- Limits indicated here were determined by the time required for the adhesive/sealant to lose no more than 50% of its original elongation when exposed to different temperatures.
- It is important to remark that for some silicone adhesives/sealants with initial elongation values in the range of 400 or 500%, losing 50% of its original value leave them with an elongation in the range of 200 or 250%.
- A material retaining 250% elongation is still highly elastomeric and this property may still be more than adequate for a great number of applications.

Conclusions

- Data reported in this paper should be used only as a guideline to establish general temperature exposure limits.
- Any specific application will require extensive testing and evaluations to determine the durability and maximum temperature exposure for the silicone, taking into consideration operating conditions and environmental factors.

Thank you!

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