Calculated Shear Stress Produced by Silicone and Epoxy Thermal Interface Materials (TIMs) During Thermal Cycling

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Abstract
Choosing a Thermal Interface Material adhesive can have an impact on the reliability of the microelectronic package in harsh thermal environments where thermal cycling temperature ranges are more extreme. This can occur during assembly with lead free solders, packages that generate heat due to their small size and processing power and applications where the package is in proximity to high temperatures. Due to the differing Coefficients of Thermal Expansion and Elastic Modulus of the materials used in hybrid electronic packages, the heating and cooling causes these materials to expand and contract, creating stress on parts of assembly where failure modes can be from warping, cracking, and delamination. Epoxy TIM adhesives have been used traditionally but silicones are becoming more popular due to their inherently low elastic modulus.

A simplified mathematical model was evaluated that calculates relative inherent stress based on CTE of substrate and TIM adhesive, temperature range, and Elastic modulus of TIM. The purpose was to evaluate if equation could be used to aid the engineer in a first order material selection based on desired relative inherent stress using literature values for properties above versus expensive empirical testing.

Three ceramic filled TIM adhesives were evaluated; an epoxy, and two Silicones (40 Type A versus 30 '00' Durometer) using the equation and then recalculated using values from empirically obtained Elastic Modulus. The substrates considered were silicon, gold, copper and aluminum.

The evaluation demonstrated that the large difference in Elastic Modulus of epoxy versus silicone did show an overall lower relative inherent stress in the package assembly.

Introduction
The engineering needed in Thermal Management designs has become a key element to the reliability of electronic devices. Sources of heat can be due to powerful processors in microelectronic packages, lead free solder reflow temperatures and the operating environment such as close to operating motors or engines. Microelectronic packages are composed of several different materials chosen for specific properties, forming a hybrid microelectronic package. Due to the differing Coefficients of Thermal Expansion (CTE) and Elastic Modulus of the materials used in hybrid electronic packages, the heating and cooling causes these materials to expand and contract, creating stress on parts of the assembly where failure modes can be caused from warping, cracking, and delamination.

Thermal Interface Material (TIM) adhesives are used to enhance the thermal contact between the heat spreader (typically copper) and the silicon die (TIM 1), and heat spreader and sink (TIM 2) (Fig. 1). The TIMs contain up to 90% (w/w) of ceramic or metallic fillers to increase the ability to transport heat and can conform to the microscopic surface contours of the adjacent solid surfaces and increase the microscopic area of contact between them.

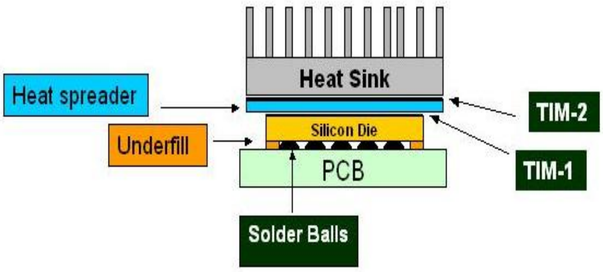


Fig. 1. Example of TIM 1 and 2 in Flip Chip Package

The thermal conductivity of the material reduces the temperature drop across this contact. One of the most common TIM adhesives used in the electronic packaging industry has been epoxy based. They are a versatile product with good adhesion and low CTE but have higher elastic modulus and are less "rubbery" than silicone, which can also be formulated with thermally conductive fillers to perform as a TIM adhesive. Silicone TIMs have a higher CTE than most epoxies but have lower Elastic Modulus. Silicone and Epoxy TIMs typically contain between 60 – 90% (w/w) thermally conductive fillers that add complexity to characterizing their behavior during temperature cycling.

An approach to choosing an adhesive to minimize shear stress is to match CTE of substrates and adhesive or chose an adhesive with low CTE. Epoxy and silicone are viscoelastic polymers that cure (thermoset) and the differences between the molecular structure of these polymers results in vastly different mechanical properties. Typically it is found cured thermoset polymers with low CTE values typically have corresponding high Elastic modulus values and are much stiffer than high CTE materials such as silicone**.**

A simplified mathematical model (Eq. 1) was evaluated that calculates relative inherent stress based on CTE of substrate and TIM adhesive, temperature range, and Elastic modulus of TIM. The purpose was to evaluate if this simple equation could be used to aid the engineer in a first order TIM material selection based on desired relative inherent stress using literature values for properties aforementioned versus expensive empirical testing.

Eq. 1

$$\sigma = (\alpha_{adh} - \alpha_{sub}) * \Delta T * E_{avg}$$

Where:

σ = Shear Stress due to adhesive bond

α_{adh} = Coefficient of Thermal Expansion of Adhesive

α_{sub} = Coefficient of Thermal Expansion of Substrate

ΔT = Temperature Range in linear region

E_{avg} = Average Modulus over the temperature range

Experimental

Silicones have an inherent large free volume within the amorphous cured polymeric 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 [1]. This gives silicone many unique properties such as thermal stability in extreme temperatures, high dielectric strength, low ionic content and low moisture absorption. Epoxy and silicone polymers have very different physical properties based on the polymer structure (Table 1).

Table 1. Typical Values of Silicone versus Epoxy

Typical Property	Epoxy C-C-C	Silicone Si-O-Si
Tg (°C) (some types may vary)	> 80	< - 60
CTE (ppm/°C)	45 - 100	120 - 1000
Bond [1] Lengths (nm)	0.154	0.164
Bond Angles [1]	109°	130 -150°

Due to the property differences of silicone and epoxies, it may be difficult to determine where to begin when choosing a TIM adhesive based on thermal cycling regime the package may experience. The study was to determine if Equation 1 could be used to reasonably calculate the relative inherent stress using literature values. The values for storage modulus and CTE from literature values can use a variety of test methods such as tensile for storage modulus at ultimate elongation and Dynamic Mechanical Analysis (DMA) or Thermo Mechanical Analysis (TMA) for CTE values. The TIM thermosets chosen for study were then tested using DMA and the theoretical results were then compared to shear stress calculated using the actual storage modulus. Equation 1 assumes that the Elastic Modulus is linear over the chosen temperature range.

Three ceramic filled TIM adhesives were evaluated; an epoxy, and two Silicones (40 Type A versus 30 '00' Durometer) using the equation and then recalculated using values from empirically obtained Elastic Modulus (Table 2).

Table 2. TIM Product Information

Property	Epoxy[6] TIM	Silicone 1 [7] TIM	Silicone 2 [8] TIM
Durometer	80 Type D	40 Type A	30 ‘00’
W/mK	0.9	1.2	1.5
CTE (in/in/^{0}C x 10^{-6})	64	145*	141*
Tg (^{0}C)	> 80	NM	< - 63
Storage Modulus (MPa)	5428.6 @ 23^{o}C	29.7 @ 23^{o}C	0.068 @ 23^{o}C

* Measured by Thermo Mechanical Analyzer ASTM E-831

The substrates considered were silicon, gold, copper and aluminum (Table 3).

Table 3. CTE of Substrates

Property	Silicon[4]	Gold[4]	Aluminum 6061 [5]
CTE (ppm/^{o}C)	2.5	14	23.4

The theoretical calculations used the average Elastic Modulus (Eavg) at 23°C and assumed Eavg and CTE were linear in temperature range 20^{o}C to 80^{o}C. This temperature range was chosen due to the Tg of the epoxy TIM. It was assumed that CTE values chosen for substrate and adhesives were the same over entire temperature range versus linear region and the same despite testing equipment used.

For the actual measurements, a DMA 2980 TA Instruments was used and modulus measurements were taken over temperature range of -75^{o}C to 250^{o}C due to the low Tg of silicone. Note that the adhesion and thickness of TIM adhesives were not taken into account for this exercise but should be considered once most likely TIM may qualify for intended application.

The theoretical calculations showed (Fig. 2) that Epoxy TIM had Eavg ~ 80X greater than Silicone 1 (40 Type A) and ~ 3000X greater than soft Silicone 2 (10 ‘00’).

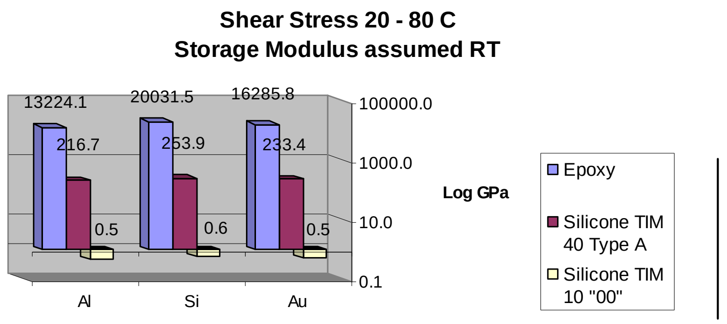
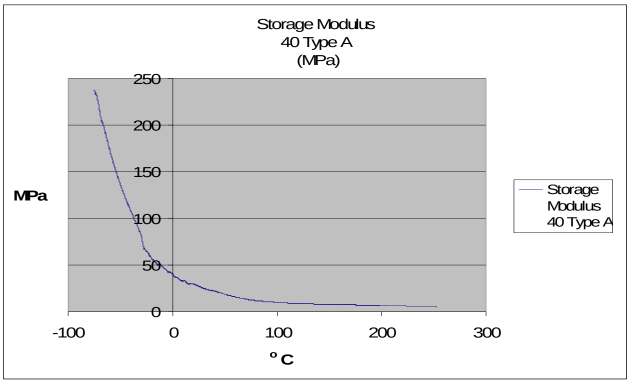


Figure. 2. Theoretical Calculated Sheer Stress

The substrate, silicon, in all cases had the highest calculated shear stress since it had the largest difference in CTE between all adhesives. Silicone 1 had a ~ 200X greater Eavg than Silicone 2. This was an interesting finding in that their CTE was relatively the same even though the Durometer and Eavg were much lower for Silicone 2 than Silicone 1.
The samples were measured via DMA and it was found that the parameters for measuring the epoxy samples were much different than the silicone and the epoxy samples were destroyed during analysis. Due to the availability of epoxy

sample, only the silicone data was available to for empirical versus theoretical calculations. The Eavg over the temperature range chosen showed between 20°C to 80°C had a correlation coefficient of >0.95 (Fig. 3).



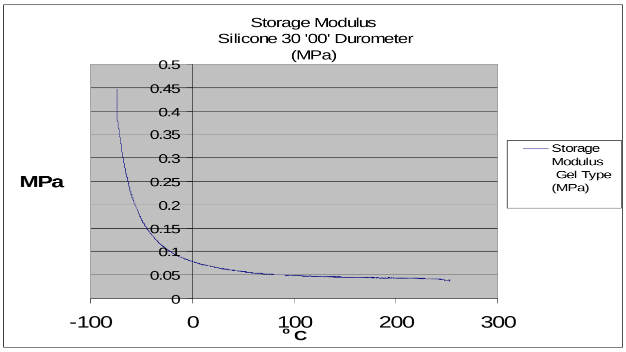


Fig. 3. Average Elastic Modulus (MPa) versus Temperature of Silicone 1 and 2

The calculated inherent shear stress using literature values versus actual CTE and Eavg over the same temperature range (Fig. 4) correlated closely and were within a statistical difference that could be considered from inherent error in testing. More samples will need to be tested to determine if there are any trends since Silicone 1 gave higher calculated shear stress values using theoretical CTE and Eavg where as Silicone 2 gave lower values.

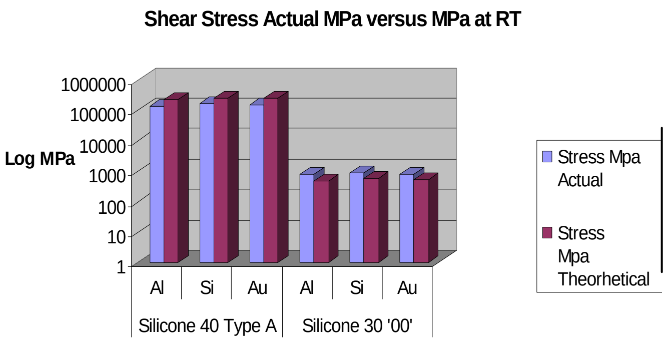


Fig. 4. Calculated Inherent Shear Stress between 20°C to 80°C

Conclusions

Elastic Modulus of Silicone 1 and 2 are much lower than Epoxy evaluated and would theoretically apply a lower shear stress against aluminum, silver and silicon. The equation does appear to be useful when evaluating materials with extreme differences in CTE and Eavg and looking in the linear range. Due to the unfortunate choice of epoxy testing parameters that did not allow DMA testing, future studies would entail obtaining Elastic Modulus at wider temperature range of epoxy and be able to directly compare to silicone. Also, choose wider temperature ranges to calculate internal stress values to better emulate the actual thermal environment and evaluate usefulness of Equation 1 as model for choosing TIMs.

Ultimately, these results should be validated in a simple package design in a reliability test and failure modes determined.

Acknowledgments

Dr. Krystyna R. Brzezinska, Assistant Project Scientist, University Of California Santa Barbara, Materials Research Laboratory

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