

Polyol-Based Phase-Change Thermal Interface Materials

YASUHIRO AOYAGI,¹ CHIA-KEN LEONG,¹ and D.D.L. CHUNG^{1,2}

1.—Composite Materials Research Laboratory, University at Buffalo, State University of New York, Buffalo, NY 14260-4400. 2.—E-mail: ddlchung@buffalo.edu

Polyol-based phase-change thermal interface materials that exhibit high thermal contact conductance and thermal stability have been developed for micro-electronic cooling. By using a diol (polycaprolactone or polyester diol in the form of 2-oxepanone) of molecular weight 1,000–2,000 amu, along with 4 vol.%-hexagonal boron nitride particles, this work attained thermal contact conductance (at 70°C, across copper surfaces) that is higher than that attained by using paraffin wax, polyether glycol, polyethylene glycol, or tetradecanol (in place of the diol) and that attained by commercial phase-change thermal interface materials. The thermal stability of the diol is superior to the other phase change materials mentioned above, although the heat of fusion is lower. Boron nitride is more effective than carbon black (also 4 vol.%) for enhancing the conductance, but carbon black diminishes the heat of fusion less than does boron nitride.

Key words: Phase change material, thermal interface material, boron nitride, carbon black, polyol, diol, triol, wax, ether, glycol

INTRODUCTION

Thermal interface materials¹ are needed to improve thermal contacts for facilitating heat transfer, such as that associated with the flow of heat from a microprocessor to a heat sink in a computer.² The performance of a thermal interface material is enhanced by conformability of the interface material to the topography of the mating surfaces, since the air residing in the valleys in the surface topography is thermally insulating and should be displaced by the interface material.

A thermal interface material is commonly in the form of a paste, which is known as a thermal paste.^{3–5} It can also be in the form of a sheet that serves to fill a gap between the two adjoining surfaces. A gap may exist when the adjoining surfaces are not parallel or not flat. A gap filling material can be in the form of a resilient sheet such as flexible graphite.⁶ The resiliency helps the conformability. It can also be in the form of a sheet that is coated by a thermal paste, which helps the conformability.⁷

A special form of thermal interface material is in the form of a phase change material.⁸ The phase change under consideration is melting, since a liquid is associated with high conformability, which is

needed for minimizing interfacial air pockets, thereby promoting the heat transfer. The phase change material should melt at a temperature above room temperature (typically below 150°C) so that the material is a liquid while it functions as a thermal interface material. The liquid is attractive in that it is conformable, but it is disadvantageous in the possibility of seepage and consequent contamination of the surrounding electronic components. By having the interface material be a solid during operation of the electronics at temperatures below the melting temperature, the seepage problem is alleviated. Furthermore, the absorption of the latent heat of fusion during melting provides an additional mechanism of heat dissipation.^{9,10}

There are two classes of phase change materials. They are the organic ones (such as paraffin wax) and the inorganic ones (most commonly metal salt hydrates, e.g., disodium hydrogen phosphate dodecahydrate^{11–19}). The organic materials are attractive in their low reactivity, stability in the phase change characteristics under thermal cycling, and low supercooling (supercooling = temperature difference between phase change onset temperatures during heating and cooling for the same thermal cycle), but they tend to be poor in thermal conductivity. The inorganic materials are attractive in their relatively high thermal conductivity, but they suffer

from relatively high reactivity, high supercooling, and poor stability in the phase change characteristics under thermal cycling. For example, by using the same testing equipment as this work, Liu and Chung²⁰ reported supercooling of -5.3°C for paraffin wax in the first thermal cycle, but $+8.9^{\circ}\text{C}$ for 99wt.% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (with 1wt.% $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$) in the first thermal cycle. Furthermore, the heat of fusion is 142.3 J/g, 142.6 J/g, and 140.1 J/g in the first, second, and third cycles, respectively, for paraffin wax, but is 97.3 J/g, 52.3 J/g, and 23.3 J/g in the first, second, and third cycles, respectively, for 99wt.% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (with 1wt.% $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{H}_2\text{O}$).²⁰

For application as thermal interface materials, the organic phase change materials are preferred and are the ones addressed in this work. Prior work mostly used paraffin wax as the matrix,²⁰ although silicone^{21,22} had also been used. The matrix materials in commercially available phase change materials are proprietary.

The thermal conductivity of a phase change material can be increased by using a filler (particles, fibers, or bars) that is thermally conductive.^{23,24} The filler does not melt, but its presence can affect the phase change characteristics, including the melting temperature and the heat of fusion. Due to the low thermal conductivity of the organic phase change materials, the use of a thermally conductive filler is important. An alternate method of increasing the thermal conductivity involves impregnating porous graphite with paraffin wax,²⁵ but this method suffers from the inability of the resulting composite to conform to the topography of the surface from which it is to absorb heat. Furthermore, the volume fraction of the component that undergoes phase change is limited.

The choice of the organic matrix of a phase change material for use as a thermal interface material depends on the melting temperature, the conformability in the molten state, the extent of undercooling during solidification, the latent heat of fusion, and the ability to withstand elevated temperatures. The conformability strongly affects the effectiveness as a thermal interface material, but it is an attribute that is difficult to measure.

A polyol (also known as polyhydric alcohol) is an alcohol having numerous hydroxyl groups. Polyols include polyethers, glycols, polyglycols, polyesters, and polyglycerols.²⁶⁻²⁸ They are low molecular weight water-soluble polymers and oligomers. Polyols are classified as diols, triols, and tetrols, depending on the number of OH end groups. A diol is linear, with an OH group at each end. A triol is branched, such that there is an OH group at the end of each of three segments that emanate from a point. A tetrol is branched, such that there is an OH group at the end of each of four segments that emanate from a point. Polyols constitute a class of organic materials that vary substantially in molecular shape, molecular length, and melting temperature, thus providing choices that can suit the requirements of phase-change thermal interface materials. Prior work on phase changes in polyols is

limited.²⁹⁻³³ An objective of this work is to investigate the use of polyols for this application.

Another objective of this paper is to provide a comparative study of a number of organic materials for use as phase-change thermal interface materials. For this purpose, the effectiveness of thermal interface materials made of various organic matrices is evaluated by thermal contact conductance measurement under identical conditions. The conditions include the testing method (the guarded hot plate method of thermal contact conductance measurement), the composition (copper) and roughness (15 μm) of the adjoining surfaces, the pressure (0.46 MPa, 0.69 MPa, and 0.92 MPa) applied to the thermal contact in the direction perpendicular to the plane of the interface, and the composition (hexagonal boron nitride or carbon black) and volume fraction (4%) of the filler. This comparative evaluation is supplemented by (1) thermal gravimetric analysis (TGA) for studying the thermal stability at elevated temperatures (i.e., ability to withstand elevated temperatures), (2) differential scanning calorimetry (DSC) for studying the melting and solidification behavior, and (3) measurement of the viscosity of the molten state.

Hexagonal boron nitride is the main filler used in this work because of its combination of high thermal conductivity and high electrical resistivity. Carbon black is a secondary filler used in this work because of its exceptional conformability, which is a consequence of its being in the form of porous agglomerates of nanoparticles.^{3-5,7} Due to its conformability, carbon black is even more effective as a filler in thermal pastes than highly conductive fillers when the mating surfaces are sufficiently smooth (such as 0.05 μm).^{3-5,7}

EXPERIMENTAL METHODS

Materials

The matrices used in this work are listed in Tables I and II. They include (1) paraffin wax ($\text{C}_n\text{H}_{2n+2}$, $n > 20$); (2) octadecane, 1-(ethylenoxy)-, homopolymer, Luwax V, ($\text{C}_{20}\text{H}_{40}\text{O}$)_n, molecular weight = 3,000 amu; (3) polyethylene glycol, PEG, $\text{H}[\text{OCH}_2\text{CH}_2]\text{OH}$, molecular weight = 1000 amu; (4) polyether glycol, Terathane, $\text{H}[\text{O}(\text{CH}_2)_4]\text{OH}$, molecular weight = 2900 amu; (5) diol, 2-oxepanone, polymer with 2,2-dimethyl-1,3-propanediol, molecular weight = 1000 amu (CAPA 2101A) and 2000 amu (CAPA 2201A); (6) diol, 2-oxepanone, homopolymer oxydi-2,1-ethanediylester, molecular weight = 1250 amu (CAPA 2125A); (7) triol, 2-oxepanone, polymer with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, molecular weight = 2000 amu (CAPA 3,201), (8) 1-tetradecanol, myristyl alcohol, $\text{CH}_3(\text{CH}_2)_{13}\text{OH}$, and (9) lauric acid, $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$. These matrices were chosen based on their melting temperatures mainly (Table II). It is not clear if the CAPA products contain anti-oxidants.

The hexagonal boron nitride (BN) particle used as a thermally conductive filler is Polartherm 180 from

Table I. Description of Phase-Change Matrix Materials

Product Name	General Name	Chemical Name
Paraffin wax (CS-2032)	Fully refined paraffin wax	
Luwax V flakes	Polyvinyl ether	1-(ethenyloxy)-, homopolymer
Polyethylene glycol MW 1000	Polyethylene glycol	
Terathane polyether glycol	PTMEG (poly tetramethylene ether glycol)	Poly (oxy-1,4-butanediyl)-a-hydro-w-hydroxyl (containing an oxidation inhibitor)
CAPA 2101A	Premium grade linear polycaprolactone diol	2-Oxepanone, polymer with 2,2-dimethyl-1,3 propanediol
CAPA 2201A	Premium grade linear polycaprolactone diol	2-Oxepanone, polymer with 2,2-dimethyl-1,3 propanediol
CAPA 2125A	Premium grade linear polyester diol	2-Oxepanone, homopolymer oxydi-2,1 ethanediyl ester
CAPA 3201	Polyester triol	2-Oxepanone, polymer with 2-ethyl-2-(hydroxymethyl)-1,3 propanediol
1-Tetradecanol 95% Lauric acid	1-Tetradecanol Lauric Acid	

GE Advanced Ceramics Corp. (Cleveland, OH). Its size range is about 5–11 μm . The average particle size is 6–9 μm . The specific gravity is 2.2. The BET surface area is 17.0 m^2/g . The thermal conductivity is about 280 $\text{W}/\text{m}\cdot\text{K}$.

The carbon black was Vulcan XC72R GP-3820 from Cabot Corp. (Billerica, MA). It was a powder with particle size 30 nm, a nitrogen specific surface area 254 m^2/g , maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm^3 . The carbon black powder was mixed with a vehicle by hand stirring to form a uniform paste. The particle size (30 nm) of the carbon black is much less than those of the metal or ceramic particles used in commercial thermal pastes. Due to the porous and nano-structured morphology of carbon black, the value of the thermal conductivity and electrical resistivity are not known for carbon black by itself. However, the electrical resistivity of a thick film obtained from a carbon black paste is $2 \times 10^{-3} \Omega\cdot\text{cm}$.³⁴

Each composition consisting of matrix and filler (4 vol.%) was prepared by manual mixing of the components for 15 min. at a temperature slightly higher than the melting point of the matrix.

Four commercial phase-change thermal interface materials, as described in Table III, are included in this study for the sake of comparison.

Testing

This work uses thermal contact conductance (in units of $\text{W}/\text{m}^2\cdot^\circ\text{C}$) to describe the quality of the thermal contact, because this quantity does not depend on the area of the contact. An alternate description is the thermal resistance (in units of $^\circ\text{C}/\text{W}$), which is given by

$$\text{Thermal resistance} = \frac{1}{(\text{Thermal contact conductance})(\text{Contact area})}$$

The thermal resistance is a quantity that depends on the contact area. For example, for a thermal contact conductance of $9 \times 10^4 \text{ W}/\text{m}^2\cdot^\circ\text{C}$ and for a contact area of 25 mm \times 25 mm, the thermal resistance is 0.018 $^\circ\text{C}/\text{W}$.

The thermal contact conductance between two 1 in. \times 1 in. (25 mm \times 25 mm) copper blocks (15- μm roughness, as attained by mechanical polishing) with a thermal interface material (25 μm or less

Table II. Specification of Phase-Change Matrix Materials

Product Name	Molecular Weight (amu)	wt. %	Specific Gravity	Melting Point ($^\circ\text{C}$)	Viscosity (cP)
Paraffin wax (CS-2032)	>283	100	0.90	52–56	SUU 34–40 (at 99 $^\circ\text{C}$)*
Luwax V flakes	3000	>1	0.93 (at 20 $^\circ\text{C}$)	46–52	—
Poly ethylene glycol MW 1000	1000	N A	1.1	35–40	—
Terathane polyether glycol	2900	100	0.97	30–43	—
CAPA 2101A	1000	>99	1.05 (at m.p.)	30–40	150 (at 60 $^\circ\text{C}$)
CAPA 2201A	2000	>99	1.07 (at 55 $^\circ\text{C}$)	40–50	480 (at 60 $^\circ\text{C}$)
CAPA 2125A	1250	>99	1.05 (at m.p.)	35–45	175 (at 60 $^\circ\text{C}$)
CAPA 3201	2000	>99	1.10 (at 20 $^\circ\text{C}$)	40–50	355 (at 60 $^\circ\text{C}$)
1-Tetradecanol 95%	214	95	0.82	38–40	—
Lauric acid	200	98	0.883	44–46	—

*Saybolt universal seconds (SUU) = Centistokes (cSt) \times 4.55.

Table III. Effectiveness of Various Thermal Interface Materials; Except for the Commercial Materials by Chomerics and Thermagon, the Filler Content is 4 vol.%

Matrix	Filler	Thermal Contact Conductance ($10^4 \text{ W/m}^2\text{°C}$)		
		0.46 MPa	0.69 MPa	0.92 MPa
Paraffin wax	BN	6.02 ± 0.54	6.09 ± 0.55	6.68 ± 0.63
Paraffin wax	C	4.65 ± 0.15	5.86 ± 0.21	5.80 ± 0.30
Luwax	BN	6.34 ± 0.57	7.13 ± 0.40	7.38 ± 0.61
Luwax	C	4.82 ± 0.45	4.84 ± 0.38	5.44 ± 0.27
PEG	BN	6.30 ± 0.67	7.11 ± 0.59	8.07 ± 0.85
Terathane	BN	6.06 ± 0.79	7.33 ± 0.82	8.28 ± 0.79
CAPA 2101A	BN	7.86 ± 0.44	7.97 ± 0.56	8.29 ± 0.65
CAPA 2101A	C	3.65 ± 0.37	3.70 ± 0.30	3.93 ± 0.30
CAPA 2201A	BN	7.46 ± 0.83	8.59 ± 0.64	8.75 ± 0.95
CAPA 2125A	BN	7.60 ± 0.58	8.22 ± 0.75	8.92 ± 0.83
CAPA 2125A	C	1.35 ± 0.08	2.12 ± 0.27	2.14 ± 0.21
CAPA 3201	BN	6.82 ± 0.74	8.23 ± 0.84	8.62 ± 0.63
Tetradecanol	BN	6.88 ± 0.49	7.36 ± 0.59	7.87 ± 0.56
Tetradecanol	C	5.44 ± 0.38	5.63 ± 0.51	6.44 ± 0.42
Lauric acid	BN	5.85 ± 0.62	5.91 ± 0.47	7.80 ± 0.49
Chomerics 1 ^a	BN	4.16 ± 0.25	4.49 ± 0.27	4.79 ± 0.38
Chomerics 2 ^b	BN	3.34 ± 0.26	3.46 ± 0.18	3.63 ± 0.23
Thermagon 1 ^c	BN	6.85 ± 0.48	7.32 ± 0.55	7.71 ± 0.61
Thermagon 2 ^d	ZnO	3.14 ± 0.16	3.44 ± 0.22	3.66 ± 0.29

^aChomerics Thermflow T 454 (without carrier), thickness = 0.005 in. or 130 μm.

^bChomerics Thermflow T 766 (with aluminum carrier of thickness 0.001 in. or 25 μm, coated on one side with a phase change material that melts at 51–58°C), thickness = 0.0035 in. or 89 μm.

^cThermagon T-pcm HP105 (without carrier), thickness = 0.005 in. or 130 μm, softening range = 50–60°C.

^dThermagon T-pcm AL 52 (with aluminum carrier of thickness 0.002 in. or 50 μm, coated on both sides with a phase change material that melts at 52°C), thickness = 0.003 in. or 76 μm.

in thickness) between them was measured using the guarded hot plate method, which is a steady-state method of heat flux measurement (ASTM method D5470). The heat in this test was provided by a 3 in. × 3 in. (76 mm × 76 mm) copper block that had two embedded heating coils (top block in Fig. 1). During the period of temperature rise, the heating rate was controlled at 3.2°C/min. by using a temperature controller. This copper block was in contact with one of the 1 in. × 1 in. copper blocks that sandwiched the thermal interface material. The cooling in this test was provided by a second 3 in. × 3 in. copper block, which was cooled by running water that flowed into and out of the block (bottom block in Fig. 1). This block was in contact with the other of the two 1 in. × 1 in. copper blocks that sandwiched the thermal interface material. Four thermocouples (type T) were inserted in four holes (T₁, T₂, T₃, and T₄ in Fig. 1, each hole of diameter 2.4 mm). Two of the four holes were in each of the 1 × 1 in. copper blocks. The temperature gradient was determined from T₁ – T₂ and T₃ – T₄. These two quantities should be equal at equilibrium, which was attained after holding the temperature of the heater at the desired value for 30 min. Equilibrium was assumed when the temperature variation was within ±0.1°C in a period of 15 min.

At equilibrium, the temperature of the hot block was 100°C, that of the cold block was in the range 22–27°C, while that of the thermal interface material was 70°C (above the melting temperature

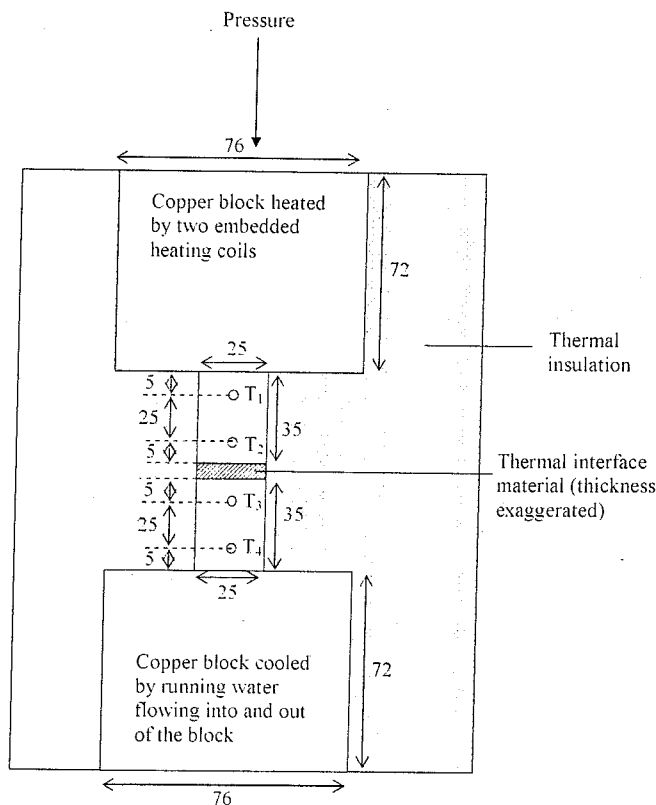


Fig. 1. Experimental setup for the guarded hot plate method of thermal contact conductance measurement. The T₁, T₂, T₃, and T₄ are holes of diameter 2.4 mm. A thermocouple (type T) is inserted in each hole. All dimensions are in millimeters.

of all of the matrix materials used in this work). The pressure in the direction perpendicular to the plane of the thermal interface was controlled by using a hydraulic press at pressures of 0.46 MPa, 0.69 MPa, and 0.92 MPa. The system was thermally insulated by wrapping laterally all the copper blocks with glass fiber cloth.

In accordance with ASTM method D5470, the heat flow Q is given by

$$Q = \frac{\lambda A}{d_A} \Delta T \quad (1)$$

where $\Delta T = T_1 - T_2 = T_3 - T_4$, λ is the thermal conductivity of copper, A is the area of the 1 in. \times 1 in. copper block, and d_A is the distance between thermocouples T_1 and T_2 (i.e., 25 mm).

The temperature at the top surface of the thermal interface material is T_A , which is given by

$$T_A = T_2 - \frac{d_B}{d_A} (T_1 - T_2) \quad (2)$$

where d_B is the distance between thermocouple T_2 and the top surface of the thermal interface material (i.e., 5 mm). The temperature at the bottom surface of the thermal interface material is T_D , which is given by

$$T_D = T_3 + \frac{d_D}{d_C} (T_3 - T_4) \quad (3)$$

where d_D is the distance between thermocouple T_3 and the bottom surface of the thermal interface material (i.e., 5 mm) and d_C is the distance between thermocouples T_3 and T_4 (i.e., 25 mm).

The thermal impedance θ is given by

$$\theta = (T_A - T_D) \frac{A}{Q} \quad (4)$$

Note that insertion of Eq. (1) into Eq. (4) causes cancellation of the term A , so that θ is independent of A . The thermal contact conductance is the reciprocal of θ .

Previous work by Leong and Chung on carbon black thermal pastes used the laser flash method (a transient method) for thermal contact conductance measurement.³⁻⁵ The guarded hot plate method used in this paper gives results that are consistent with those given by the laser flash method, as shown by testing the same interface material and the same mating surfaces using the two methods.

A thermal paste should be able to withstand elevated temperatures (e.g., up to about 150°C in case of use for microelectronic cooling). Thermal stability is indicated by a small degree, if any, of weight loss upon heating. Therefore, this work includes measurement of the weight loss during heating in air, using a Perkin-Elmer Corp. (Norwalk, CT) TGA7 thermogravimetric analyzer. The temperature was raised from 25°C to 100°C at a rate of 3°C/min. Then the temperature was held at 100°C for 25 h (1500 min.).

For DSC testing, specimens were put in aluminum pans and covered by aluminum lids (without sealing). Testing was conducted in air, using a Perkin-Elmer Corp. DSC 7 system equipped with

an ice filled cooler for operation below room temperature. The heating and cooling rates were 2.0°C/min.

The phase change kinetics were also studied isothermally by visual observation and by measuring the time required for melting of a matrix material (without filler, volume = 9.6 mL) at 65°C (provided by a water bath) and the time required for subsequent solidification at 18°C (room temperature). In particular, the times for solidification to start and to finish were both measured.

The phase change onset temperature (T_s)²⁰ corresponds to the point of intersection of the tangent (drawn at the point of maximum slope of the leading edge of the DSC peak) and the extrapolated baseline on the same side as the leading edge of the peak, as illustrated in Fig. 2, which is for paraffin wax. The temperature corresponding to the DSC peak is referred to as T_p , as shown in Fig. 2. Thus, the tangent and the baseline are on the left side of the DSC peak during heating, but they are on the right side of the peak during cooling. The melting and solidification points mentioned in the following sections are both T_s . The T_s and heat of fusion (ΔH) were calculated by using programs provided by Perkin-Elmer Corp. for this purpose. The supercooling (ΔT) is the temperature difference between T_s during heating and T_s during cooling for the same thermal cycle. The supercooling is positive if T_s during heating is higher than that during cooling, and is negative if T_s during heating is lower than that during cooling.

The viscosities of the thermal interface materials in the molten state were measured at 70°C \pm 0.5°C by using a rotational viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, MA, Model LVT Dial-Reading Viscometer, equipped with a Model SSA-18/13R small sample adaptor).

RESULTS AND DISCUSSION

Table III lists the thermal contact conductance values for various thermal interface materials. In general, the conductance increases

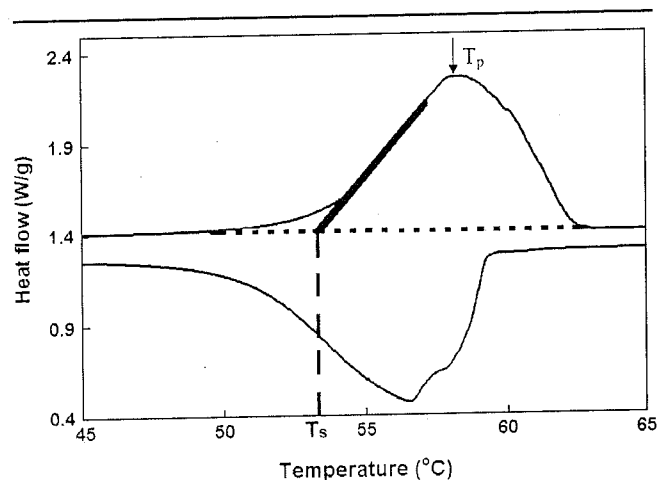


Fig. 2. DSC thermogram during heating and subsequent cooling for paraffin wax. The phase change (melting) onset temperature during heating (T_s) is given by the intersection of the tangent (thick line) and the extrapolated baseline (dotted line).

with increasing pressure. CAPA 2101A/2201A/2125 in combination with BN is most effective as a thermal interface material. The conductance attained is higher than all of the commercial materials investigated. In the case that carbon black is the filler, tetradecanol, paraffin wax, and Luwax are more effective than CAPA. For any matrix, BN is more effective than carbon black, due to the higher thermal conductivity of BN. If the mating surfaces were smoother, carbon black might have been more effective than BN, as suggested by prior results on thermal pastes (not phase change materials).³⁻⁵

The compatibility of CAPA 2101A/2201A/2125 with BN is attributed to the OH groups at both ends of each CAPA molecule and the interaction of the OH groups with the functional groups on the surface of the BN particles. In contrast, paraffin wax does not have functional groups for interacting with the surface functional groups of BN, so it is not as compatible with BN as is CAPA. On the other hand, the compatibility of tetradecanol with carbon black is because tetradecanol has an OH group at one end only, so that it has a hydrophobic end for interacting with the surface of carbon black. The compatibility of paraffin wax or Luwax with carbon black is attributed to the hydrophobic nature of carbon black and the absence of OH groups in paraffin wax or Luwax. The relative incompatibility of CAPA with carbon black is attributed to the hydrophobic nature

of carbon black and the presence of hydrophilic OH groups at both ends of a CAPA molecule.

Table IV shows that the various matrices (without filler) differ considerably in the supercooling (ΔT) and the heat of fusion (ΔH). Paraffin wax and Luwax have relatively high melting temperatures (Tables IV and V). Paraffin wax and PEG exhibit less supercooling than the other phase change matrices. The heat of fusion is relatively high for tetradecanol, due to the OH group present at an end of each of these molecules and the consequent hydrogen bonding, which enhances the intermolecular interaction.

Table V shows that the filler and its composition affect the phase change characteristics. The heat of fusion ΔH (latent heat absorbed during melting) is decreased by the addition of a filler, since the filler does not melt and takes up a part of the mass. For a given matrix, carbon black reduces ΔH less than BN. This may be related to the higher degree of suspension attained by carbon black than BN. The better suspension is due to the porosity and surface chemistry of carbon black. It is difficult for polymer molecules (particularly those with high molecular weights) to fill the pores in carbon black. The high degree of suspension results in greater influence of the filler on the solidification process.

Table VI shows that paraffin wax, Luwax, tetradecanol, and lauric acid are fast in solidification, whereas Terathane and CAPA 2101A are slow in

Table IV. Phase Change Characteristics for Various Matrices (without Filler); Two Values Given in the Same Entry Refer to the Attributes for Two Peaks Observed in the Same DSC Thermogram

Matrix	T_s (°C)		T_p (°C)		ΔT (°C)		ΔH (J/g)	
	Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
Paraffin wax	53.4	59.4	58.2	56.6	-6.0	-6.0	142.0	-141.3
Luwax	55.5	48.2	58.1	44.4	7.3	7.3	111.0	-98.0
PEG	28.6	35.7	43.6	33.3	-7.1	-7.1	154.3	-128.9
Terathane	40.6	19.6	48.8	-52.8	21.0	21.0	123.3	-52.8
CAPA 2101A	36.3	—	40.0	—	—	—	18.5	—
CAPA 2201A	36.7/49.4	33.8	58.1	31.3	2.9/15.6	2.9/15.6	81.0	-67.8
CAPA 2125A	29.0/41.0	25.5	47.2	21.1	3.5/15.5	3.5/15.5	56.8	-39.1
CAPA 3201	27.0/41.5	19.5	44.9	12.3	7.8/22.0	7.8/22.0	48.7	-31.1
Tetradecanol	42.6	41.1/34.7	45.1	40.0	1.5/7.9	1.5/7.9	216.1	-206.8
Lauric acid	48.9	47.1	50.8	45.2	1.8	1.8	176.2	-173.0

Table V. Effect of Filler (4 vol.%) on the Phase Change Characteristics

Matrix	Filler	T_s (°C)		T_p (°C)		ΔT (°C)		ΔH (J/g)	
		Heating	Cooling	Heating	Cooling	Heating	Cooling	Heating	Cooling
CAPA 2125A	None	41.0	25.5	47.2	21.1	15.5	15.5	56.8	-39.1
CAPA 2125A	BN	30.5	38.8	44.1	32.5	-8.3	-8.3	55.1	-32.7
CAPA 2125A	C	26.5	31.5	40.2	28.6	-5.0	-5.0	56.3	-45.6
Paraffin wax	None	53.4	59.4	58.2	56.6	-6.0	-6.0	142.0	-141.3
Paraffin wax	BN	53.1	59.4	60.7	56.7	-6.3	-6.3	126.0	-125.6
Paraffin wax	C	53.0	58.7	60.0	57.0	-5.7	-5.7	131.8	-130.3
Luwax	None	55.5	48.2	58.1	44.4	7.3	7.3	111.0	-98.0
Luwax	BN	52.5	50.1	55.3	45.1	2.4	2.4	89.8	-86.2
Luwax	C	52.0	49.7	54.5	45.5	2.3	2.3	91.6	-91.3

solidification. In spite of fast solidification, melting is slow for paraffin wax and Luwax. In spite of slow solidification, melting is fast for CAPA 2101A and Terathane. Moderately fast melting and solidification were observed for CAPA 2201A, CAPA 2125A, tetradecanol, and lauric acid.

Table VII shows that tetradecanol and lauric acid are exceptionally poor in thermal stability. PEG and Terathane are better, but they are inferior to the remaining matrices. CAPA 2201A is the best in thermal stability, although it is closely followed by CAPA 3,201. Paraffin wax and Luwax suffer from continuous and significant weight loss as the time spent at 100°C increased up to 1500 min., whereas CAPA 2201A, 3,201, 2125A, and 2101A suffered from weight loss mainly in the first 100 min. at 100°C; after the initial 100 min., the weight loss was very little.

The CAPA products are more stable thermally than PEG. This is partly because PEG has ether in its molecular structure, i.e., -R-O-R-O-R-O-R-OH, where R is (CH₂)₂, whereas CAPA has ester instead, i.e., -R'-OOC-R'-OOC-R'-OH, where R' is (CH₂)₅. When a PEG molecular chain is cut due to heat, the molecule becomes radicals such as -R-O-R-O-R-O· (structure of radical not determined); this end group is similar to the OH group, which is known to be not stable thermally. When a CAPA molecular chain is cut due to heat, the molecule becomes radicals such as -R'-COO-R'-COO· (struc-

ture of radical not determined); this end group is similar to the carboxylic group, which is known to be more stable thermally than the OH group, due to the polar nature of the C=O bond in the carboxylic group. The high degree of thermal stability of the CAPA products may also be due to the possible presence of antioxidants.

The thermal stability is better for CAPA 2201A/3201 than CAPA 2101A/2125A, due to the higher molecular weight of the former. CAPA 2125A is less thermally stable than the other CAPA products, probably because of its higher content of oxygen (ether). The relatively poor thermal stability of tetradecanol is attributed to the OH group at an end of the molecule. Lauric acid is more stable than tetradecanol due to the carboxylic group in lauric acid. Terathane is more thermally stable than PEG because of its higher molecular weight, lower content of oxygen, and inclusion of an antioxidant. Paraffin wax is more thermally stable than tetradecanol or lauric acid, due to its methyl group, but its short molecular length makes it limited in thermal stability.

Table VIII shows that Paraffin wax, lauric acid, and tetradecanol have relatively low viscosities, due to their low molecular weights. Terathane and Luwax have relatively high viscosities. The matrices CAPA 2201A/2125A/3201/2101A have intermediate values of the viscosity. The viscosity is higher for CAPA 2201A than for CAPA 2101A, due to the higher molecular weight of the former. These

Table VI. Phase Change Kinetics of Various Matrices (without Filler)

Matrix	Time to Melt (min.)	Time for Solidification to Start (min.)	Time for Solidification to Finish (min.)
Paraffin wax	12	0.08	5
Luwax	9	0.3	5
PEG	12	0.5	15
Terathane	8	20	>60
CAPA 2101A	3	>60	>60
CAPA 2201A	8	2	14
CAPA 2125A	7	9	19
Tetradecanol	7	0.3	13
Lauric acid	6	0.3	9

Table VII. Weight Loss during Isothermal Heating of Various Matrices (without Filler) at 100°C

Matrix	Residual Weight (%)			Weight Loss* (%)		
	500 min.	1,000 min.	1,500 min.	0-500 min.	500-1,000 min.	1,000-1,500 min.
Paraffin wax	99.66	98.77	97.87	0.34	0.89	0.90
Luwax	100.45	99.30	97.74	-0.45	1.15	1.56
PEG	94.60	85.54	73.26	5.40	9.07	12.28
Terathane	99.74	99.65	92.62	0.26	0.09	7.03
CAPA 2101A	98.52	98.44	98.37	1.48	0.08	0.07
CAPA 2201A	99.26	99.21	99.17	0.74	0.05	0.04
CAPA 2125A	98.95	98.81	98.69	1.05	0.14	0.12
CAPA 3201	99.02	98.99	98.94	0.98	0.03	0.05
Tetradecanol	50.27	9.84	1.09	49.7	40.4	8.8
Lauric acid	71.13	47.89	28.91	28.9	23.2	19.0

*Relative to the weight prior to heating.

Table VIII. Viscosity (cP) at $70 \pm 0.5^\circ\text{C}$ for Various Matrices (without Filler) and Various Shear Rates

Matrix	Shear rate					
	0.79 s^{-1}	2.0 s^{-1}	4.0 s^{-1}	7.9 s^{-1}	16 s^{-1}	40 s^{-1}
Paraffin wax	—	—	—	—	6.5	5.9
Luwax	—	1050	980	—	—	—
PEG	—	—	—	48	48	46
Terathane	1420	1340	—	—	—	—
CAPA 2101A	—	—	100	98	99.5	—
CAPA 2201A	—	340	335	325	—	—
CAPA 2125A	—	—	148	143	137	—
CAPA 3201	—	260	262	260	—	—
Tetradecanol	—	—	—	—	6.3	6.3
Lauric acid	—	—	—	—	6.8	5.5

results indicate that the high conductance of CAPA 2201A/2125A/3201/2101A is not due to low viscosity, though low viscosity tends to be associated with high conformability, which helps the effectiveness of a thermal interface material.

CAPA 2101A, 2201A, and 2125A are all diols, whereas CAPA 3,201 is a triol. The branched nature of a triol molecules may make triol harder to conform to the surface topography than diol. Tetrol is not included in this study, in spite of its symmetrical molecular configuration possibly enhancing the conformability and its presence of four segments in a molecule possibly enhancing the thermal stability. The main reason for not including tetrol in this work is that tetrol with a melting point in the range $40\text{--}50^\circ\text{C}$ is not commercially available.

Among the various thermal interface materials studied in this work, CAPA 2201A containing BN has the best overall performance, as shown by a high thermal contact conductance of $8 \times 10^4 \text{ W/m}^2\cdot^\circ\text{C}$, suitable T_s values of 37°C during heating and 34°C during cooling, moderately fast melting and solidification, and a high degree of thermal stability. The compatibility of CAPA 2201A with BN relates to the OH groups at the ends of the molecule. The compatibility of CAPA 2201A with carbon black is less, as shown by the much lower conductance (Table III).

The main disadvantage of CAPA 2201A lies in its low value of ΔH (Table IV). However, a high value of ΔH is not essential to a thermal interface material, as the main function of a thermal interface material is not heat storage.

In the case of applications that are focused on heat storage, paraffin wax is recommended. This is due to its high ΔH , negative supercooling, and thermal stability. In addition, paraffin wax is attractive in its excellent thermal cycling stability.⁹ The addition of carbon black or BN to paraffin wax is attractive, due to the expected increase in thermal conductivity, though ΔH is diminished (Table V). Carbon black is advantageous over BN in that it is associated with less reduction in ΔH . Although tetradecanol, PEG, and lauric acid have even higher values of ΔH (Table IV) than paraffin wax, they suffer from poor thermal stability.

The use of antioxidants is expected to improve the thermal stability of at least some of the phase change materials studied in this work. The effect of antioxidants is the subject of a separate paper by Aoyagi and Chung.

CONCLUSIONS

A polycaprolactone diol (molecular weight = 2000 amu) filled with hexagonal boron nitride particles (4 vol.%) is an effective phase-change thermal interface material. It exhibits a melting onset temperature of 37°C and a solidification onset temperature of 34°C . The thermal contact conductance across copper mating surfaces ($15\text{-}\mu\text{m}$ roughness) is $8 \times 10^4 \text{ W/m}^2\cdot^\circ\text{C}$ at 70°C and a pressure of 0.69 MPa. The combination of high conductance and high resistance to elevated temperatures makes this material superior as a phase-change thermal interface material to BN-filled paraffin wax, polyvinyl ether, polytetramethylene ether glycol, tetradecanol, lauric acid, polyester diol, polyester triol, or polycaprolactone diol (molecular weight = 1000 amu). However, the heat of fusion is lower for the polyols than the other organic materials studied. The conductance attained by BN filled diols is higher than that attained by commercial phase-change thermal interface materials. BN is more effective as a filler than carbon black for providing high conductance, but carbon black reduces the heat of fusion by a smaller amount than does BN.

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