Solvent Resistance of Silicones used for Electronic Packaging Applications

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Abstract

Silicones are becoming more popular in advanced packaging for their thermal stability above 200^oC and ability to protect the electronic package from environmental factors. The electronic package may be exposed to a variety of different solvents by fabricators in the cleaning process. Problems arise when the silicone swells with solvent. When the solvent evaporates, the silicone will become harder and put stress on the metal bonds, potentially bending and even shearing them. Fundamentals of silicone manufacturing allow silicones to have different chemical characteristics that can respond differently to various solvents. For example, some silicones are more resistant to hydrocarbon solvents, whereas others are more resistant to halogenated solvents. The purpose of this study is to evaluate the solvent resistance of silicone materials that can be used for electronic packaging. The solvents chosen for this study are commonly used solvents used in the electronics industry and the silicone materials chosen were based on the chemical composition. The change in thickness and specific gravity (% Swell) was measured over time after silicone was exposed to various solvents. By understanding how the electronic package is affected by different solvents, the appropriate solvent and silicone system can be chosen.

1.0 Introduction

Silicones are becoming more popular for their use as adhesives, encapsulants and interface materials due to their thermal stability and low modulus which can protect the components within the microelectronic package [1,2,3]. The "electronic package" is the term used to describe the semiconductor's entire assembly that can be used as an integrated circuit (IC). The electronic package may be exposed to a variety of different solvents by fabricators in the cleaning process.

Problems arise when the silicone swells with solvent and becomes soft. When the solvent evaporates, the silicone will reduce in size and become harder and put stress on the metal bonds, potentially bending and even shearing them. If the solvent is unable to be removed, it can also cause out gassing (bubbles) once the equipment is in use.

This paper will briefly explore how silicones can be used as an encapsulant, interface material and/or as an adhesive for microelectronic applications and their benefits. It will also discuss what can distinguish one type of silicone from another based on the chemical composition and reinforcement mode of the silicone polymers. The focus will be on how the chemical composition of the silicone can have a direct effect on the solvent resistance, as measured by % swell and change in thickness, after prolonged exposure to common solvents used in the electronics industry.

By understanding how the electronic package is affected by different solvents, the appropriate solvent can be chosen for cleaning.

1.1 Silicone in Microelectronic Packaging

Silicones have an inherent large free volume within the amorphous structure due to the large bond lengths and angles between the repeating silicon and oxygen atoms that make up the majority of the polymeric structures [4]. This, along with unusually weak intermolecular forces, gives silicone many unique properties such as thermal stability in extreme temperatures. Other unique properties are:
• Tg typically < - 115 $^{\circ}$ C
• Low Modulus
• Low shrinkage, < 1%
• Dielectric Strength 500V/mil (0.001 inch) or 20 kV/mm
•Versatile usage configurations:

–Optically Clear, Thermally Conductive, Electrically Conductive, Silica filled

1.2 Silicones for Microelectronic Packaging

There are several areas within, and on, a microelectronic assembly that may need an elastomeric or 'rubber' material such as an adhesive, encapsulant or interface material. Thermal Interface Materials (TIMs) are typically a polymeric material that is able to absorb stress and transfer heat away from heat sensitive components. They can be electrically and/or thermally conductive, as well as have a consistency such as grease or a hard elastomer. Below are examples of where silicone can be applied within a Flip Chip assembly. They also can be used directly in contact with the die as die attach or underfill. Another common application for silicones is as an encapsulant, also known as "glob top", that protect the entire microelectronic assembly from damage during transport, and other environmental conditions that can damage the components.
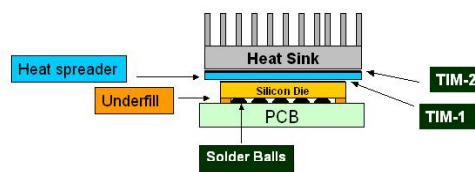

Figure 1: Example of Flip Chip assembly

1.3 Silicone Polymer Chemistry

The primary structure of many silicone products used in microelectronics are silicone polymers, which can be up to 70 percent of the total formulation. These are linear structures with alternating silicon-oxygen atoms that make up the backbone of the polymer. For a given silicone polymer formulation; the number of monomeric units dictates the chain length which affects viscosity, the R group will affect the chemical performance and the "end blocker" typically contains the functional group that partakes in the crosslinking (curing) reaction. The resulting polymer comprised of several repeating monomers is a poly (diorgano) siloxane polymer (see Figure 2)
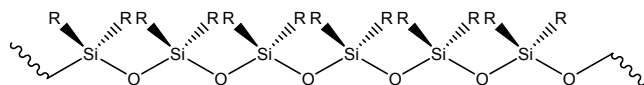

Figure 2: Diorganodisiloxane polymer. R can be methyl, trifluropropyl, phenyl, etc.

The diorganodisiloxane structures in Figure 3 shows that the R groups on the back bone can vary which allows different types of organic groups to be incorporated as pendant groups within one polymer chain (R and R').
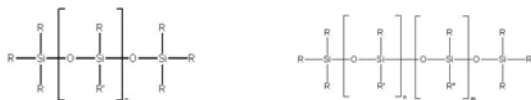

Figure 3: Generic polymer and Generic Co-Polymer

Different pendant groups can provide a variety of excellent properties that can be chosen according to the specific application. The organic pendant groups that will be evaluated for this discussion are methyl and trifluoropropylmethyl substituents [5].

Dimethylsilicones:
Dimethylpolysiloxanes (PDMS), are the most common silicone polymers used industrially. These polymers are typically the most cost effective to produce and generally yield good physical properties in silicone elastomers and gels (see Figure 4).
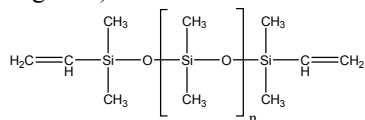

Figure 4: Vinyl terminated polydimethysiloxane

Fluorosilicones are based on trifluoropropyl methyl polysiloxane polymers and historically used for applications that require fuel or hydrocarbon resistance. The trifluoropropyl group contributes a slight polarity to the polymer, resulting in swell resistance to gasoline and jet fuels (Figure 5).
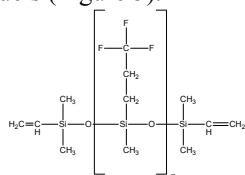

Figure 5: Vinyl terminated polytrifluoropropylmethylsiloxane

1.4 Silicone Polymer Reinforcement:
When silicone polymers alone are crosslinked together, the cured material is typically referred to as a "gel" since the cured silicone has minimal tensile and tear strength properties. Gels are also soft and have very low modulus. Silicone polymers can be reinforced by adding reinforcing fillers, such as fumed silica, and/or silicone resins, that increase the elastic properties of cured silicone.

Silica reinforces the cured silicone polymers through van der Waals forces and hydrogen bonding between hydroxyl groups on silica surface and siloxane backbone of polymer. These weak interactions allow the cured silicone to absorb stresses as well as increase the viscosity of uncured silicone through the same polymer-filler interaction [6]. The silica is typically added to the polymer and treated with organosilicones to help increase the compatibility of silica in polymer, which subsequently stabilizes the viscosity to a certain degree. Silica reinforced silicones typically have non-Newtonian flow characteristics where the viscosity will decrease when shear is applied and are also translucent.

Silicone resins are highly branched polyorganosiloxanes. Silicone resins can reinforce the silicone polymer through more complex crosslinked architecture once cured, which helps distribute applied stress as well as entanglement of resin and polymer molecules. Of course, van der Waals forces and hydrogen bonding also play a role in stress response. Resin reinforced silicones are typically transparent and have Newtonian flow characteristics where the viscosity is not greatly affected by the applied shear.

2.0 Solvent Resistant Evaluation

The general rule for dissolving substances is "likes dissolve likes" [7]. The more chemically similar the solute (in this case silicone rubber) is to the solvent, the more the silicone will absorb the solvent into its cured matrix. Solvents can be readily removed by exposing the elastomer to moderate heat. Within those elastomer systems high molecular weight, unreacted siloxane polymers are readily dissolved and removed from the cured elastomer systems when exposed to certain solvents. As a result, silicones can lose volume upon exposure to solvent systems. This volume loss can impact the package in several ways such delamination of the silicone from the substrate surface. It is important to note the stresses associated with solvent shrinkage are considerable (roughly 3 orders of magnitude more) when compared to expansion and contraction due to thermal cycling in the solder reflow and operating phases of package. The more dissimilar they are chemically, the less

solvent the cured silicone will absorb, leading to less swelling.

Polarity is the chemical property most responsible for how similar the solute and solvents are. Organic solvents may have a polar functional group such as alcohol (-OH) or a halogen (-F, -Cl, or -Br) to increase the ability to dissolve substances that have similar functional groups on them.

2.1 Materials:
The solvents chosen for this study are commonly used solvents (or solvent families) used in the microelectronics industry (Table 1). The silicone materials were chosen based on polymer chemical composition and mode of reinforcement (resin or silica). Table 2 shows the abbreviations given to the silicone systems used for the study. The polymers used for DMR and DMS are the same but one uses silica for reinforcement (DMS) and the other silicone resin (DMR). Since one mode of reinforcement for resins is additional crosslinks, the durometer for DMR is higher than DMS. The flurosilicones, FS1 and FS2, use similar polymers but have different formulations where FS1 is an adhesive and FS2 is an encapsulant.

Table 1: Solvents

Solvent	General Description and Use
Isopropyl alcohol (IPA)	Polar solvent and commonly used to wipe down a surface before applying silicone.
HFE [8]	Fluorinated ether solvents are polar compared to hydrocarbon solvent. Common family of solvents used for cleaning microelectronics.
Terpene [9]	Limonene/Ester mixture. Aromatic product of citrus fruits and replacement for CFC.
Hexane	Hydrocarbon solvent with no double bonds. Least polar of solvents evaluated.

Table 2: Silicones:

2.2 Experimental
% Swell **(Ref ASTM D-471)**, which measures change in volume based on specific gravity, was measured to evaluate the differences before and after exposure to solvent. The method and calculations were adapted from ASTM D 471-79 where the higher % change in volume, the more solvent the silicone was absorbing.

% change in thickness was also measured before and after submersion. The thickness was measured again after a 48 hour dry out period to evaluate how much solvent would evaporate in ambient conditions after 48 hour exposure to solvent and see if there were any further dimensional changes.

2.3 Calculations
a. % Swell (% V)

$$\% \, Swell = \frac{(M3 - M4) - (M1 - M2) \times 100}{M1 - M2}$$

M1 = initial weight of sample in air
M2 = initial weight of sample in water
M3 = weight of sample in air after immersion
M4 = weight of sample in water after immersion

b. Δ % Thickness (%ΔT)

$\% \, \Delta \, Thickness = \{(T2 - T1)/T1] \times 100$

T1 = Original sample thickness
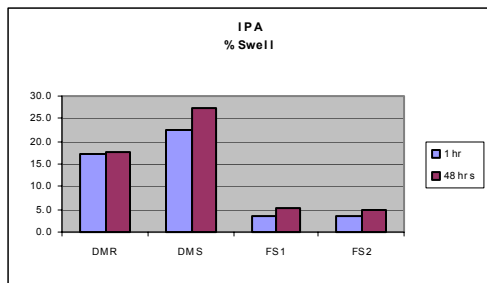T2 = Final sample thickness

2.4 Sample Preparation
1. Silicones were cured per standard cure schedule
2. Sample size 1" x 1" x 0.025"
3. Volume of the solvents was 50 ml in 2 oz glass container
4. The samples were submersed for 1 hour, 6 hours and 48 hours and kept at 25° C
5. Specific Gravity and Thickness were measured immediately after submersion (after excess solvent was allowed to drip off)
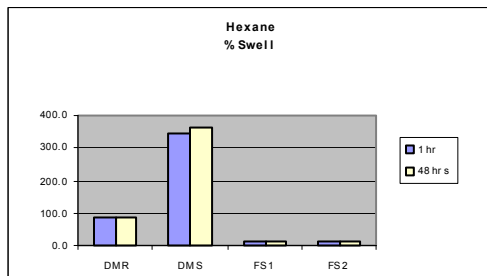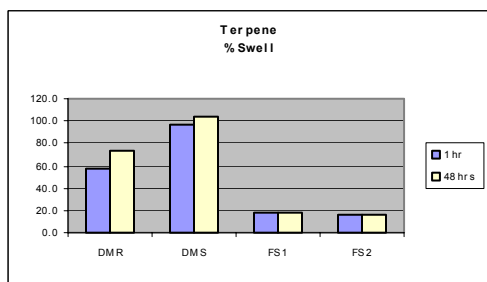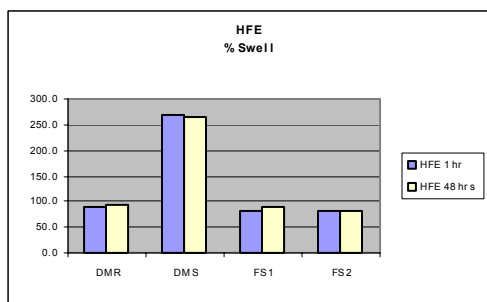
3.0 Results
3.1 % Swell
The silicone absorbed not much more solvent between 1 and 48 hours so the 6 hour results are not reported.

Sample Code	Polymer Chemical Composition	Reinforcement	Durometer Type A
DMR [10]	Dimethyl	Resin	50
DMS [11]	Dimethyl	Silica	25
FS 1 [12]	Fluoro	Silica	30
FS 2 [13]	Fluoro	Silica	45

IPA
% Swell

(chart: DMR, DMS, FS1, FS2 — series: 1 hr, 48 hrs)

3.1 % Swell, continued

HFE
% Swell

(chart: DMR, DMS, FS1, FS2 — series: HFE 1 hr, HFE 48 hrs)

Terpene
% Swell

(chart: DMR, DMS, FS1, FS2 — series: 1 hr, 48 hrs)

Hexane
% Swell

(chart: DMR, DMS, FS1, FS2 — series: 1 hr, 48 hrs)
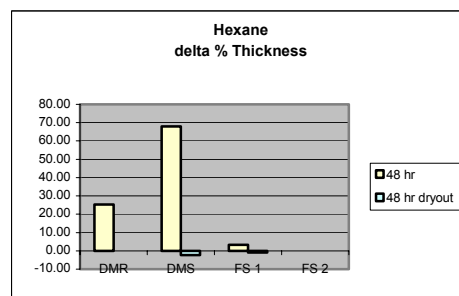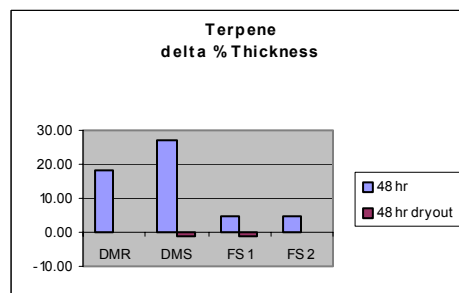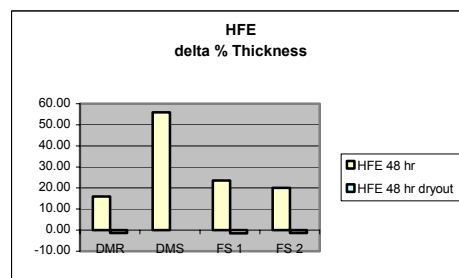
3.2 % Thickness

There were minimal changes in thickness between 1, 6 and 48 hours so only the change in thickness after 48 is reported to show "worst case scenario".

IPA
delta % Thickness

(chart: series: IPA 48 hr, IPA 48 hr dryout)

HFE
delta % Thickness

(chart: DMR, DMS, FS 1, FS 2 — series: HFE 48 hr, HFE 48 hr dryout)

Terpene
delta % Thickness

(chart: DMR, DMS, FS 1, FS 2 — series: 48 hr, 48 hr dryout)

Hexane
delta % Thickness

(chart: DMR, DMS, FS 1, FS 2 — series: 48 hr, 48 hr dryout)
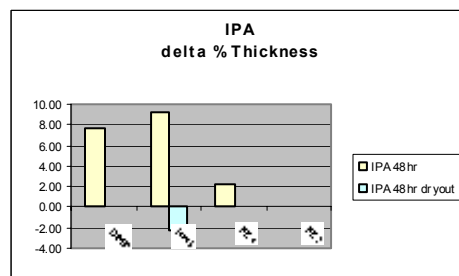
3.3 Relative Differences:

Solvent Resistance	% V	% Δ T
4 Excellent	≤5	≤1
3 Good	≤7	≤2
2 Fair	≤10	≤3
1 Poor	>10	> 3

Silicone	IPA		HFE	
	%* V	% Δ¤T	%* V	% Δ¤T
DMR	1	1	1	1
DMS	1	1	1	1
FS 1	4/3	4	1	1
FS2	4	4	1	1

Silicone	Terpene		Hexane	
	%* V	% Δ¤T	%* V	% Δ¤T
DMR	1	1	1	1
DMS	1	1	1	1
FS 1	1	1	1	1
FS2	1	1	1	4

4.0 Discussion:

There were no significant differences in results between 1 and 48 hours for % V and % Δ T. % Δ T gives a more accurate idea of effect of solvent on silicone materials based on dimensional change. The % Δ T does not have to take into account the specific gravity of solvent or silicone in the dimensional change after submersion.

All the silicones and solvents used contained some methyl (-CH3) groups so they all exhibited some solvent absorption. Fluoro silicones performed very well against IPA and hexane even though one solvent is non-polar (hexane) and the other polar (IPA). We can deduce that hexane is much less polar than the fluorosilicones and IPA must be much more polar than the fluorosilicone since performs well with both.

The terpene is an aggressive solvent. Fluorosilicones did perform better than the standard dimethyl silicones where FS1 and FS2 had 115 Relative Percent Difference (RPD) % *lower* % Δ T than DMR.

DMR was most resistant to HFE and had 22 % RPD lower % Δ T than FS1 and FS2. Standard Silica reinforced dimethylsilicone (DMS) is least resistant to all solvents.

5.0 Conclusion:

Not all silicones are the same with respect to their response to solvent cleaning processes. Fundamentals of silicone manufacturing allow silicones to have different chemical characteristics that can respond differently to various solvents.

The fluorosilicones (FS1 and FS2) were much more resistant to IPA and hexane than the other silicones evaluated. FS2 had the best overall solvent resistance.

In general, even though IPA is a polar organic solvent, this demonstrates that solubility is a complex subject and experiments may be used to determine the effects of a particular solvent on silicone.

Solvents are designed to remove contamination that can be from chemical compounds that have a wide range of polarity. By understanding how the electronic package is affected by different solvents, the appropriate silicone/solvent can be chosen.

6.0 References

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