Low Temperature Characteristics of Silicones

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Silicones are often used to protect electronic applications designed for cold environments. The low temperature flexibility of silicones is well recognized, but not as well understood. While the actual Tg of silicones is about -120°C, they do transition from a soft rubber to a harder rubber around -45°C. At the transition their hardness, strength and modulus increase slightly while elongation decreases slightly. Very soft silicone gels show the greatest change, becoming more rubbery and in some cases showing tears. These tears can self-heal within a few weeks at warmer temperatures.

The specific temperature where these changes take place is shown to be dependant on the rate of cooling. Slow cooling will show this transition around -45°C for many silicone elastomers. Analytical tests may indicate performance limits that are too conservative. On the other hand, rapid cooling and short dwell times often used in thermal shock and cycling tests may not detect stress changes that could occur in slower cooling conditions unless a sufficiently long low temperature soak is included in the testing regime. Lower temperature versions of silicones are available that do not show property transitions until -80°C or even until -120°C.

Introduction

Many of today's electronic devices must withstand harsh environmental conditions. Low temperature requirements for many outdoor applications are designed for -40°C or lower. At these temperatures materials can become brittle and break under vibration or mechanical shock. In addition, changing mechanical properties must be taken into consideration during design, as many materials become stiffer and less stress reliving.

Low temperature property testing commonly involves hundreds or thousands of cycles between the upper and lower temperature specifications. To increase the stress this cycling is often done with rapidity in thermal shock.

For many materials sudden and large temperature swings will generate the greatest stress. Large parts, however, can take time for the entire thermal mass to reach the set temperature. Here it is typical to include a time lag at the extremes of the test cycle, referred to as a temperature or thermal "soak". The duration can either be an arbitrary value or determined with thermocouples to see how long is required for the entire module to reach the temperature set point.

This technique does not always take into consideration the potential for longer term "chronic" changes that only occur in some materials after extended low temperature exposure or the related phenomena of "super-cooling" wherein some materials like particulate-free water can be cooled to well below their normal freezing point before they undergo a phase transition.

Electronics in harsh environments often need special protection. Coating or encapsulating sensitive items with a material that can provide electrical isolation is commonly employed. A soft encapsulant can allow for thermal movements without overly stressing sensitive wires and solder joints. Silicone adhesives, coatings and encapsulants are commonly used for such purposes[1-3]. Silicone encapsulants range from hard to soft thermosetting rubbers to extremely soft gels. Silicone gels are thermosetting semi-solids whose properties begin to cross the boundary between solids and liquids, and have been shown to be highly stress-relieving when encapsulating solder joints.[4]

Silicones have some unique low temperature characteristics that should be taken into consideration when setting up test matrices for low temperature evaluations.

Silicone's Low Temperature Transitions

The glass transition temperature (T_g) of silicones is between -115 and -120°C, where they become hard, brittle and glass-like. However, most silicone products go through another transition around -45°C that is sometimes called a melting/freezing point (T_m or T_f) or even a *pseudo* melting/freezing point. Here many silicones undergo a partial crystallization characterized by a rather sudden increase in hardness, a small shrinkage, and lesser changes in other mechanical properties[5].

These changes may be slight enough to have no real impact on module performance. However, in some cases the hardening may reduce the normal stress relieving properties for which the silicone product was chosen. A few silicone products have been specially modified to enable this property transition to occur at -80°C, or to show no nearly no property changes until the T_g is reached. Most silicones will however experience property changes in the -35 to -55°C range with a transition which will be referred to as the material's T_f.

Determining where this transition takes place and what property changes occur has caused some confusion. Early analytical techniques often showed few changes in silicones until about -65°C. Also, an early low temperature test for coatings was referred to as a "Brittle-point" test[6] and people came to think of the low temperature rating as when a material became glass-like and easily damaged.

Part of the confusion is because silicones show a strong rate dependency in where the low temperature transition occurs. When fast cooling the property changes occur near -65°C while at slower at -40 to -50°C. While newer analytical techniques do present a more accurate temperature for the transition, these methods can be overly conservative to show the transition between -35 and -40°C.

While in some applications these may be minor or even trivial differences, in other applications with a low temperature requirement of -40 or -45°C these differences may become more significant. In particular, this "super-cooling" phenomenon may give false positive results in rapid thermal shock testing with minimal soak times at the low temperature end of the cycle.

The evaluations described in this paper were carried out to show the types of changes that occur to silicone adhesives, encapsulants and gels as they go through the low temperature transition and the magnitude of the effects of cooling and warming rates.

Property Changes During Cooling

Shrinkage

As materials are cooled they contract according to their Coefficient of Thermal Expansion/Contraction (CTE). For many silicones the linear CTE is about 300 microns/meter degree C or shortened to 300 ppm/°C. This value is remarkably constant from +200°C down to their T_f. The volumetric dimensional change is three times the linear change. A representative silicone adhesive was used to generate the following data.

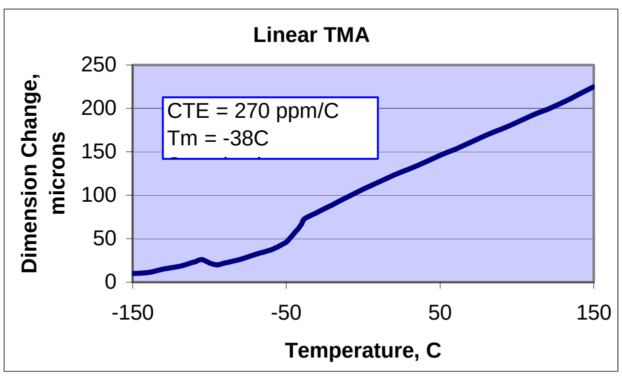


Figure 1 - TMA of a typical silicone adhesive

As these materials go through their T_f they contract at a much higher rate over the course of a few degrees and then return to a rate similar in magnitude to the CTE found above the T_f.

In an effort to evaluate the dimensional changes in the same silicone elastomer under cooling conditions, caliper measurements were made on samples subjected to a very slow cooling rate. Samples were placed in a –30°C chamber that was then further cooled at 1°C every 3 days.

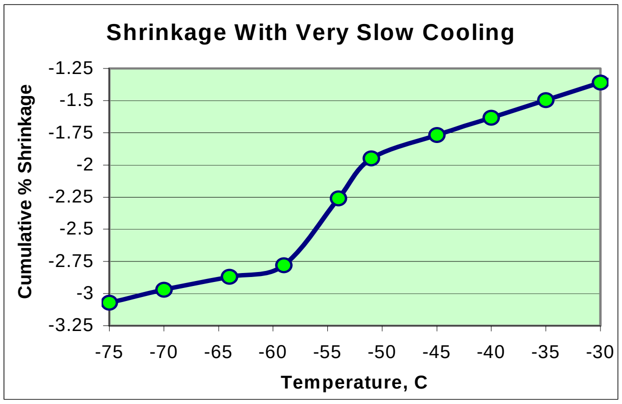


Figure 2 - Shrinkage of a silicone adhesive under very slow cooling

Note that slow cooling produced a T_f of –52°C, substantially cooler than the –38°C obtained by TMA. A cumulative shrinkage graph for the slowly cooled material shows a larger shrinkage associated with the transition - about 0.9%. Slowly cooling silicone gels has produced shrinkages of up to 1.5% associated with their T_f.

Tensile Strength, Modulus and Elongation

As silicones are cooled their tensile strength and tensile modulus change very little until the T_f is reached, then these properties increase by about 40%.

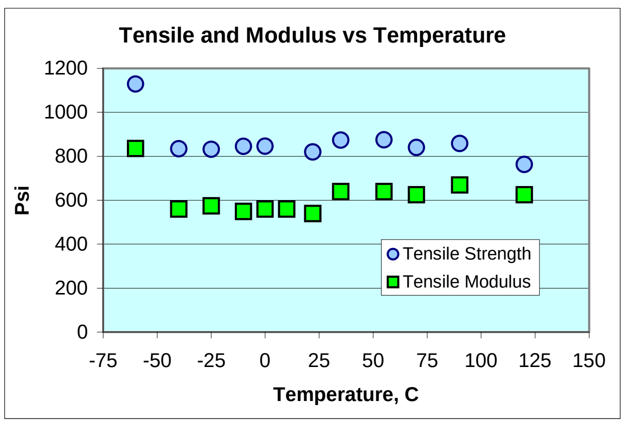


Figure 3 - Tensile strength and Elastic Modulus of a silicone adhesive under slow cooling

A common instrumental technique to measure low temperature moduli of elastomers is Dynamic Mechanical Thermal Analysis, or DMTA. A typical procedure is to cool a sample below its T_g and then to warm at a rate between 1 and 10°C per minute while measuring the storage (G') and loss (G") moduli of a sample in cyclic torsion. DMA testing for the materials discussed in this paper show a melting point of about –45°C.

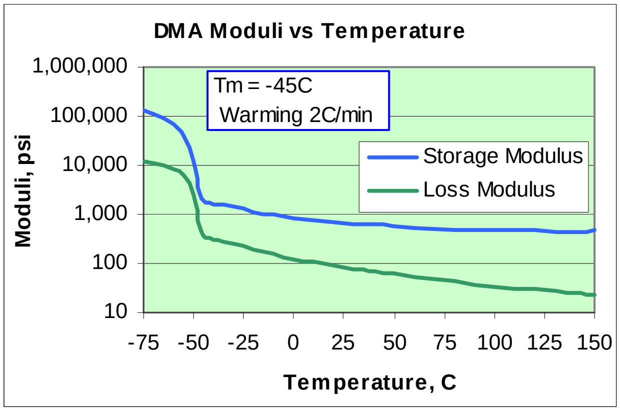


Figure 4 - DMA of a typical silicone adhesive

The elongation values show a distinct and approximately linear increase as temperatures are lowered until the T_f is reached. At that point the elongation drops rapidly, becoming essentially zero at the T_g.

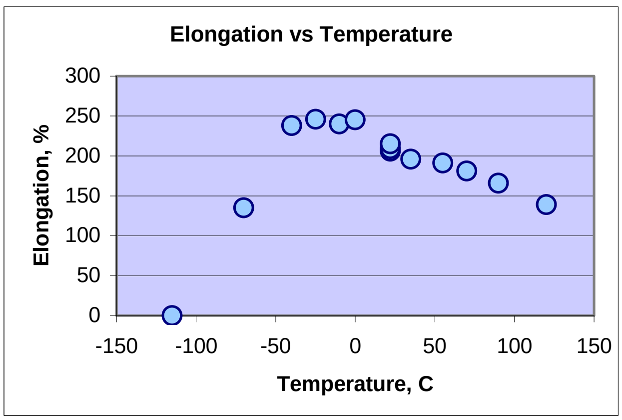


Figure 5 - Elongation of a silicone adhesive vs temperature

Adhesion

Lap shear adhesion strength is somewhat influenced by temperature above the T_f. As the silicone elastomer is cooled the bond strength increases in a roughly linear manner until the T_f is reached. At that point the adhesive strength greatly increases and continues to rise at a fairly rapid rate to the T_g.

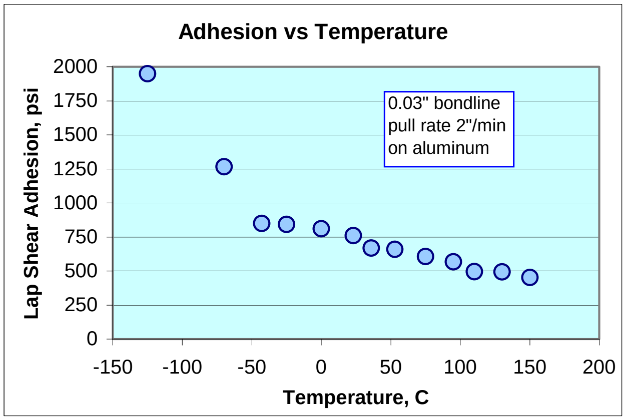


Figure 6 Adhesion of a silicone adhesive vs temperature

Hardness

As silicone elastomers are cooled their durometer decreases slowly throughout most of their useful temperature range. Just before the T_f is reached the durometer may dip slightly lower, and then increase significantly during the transition.

For the example product used so far in this paper, the durometer increase was 20-30 Shore A points above the room temperature value. Other products showed similar changes; some had a slightly less durometer increase, or the increase was spread out over a temperature range of 3-6 degrees C. The slow cooling freezing point shown in Figure 7 was about –50°C.

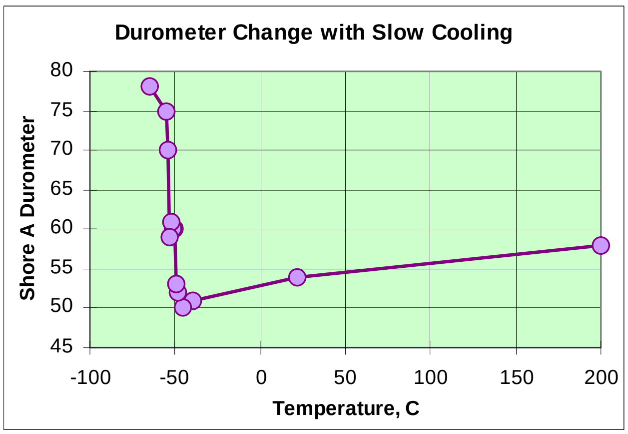


Figure 7 - Hardness changes in a silicone adhesive vs temperature

Silicone gels had the largest hardness changes. Very soft gels became medium-hard rubbers with durometers from 30-50 Shore A. Along with the increase in durometer, cracks formed in many of the gels as they passed through T_f.

When the gels were re-warmed the cracks remained. These samples were held at room temperature and after several weeks the cracks disappeared.   The relatively high molecular motion allowed by sparse crosslinking in the gels allowed them to "self-heal" from the damage. However, in some cases a small air bubble became permanently trapped in the crack area.

Figure 8 - Picture of silicone gels cooled below Tf and re-warmed to room temperature (1 day after warming)

Thermal Change Rate Effects
A study was conducted to look at durometer derived T_m and T_f at two slow rates of thermal change and couple this data with that from two more rapid rates of cooling and warming using Differential Scanning Calorimetry. DSC measures the slight changes in temperature materials undergo during crystallization or other phase changes. Nearly always a T_m is reported with DSC with samples rapidly cooled and then allowed to warm at a controlled rate such as 10°C/minute.

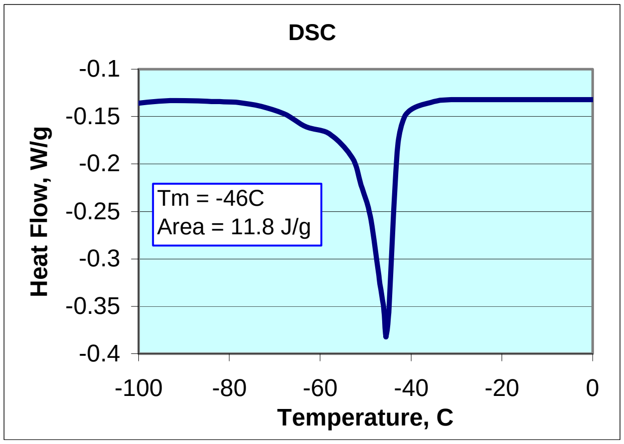
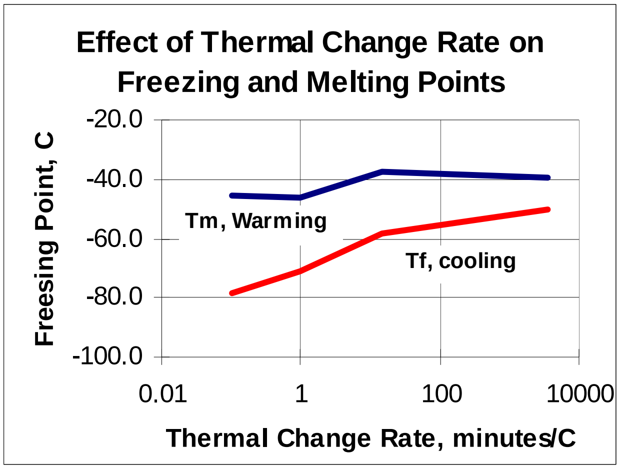


Figure 9 - DSC of a typical silicone adhesive

Fourteen products were evaluated, covering a range of silicone adhesives and encapsulants. DSC scans were made at 1 and 10°C per minute warming and again at these same rates of cooling. Durometer samples were manually measured at both cooling and warming rates of 1°C change every 15 minutes (4°C/hr) and at 1°C change every 3 days (0.35°C/day).

The melting point appears to be much less sensitive to the rate of thermal change than does the freezing point. Slower warming allows the materials to equilibrate at the temperature tested and requires the temperature to be slightly higher before the melting transition occurs. Freezing points were found to be very sensitive to the rate of temperature change.



Conclusion

Silicone elastomers undergo a property transition whose exact temperature is dependant on the rate of thermal change. Analytical techniques may indicate the transition at -40 to -45°C, but slow cooling can show it at a temperature 5-15 degrees C lower.

During the transition silicone elastomers can see a linear shrinkage of up to 1.5% and a durometer increase of 20-30 Shore A points. A moderate increase in strength and modulus also occurs. Silicone gels turn into semi-hard rubbers and cracks may form. These cracks often self-heal after the gels are warmed.

Freezing points for several elastomeric silicone adhesives were found to be –50 to –60°C when measured using slow cooling techniques, while for several silicone gels it was –48°C. Low temperature reliability testing with applications using silicones should take into account the described phenomena and should include a thermal soak for several hours or even days to simulate slow cooling to obtain a complete

Even below their freezing point, silicones still retain many very beneficial properties. Actual low temperature use limits will be application dependant. For applications requiring silicone elastomers and 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 –80°C or even to a glass transition temperature of –115°C or lower.

References

(1) S. Dent, K. Mine, Y. Ushio, M. Watson, "Technology Roadmap for Silicone Adhesives in Thin Multi-Chip Packages", SMTA Pan Pacific Symposium, Feb., 2003.

(2) C. Wong, J. Segelken, J. Balde, "Understanding the Use of Silicone Gels for Non-Hermetic Plastic Packaging", Electronic Components Conference, 1989, Proceedings, 39th, p 769-776.

(3) S. Dent, "Development of Microelectronic Grade Silicone Materials for Chip Scale Packages", SMTA Pan Pacific Symposium, Jan., 2000.

(4) T. Barcley, P. Berry "Investigation Into the Effect of Gel Hardness on Solder Joints", SAE 2001 World Congress, Doc. No. 2001-01-0689.

(5) A. Lee Smith, The Analytical Chemistry of Silicones, Wiley Interscience, 1991 p.161-163.

(6) ASTM D-2137.

Low Temperature Reliability of Silicones

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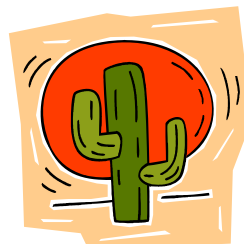
Many electronic devices must operate dependably at both

+150C

+105C

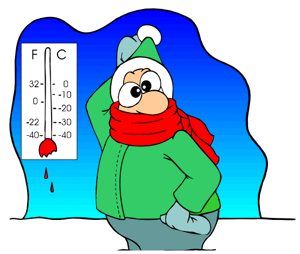
+85C

HIGH



and

LOW



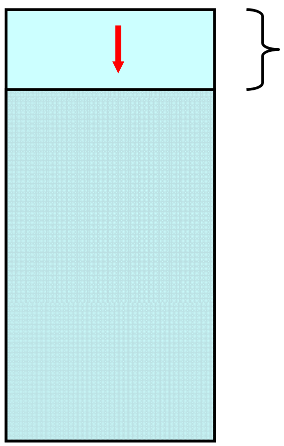
+5C

-20C

-45C

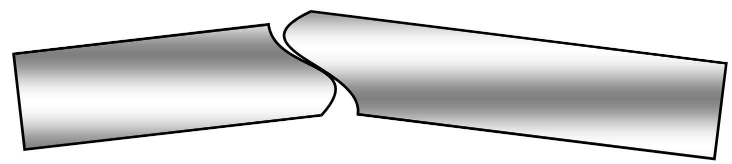
temperature extremes.

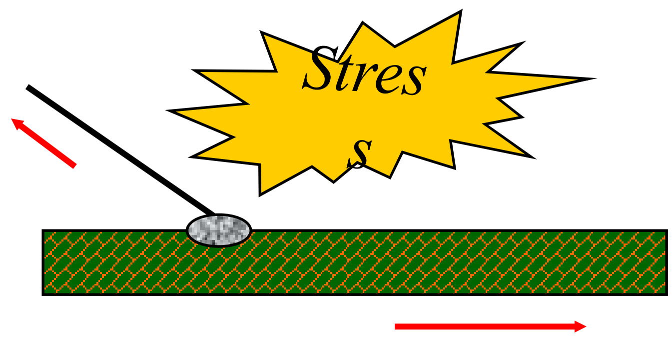
What happens to materials as they are cooled?



Shrinkage

Embrittlement





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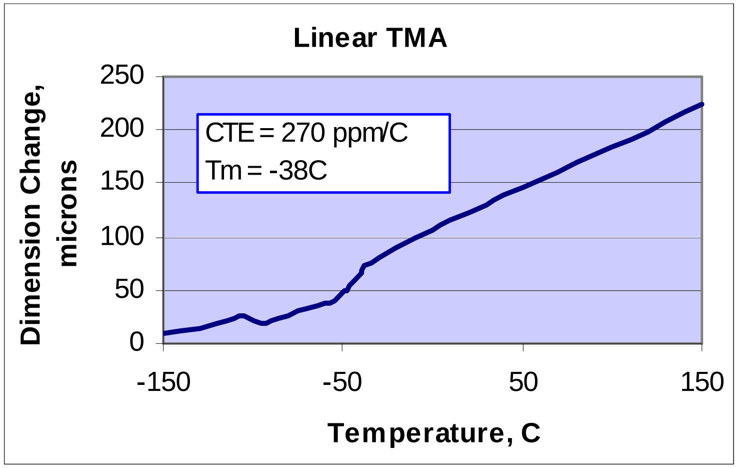
What happens to silicones as they are cooled?

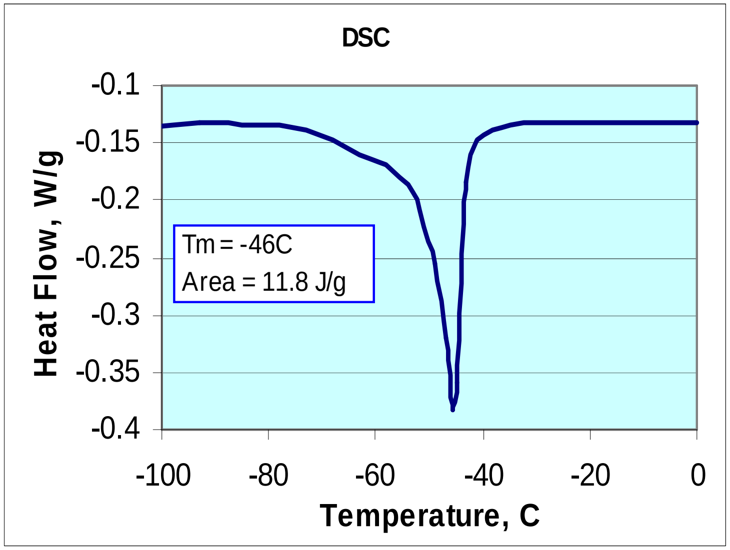
Glass transition temperature of most silicones = **-120C**

Silicones are always used ABOVE their Tg!

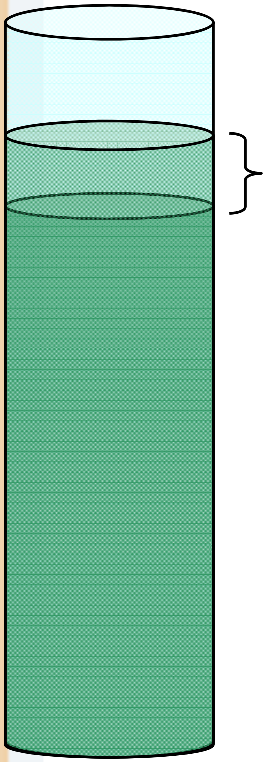
What happens to silicones as they are cooled?

A "stiffening" transition does occur around -40 to -45C.





What happens to silicones as they are cooled?

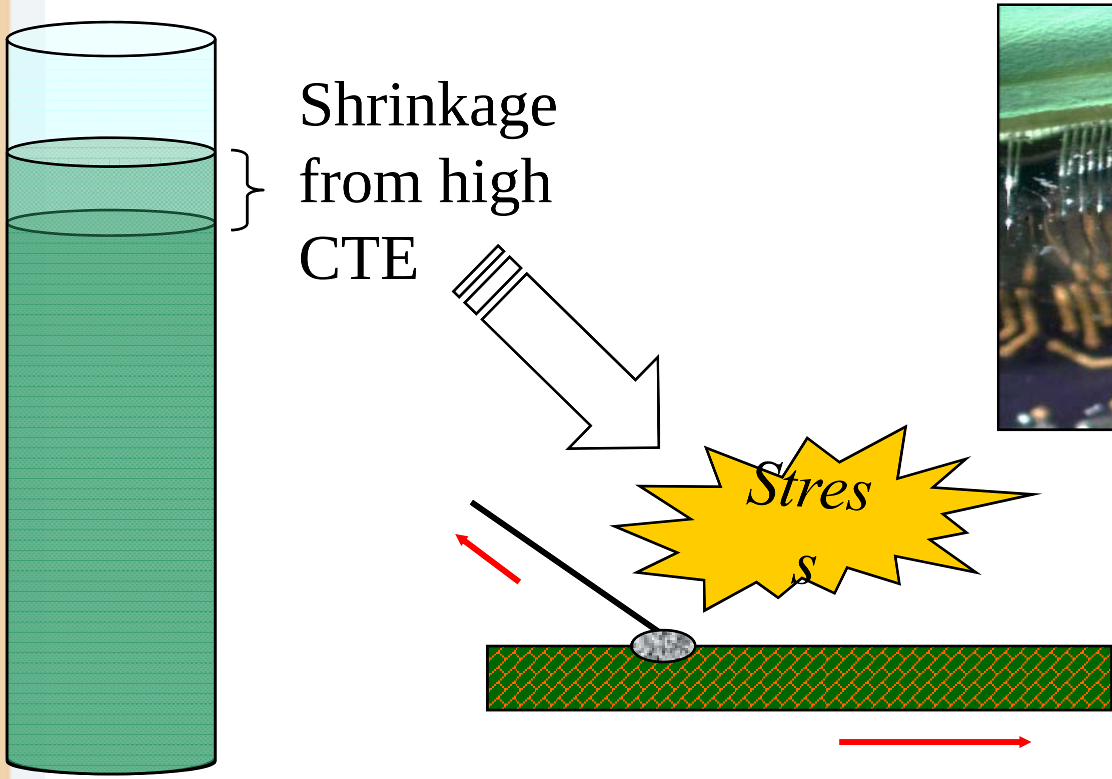


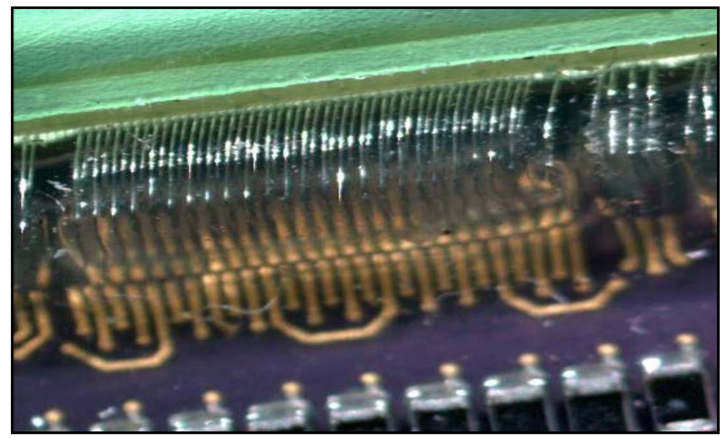
Shrinkage from high CTE

Volumetric CTE for silicones ranges from 500 ppm/C for highly filled products to 1200 ppm/C for unfilled materials like gels.

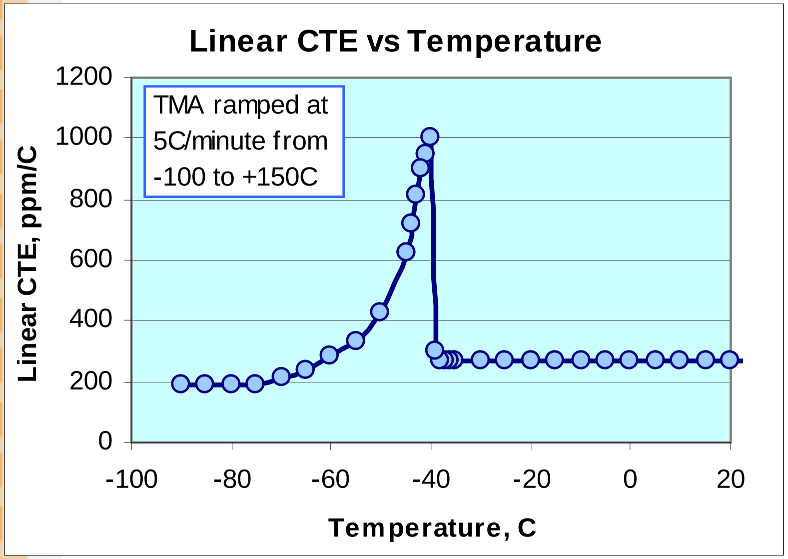
A 12% volume change over a 100C temperature change is very large, but extremely low modulus allows silicones to remain stress RELIEVING even during these thermal movements.

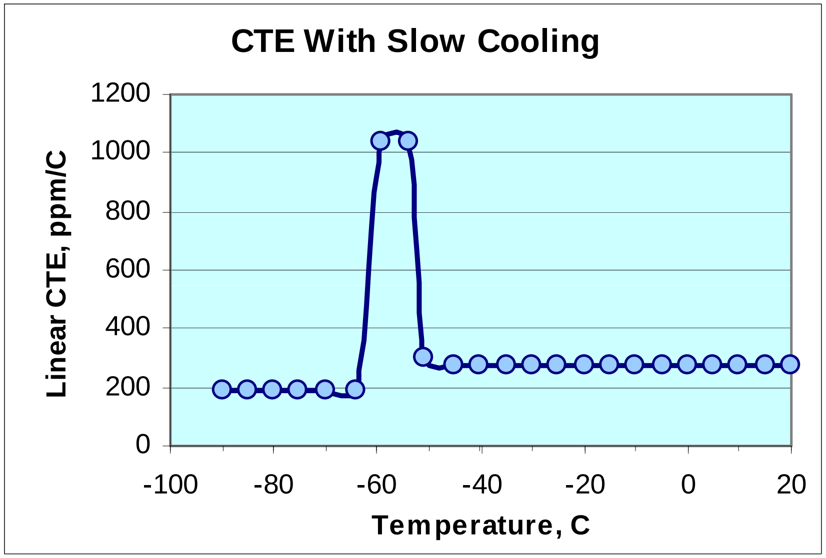
What happens to devices as they are cooled?





Typical analytical testing shows a transition in silicones at about -40C, while a slow cooling may show it at -50C or lower.





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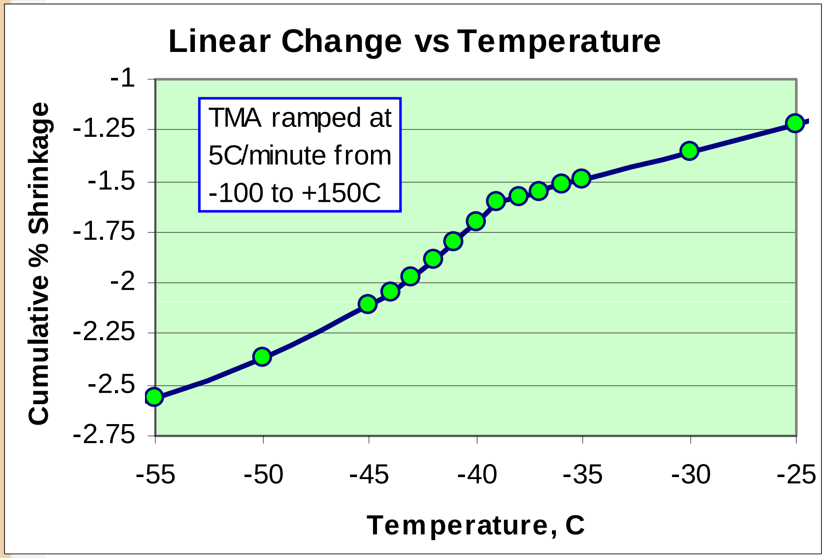
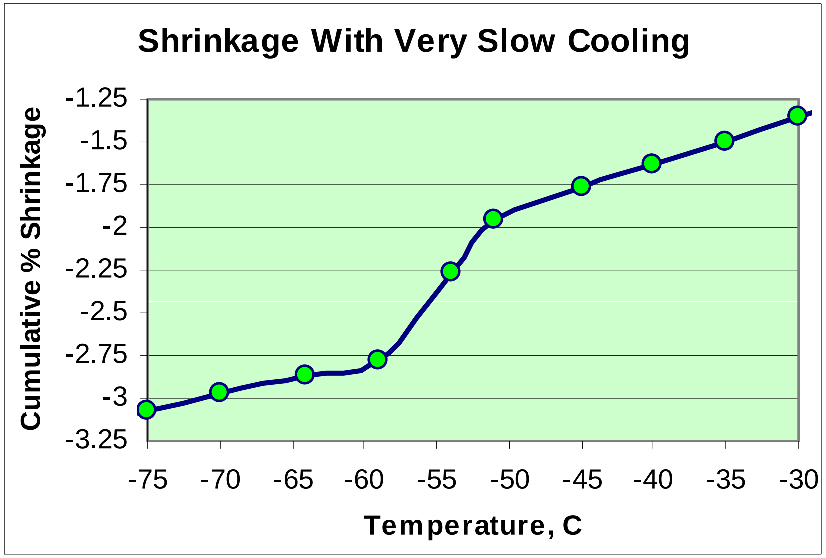
Is this important? It can be if your low temperature specification is between -35 and -60C.





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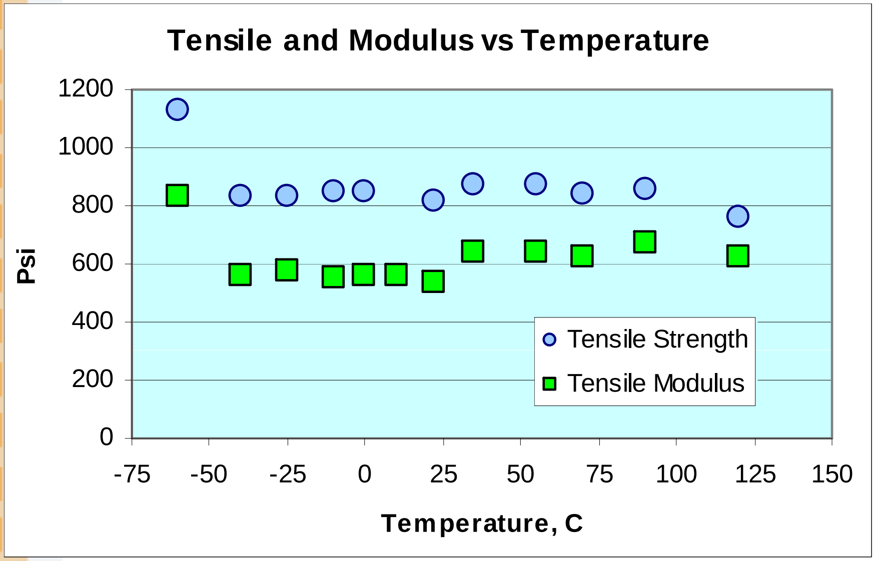
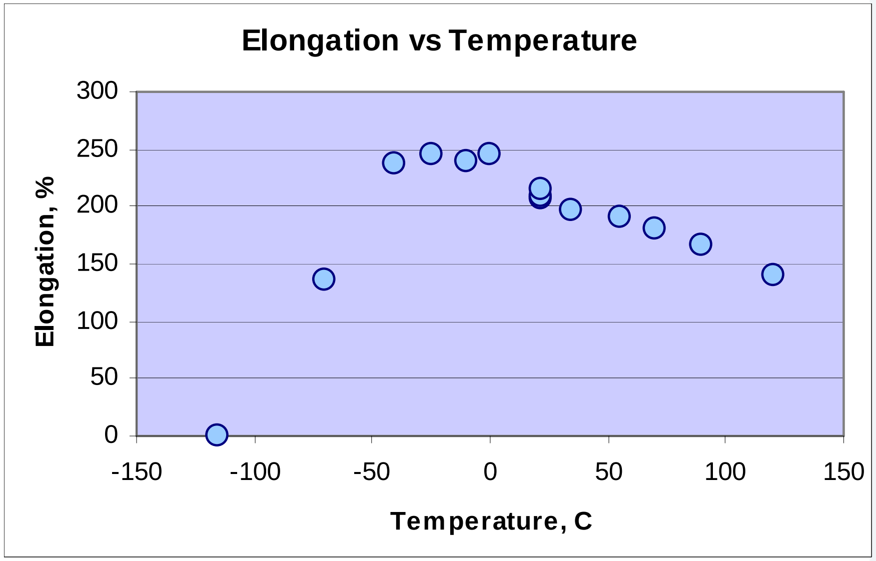
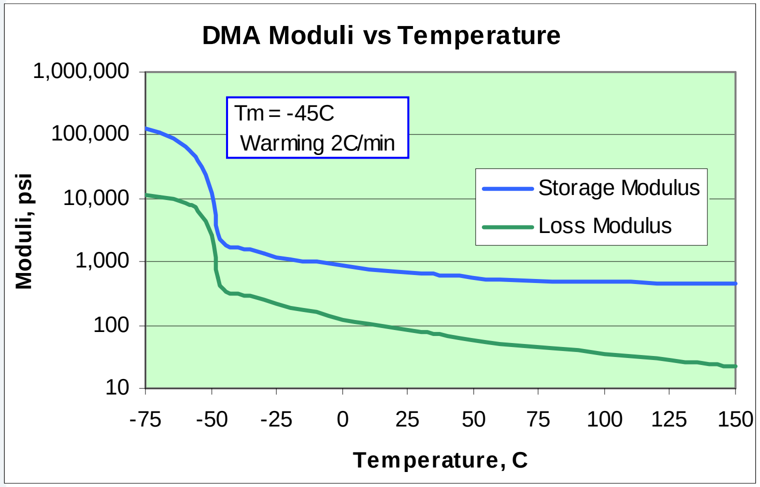
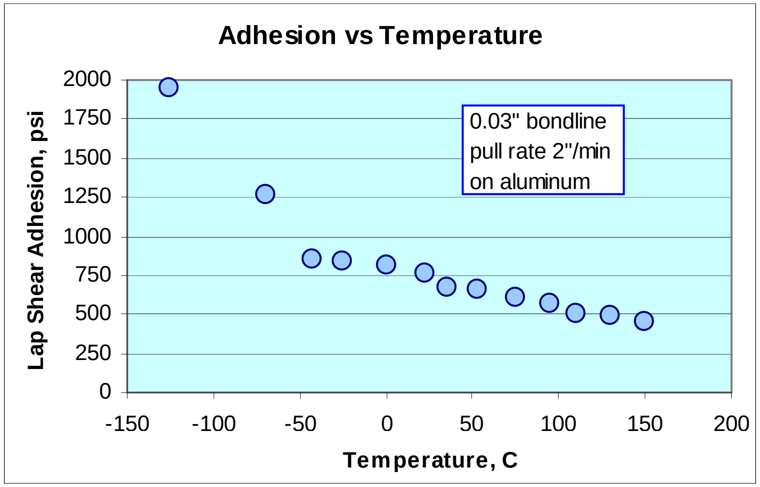
Tensile Strength, Elongation and Elastic Modulus





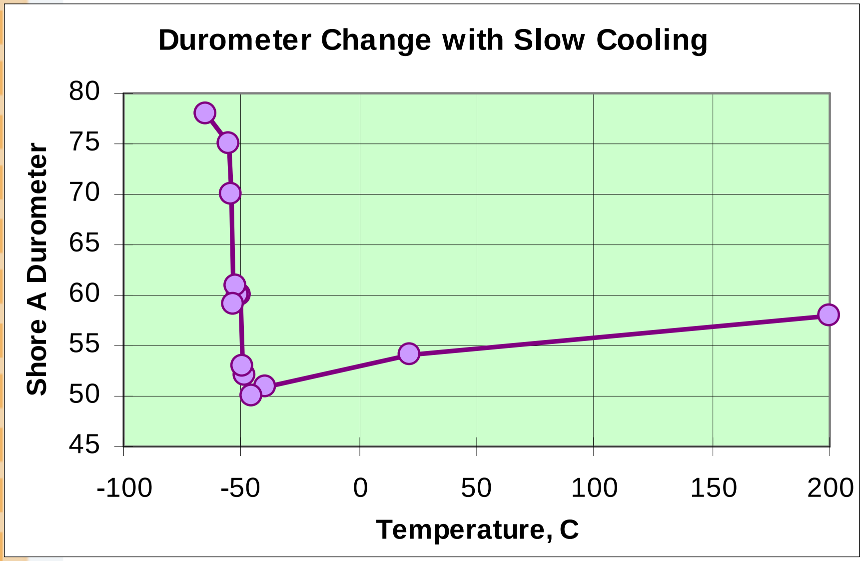
Storage & Loss Moduli and Adhesion

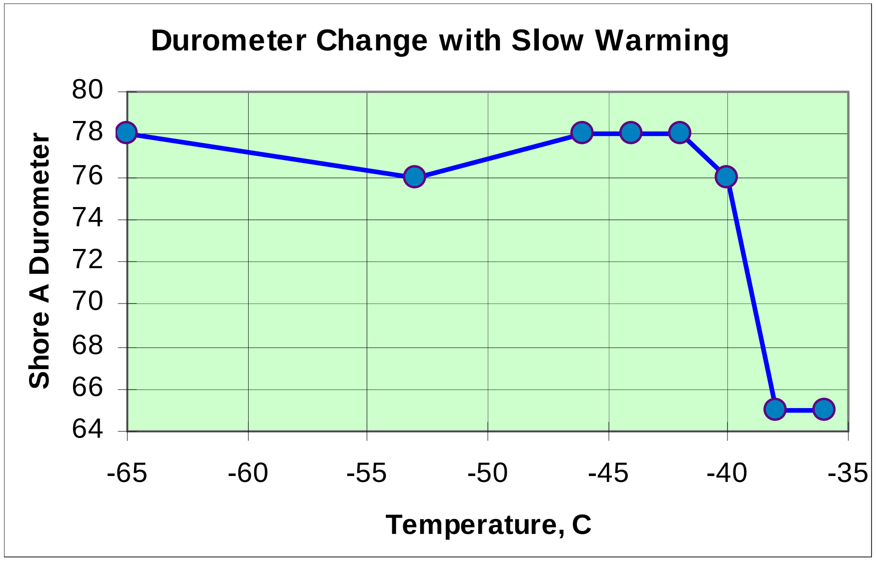




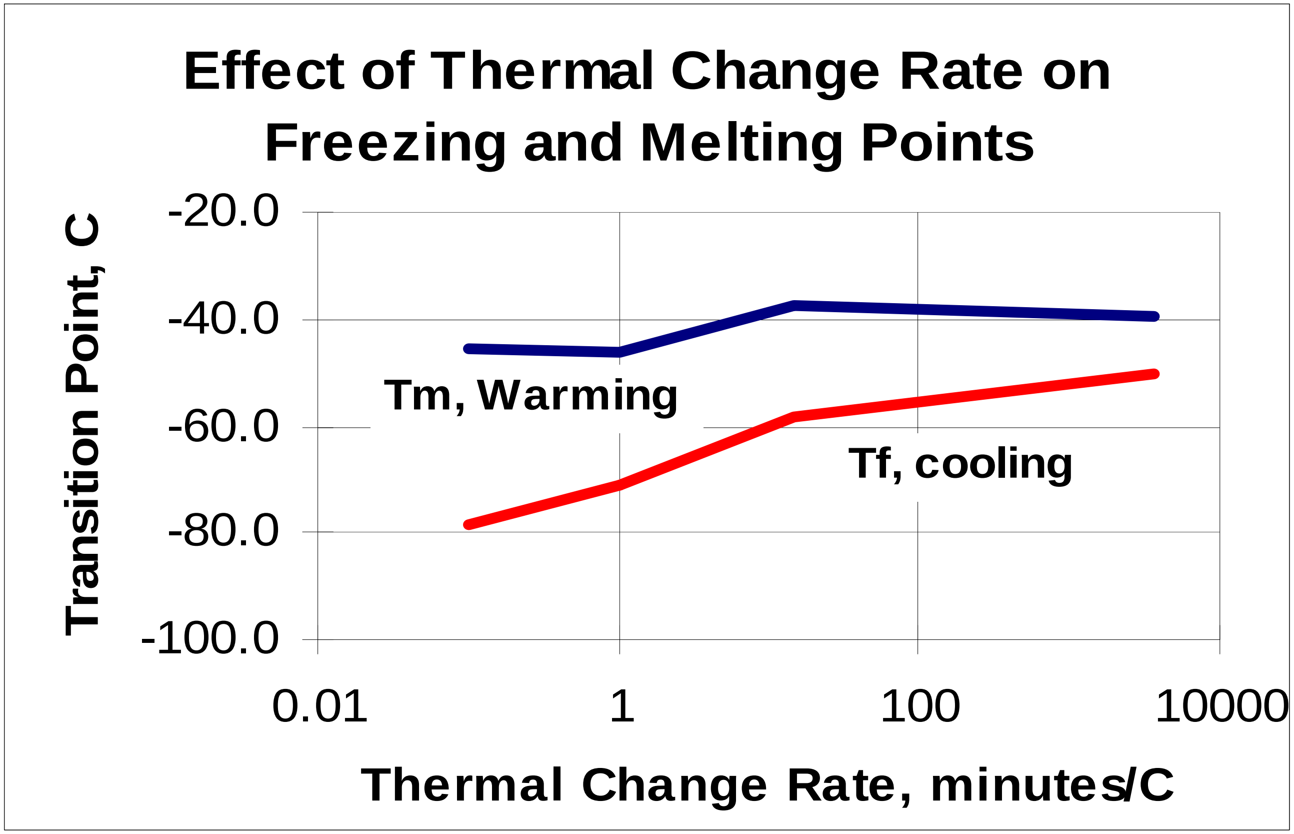
Durometer changes cooling vs warming

Note that most analytical techniques cool to -100C and then warm samples – and will give a transition value that may be overly conservative (-38C vs -48C, for example).





Cooling and Warming Rate Effects



Silicone Gels may show cracks and voids when cooled below -40C.

After 3 weeks at room temperature all cracks were gone … the gels appeared to self-heal from the low temperature induced damage.

Low Temperature Reliability of Silicones

As silicones are cooled they tend to:

- Slightly increase in strength, modulus and elongation
- Very slightly decrease in durometer
- Shrink according to their relatively high CTE

Low Temperature Reliability of Silicones

- Around -45 to -50C most silicones transition from soft rubbers to harder rubbers and may shrink 0.5-1.5%.
- Cracks may form in silicone gels during this transition, but most to all damage tends to self-heal over time when warmed above this temperature.

Low Temperature Reliability of Silicones

- The temperature at which this transition to a harder rubber occurs is cooling rate dependant.
- Below this transition, silicones will not be as stress-relieving.
- Fast cooling and/or relatively short duration low temperature soak times may not identify when this occurs.

Low Temperature Reliability of Silicones

Recommendations when testing silicones at low temperatures:

- Cool slowly or
- Include a low temperature heat soak/ residence time of at least 1 hour when at or below -40C.