

FRACTURE TOUGHNESS OF THERMALLY CONDUCTIVE ADHESIVES

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ABSTRACT

Thermally conductive adhesives provide many advantages over traditional mechanical fastening techniques. Specifically, they use less material and space and are more amenable to automation than existing solutions. The thermal and mechanical properties of these materials are well understood but little work has been done to characterize and understand their toughness and fracture behavior. This paper presents the effects of filler loading as well as matrix composition on the fracture toughness of thermally conductive silicone adhesives. It was observed that the fracture toughness of these materials increased significantly with initial filler loading, and that the mechanical properties and fracture toughness depended on the molecular architecture of the matrix used.

Key words: Thermal management, fracture toughness, adhesives

INTRODUCTION

Modern electronic devices require thermal interface materials to effectively transfer heat from operating components to ensure consistent and reliable performance. These materials range from greases and pads to gap fillers and liquid adhesives.

Liquid adhesives have a variety of advantages over pads. Specifically, they eliminate the need for mechanical fasteners, reduce the amount of material needed in a given application, decrease the residual stresses on electronic components, and enable automated assembly. These advantages lead to electronic devices that are smaller, more reliable, and more efficient than previous devices [1, 2].

The mechanical properties of thermally conductive adhesives are well-known and documented, but the fracture behavior of these materials is less understood [3]. The fracture toughness of a thermally conductive adhesive can have important effects on the performance of an electronic assembly, especially as it relates to issues of fatigue and reliability.

BACKGROUND

Thermal Material Composition

Thermal interface materials are typically composed of a polymeric matrix that is combined with one or more fillers. This forms a composite structure that conducts and/or absorbs heat. The matrix keeps the fillers in place and provides the necessary thermal stability and chemical properties of the composite. Some applications may require a material with a high decomposition temperature or resistance to a specific chemical, while others may not. For example, in automotive applications, resistance to automotive transmission fluid may be a necessary characteristic of the material.

In some cases, such as an adhesive, a more rigid or tough matrix may be desirable. In other cases, like a GAP PAD or gap filler, a soft, compliant material would be ideal to prevent residual stresses on components and to absorb vibration and thermal expansion. The modulus of the filler is generally much higher than that of the matrix, so the mechanical properties of the finished material are largely determined by the matrix modulus and the filler volume fraction.

The thermal conductivity is generally provided by metal oxides to give a balance between costs, performance, and minimize electrical conductivity. In more specialized cases, other ceramics such as boron nitride, aluminum nitride, and silicon carbide or metals are used. Thermal absorption typically comes from materials that undergo a phase transition at the temperature of interest. Waxes and low melting metal alloys often fall into this category [4, 5].

The form factor or method of delivery and use of thermal management materials is widely varied. These solutions come in the form of thick, compliant pads, thin tapes and sheets, reactive materials that cure to form soft interfaces, structural adhesives, and uncured pastes. This study will focus on liquid thermally conductive materials, specifically two-part silicone adhesives filled with aluminum oxide.

Thermal Background

A thermal interface material (TIM) serves to transfer heat from one location to another in an electronic assembly so the necessary components do not overheat. This effect is achieved by reducing the thermal resistance between two or more substrates. Microscopic irregularities on a given substrate trap air at the interface, which then acts to insulate the materials from each other. The thermal interface material displaces the air and provides a thermal path for heat transfer. Improving the thermal conductivity of the interface material is one way to reduce the thermal resistance, but decreasing the bondline between the two substrates is also critical for improving heat transfer. The relationship between thermal conductivity and the bondline and thermal resistance is shown below [4].

$$k = \frac{dq}{dt} \cdot \frac{z}{A\Delta T}, R_{\theta} = \frac{z}{kA} + R_i, Z_{\theta} = \frac{z}{k} \quad (1)$$

k = thermal conductivity, q = heat flow, t = time, z = thickness, A = area, T = temperature, R_{θ} = overall thermal resistance, R_i = interfacial thermal resistance, Z_{θ} = overall thermal impedance

In addition to the thermal conductivity and bondline, additional factors such as reliability, mechanical properties, thermal and chemical stability, electrical conductivity, and dielectric constant also come into play when selecting a thermal interface material.

Fracture Testing Background

Generally, the fracture toughness of a material refers to the amount of energy required to propagate an existing crack in a material [6]. This information is useful as real materials contain flaws and it can be used to predict the performance of materials in applications as well as failure that may occur below the yield strength of an unflawed material.

Two types of tests were used to characterize the fracture properties of the adhesives in this study. Both of these tests examine the properties of a material in a cleavage/an opening mode, which is also referred to as Mode I. This mode is the most common, which is why it was chosen for this study; tests can also be performed for shear (Mode II) or tearing (Mode III) [6, 7]. The first measurement, the plane strain fracture toughness (K_{IC}) of the adhesive on its own, was measured with a single-end-notch bending test, which is shown schematically in Figure 1 [8]. This test measures the inherent fracture toughness of the adhesive by applying a load to a pre-cracked material in a 3-point bending apparatus until the crack propagates catastrophically.

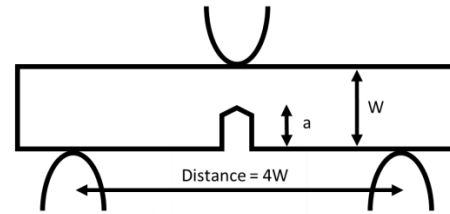


Figure 1. Single-end-notch bending test [8]

The second method measures the fracture toughness, or strain energy release rate (G_{IC}), of an adhesive bond using the dual cantilever beam method. This method gradually opens the bond between the substrates until the crack propagates at which point the load and crack length are measured and the procedure is repeated. A drawing of the test method specimen can be seen in Figure 2.

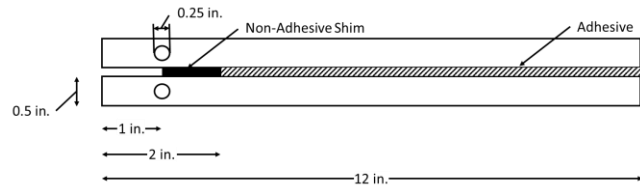


Figure 2. Dual cantilever beam test [9]

TEST PROCEDURES

Mechanical Testing

Tensile testing was performed on the materials in this study in accordance with ASTM D412 [10]. Lap shear strength testing was performed according to ASTM D1002 [11] on 5052 aluminum substrates using a 1" overlap and a roughness of 40 μin .

The plane strain fracture toughness (K_{IC}) measurements of the adhesives themselves were conducted using the single-edge-notch bending (SENB) method described in ASTM D5045 [8]. Experimentation prior to testing showed that the material geometry was sufficient to meet the plane strain criterion.

The Mode I fracture toughness of the adhesives in cleavage (G_{IC}) was tested using the dual cantilever beam (DCB) method according to ASTM D3433 [9]. The substrates were composed of 6061 aluminum substrates with a 12.7 x 12.7mm cross section and a length of 304.8mm. Surface roughness measurements (R_a) on the substrates showed a value of 150 μin which, while relatively high, were within the ASTM specifications. Note that for all of the test results reported the error bars represent one standard deviation.

Materials Tested

The adhesives evaluated in this work were based on typical thermally conductive silicone adhesive formulations used in electronic applications. Two silicone resins were used in the formulations. Both of the materials were vinyl/hydride addition cured silicones with similar hydride to vinyl ratios, but the molecular weight between crosslinks was varied from 45000 Da for the first resin to 9300 Da for the second. The hydride functional crosslinkers had similar molecular weights and backbones that alternated hydride functional and non-functional groups. The change in the molecular weight between crosslinks was achieved by modifying the molecular weight of the vinyl terminated silicone component. This change was made to evaluate the effect of molecular architecture on the mechanical properties of the adhesives. It was expected that the adhesive that had a lower molecular weight between crosslinks would be more brittle and higher in modulus than the material with the higher molecular weight between crosslinks.

In order to achieve an increase in thermal conductivity, the resins were filled with 0, 400, 700, and 1000phr of alumina powder. These loading levels were chosen to be representative of typical products. In all cases, the filler package consisted of a trimodal blend of $<50\mu\text{m}$ spherical alumina powders. The same filler package was used in all of the adhesives to minimize any effects of changing particle morphology or maximum packing fraction. In all cases, the materials were cured for 30min at 100°C .

RESULTS AND DISCUSSION

Mechanical Properties

Prior to testing the fracture behavior of the materials in this study, their mechanical properties in tension were established. Figures 3-5 below show the tensile strength, modulus, and elongation to break of the eight materials studied.

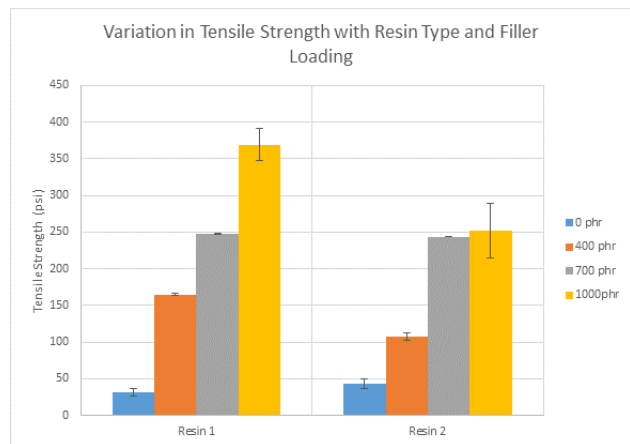


Figure 3. Variation in Tensile Strength with Composition

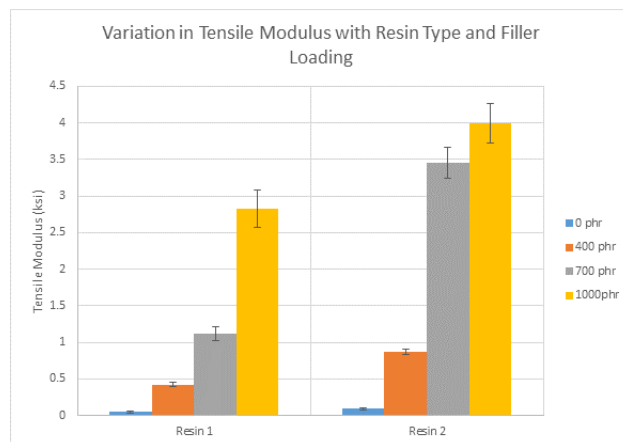


Figure 4. Variation in Tensile Modulus with Composition

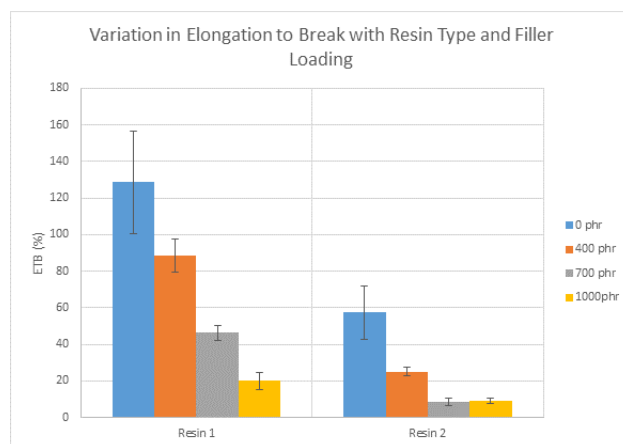


Figure 5. Variation in Elongation to Break with Composition

As would be expected from the difference in molecular weight between crosslinks between resins 1 and 2, resin 1 showed a larger elongation to break and a lower modulus than resin 2. The effect of resin type on tensile strength was less pronounced. Increasing the filler content also had the result of increasing strength and modulus but decreasing the elongation to break of the material. Without reinforcing fillers, silicone materials are well known for being quite weak, so this observation was expected. [12].

Lap shear testing on the materials showed a large initial increase in strength when filler was added followed by a more gradual increase as can be seen in Figure 6. In all cases, the lap shear specimens failed cohesively.

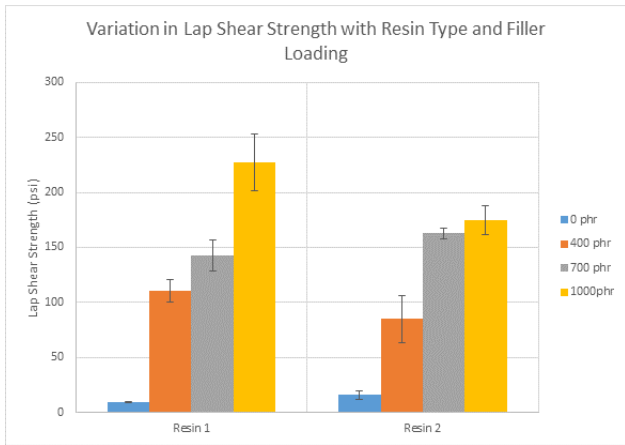


Figure 6. Variation in Lap Shear Strength with Composition

These adhesion results follow what would be expected from the increase in tensile strength and modulus with filler loading from the tensile testing. Formulations containing resin 1 showed larger adhesion values than those containing resin 2, suggesting a link between the molecular weight between crosslinks and the lap shear strength. Figures 7 and 8 below show the correlation between the lap shear strength and the tensile modulus and tensile strength of the adhesives. At higher filler loading the modulus and strength of the adhesives increased, which both correlated with an increase in the lap shear strengths of the adhesives.

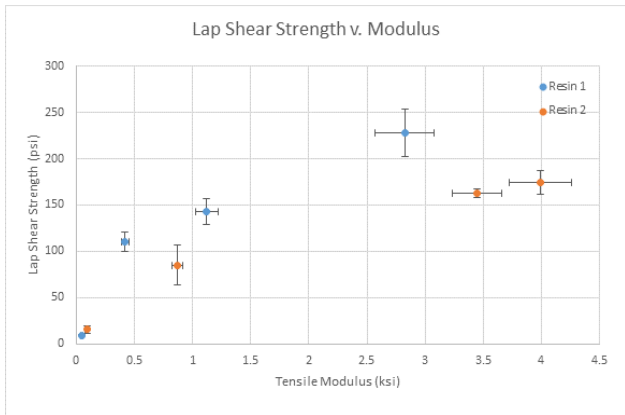


Figure 7. Variation in Lap Shear Strength with Tensile Modulus

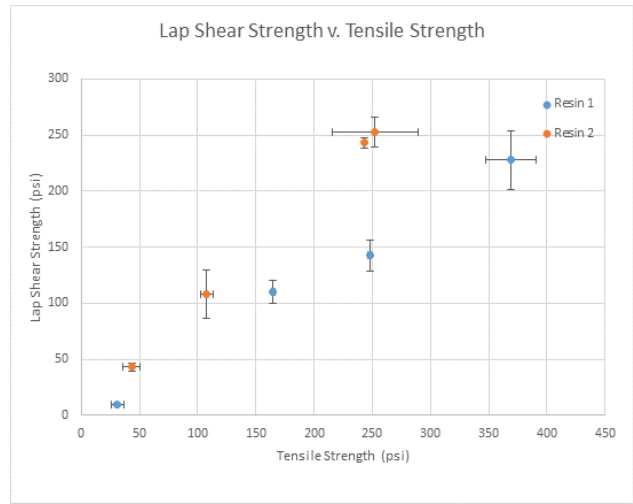


Figure 8. Variation in Lap Shear Strength with Tensile Strength

Fracture Testing

In this section, the fracture toughness properties of the dispersions and adhesively bonded specimens will be presented and discussed. In Figure 9 below, the fracture toughness properties of the adhesives are presented.

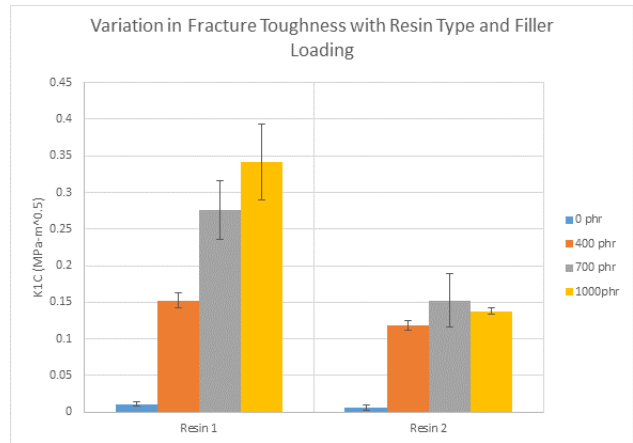


Figure 9. Variation in Dispersion Fracture Toughness with Composition

There is a significant increase in fracture toughness that is associated with the addition of filler to the formulation. No significant difference between the two unfilled resins was observed. However, the fracture toughness at 700 and 1000phr loading was significantly larger for the dispersions containing resin 1 as compared to resin 2.

Scanning electron micrographs were taken of the failure surfaces for all of the specimens tested. No significant difference in the failure surfaces that correlated with the resin type or filler loading above 400phr was seen. Figure 10

below shows the transition from the pre-cracked region (bottom) to the fracture surface (top) of resin 2 without any filler. Secondary electron imaging was used to obtain this picture.

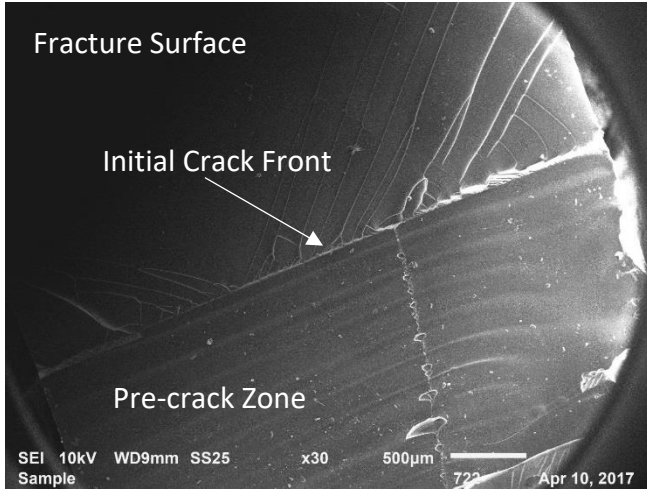


Figure 10. SEM Image of the Resin 2 SENB 0 phr Failure Surface, 30x

Figures 11 and 12 below show backscatter SEM images of the pre-crack and failure surface for resin 2 containing 1000phr of filler, respectively. As the image shows, significant filler pull-out occurs during the crack propagation, which likely plays a role in the improvement of the fracture toughness.

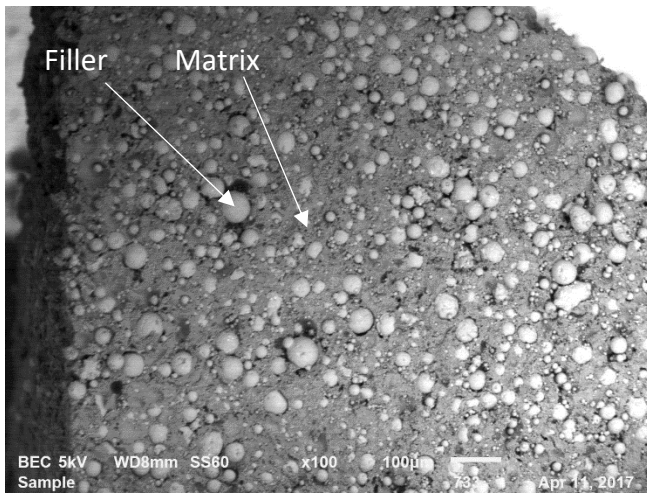


Figure 11. SEM Image of the Resin 2 1000phr Pre-crack Surface, 100x

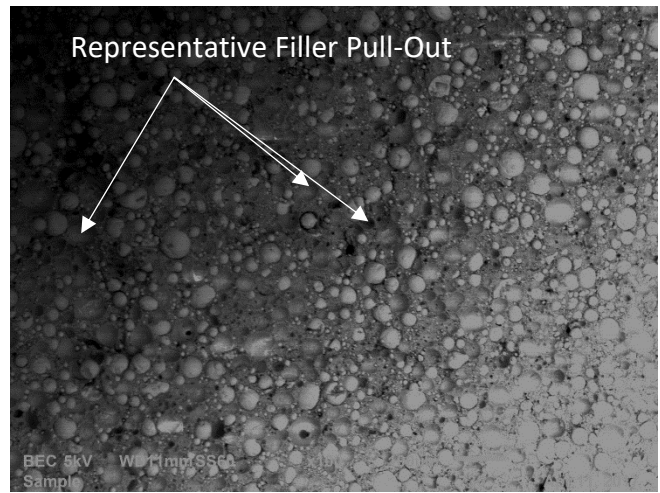


Figure 12. SEM Image of the Resin 2 1000phr Failure Surface, 100x

It was discovered that the K_{IC} fracture toughness values of the dispersions correlated with the tensile strength of the specimens. Figure 13 displays this relationship. As the figure shows, the tensile strength of the material increases as the fracture toughness of the material increases.

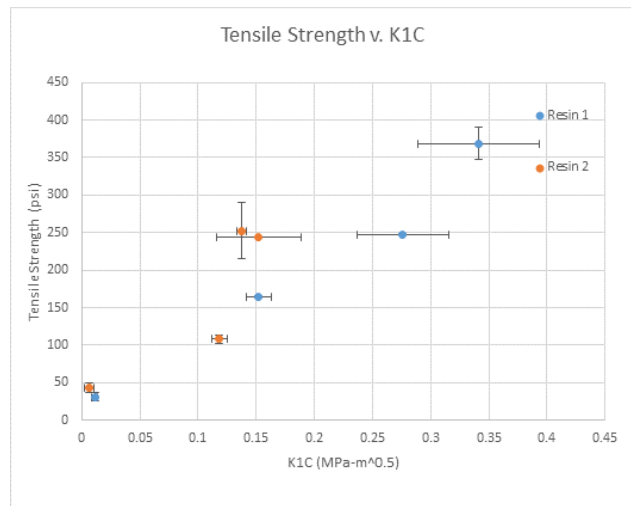


Figure 13. Variation in Tensile Strength with Fracture Toughness and Composition

After testing the fracture toughness of the adhesives outside of an application, they were tested when used to bond substrates together to determine their performance. In Figure 14 we can see the G_{IC} values for the adhesives studied.

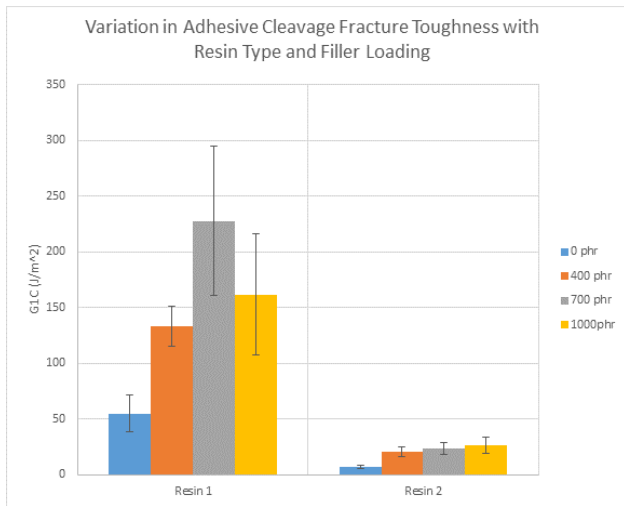


Figure 14. Variation in Cleavage Fracture Toughness with composition

It can be seen that the adhesive that contained the resin with the higher molecular weight between crosslinks (resin 1) showed a much higher fracture toughness than resin 2. As was observed with the K_{IC} values, adding filler increased the toughness, but to a less significant degree. All of the specimens failed cohesively and images were recorded, although significant differences between the systems were not seen. Figures 15 and 16 show representative failure surfaces for unfilled and filled systems, respectively.



Figure 15. Dual Cantilever Unfilled Resin 2 Failure Surface



Figure 16. Dual Cantilever 1000phr Resin 2 Failure Surface

CONCLUSIONS

The effects of molecular weight between crosslinks as well as filler loading were shown to influence the mechanical properties of thermally conductive adhesives, particularly their fracture toughness. Increased levels of filler, which correlate with higher thermal conductivities, led to increases in modulus, strength, and fracture toughness but a decrease in elongation to break. An increase in molecular weight between crosslinks improved the strength, toughness, and elongation to break of the materials.

FUTURE WORK

Future work is planned to investigate material performance at elevated and sub-ambient temperatures. In particular, the properties of the adhesives above and below T_g will be studied. Additional experimentation around a wider variety of matrix types and matrix formulations is also expected.

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As previously published in the proceedings of SMTA International.