SILICONE MIGRATION CONCERNS IN THERMAL MATERIALS – HOW REAL ARE THEY?

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Thermal interface materials (TIMs) are ubiquitous in electronics cooling in a wide variety of applications in Industrial, Automotive and Consumer electronics [1]. These materials are typically comprised of a soft polymeric matrix with thermally conductive fillers. By far the majority of TIMs are based on silicone polymers due to the special characteristics of thermal stability and ability to fine tune the modulus across a wide range [2]. Silicone migration concerns – both with vapor phase (outgassing) and liquid phase (bleed) have been of concern (although not always accompanied by specifics). With proper analysis of the application these concerns can be addressed by designing materials specifically for such applications. Migration is dependent on both TIM microstructure and application details like power density, thermal stack up and physical layouts. We will describe the underlying cause of polymer migration, possible risks, and mitigation measures.

Polymeric TIM Structure and Migration

Polymeric TIMs are comprised of polymers, which typically have a low thermal conductivity (O ~ 0.1 W/m-K) that are filled with thermally conductive fillers (O ~ 1-1000 W/m-K), yielding useful TIMs from 1 – 15 W/m-K [3]. The polymeric portion of the TIM is a complex network structure of polymer chains that are "tied" or cross linked to provide the final physical form. Very long chains can also form networks through entanglements. The polymer TIM structure contains large, gelled clusters but also polymer chains that are not chemically bound to the structure. If these chains are short enough, they do not entangle and can bleed out of the material, as a liquid, under some conditions. Extremely small molecules can migrate in vapor phase as outgassed material and can potential interact or condense with components in the electronics assembly.

The vast majority of TIMs are based on silicone polymers as they are chemically stable and have very low temperature coefficient of properties like viscosity or modulus [2]. This makes them uniquely suited to perform well in applications where temperature or power swing can cause significant temperature changes in operation.

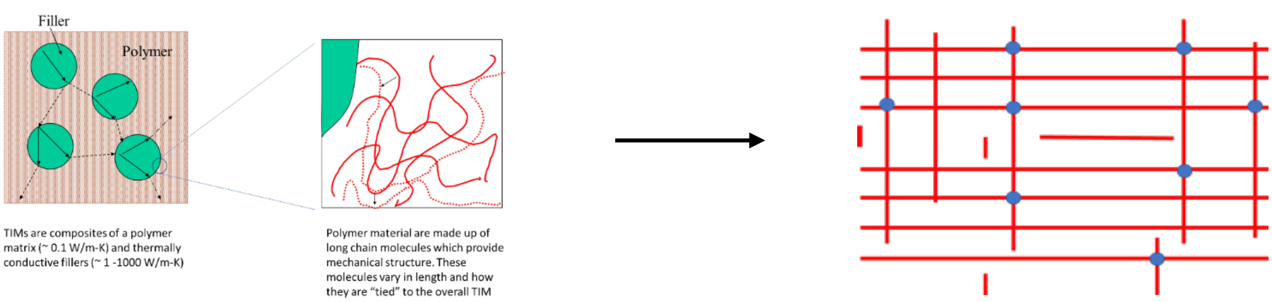

Figure 1. Microstructure of the Polymeric Portion

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Performance Analysis

The polymer portion of the TIM can be broadly classified into 4 categories, based on the ability to migrate – which in turn depends upon the molecular weight (MW) of the category [4].

Extractable = Volatile + Bleedable + Entangled, where

- Extractable is the total amount of free silicone that can be extracted from the **TIM by solvent.**
- Volatile represents the **low molecular weight** silicones that can volatilize and migrate through **vapor phase migration**.
- Bleedable is the **medium molecular weight** liquid silicone portion that can bleed out of the rubber through **liquid phase migration**.
- Entangled or Residual is the higher molecular weight liquid silicone portion that remains in the TIM

In general, for silicone polymers the molecular weight distribution (MWD), of these portions looks as follows:

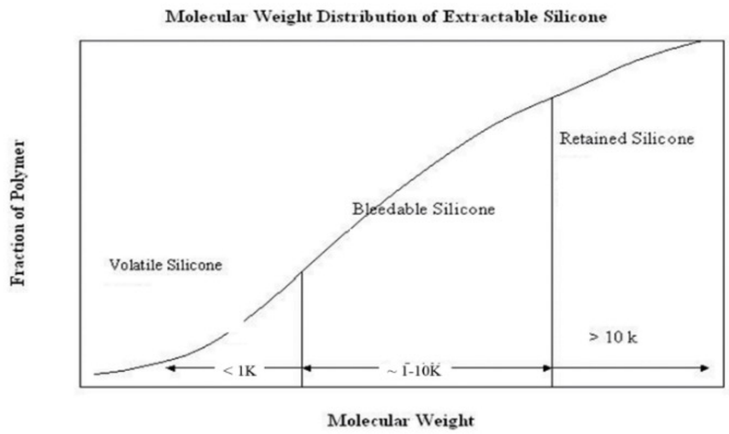

Fig 2. Typical MWD Associated with Migratory Species

The volatile portion can be tailored to a large extent to mitigate migration effects, whereas the bleedable portion is more complex to define and mitigate. This is because the drivers of each of these migrations are different. More on this below.

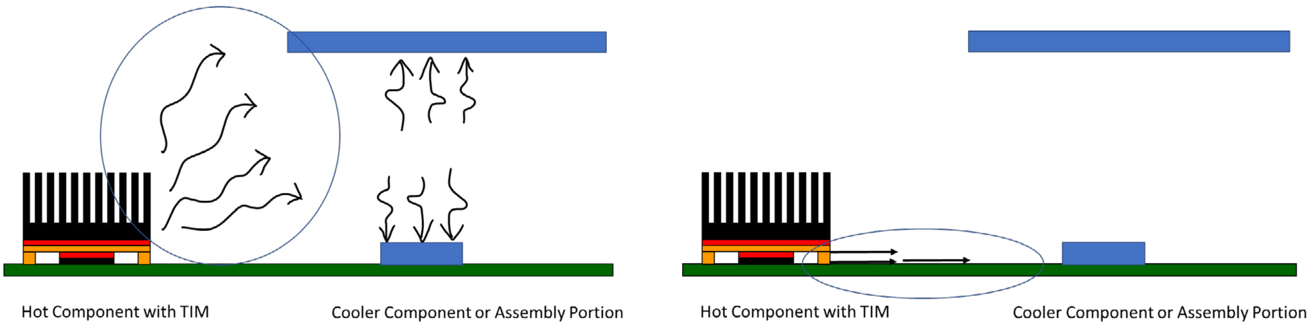

Fig 3. Vapor Phase vs, Liquid Phase Migration

The volatile portion can be tailored to a large extent to mitigate migration effects, whereas the bleedable portion is more complex to define and mitigate. This is because the drivers of each of these migrations are different.

In liquid phase migration, a DIRECT path is required for affected components/surface. This liquid migration is driven by thermocapillary flow due to surface tension gradient. The surface tension gradient exists in the TIM due temperature gradient – hot near active component and cooler further away. As the temperature gradient causes bleed, rate of bleed depends on temperature gradient. Once the material bleeds, the spreading is controlled by surface tension of the bled material and its viscosity.

Migration Risks, Quantification and Mitigation

Markets	Applications	Risk of Silicone TIM	Risk of non-Silicone TIM	Silicone Risk Mitigation
Automotive Electronics	• In-Cabin Electronics	• OEMs siloxane criteria • Passivation of open relays • Hard drive failures	• Few Risks	• Low volatility silicones
Lighting	• LED	• Fogging	• Fogging	• Low volatility silicones
Telecom Datacom	• Optical	• Fogging	• Fogging	• Low volatility silicones
Automotive/Industrial	• Brushed Motor	• Passivation related failures	• Few Risks	• Low volatility silicones
Consumer	• HDD	• Stiction / Head-Crash	• Stiction / Head-Crash	• Low volatility silicones
	• SSD (Multi-format)	• Shared HDD mfg facility	• Shared HDD mfg facility	• Low volatility silicones
Industrial Controls	• General use	• OEM Demand • Paint adhesion • Open contacts	• Few Risks	• Low volatility silicones

Table 1. Vapor Phase Migration Risks

Markets	Applications	Risk of Silicone TIM	Risk of non-Silicone TIM	Silicone Risk Mitigation
All Markets	• All applications	• Cosmetic defect caused by visual bleed presence	• Lower risk due to higher surface tension	• Higher MW (Higher cross-linking leading to possibly higher viscosity/modulus)
All Markets	• All applications	• Contamination may be attracted to bled oil and *may* cause electrical malfunction	• Lower risk due to higher surface tension	• Higher MW (Higher cross-linking leading to possibly higher viscosity/modulus)
Lighting	• Lighting	• Components in vicinity may be affected	• Lower risk, but possible	• Higher MW (Higher cross-linking leading to possibly higher viscosity/modulus)
Communication Equipment	• Optical Components	• Components in vicinity may be affected	• Lower risk, but possible	• Higher MW (Higher cross-linking leading to possibly higher viscosity/modulus)

Table 2. Liquid Phase Migration Risks

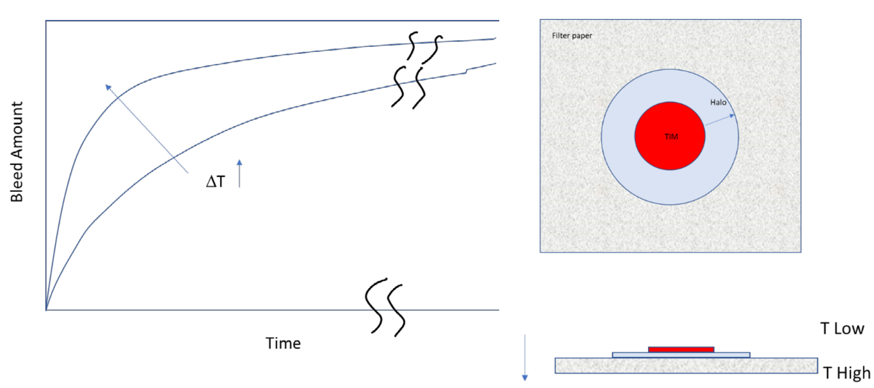

Fig. 4 Bleed Rate Increase with Temp Gradient – Same TIM

Vapor phase migration is mainly comprised of very low molecular weight cyclic silicones that serve as precursors for silicone polymer and well as low MW oligomers [2]. These can be quantified using well documented methods like ASTM E595 [4] – which characterizes total amount of volatilizable material (Total mass Loss - TML) in vacuum as well as the portion that can condense and fog cooler surfaces (collectable volatile condensable material – CVCM). Another well documented method is headspace GC-MS analysis [5], that measures the outgassing of species of specific MWs that are related to failures. As we note, in table 1, while silicone outgassing is concerning for a wide variety of applications, these are largely mitigated by proper design using low volatility silicones. In addition, failure modes like fogging are also a concern for non-silicone materials.

Liquid phase migration, or bleed, is driven by the temperature gradient in an assembly [7]. As silicones have a high spreading coefficient they spread easily on the surface once they are driven out of the interface. If bleed is a real concern for functionality, non-silicone TIMs generally perform better. Some avenues are available for reducing silicone bleed through design, although they don't translate easily across applications. This is because bleed rate depends on the temperature gradient across the TIM, which can vary from one application to another. As shown below, the same TIM can bleed differently depending upon the temperature driver. Since this depends on device power density, thermal stack and general layout, bleed issues are complex interaction between TIM microstructure and the application itself [4].

Typical methods for bleed characterization are centered around: (1) Capillary forces driven bleed into porous filter paper accompanied by measurement of the halo diameter around the TIM or the weight gain of the paper, and/or (2) Temperature gradient driven flow into the paper to characterize the application influence on bleed. These methods are more suitable for comparing different materials for bleed risk, rather than providing a quantitative assessment of suitability in use.

Summary

While silicone outgassing has a higher risk for failure it can also be addressed more robustly and in a quantifiable manner through fundamental TIM design. Nearly all applications at risk can be addressed by low volatility silicone TIMs and a robust product design can transcend markets and applications. Liquid migration is more complex both in terms of assessing risk but also qualifying a TIM, since this is application dependent. Even so, if bleed is a real risk, some design options are available for silicone TIMs but are not universal across applications. Replacing silicones with non-silicones should also be considered carefully since the mechanical properties of the latter have a higher temperature dependence that can affect assembly stress and robustness in thermal/power cycling.

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