Exploring the Performance of Silicone Gels at High and Low Temperature

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ABSTRACT
Silicones have been used in the electronics industry as protective/assembly materials for operations that will have a wide temperature variation. A large variety of silicone products are available to satisfy the needs for the majority of these operations, including: coatings, adhesives and encapsulants. Special kinds of encapsulants, subject matter of this study, are the gels. Silicone gels are a special kind of encapsulating materials with unique characteristics. They are extremely soft elastomers (solids with liquid characteristics) that are used to provide high levels of stress relief to sensitive circuitry when operating at adverse environments. They provide protection by functioning as dielectric insulators, forming environmental barriers and relieving mechanical and thermal stress on components.
Advances in miniaturization technologies have had dramatic impacts on our lives. Radios, computers, and telephones that once occupied large volumes now fit in the palm of a hand. This miniaturization has brought the need to use more delicate components/circuits that have to work in harsh environments and withstand exposures to high or low temperatures. Silicone gels are products that gather many of the special requirements to protect these sensitive assemblies working in a highly demanding environment. The purpose of this paper is to explore the performance of silicones gels when operating at high or low temperature to better establish the reliability temperature limits for these kinds of products.

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. In electronics silicones can be used for several applications, including: adhesives and sealants, 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 with wide operating temperature range, flexibility, moisture resistance, excellent electrical properties, UV resistance, good chemical resistance, adhesion to many common substrates used in electronics, low ionic impurity and compatibility with common processing techniques (easy to use). 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.
From all the different silicone products available for the electronics applications one material has been gaining great acceptance within the industry. These products are the silicone gels. Electronics components are in a constant evolution. Major efforts are made to reduce the size of the components and at the same time increase its power and efficiency. This trend has allowed the use of electronic components in environments and places never imagine, finding electronics components working in harsh environments and being exposed to severe temperature variations. The miniaturization of components and exposure to more severe environments has brought the need to work with protective materials that can withstand such condition. Silicone gels offer unique characteristics as protective materials that make them very suitable for a multitude of applications. It is the goal of this paper to provide information to better understand the nature of the silicone gels, properties and characteristics; and to review the performance of some of these products when they are exposed to different temperatures as a way to provide valuable guidance in the proper selection of a protective material for an electronics application.

What is a Silicone Gel?
Silicone gels are special class of products that cure to an extremely soft material with excellent cushioning, resiliency and self healing properties (fig. 1). It is hard to provide a precise definition of what a silicone gel is. Because of it very soft and gooey consistency, silicone gels commonly are described as a gelatins or marshmallows. These products are very unique materials with properties that might easily fall between a liquid and a solid. Because of its exceptional physical form,

silicone gels provide the ultimate in thermal and mechanical stress relief, while retaining the dimensional stability of an elastomer. They are typically used in electronics applications as encapsulating materials applied in thick layers to completely wrap around high components in an electronic board (such as transformers or capacitors), and particularly high standing wire bonds. Specific silicone gels can be formulated for enhanced properties such as high optical transmission (high transparency or clarity), solvent and fuel resistance, controlled volatility or flame resistance.

Fig. 1 Silicone Gel Physical Form (AV12003)

The silicone gel cure chemistry is known as "Addition Cure", using a platinum based catalyst system. Silicone gels are solventless formulations, typically supplied as 2-part, low viscosity liquids with a 1:1 mix ratio. One part materials are also available, eliminating the need for metering and mixing equipment. Most of these silicone gels will cure at room temperature with speeds ranging from 1 to 24 hours. Heat can also be used to accelerate these times down to a few minutes. Products can be formulated which will only cure with the use of heat and therefore, have a very long pot life. A few specialized gels are formulated for extremely rapid UV cure for high speed processing.

When a silicone gel cures a cross-linking reaction occurs, transforming the liquid into a soft solid material. There are basically two key molecules forming the composition of a silicone gel, the long chain polymer and the cross-linker (fig. 1). The cross-linker is a short molecule with many reactive sites. The long chain polymer has a reactive site on each end of the chain. When reacting, two polymers get linked together with the cross-linker forming a larger molecular structure. Differently from silicone hard elastomers, the number of cross-linked molecules present in a silicone gel is much lower, allowing a more flexible polymeric matrix. The cure reaction begins when two polymers get linked together with the cross-linker. Then a third links in, then those get linked to others, and all the rest begin to link and the mass solidifies.

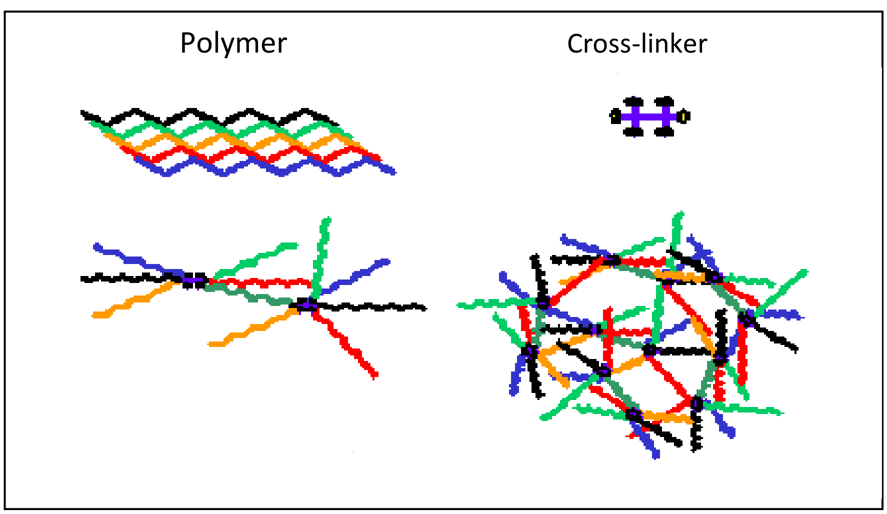

Figure 2 – Cross-linking reaction for Silicone Gels

A key characteristic of a silicone gel, as described above, is its naturally tacky surface after cure, which allows it to attain physical adhesion to most substrates without the need for a primer. This tackiness also gives silicone gels the unique ability to heal themselves if the cured gel has been torn or cut, effectively re-sealing the assembly. This self-healing capability also permits the use of test probes directly through the gel for circuit testing, without compromising the material's protection capability. This same property allows rework and repair that would not be possible with other material chemistries. The self-healing characteristics of a silicone gel can be explained by the fact of the loose polymeric matrix of the cured material. The mobility of silicone molecules in the cured state allows small cracks and tears to practically disappear over time. However, large tears to the gel structure may not completely heal and air bubbles can be trapped in the damaged areas, as shown in figure 3 below.

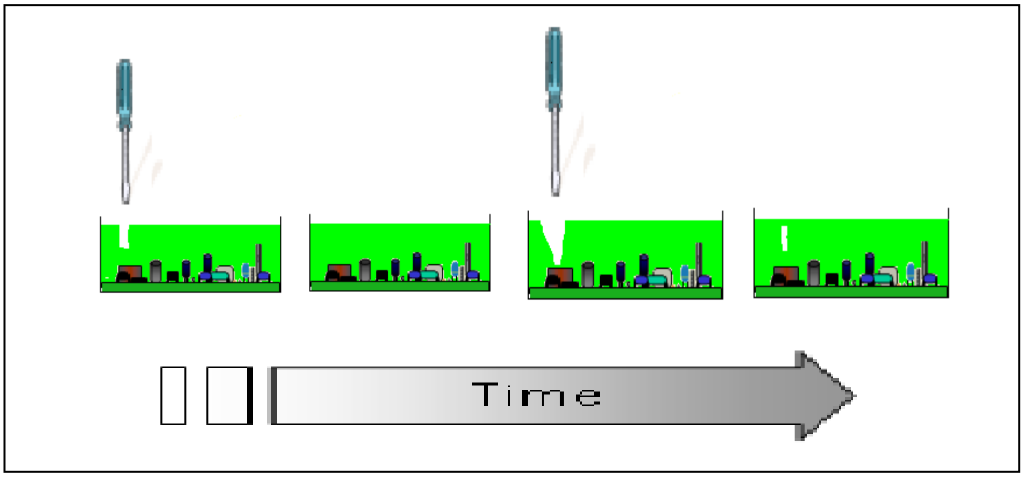

Figure 3 – Self Healing Property for Silicone Gels

As in other family of silicone materials, gels achieve very good wetting and intimate contact with substrates and components, minimizing microscopic voids that can trap moisture. Cured gels easily exclude liquid water, while allowing vapor from ambient humidity to permeate through. With no opportunity to collect in voids or at the covered surface, the water vapor in the air causes no ill effects.

The electronics industry is in the constant evolution trying to develop smaller and more powerful components. For many applications, as described above, electronics components and modules are exposed to severe environments. To improve reliability and proper function of the electronic modules working in extreme environments protective materials, such as silicone gels, have proved to be of great importance. One of the main characteristics of the silicone gels is their capability to relieve stress when working at high or low temperatures. This special condition relies in part in the low modulus these products exhibit. Due to this special feature, it is of paramount importance to verify how the modulus (or hardness) of a silicone gel is impacted when working at different temperatures, high or low. Silicone gels behave in different ways when exposed to high or low temperatures. Due to this difference in behavior and performance product properties have to be evaluated in a different manner when working at high or low temperature.

This paper is then divided in two parts to analyze the performance of silicone gels when exposed to high and low temperature.

High Temperature

Thermo gravimetric 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 depolymerisation 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 needs to be linked to the degradation of physical properties, such as: tensile strength, elongation, hardness, etc. In the case of silicone gels, the thermal stability of these products may be linked directly to the change in hardness. Silicone gels are characterized by their ability to relieve stress due to their low modulus. Therefore, a change of this property represents a parameter that is of relevant importance in the performance of the product.

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. As silicone gels are exposed to high temperatures, new cross-links are formed in the polymeric matrix, resulting in an increment in the hardness of the product. Gel hardness is the property identified to monitor the thermal stability of silicone gels. There are several methods to determine the hardness of a silicone gel. For this study the method utilized was the texture analyzer, which provides a more accurate way to determine the hardness of the silicone gel. The group of products used for this study was formed by two different gel formulations: a standard dimethyl gel (general purpose silicone gel) and a gel formulated with a special branched polymer (a silicone gel that exhibits better thermal stability). Hardness of both silicone gel formulations were evaluated at four different temperatures: 85, 125 and 150 °C. Time of exposure was extended until completing 1000 hrs. Hardness of the silicone gel was measured after 24, 48, 100, 500 and 1000 hour respectively.

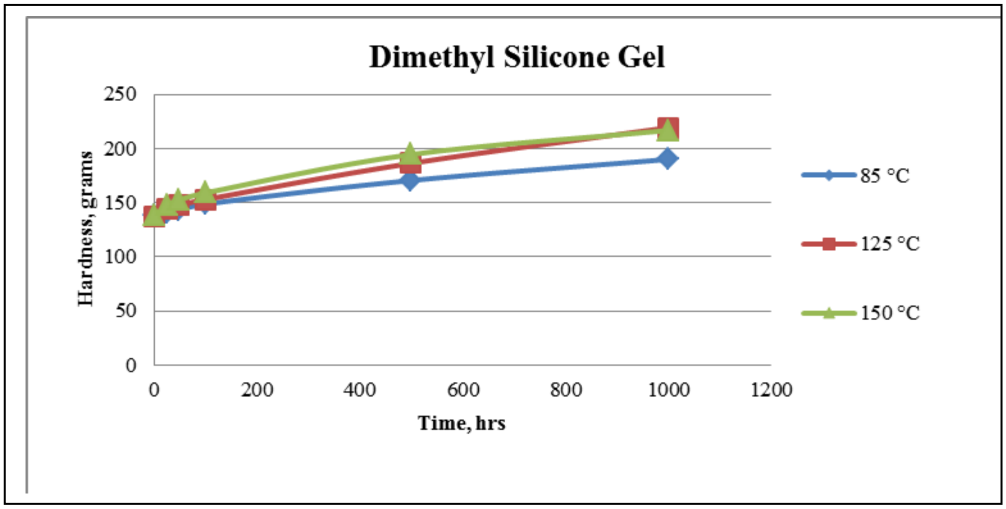

Figure 4 - Gel Hardness vs. High Temperature Aging

Figure 4 shows the behavior of the dimethyl silicone gel when it is exposed to high temperatures (85, 125 y 150 °C respectively). It is observed that the higher the temperature and exposure time the larger hardness is obtained. However, it is important to remark that the hardness increment of the gel is not significantly high, considering the hardness range for these kinds of products, where it can be found products with hardness as low as 50 grams and as high as 400 grams (this in the category of soft silicone gels). After an exposure period of 1000 hrs at 150 °C, the gel increased its hardness from an initial value of 148 grams to a final value of 215 grams. This represents an increment of 48% approximately. At 215 grams, the silicone gel is still very soft and retains most of its stress relieving properties.

More rigorously, the performance and life expectancy of the silicone gel studied here when exposed to high temperatures can be expressed in a more useful way following the guidelines offered by the UL Standard 746B10. This standard relates the useful life of a polymeric material as the time required to lose no more than 50% of any application-important property. Considering this parameter, the dimethyl silicone gel studied here would be within its life expectancy at temperature exposures up to 150 °C.

Likewise, figure 5 shows the behavior of the branched chain polymer gel. A branched chain silicone polymer is a technology used for Dow Corning to prepare products with a higher thermal stability. When compared this gel with the standard dimethyl gel, it is easy to observe a more stable behavior. Hardness of the gel when exposed 1000 hours at 150 °C goes from an initial value of 75 grams to a final value of 95 grams. This represents a change of 26%, compared to a change of 48% for the dimethyl silicone gel. This value is also below the 50% marked by the UL standard guideline to determine the useful life of a polymeric material.

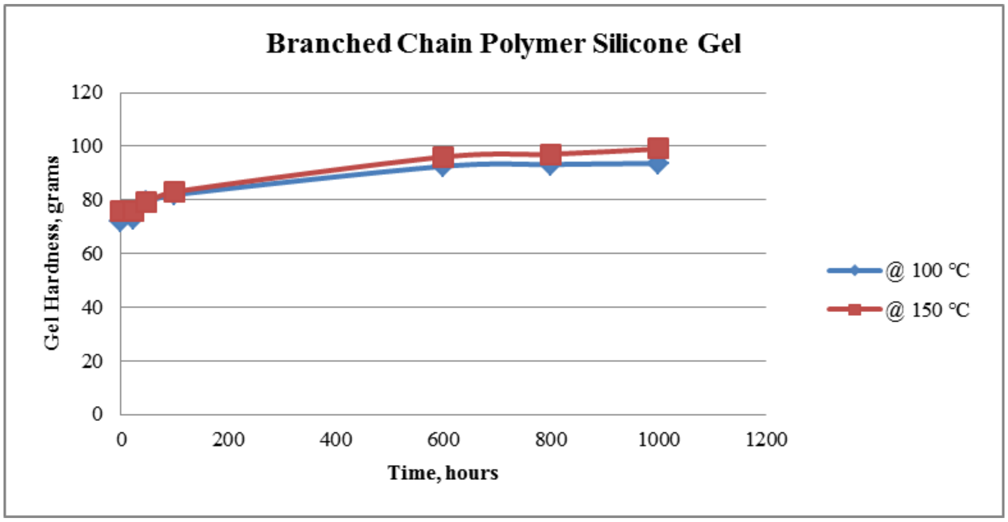

Figure 5 – Gel Hardness vs. High Temperature Aging

Low Temperature

Contrarily to what happen to silicones when exposed to high temperatures, these products do not suffer a chemical degradation when exposed to low temperatures. When silicones are cooled down they become harder and brittle and can put some extra stress to very sensitive components in electronic modules operating at low temperatures.

The glass transition temperature (Tg) for silicones is between -115 and -125 °C. However, silicone elastomeric materials, such as adhesives, encapsulants and gels go through a transition around -45 °C, known as hardening point or freezing/melting point (Tf). This transition is characterized by a partial crystallization of the elastomeric structure with an increase in hardness and small shrinkage. For some applications these changes may not generate any problem. However, there are applications where this sudden increase in hardness may reduce the stress relieving properties of the silicone, possibly damaging the performance of the electronic module. Silicones exhibit a great dependency on the rate at which they are cooled down. Fast cooling procedure frequently produces a "super-cooling" effect and sometimes the silicone elastomers do not exhibit a crystalline freezing point or the point is reached at a much lower temperature, regularly in the -65 °C range. Cooling a silicone elastomer very slowly through the freezing temperature range provides the greatest opportunity for the material to freeze in its most stable crystalline form, exhibiting a crystalline freezing point in the range between -40 to -50 °C. This behavior can cause some confusion when evaluating a silicone product for extreme low temperature applications. In particular, this "super-cooling" effect may give false positive results in thermal shock testing with rapid temperature changes and minimal soaking times at the low temperature end of the cycle.

When the soft silicone gels are cooled down they became semi-hard rubbers with durometers from 30 to 50 Shore A points. Likewise, some cracks appeared in many of the soft gels when going through the hardening point. The transparent products became cloudy and opaque. When these same gels were warmed up, either slowly or rapidly, they again became transparent and soft; however, sometimes the cracks remained even when the gels were returned to room temperature. These samples were held at room temperature and over the course of several weeks the cracks were all observed to disappear. The relatively high molecular motion allowed by the sparse cross-linking in the gels allowed the materials to "self-heal" from the cracks. However, in many cases a small air bubble became permanently trapped in the crack area within the gel.

This special behavior of silicone gels is of notable importance since these products are used in many applications to protect stress sensitive electronic components/modules. The drastic changes in the gel's hardness when exposed to low temperatures (below the hardening point) that could limit its stress relief capability should be considered when evaluating a product for such low temperature applications.

For this part of the study two different gel formulations were evaluated: a standard dimethyl gel (general purpose silicone gel) and a gel formulated with a special branched polymer (a silicone gel that exhibits better thermal stability). Samples of these two gel formulation were exposed to -40 and -50 °C for different time exposures. Hardness of the gels was measured then. For this section, hardness was measured using a pentrometer. The measured values of the test are showed in figure 6 and 7 below. Results showed no signs of solidification/crystallization for either of the gel formulations when exposed at -40 °C for periods up to 3 days (72 hours). However, when dimethyl silicone gel was exposed to -55 °C after a period of 12 hrs the gel became hard and brittle. The branched polymer silicone gel stayed flexible when exposed to -55 °C for an extended period of time.

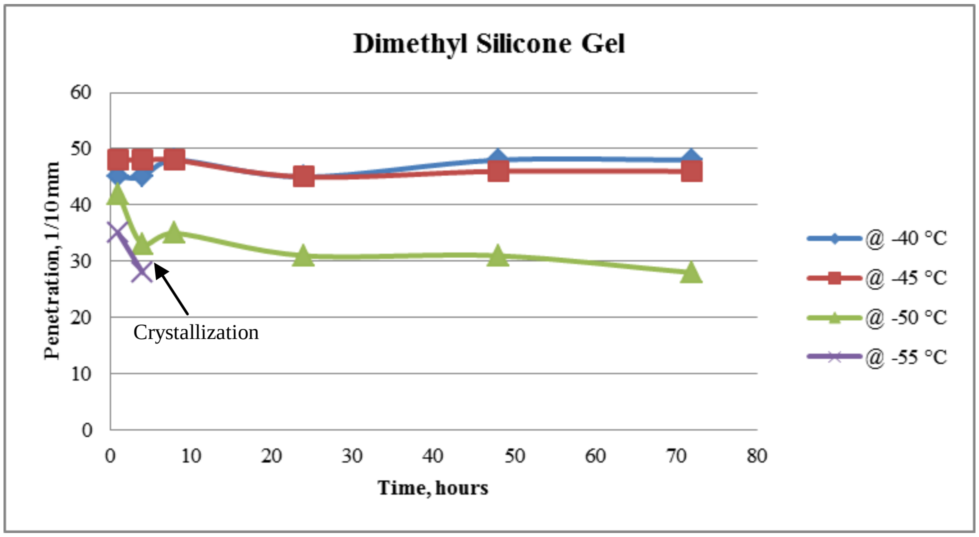

Figure 6 – Gel Penetration vs. Low Temperature Aging

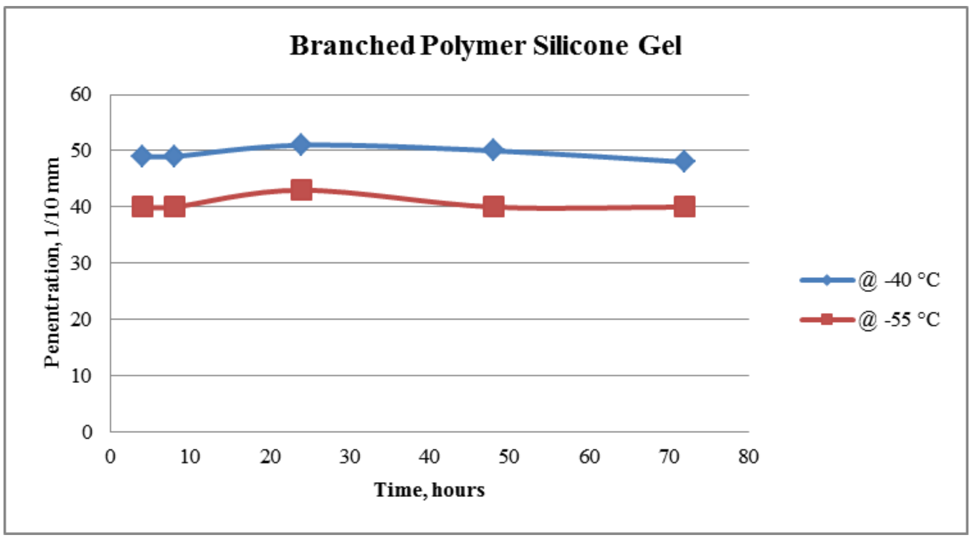

Figure 7 – Gel Penetration vs. Low Temperature Aging

It is important to remark that for those applications requiring silicone gels to be used at temperatures lower than the typical freezing points described in this paper, special products have been formulated that do not show a significant thermal transition to –85°C or even to a glass transition temperature of –115°C or lower.

Conclusion

When silicone gels are exposed to temperatures above 150 °C some chemical degradation starts impacting some of the physical properties of the elastomers. This chemical degradation is promoted by a variety of processes, including oxidation, siloxane rearrangement and hydrolysis. From this study conducted over two different gel formulations (dimethyl silicone and branched chain polymer) it was observed that the property that shows the highest and fastest degree of degradation for these products is the hardness. Hardness was used then to predict the high and low temperature performance for the silicone gels evaluated under the scope of this paper. In this way, the high temperature performance of the silicone gels were determined by the time required for the product to lose no more than 50% of its original hardness when exposed to temperatures up to 150 °C, following the guidelines of UL Standard 746B10. It is important to remark that for some very soft silicone gels, with initial hardness of 50 or 75 grams, changing more than 50% of its original value leave them with a hardness in the range of 75 or 113 grams. A silicone gel with a hardness of 113 gram is still very soft, retaining most of its stress relieving characteristics and is likely still more than adequate for even a majority of end-use 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 gel.

Likewise, low temperature reliability limits for silicone gels are more difficult to establish as the elastomeric structure of the silicone does not suffer of any chemical degradation when exposed to very low temperatures. However, it will be very important to consider the changes the polymeric structure suffers when passing through the hardening point as the capability to relieve stress at this point is drastically reduced due to the hardening and stiffening of the silicone gel. Even below their hardening point, silicone gels still retain many very beneficial properties. Therefore, actual low temperature use limits will be application dependant and extensive testing and evaluation is encouraged to determine feasibility of use a silicone gel for these conditions.

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  EP&A Marketing

Goals

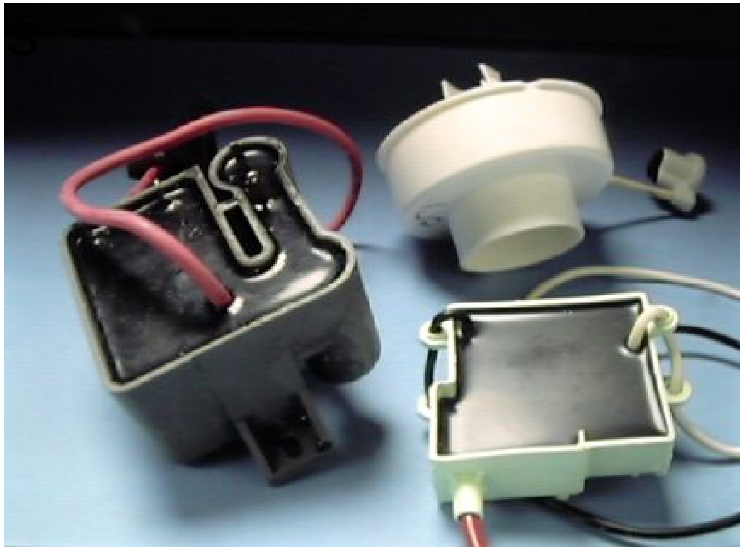
- Provide information to better understand the nature of the silicone gels, properties and characteristics.

- Review the performance of some silicone gels when they are exposed to different temperatures as a way to provide valuable guidance in the proper selection of a protective material for an electronics application.

Silicone Products

Silicone is the generic name used for many to identify a family of products based on the polydimethyl siloxane (PDMS) molecule with unique characteristics.

Encapsulant



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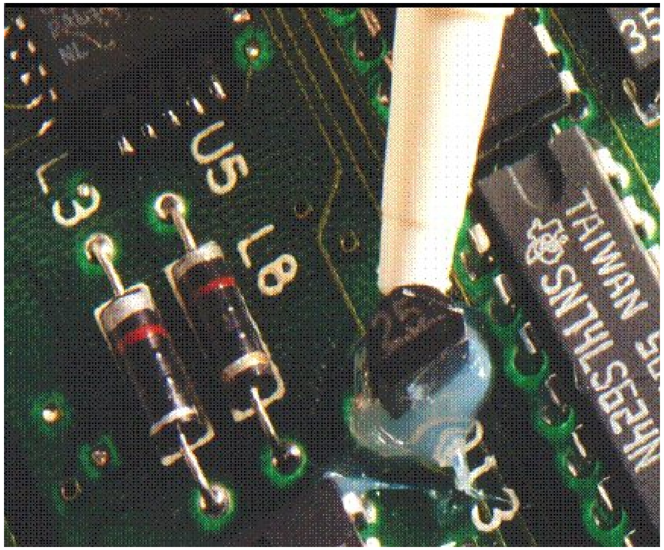
Adhesives and Coatings



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Silicone Properties

- Thermal Stability
- Moisture resistance
- Low Temperature Flexibility
- Good adhesion to many substrates
- Low ionic impurity
- Compatibility with common processing techniques.

Silicones Thermal Stability

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

- Some approaches point out to: -45 to 200 °C
- Less Conservative approach: -50 to 200 °C

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

Operating Temperature for Silicones

- There is 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.

What is a silicone gel?

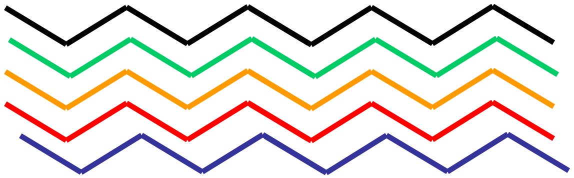
- Silicone gels are special class of products that cure to an extremely soft material with excellent cushioning, resiliency and self healing properties.

Silicone Gel

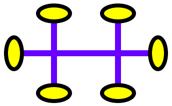
- Silicone gels provide the ultimate in thermal and mechanical stress relief, while retaining the dimensional stability of an elastomer.

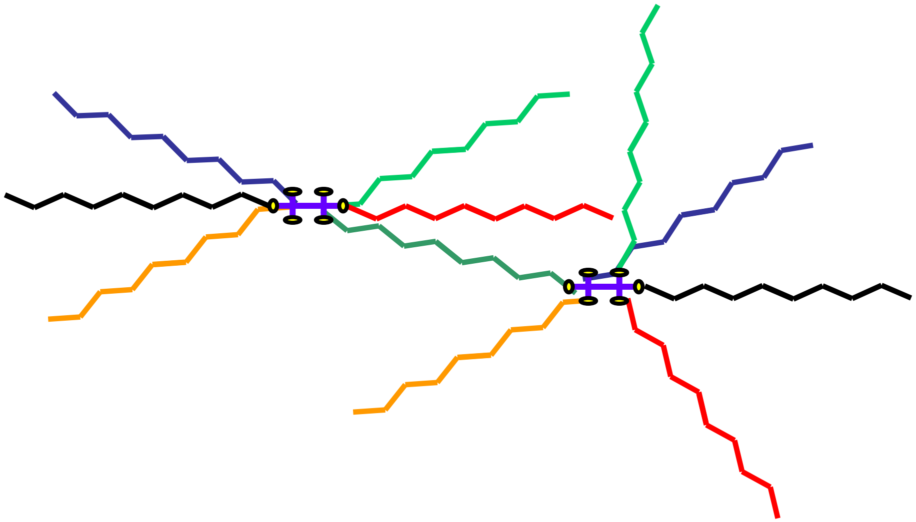
- Silicone gels are typically used in electronics applications as encapsulating materials.

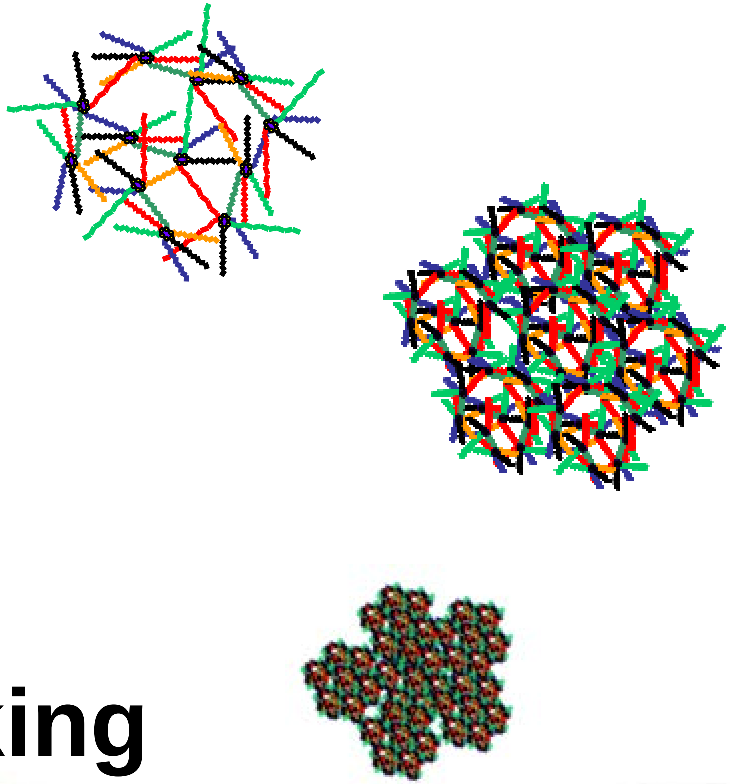
Polymer



Crosslinker

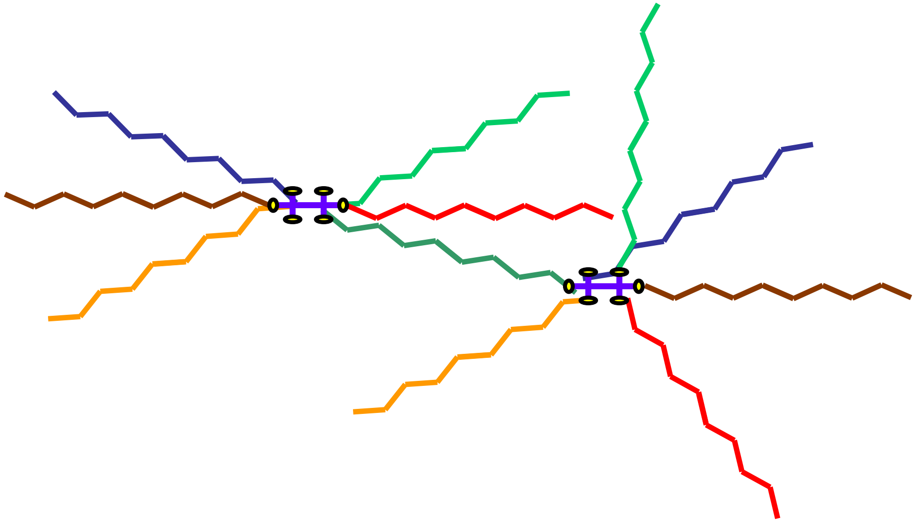


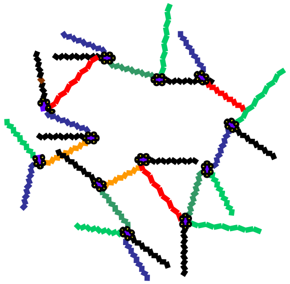


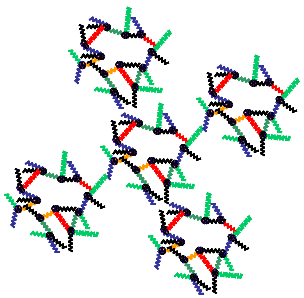


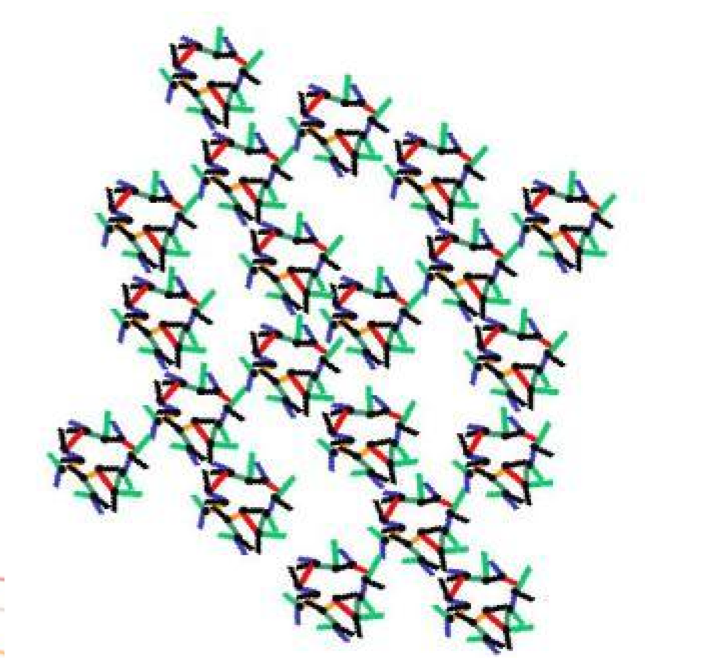
Crosslinking

Gels are "loosely" crosslinked

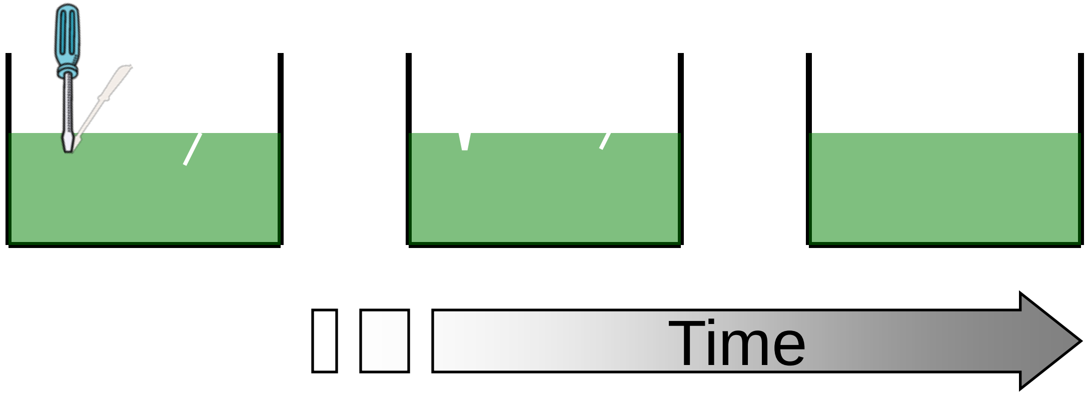








What makes gels so special?



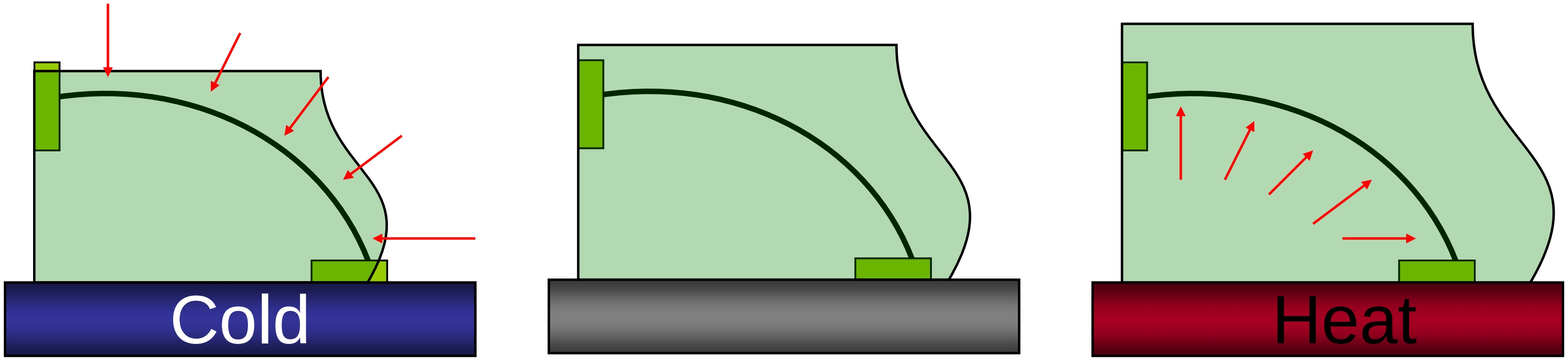
Self-Healing

Silicone Gel

- Silicone gels achieve very good wetting and intimate contact with substrates and components, minimizing microscopic voids that can trap moisture.
- Cured gels easily exclude liquid water, while allowing vapor from ambient humidity to permeate through.
- With no opportunity to collect in voids or at the covered surface, the water vapor in the air causes no ill effects.

Silicone Gel

- One of the main characteristics of the silicone gels is their capability to relieve stress when working at high or low temperatures.



Lowest Stress

Proposed Work

- Two different Gel Formulations:
  - Dimethyl silicone polymer
  - Branched chain silicone polymers

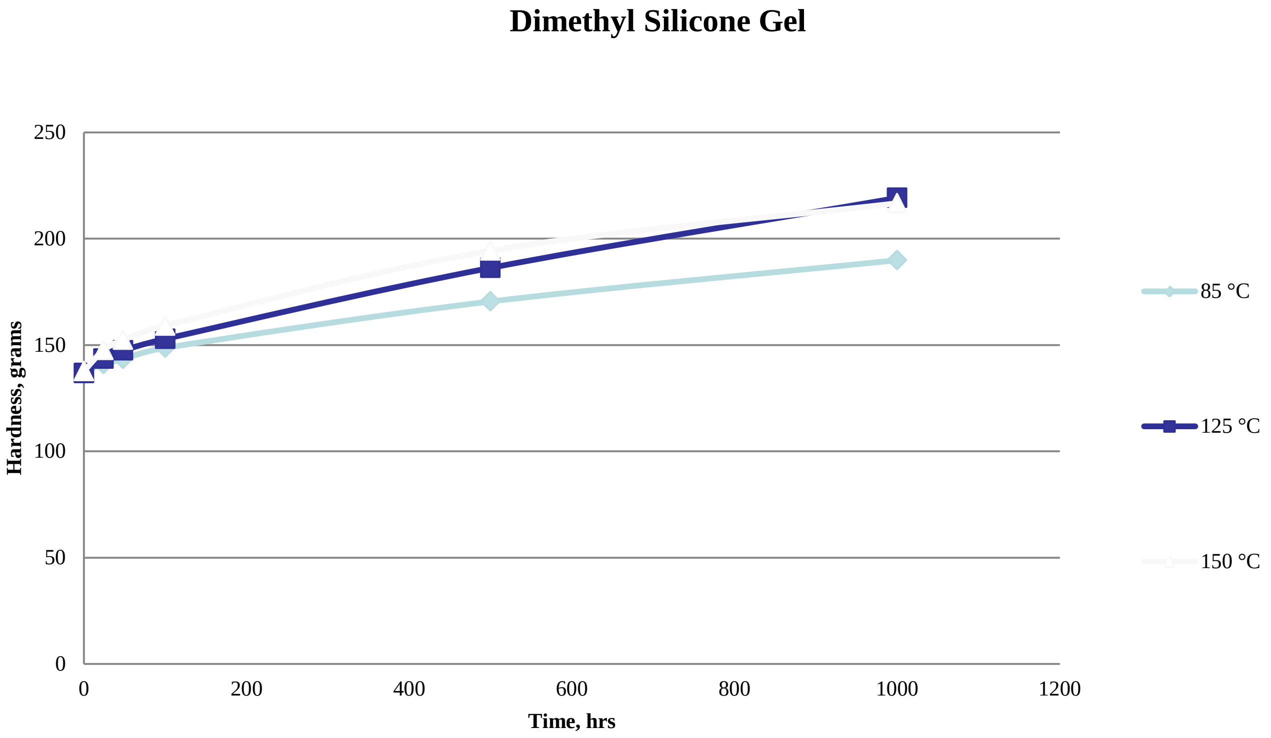
- 1000 hours exposure:
  - High Temperature: 85, 100, 125 and 150 ° C
  - Low Temperature: from -40, -45, -50 and -55 ° C

- Gel Hardness was the property identified to verify performance.

- Silicone gels are characterized by their ability to relieve stress due to their low modulus. Therefore, a change of this property represents a parameter that is of relevant importance in the performance of the product.

- As silicone gels are exposed to high temperatures, new cross-links are formed in the polymeric matrix, resulting in an increment in the hardness of the product.

Gel Hardness vs. High Temperature Aging



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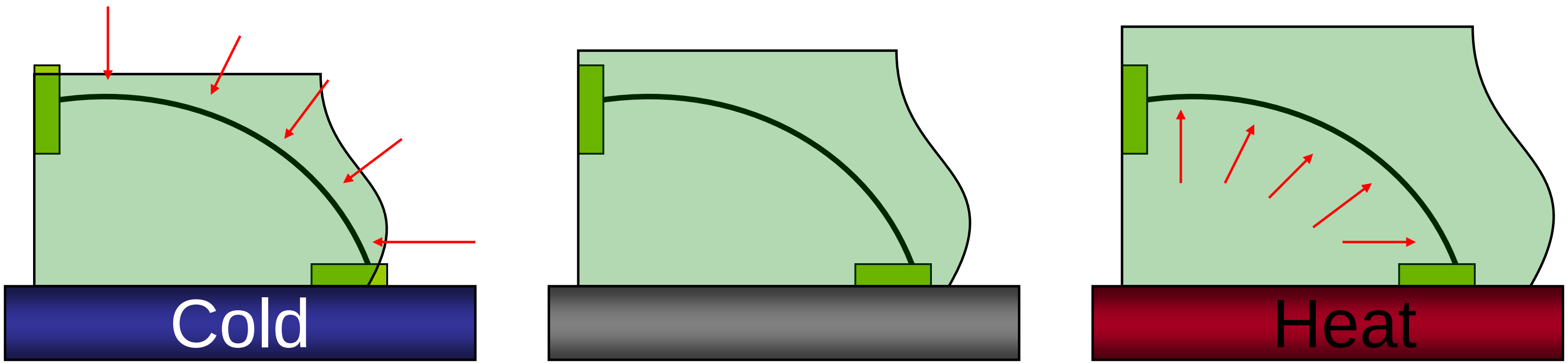

Lowest Stress

Liquid-like flexibility **Solid-like structure**