

# Lithium Doped Polyethylene-Glycol-Based Thermal Interface Pastes for High Thermal Contact Conductance

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*Polyethylene-glycol-based thermal interface paste containing trifluoroacetic acid lithium salt (1.5 wt. percent optimum) and boron nitride particles (~18.0 vol. percent optimum), as well as water and N, N-dimethylformamide for helping the dissociation of the salt to release Li<sup>+</sup> ions, gives thermal contact conductance that is almost as high as that given by Sn-Pb solder, similar to that given by boron nitride particle filled sodium silicate, and much higher than that given by boron nitride particle filled silicone.*

[DOI: 10.1115/1.1477191]

*Keywords:* Polymer, Polyethylene Glycol, Lithium, Boron Nitride, Thermal Interface, Thermal Contact, Thermal Conductance, Composite

## Introduction

Thermal contacts are commonly encountered in industry and in homes. A thermal contact can be between a hot (or cold) plate and an object to be heated (or cooled), and between two objects (at different temperatures) in an assembly. An example is the thermal contact between a printed circuit board and a heat sink in an electronic package. Heat dissipation is a critical problem that limits the reliability, performance, and further miniaturization of microelectronics [1,2]. The thermal resistance at a contact results in a thermal barrier, which leads to inefficient heating or cooling, and hence the wasting of energy. To decrease the thermal resistance at the contact, a thermal interface material (commonly in the form of a paste) can be placed at the interface between the two objects. The saving of energy through the use of thermal interface materials has received much less attention than the saving of energy through microprocessors and other control electronics for the heating (cooling) device. The reason for the little attention on the use of thermal interface materials is that the development of these materials has not matured and the available thermal interface materials are limited in the heat transfer ability, temperature resistance, and durability. Thermal pastes are predominantly based on polymers, particularly silicone [3–6], although thermal pastes based on sodium silicate have been reported to be superior in providing high thermal contact conductance [7]. The superiority of sodium-silicate-based pastes over silicone-based pastes is primarily due to the low viscosity of sodium silicate compared to silicone, and the importance of high fluidity in the paste so that the paste can conform to the topography of the surfaces which it interfaces and can be spread very thin.

In general, the effectiveness of a thermal interface material is enhanced by its thinness, conformability, and thermal conductivity. For example, an interface material with a high thermal conductivity may not be effective, if it is thick or if it is not conformable. This effectiveness is indicated by the thermal contact conductance between two thermally conducting disks that sandwich the thermal interface material. As the thermal conductivity of the thermal interface material is only one of the parameters that

impact the effectiveness of the interface material, it cannot be used as an indicator of the effectiveness of a thermal interface material.

This work provides thermal pastes based on polyethylene glycol (PEG, a polymer) of a low molecular weight (400 amu). These pastes are superior to silicone-based pastes and are as good as sodium-silicate-based pastes due to the low viscosity of PEG and the contribution of lithium ions (a dopant) in the paste to the thermal conduction. Compared to the sodium-silicate-based pastes, the PEG-based pastes are advantageous in their long-term compliance (mechanical softness), in contrast to the long-term rigidity (mechanical stiffness) of sodium silicate. Compliance is attractive for decreasing the thermal stress, which can cause thermal fatigue.

Polyethylene glycol of a high molecular weight and doped with Li<sup>+</sup> ions has been previously studied due to its ionic conductivity [8]. However, polyethylene glycol has not been previously used as a thermal paste. The Li<sup>+</sup> ions are used in this work to enhance the thermal conductivity.

## Experimental Methods

**Materials.** The polyethylene glycol (PEG, or HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H) used was PEG 400 from EM Science (Gibbstown, NJ). It had a molecular weight of 400 amu. It was a liquid at room temperature.

Lithium (Li<sup>+</sup>) ions were provided by trifluoroacetic acid lithium salt (CF<sub>3</sub>CO<sub>2</sub>Li) from Aldrich Chemical Company, Inc. (Milwaukee, WI). The salt was a solid, which we dissolved in ethanol.

N, N-dimethylformamide (DMF, or HCON(CH<sub>3</sub>)<sub>2</sub>) from Aldrich Chemical Company, Inc., and water, were used to help the dissociation of the lithium salt for the purpose of releasing Li<sup>+</sup> ions.

Hexagonal boron nitride (BN) particles (Polartherm 180 from Advanced Ceramics Corp., Cleveland, OH) were used as a thermally conductive filler in the pastes. The particle size was 5–11 μm. The thermal conductivity was 280 W/m.K.

**Sample Preparation.** The lithium salt was dissolved in ethanol under heat (optional). Then, the solution was added to PEG liquid (referred to as A) and mixed. After that, the solution was heated in a vacuum oven to remove the ethanol, thereby resulting in a liquid consisting of PEG and the lithium salt (referred to as

Contributed by the Electronic and Photonic Packaging Division for publication in the JOURNAL OF ELECTRONIC PACKAGING. Manuscript received by the EPPD May 3, 2001. Associate Editor: Z. Suo.

C). Boron nitride particles were added to C and then mixed in a ball mill for 4 h, thereby resulting in a BN particle filled paste (referred to as D).

Boron nitride particles were added to PEG (i.e., A) and then mixed in a ball mill for 4 h, thereby resulting in a BN filled paste that had no lithium salt (referred to as B).

Water and DMF (together at 5 wt. percent) were added to PEG (all liquids) and were mixed by stirring, thus resulting in a solution referred to as J. The lithium salt in various amounts was dissolved in J by stirring, thus resulting in solutions referred to as E, F, G, H and I for Li salt in amounts of 0.75, 1.5, 3.0, 4.5, and 6.0 wt. percent, respectively.

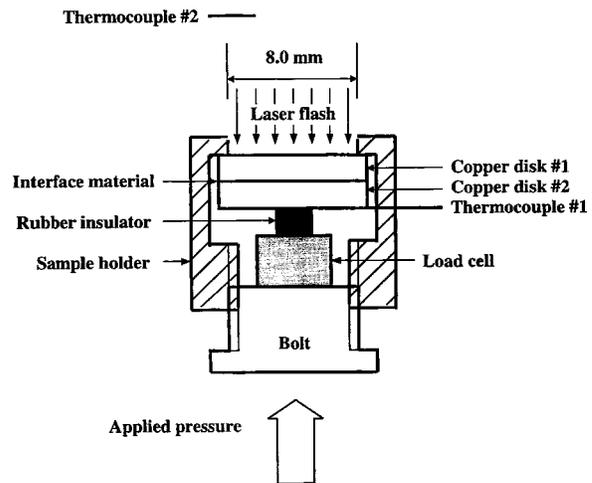
Boron nitride particles in various amounts were added to F and mixed in a ball mill for 4 h, thus resulting in BN filled pastes referred to as  $F_1$ ,  $F_2$ ,  $F_3$ , and  $F_4$  for BN in amounts of 16.0, 18.0, 19.5 and 21.5 vol. percent, respectively.

Boron nitride particles in various amounts were added to G and mixed in a ball mill for 4 h, thus resulting in BN filled pastes referred to as  $G_1$ ,  $G_2$ ,  $G_3$ , and  $G_4$  for BN in amounts of 16.0, 18.0, 19.5, and 21.5 vol. percent, respectively.

Boron nitride particles in the amount of 18.0 vol percent were added to H and mixed in a ball mill for 4 h, thus resulting in a BN filled paste referred to as  $H_1$ .

**Thermal Contact Conductance Measurement.** Various thermal pastes were sandwiched between the flat surfaces of two copper disks (both surfaces of each disk having been mechanically polished by using  $0.05 \mu\text{m}$  alumina particles), which had diameter 12.6 mm and thickness 1.16 mm for one disk and 1.10 mm for the other disk. The thermal contact conductance between two copper disks with and without a thermal interface material was measured using the transient laser flash method [7,9,10]. The pressure on the sandwich was controlled at 0.46 MPa. This is because the pressure affects the thermal contact conductance [7]. The thickness of the thermal interface material was 0.001 in ( $25 \mu\text{m}$ ), unless noted otherwise. The uniform distribution of the paste in the plane of the sandwich was made possible by the fluidity of the paste and the use of pressure. Except for the case of solder as the interface material, the interface material thickness was obtained by subtracting the thicknesses of the two copper disks from the thickness of the sandwich, such that all thicknesses were measured using a micrometer. For the case of solder as the interface material, the thickness of the interface material was measured by optical microscopy. The interface material thickness for all cases was the same before and after the conductance measurement. The finite element program ABAQUS was used to calculate the thermal contact conductance through temperature versus time curves, which were experimentally obtained. The calculation [7] assumed no thickness and no heat capacity for the interface between the two copper disks. In addition, it assumed no heat transfer between specimen and environment except for the absorption of laser energy by the specimen. Moreover, it assumed that the laser energy was uniformly absorbed on the surface of the specimen, that the heat flow was one-dimensional, and that the thermal contact conductance between the two copper disks was uniform. The validity of these assumptions is supported by the calibration result and error analysis given below.

A Coherent General Everpulse Model 11 Nd glass laser with a pulse duration of 0.4 ms, a wavelength of  $1.06 \mu\text{m}$  and a pulse energy up to 15 J was used for impulse heating. The laser power was adjusted to allow the temperature rise of the specimen to be between 0.5 and 1.0 deg C. The upper surface of disk #1 on which the laser beam would directly hit had been electroplated by black nickel in order to increase the extent of laser energy absorption relative to the extent of reflection (Fig. 1). An E-type thermocouple (#1) was attached to the back surface of disk #2 for monitoring the temperature rise. Another thermocouple (#2) of the same type was put  $\sim 30$  cm above the specimen holder to detect the initial time when the laser beam came out. A National Instruments DAQPad-MIO-16XE-50 data acquisition board with a data



**Fig. 1 Experimental setup for thermal contact conductance testing**

acquisition rate up to 20,000 data points per second at 16 bits resolution, along with NI-DAQ interface software coded in Visual Basic, was used to monitor the response of both thermocouples simultaneously. A plexiglass holder (Fig. 1) was used to facilitate pressure application. An Omega LCKD-100 load cell was used for pressure measurement. Calibration using a standard graphite specimen was performed before testing each specimen in order to ensure measurement accuracy. The data acquisition rate used for each test was adjusted so that there were at least 100 temperature data points during the temperature rise.

The experimental error in transient thermal contact conductance measurement consists of random error due to experimental data scatter, and systematic error mainly due to the lag of the thermocouple response and partly due to the method used to calculate the conductance from the temperature data. The higher the thermal contact conductance, the greater is the error. The thermal diffusivity of a standard NBS 8426 graphite disk (thickness= $2.62$  mm), which had a similar transient temperature rise time as the copper sandwich with the highest thermal contact conductance, was measured prior to testing each specimen in order to determine the systematic error. The measured thermal diffusivity of the graphite was about seven percent less than the reference value, which corresponds to a time lag of about 0.0006 s. Moreover, a single copper disk (thickness= $2.66$  mm) was also tested and a time lag of about 0.0008 s was found upon comparison of the measured thermal diffusivity with the reference value. From multiple measurements of both copper and graphite, the time lag of the thermocouple was found to be about 0.0007 s, which was used to correct for the measured rise time for each specimen. The conductance reported in Table 1 for each specimen was based on the corrected rise time. The random error shown by the  $\pm$  value in Table 1 was determined by six or more measurements of each specimen.

## Results and Discussion

Table 1 gives the thermal contact conductance for different thermal interface materials. Included in the comparison are results obtained with the same method on silicone-based paste, sodium-silicate-based pastes and solder [7]. PEG (i.e., A) gives much higher thermal contact conductance ( $11.0 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ ) than silicone ( $3.08 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ ), due to its relatively low viscosity, but the conductance is lower than that given by sodium silicate ( $14.1 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ ), in spite of its low viscosity, due to the molecular nature of PEG. The addition of the Li salt (1.5 wt. percent) to PEG (i.e., to obtain C) raises the conductance from  $11.0 \times 10^4$  to  $12.3 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ , even though the viscosity is

**Table 1 Thermal contact conductance for various thermal interface materials between copper disks at 0.46 Ma contact pressure**

Thermal interface material		Interface material thickness ( $\mu\text{m}$ ) ( $\pm 10$ )	Thermal contact conductance ( $10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ )	Viscosity (cps) ( $\pm 0.3$ )	Ref.
Description	Designation				
PEG	A	<25	11.0 $\pm 0.3$	127 <sup>b</sup>	This work
PEG+BN (18 vol. %)	B	25	12.3 $\pm 0.3$	/	This work
PEG+Li salt (1.5 wt. %)	C	<25	12.3 $\pm 0.3$	143 <sup>b</sup>	This work
PEG+Li salt (1.5 wt. %) +BN (18 vol. %)	D	25	13.4 $\pm 0.4$	/	This work
PEG+water+DMF	J	<25	12.5 $\pm 0.2$	75.6 <sup>b</sup>	This work
J+Li salt (0.75 wt. %)	E	<25	11.4 $\pm 0.3$	79.7 <sup>b</sup>	This work
J+Li salt (1.5 wt. %)	F	<25	16.0 $\pm 0.5$	85.6 <sup>b</sup>	This work
J+Li salt (3.0 wt. %)	G	<25	11.6 $\pm 0.2$	99.0 <sup>b</sup>	This work
J+Li salt (4.5 wt. %)	H	<25	9.52 $\pm 0.25$	117 <sup>b</sup>	This work
J+Li salt (6.0 wt. %)	I	<25	7.98 $\pm 0.16$	120 <sup>b</sup>	This work
F+BN (16.0 vol. %)	F <sub>1</sub>	25	18.5 $\pm 0.8$	/	This work
F+BN (18.0 vol. %)	F <sub>2</sub>	25	18.9 $\pm 0.8$	/	This work
F+BN (19.5 vol. %)	F <sub>3</sub>	25	15.3 $\pm 0.2$	/	This work
F+BN (21.5 vol. %)	F <sub>4</sub>	25	14.0 $\pm 0.5$	/	This work
G+BN (16.0 vol. %)	G <sub>1</sub>	25	17.0 $\pm 0.5$	/	This work
G+BN (18.0 vol. %)	G <sub>2</sub>	25	17.3 $\pm 0.6$	/	This work
G+BN (19.5 vol. %)	G <sub>3</sub>	25	14.9 $\pm 0.6$	/	This work
G+BN (21.5 vol. %)	G <sub>4</sub>	25	13.4 $\pm 0.4$	/	This work
H+BN (18.0 vol. %)	H <sub>1</sub>	25	13.9 $\pm 0.4$	/	This work
Solder (63Sn-37Pb)	/	25	20.8 $\pm 0.6^a$	/	7
Sodium silicate+BN (16.0 vol. %)	/	25	18.2 $\pm 0.7$	/	7
Sodium silicate+BN (17.3 vol. %)	/	25	15.5 $\pm 0.4$	/	7
Sodium silicate	/	<25	14.1 $\pm 0.5$	206 <sup>c</sup>	7
Silicone/BN	/	25	10.9 $\pm 1.5$	/	7
Silicone	/	<25	3.08 $\pm 0.03$	8800 <sup>d</sup>	7
None	/	/	0.681 $\pm 0.010$	/	7

<sup>a</sup>At zero contact pressure (not 0.46 MPa).

<sup>b</sup>Measured using the Ubbelohde Method.

<sup>c</sup>Measured using the Ostwald Method.

<sup>d</sup>Value provided by the manufacturer.

increased. The further addition of water and DMF (i.e., F) raises the conductance to  $16.0 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  and decreases the viscosity. Thus, the addition of water and DMF is very influential, as water and DMF help the dissociation of the lithium salt. The still further addition of BN (18.0 vol. percent) (i.e., F<sub>2</sub>) raises the conductance to  $18.9 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$ . The positive effect of BN is also shown by comparing the results of C and D (which are without water and DMF) and by comparing the results of A and B (which are without Li<sup>+</sup>). In the absence of the lithium salt, water and DMF also help, though not greatly, as shown by comparing A and J. The viscosity increases with the lithium salt content, as shown by comparing J, E, F, G, H and I. Comparison of E, F, G, H and I shows that the optimum lithium salt content for the highest conductance is 1.5 wt. percent. That an intermediate lithium salt content gives the highest conductance is probably because of the enhancement of the thermal conductivity by the Li<sup>+</sup> ions and the increase of the viscosity caused by the lithium salt addition. Both high conductivity and low viscosity (good conformability) are desirable for a high contact conductance. Comparison of F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub>, and F<sub>4</sub> shows that the optimum BN content is around 18.0 vol. percent, as also indicated by comparing G<sub>1</sub>, G<sub>2</sub>, G<sub>3</sub>, and G<sub>4</sub>. Among all the PEG-based pastes, the highest conductance is given by F<sub>2</sub>, as it has the optimum lithium salt content as well as the optimum BN content. The presence of an optimum in the BN content was previously reported for BN filled sodium-silicate-based pastes [7]. It is due to the increase in both the thermal conductivity and the viscosity of the paste as the BN content increases. The best PEG-based paste (i.e., F<sub>2</sub>) is similar to the best sodium-silicate-based paste in the conductance. Both are better than BN filled silicone, but both are slightly inferior to solder. Although solder (63Sn-37Pb eutectic alloy) gives the highest con-

ductance, it suffers from the need of heating during soldering. In contrast, heating is not needed in the use of PEG-based pastes, silicone-based pastes or silicate-based pastes.

## Conclusion

PEG-based thermal pastes containing a lithium salt and BN particles, as well as water and DMF for helping the dissociation of the lithium salt to release Li<sup>+</sup> ions, give thermal contact conductance that is similar to that given by BN filled sodium silicate, that is almost as high as that given by solder, and that is much higher than that given by BN filled silicone. For the PEG-based pastes, the optimum lithium salt (trifluoroacetic acid lithium salt) content is 1.5 wt. percent, and the optimum BN content is ~18.0 vol. percent. These optima together give a paste that provides a thermal contact conductance of  $18.9 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  between copper disks at 0.46 MPa contact pressure, compared to a value of  $20.8 \times 10^4 \text{ W/m}^2 \cdot ^\circ\text{C}$  for Sn-Pb solder as the thermal interface material. The PEG-based thermal pastes are potentially attractive as a replacement for solder.

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