

Antioxidant-Based Phase-Change Thermal Interface Materials with High Thermal Stability

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This work provides phase-change thermal interface materials (TIMs) with high thermal stability and high heat of fusion. They are based on antioxidants mainly in the form of hydrocarbons with linear segments. The thermal stability is superior to paraffin wax and four commercial phase-change materials (PCMs). The use of 98.0 wt.% thiopropionate antioxidant (SUMILIZER TP-D) with 2.0 wt.% sterically half-hindered phenolic antioxidant (GA80) as the matrix and the use of 16 vol.% boron nitride particles as the solid component give a PCM with a 100°C lifetime indicator of 5.3 years, in contrast to 0.95 year or less for the commercial PCMs. The heat of fusion is much higher than those of commercial PCMs; the values for antioxidants with nonbranched molecular structures exceed that of wax; the value for one with a branched structure is slightly below that of wax. The phase-change properties are degraded by heating at 150°C much less than those of the commercial PCMs. The stability of the heat of fusion upon phase-change cycling is also superior. The viscosity is essentially unaffected by heating at 150°C. Commercial PCMs give slightly lower values of the thermal contact conductance for the case of rough (12 μm) mating surfaces, in spite of the lower values of the bond-line thickness.

Key words: Thermal interface material, thermal paste, thermal contact conductance, thermal stability, phase-change material, antioxidant

INTRODUCTION

Thermal interface materials (TIMs) are materials that are applied to the interface between a heat source (e.g., central processing units in computers) and a heat sink in order to improve the thermal contact. The surface of a heat source or heat sink is never perfectly smooth, and the air pockets between the mating surfaces impede the heat flow. A good thermal contact is necessary for heat to flow effectively from the heat source to the heat sink. A TIM can be in the form of a paste, an adhesive or a phase-change material (PCM). In relation to a PCM,¹ the relevant phase change is melting, since a liquid is associated with high conformability, which is

needed for minimizing interfacial air pockets, thereby promoting the heat transfer. The PCM should melt at a temperature above room temperature (typically below 50°C), so that the material flows and minimizes the interfacial air pockets, while it functions as a TIM. The liquid is attractive in that it is conformable, but it is disadvantageous due 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 (e.g., during transportation of the electronics), the seepage problem is alleviated. In addition, at the operating temperature, its relatively high viscosity reduces the possibility of seepage. Furthermore, the absorption of the latent heat of fusion during melting provides an additional mechanism of heat dissipation.^{2,3}

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There are two classes of PCMs: organic materials (such as paraffin wax) and inorganic materials (most commonly metal salt hydrates).⁴⁻⁶ The organic materials are attractive in terms of their chemical inertness, the thermal stability of the phase-change characteristics under thermal cycling, and low supercooling (the temperature difference between the phase-change onset temperatures during heating and cooling for the same thermal cycle), but they tend to have poor thermal conductivity. Inorganic materials are attractive in terms of 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.⁷

For application as TIMs, organic PCMs are preferred, due to their low tendency to cause ionic contamination, and are the ones addressed in this work. Prior work mostly used paraffin wax as the matrix,⁷ although silicone^{8,9} had also been used. Another novel organic phase-change matrix is polyol.¹⁰ The matrix materials in commercially available PCMs are mostly proprietary. Comparative evaluation of various organic PCMs, including commercial ones, is included in this work.

Since computer users usually do not change the TIMs until the computer has developed a problem, the thermal stability of the PCMs is practically important. Therefore, this paper is directed at developing organic PCMs that exhibit superior thermal stability.

The thermal conductivity of a PCM can be increased by using a filler (particles, fibers or bars) that is thermally conductive.^{11,12} 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 PCMs, the use of a thermally conductive filler is important. An alternate method of increasing the thermal conductivity involves impregnating porous graphite with paraffin wax,¹³ 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 the phase change is limited.

The choice of the organic matrix of a PCM for use as a TIM 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 extent of undercooling depends on the phase-change matrix and the solid component.¹⁰ The conformability strongly affects the effectiveness as a TIM, but it is an attribute that is difficult to measure. The ability to withstand elevated temperatures can be enhanced significantly by the addition of antioxidants to polyol esters.¹⁴ However, the antioxidant itself has not been investigated previously as a phase-change matrix material.

The combined use of two types of antioxidant significantly improves the thermal stability.¹⁵ In particular, the combination of a half-hindered primary antioxidant and a thiopropionate secondary antioxidant in polyol ester showed a synergistic effect. Furthermore, boron nitride (BN) as the solid component showed a synergistic effect with the two antioxidants in polyol ester, thereby resulting in a paste with a high degree of thermal stability, with the lifetime indicator reaching 19 years at 100°C.¹⁴ Due to the requirements of thermally stable phase-change characteristics, the attainment of high thermal stability for a TIM in the form of a PCM tends to be more challenging than that for a TIM that is not in the form of a PCM.

There is no reported prior work on phase changes in antioxidants. However, the fact that some antioxidants are in the form of hydrocarbons with linear segments suggests the possibility of these antioxidants as attractive PCMs. An objective of this work is to investigate the use of antioxidants for attaining thermally stable TIMs in the form of PCMs. Another objective of this work is to provide a comparative study of paraffin wax, antioxidants, and commercial PCMs for use as phase-change TIMs. For this purpose, the effectiveness of TIMs 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 for thermal contact conductance measurement), the composition (copper) and roughness (15 μm) of the adjoining surfaces, the pressure (0.46, 0.69, and 0.92 MPa) applied to the thermal contact in the direction perpendicular to the plane of the interface, and the composition (either hexagonal BN or carbon black (CB)) and volume fraction (4%) of the filler, and the temperature and time of prior heating. This comparative evaluation is supplemented by (i) thermal gravimetric analysis (TGA) for studying the thermal stability at elevated temperatures (i.e., the ability to withstand elevated temperatures), (ii) differential scanning calorimetry (DSC) for studying the melting and solidification behavior, and (iii) the measurement of the viscosity of the molten state.

Hexagonal BN is the main filler used in this work because of its combination of high thermal conductivity and high electrical resistivity. CB 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.¹⁶⁻¹⁹ Due to its conformability, CB 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).¹⁶⁻¹⁹

EXPERIMENTAL

Materials

The various antioxidants used in this work are listed in Table I. A primary antioxidant used is

Table I. Trade Name and Molecular Structure of Each Antioxidant

Name	Structure
SUMILIZER GA80	
CYANOX 1790	
SUMILIZER TP-D	$(\text{H}_{25}\text{C}_{12}\text{SCH}_2\text{CH}_2\text{COOCH}_2)_4\text{C}$
SUMILIZER TPM	$(\text{H}_{29}\text{C}_{14}\text{OOCCH}_2\text{CH}_2)_2\text{S}$
CYANOX LTDP	$(\text{H}_{25}\text{C}_{12}\text{OOCCH}_2\text{CH}_2)_2\text{S}$

3,9-bis[2-[3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionyloxy]-1,1-dimethylethyl] 2,4,8,10-tetraoxaspiro-[5.5] undecane. It is a half-hindered phenolic compound and is a commercial product (SUMILIZER GA80, Sumitomo Chemical Corp.) in the form of a powder with a melting point $>110^\circ\text{C}$ and molecular weight 741 amu. Its weight-loss onset temperature (15%) is 401°C under nitrogen.

Another primary antioxidant used is 1,3,5-tris(4-*tert*-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione. It is a half-hindered phenolic compound and is a commercial product (CYANOX 1790, Cytec Industries, Inc.) in the form of a powder with melting point of 159 to 162°C and a molecular weight of 699 amu.

A secondary antioxidant is pentaerythrityl tetrakis-(3-dodecylthiopropionate). It is a commercial product (SUMILIZER TP-D, Sumitomo Chemical Corp.) in the form of a powder with a melting point of $>46^\circ\text{C}$ and a molecular weight of 1162 amu. The purity is 100%. Its weight-loss onset temperature (5%) is 335°C under nitrogen.

Another secondary antioxidant is dimyristyl 3,3'-thiodipropionate. It is a commercial product (SUMILIZER TPM, Sumitomo Chemical Corp.) in the form of a powder with a melting point of $49\text{--}54^\circ\text{C}$ and a molecular weight of 571 amu. The purity is 100%. Its weight-loss onset temperature (5%) is 334°C under nitrogen.

Yet another secondary antioxidant is dilaurylthiodipropionate. It is a commercial product (CYANOX LTDP, Cytec Industries, Inc.) in the form of flakes with a melting point of 39.5°C and a molecular weight of 514 amu.

These antioxidants are chosen for the following reasons. The antioxidant molecules to be used as a PCM should have a phase-change ability at or near 50°C , which requires the molecules to be a hydrocarbon or a related species with linear segments. In order for the molecules to melt at or near 50°C and subsequently align upon cooling with little, if any, supercooling, the segments should not include any bulky side groups or heteroatoms. Bulky side groups and heteroatoms tend to increase the extent of supercooling, due to the poor alignment of the molecules upon solidification. Although aromatic rings in the molecules improve the thermal stability, their presence increases the melting point. Therefore, hydrocarbons with linear segments (e.g., wax, lauric acid, etc.) are often used as PCMs. However, in the absence of appropriate additives, their thermal stability is poor,¹⁰ because of their small molecular size and low dissociation energy.

In contrast to the conventional use of antioxidants as minor additives to improve the thermal stability of the host, in this work antioxidants are used as the matrix medium. This is akin to using the antioxidant as the host. In this context, the antioxidant reacts with radicals formed from some of the antioxidant molecules upon heating, thereby inhibiting the decomposition of the antioxidant. Thiopropionate is an antioxidant that is known for its good thermal stability. SUMILIZER TPM and CYANOX LTDP are thiopropionate antioxidants with linear molecular structures, in contrast to SUMILIZER TP-D (another thiopropionate antioxidant), which has linear segments in a branched molecule. Due to this difference in structure, SUMILIZER TPM and CYANOX LTDP are expected to exhibit little supercooling and high heat of fusion, but poor thermal stability compared to SUMILIZER TP-D.

Paraffin wax ($\text{C}_n\text{H}_{2n+2}$, $n > 20$) in the form of a fully refined paraffin wax (CS-2032) from Crystal, Inc., PMC, Lansdale, PA, is a powder with purity 100%, specific gravity 0.90, melting point $52\text{--}56^\circ\text{C}$, viscosity 6.7×10^{-3} to 7.9×10^{-3} Pa s at 99°C , and molecular weight exceeding 283 amu.

The CB is Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It is a powder with particle size 30 nm, a nitrogen specific surface area $254 \text{ m}^2/\text{g}$, maximum ash content 0.2%, volatile content 1.07%, and density $1.7 \text{ g}/\text{cm}^3$ to $1.9 \text{ g}/\text{cm}^3$. The particle size (30 nm) of the CB is much lower than those of the metal or ceramic particles used in commercial thermal pastes.

The BN particles are hexagonal BN, equiaxed in shape (as shown by scanning electron microscopy), with a size of $5 \mu\text{m}$ to $11 \mu\text{m}$, surface area $17 \text{ m}^2/\text{g}$, oxygen content 0.5%, sulfur content <50 ppm, thermal conductivity $280 \text{ W}/\text{m K}$, and specific

gravity 2.2, as provided by GE Advanced Ceramics Corporation, Cleveland, OH (Polartherm 180). No functional group is present on the basal plane, but functional groups such as OH, BOH, NH, and NH₂ are present on the edge plane (GE Advanced Ceramics, private communication).

A number of commercial phase-change TIMs are also evaluated in terms of the thermal stability and phase-change characteristics for the sake of comparison. These commercial materials are Thermagon T-pcm HP105 (a PCM with a phase-change softening temperature of 50–60°C and thickness of 0.005 in. = 125 μm, from Laird technologies), Thermagon T-pcm FSF 52 (a PCM that melts at 52°C and has a thickness of 0.005 in. = 125 μm, from Laird technologies), Thermagon T-pcm 583 (a PCM that melts at 50°C and has a thickness of 0.003 in. = 76 μm, from Laird technologies), and HeatPath PCM 1052 A011 from Tyco Electronics Corporation.

Thermal Stability Testing

Thermogravimetric analysis (TGA) under isothermal or constant heating rate conditions was conducted.^{20,21} In particular, the isothermal method, as conducted at various constant temperatures as a function of time, is attractive for detailed kinetic study.^{22–24} Although the constant heating rate condition requires less measurement time than the isothermal condition,²¹ the isothermal condition is used herein, due to the small range of temperatures involved.

The degree of degradation, α ,²² is defined as the fractional loss in weight due to the heating. It is expressed as

$$\alpha = (w_0 - w)/w_0, \quad (1)$$

where w_0 is the initial weight of the specimen before heating and w is the actual weight at a point during the heating.

Cracking of a paste was observed in prior work when a commercial thermal paste (Arctic Silver[®] 5) was heated at 200°C and the remaining weight was 92.3%.¹⁴ This suggests that a weight loss of 7.7% may reduce the performance of a thermal paste. Therefore, the time for 3% weight loss (i.e., a remaining weight of 97%) is used in this work as an indicator of the lifetime of a thermal paste.

The isothermal heating time (τ) for attaining a weight loss of 3% is determined for each of several temperatures, namely 120 ± 2°C, 140 ± 2°C, 160 ± 2°C, 180 ± 2°C, 200 ± 2°C, and 220 ± 2°C. Zero time is taken as the time at which the temperature just reaches the set isothermal temperature. The time τ is considered as a lifetime indicator; it is not the true lifetime of the paste under use condition. Nevertheless, the determination of τ for various thermal pastes allows comparison of the thermal stability of the pastes.

The rate of degradation, da/dt (where t is the time), describes the rate of weight loss. It is expressed as

$$da/dt = k(T)f(\alpha), \quad (2)$$

where k is the temperature-dependent rate constant, T is the temperature in K, and $f(\alpha)$ is a function of α . The rate constant k increases with temperature, following the Arrhenius form, i.e.,

$$k(T) = A \exp(-E/RT), \quad (3)$$

where E is the activation energy, A is the pre-exponential factor, and R is the gas constant.

Substitution of Eq. 3 into Eq. 2 gives

$$da/dt = A \exp(-E/RT)f(\alpha). \quad (4)$$

Integration of Eq. 4 with respect to time gives

$$g(\alpha) = \int [da/f(\alpha)] = A [\exp(-E/RT)] t. \quad (5)$$

Rearrangement of Eq. 5 gives

$$\ln t = E/RT + \ln[g(\alpha)/A]. \quad (6)$$

Based on Eq. 6, E can be determined from the slope of the plot of $\ln t$ versus $1/T$.

The thermal stability is evaluated in this work by two methods, namely (i) oven aging, i.e., weighing before and after isothermal heating in air at 150 or 200°C for 24 h, with the heating and cooling rates being 3.0 °C/min, and (ii) isothermal TGA in air, the heating rate being 3.0 °C/min prior to the isothermal period. The TGA testing was conducted by using a Perkin-Elmer Corp. (Norwalk, CT) TGA 7 system. Both oven-aging and TGA specimens were contained in aluminum pans.

In the oven-aging testing, each specimen was contained in an aluminum weighing dish (57 mm in diameter and 10 mm in depth, VWR International) and was heated for 24 h in air in a box furnace (0.004 m³ in volume, without forced convection, Isotemp[®] Programmable Muffle Furnace, Fisher Scientific Co.) at either 150 ± 5°C or 200 ± 5°C. The maximum operation temperature of thermal pastes used in computers is typically around 100°C. A testing temperature of either 150 or 200°C was chosen for oven-aging testing in this work in order to compare rapidly the thermal stability of pastes containing various combinations of antioxidants and solid components. The weight was measured before heating and after the heating by using an electronic balance (Mettler MT, Mettler-Toledo, Inc.). The specimen weight (excluding the solid component) was 2000 ± 1 mg, except for the commercial samples. The weight of the commercial sample was 200 ± 25 mg. In addition, each specimen was visually inspected for surface cracks after the heating and subsequent cooling. Two specimens of each type are tested. The same oven-aging testing method was used for

all types of specimen, including the commercial TIMs.

In both the oven-aging and TGA testing, an antioxidant (or an antioxidant combination) or another PCM was placed in an aluminum pan and heated until the solid component in the pan had melted completely. After that, the solid component (either CB in the amount ranging from 2.4 vol.% to 6.0 vol.%, or BN in the amount ranging from 4.0 vol.% to 16 vol.%) was optionally added and the mixture was stirred manually for 10 min. These proportions of solid component have been previously used in relation to thermal paste performance evaluation.¹⁶ The specimen weight was 12.0 ± 0.5 mg. Each specimen was contained in an aluminum pan (6.4 mm in diameter and 1.6 mm in depth, Perkin-Elmer Corp.). The aluminum pan used in TGA is much smaller than that used in the oven aging. This difference in size contributes to the difference in percentage weight loss between the two cases.

The tendency for cracking of PCMs was studied after heating by visual inspection. Cracking is related to the conformability of the paste. A non-conformable PCM may cause the detachment of the heat sink from the central processing unit (CPU) or give rise to more interfacial air, which may reduce the thermal contact conductance.

Viscosity Testing

The viscosities of the TIMs in the molten state are measured at $70 \pm 0.5^\circ\text{C}$ 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). The measurement was conducted after heating at 150°C for various lengths of time up to 72 h.

Thermal Contact Conductance Testing

Various TIMs were sandwiched between the 1 in. \times 1 in. (25 mm \times 25 mm) surfaces of two copper blocks. Both 1 in. \times 1 in. surfaces of each block had either rough surfaces (12 μm or 800 grit roughness, prepared by mechanical polishing by Hardric Laboratories, Inc., N. Chelmsford, MA) or smooth surfaces (0.009 μm roughness and 0.040 μm to 0.116 μm flatness, as attained by diamond turning). Each copper block had a height of 35 mm.

The thermal contact conductance of the interface between two 1 in. \times 1 in. (25 mm \times 25 mm) copper blocks with a TIM between the mating surfaces was measured using the guarded hot-plate method, which is a steady-state method of heat flux measurement (ASTM method D5470). The testing method is the same as that in prior work,²⁵ which showed that this method gives results that are consistent with those obtained by measuring the temperature rise in an operating computer that uses the thermal paste at the interface between the

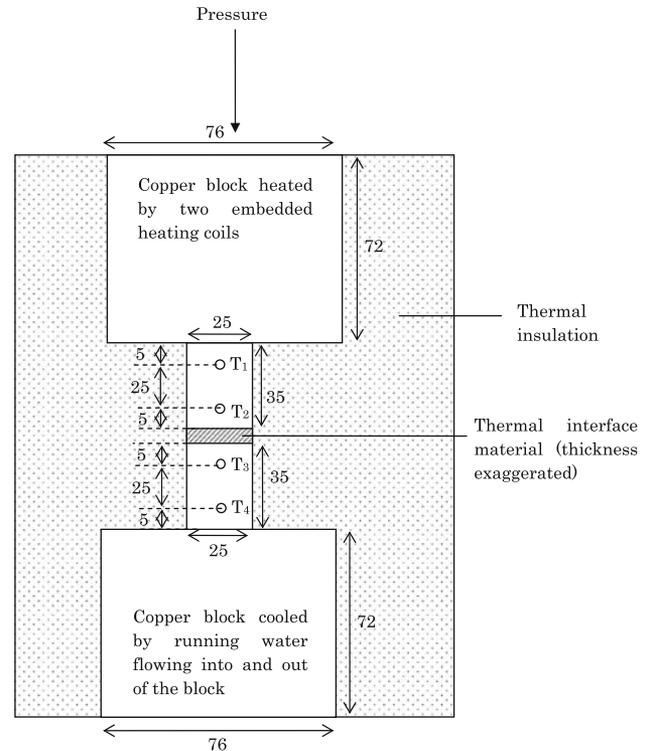


Fig. 1. A schematic representation of the steady-state method (guarded hot-plate method) of thermal contact conductance measurement. T_1 , T_2 , T_3 , and T_4 are holes of diameter 3.3 mm. An RTD probe is inserted in each hole. All dimensions are in mm.

microprocessor and the heat sink. The heat in this test is provided by a 3 in. \times 3 in. (76 mm \times 76 mm) copper block that has two embedded heating coils (top block in Fig. 1). During the period of temperature rise, the heating rate is controlled at $3.2^\circ\text{C}/\text{min}$ by using a temperature controller. This copper block is in contact with one of the 1 in. \times 1 in. copper blocks that sandwich the TIM. The cooling in this test is provided by a second 3 in. \times 3 in. copper block, which is cooled by running water that flows in and out of the block (bottom block in Fig. 1). This block is in contact with the other two 1 in. \times 1 in. copper blocks that sandwich the TIM. A resistance temperature detector (RTD) probe (connected to Digi-Sense ThermoLogR RTD Thermometer from Fisher Scientific Co., with an accuracy of $\pm 0.03^\circ\text{C}$) is inserted in four holes (T_1 , T_2 , T_3 , and T_4 in Fig. 1, each hole of diameter 3.3 mm) one after the other. Two of the four holes were placed in each of the 1 in. \times 1 in. copper blocks. The temperature gradient was determined from $T_1 - T_2$ and $T_3 - T_4$. These two quantities should be equal at equilibrium, which is attained after holding the temperature of the heater at the desired value for 30 min. Equilibrium is assumed when the temperature variation is within $\pm 0.1^\circ\text{C}$ for a period of 15 min. At equilibrium, the temperature of the hot block is 100°C , that of the cold block is in the range $12\text{--}25^\circ\text{C}$, while that of the TIM is in the range $50\text{--}63^\circ\text{C}$.

The pressure in the direction perpendicular to the plane of the thermal interface was controlled by using a hydraulic press at a pressure of 0.46, 0.69, or 0.92 MPa. The system was thermally insulated by wrapping all the copper blocks laterally with glass-fiber cloth.

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

$$Q = \lambda A \Delta T / d_A \quad (7)$$

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. (25 mm \times 25 mm) copper block, and d_A is the distance between the thermocouples T_1 and T_2 (i.e., 25 mm). The temperature at the top surface of the TIM is T_A , which is given by

$$T_A = T_2 - d_B(T_1 - T_2) / d_A, \quad (8)$$

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

$$T_D = T_3 + d_D(T_3 - T_4) / d_C, \quad (9)$$

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

The thermal impedance θ is given by

$$\theta = (T_A - T_D)A / Q \quad (10)$$

Note that insertion of Eq. 7 into Eq. 10 causes cancellation of A , so that θ is independent of A . The thermal contact conductance is the reciprocal of θ .

Each type of TIMs was tested for thermal contact conductance at least twice, each time with measurement at the three pressures (0.46, 0.69, and 0.92 MPa) in the order listed.

The thermal resistance of a system consisting of a thermal paste sandwiched by a heat source and a heat sink can be simply modeled by thermal resistances in series:

$$R = h / kA + R_1 + R_2, \quad (11)$$

where h is the bond-line thickness, A is the area of the thermal contact, k is the thermal conductivity of the TIM, R is the total thermal resistance of the sandwich, and R_1 and R_2 are the contact resistances of the interface between the TIM and the two surfaces that sandwich the interface material. Equation 11 indicates that a thicker bond line will give a higher thermal resistance, i.e., a lower thermal conductance.²⁶

Bond-Line Thickness Measurement

The bond-line thickness refers to the thickness of the TIM. It was measured by sandwiching the thermal paste at a pressure of 0.46 MPa with the

rough copper surfaces used for the thermal contact conductance measurements. A low value of the bond-line thickness is associated with high spreadability of the thermal paste. A strain gage mounted between the surfaces that sandwich the TIM, as shown in Fig. 2, was used for the bond-line thickness measurement. The strain gage works by sensing the deformation induced by the distance change between the two mating surfaces. The bond-line thickness was calculated from the electrical output of the strain gage. The measurement was conducted at elevated temperature in order to melt the PCMs. The temperature of the hot block was 100°C, while that of the TIM was in the range of 50–69°C; these temperatures are taken from the temperature T_3 and T_2 of the copper blocks (Fig. 1). First, two copper blocks that are in contact in the absence of an interface material were heated, and the voltage output of the strain gage was adjusted to 0 mV. After heating the copper blocks for 15 min, a PCM was applied between blocks. After subsequent heating at a pressure of 0.46 MPa for 10 min, the strain gage output was recorded.

Phase-Change Characteristics

For the DSC measurements, a specimen was contained in an aluminum pan and covered by an aluminum lid (without sealing). Testing was conducted in air, using a Perkin-Elmer Corp. (Norwalk, CT) DSC 7 system equipped with an ice-filled cooler for operation below room temperature. The heating and cooling rates were both 2.0 °C/min.

The phase-change onset temperature (T_s)⁷ 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. The temperature corresponding to the DSC peak is referred to as T_p . 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

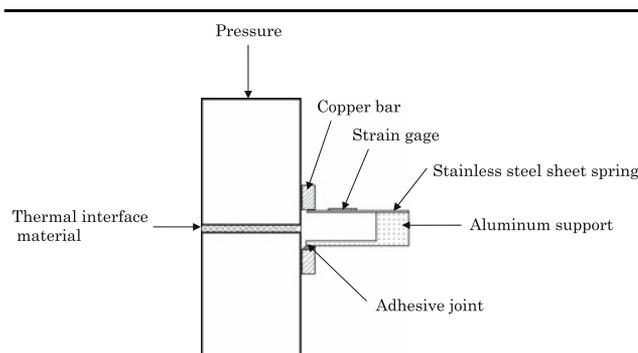


Fig. 2. A schematic representation of the bond-line thickness measurement method.

purpose. The supercooling (ΔT) was defined as 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 is higher during heating than that during cooling, and is negative if T_s is lower during heating than that during cooling.

Phase-Change Cyclability

Differential scanning calorimetry was used to monitor the phase-change cyclability. In the first cycle, the specimen was heated from 30°C to 130°C at a heating rate of 5 °C/min and then immediately cooled from 130°C to 30°C at a cooling rate of 5 °C/min. In subsequent cycles, the procedure was identical, except that the temperature was held at the maximum temperature of 130°C for 100 min.

RESULTS AND DISCUSSION

Thermal Stability Evaluation by Oven-Aging Testing

Table II shows the oven-aging results of the thermal stability evaluation for various PCMs. The degradation of the phase-change properties and the weight loss of the material may cause an increment of air void content and change the filler proportion, in addition causing either a reduction of the viscosity (the pump-out problem) or an increase of the viscosity (loss of conformability), consequently degrading performance. Among all the samples tested in this work, the PCM including 2.0 wt.% GA80, 98.0 wt.% TP-D, and BN showed the greatest thermal stability, as shown by the high residual weight after heating at 150°C for 24 h. In addition, they retained their ability to change phase after this heating. The addition of the BN enhances the thermal stability more than the addition of CB. This is consistent with the prior report of the superior

thermal stability of polyol-ester-based BN interface material with antioxidant compared to polyol-ester-based CB interface material with antioxidant.¹⁴ Surface functional groups (such as the amine group) on BN exhibit a stronger synergistic effect with two antioxidants than the functional groups (such as phenolic and carbonyl groups) on CB. The amine group on BN may trap an alkyl radical.^{14,27} In addition, the PCM containing 2.0 wt.% GA80, 98.0 wt.% TP-D, and BN also showed greater thermal stability than the commercial PCMs.

Paraffin wax does not have a high thermal stability, as shown by the low residual weight after heating at 150°C. Even in the presence of antioxidants, which enhance thermal stability, the thermal stability of the wax remains poor compared to antioxidant-based PCMs (2.0 wt.% GA80 plus 98.0 wt.% of either TP-D or TPM). All four commercially available PCMs were less thermally stable than the antioxidant-based PCMs containing BN or CB.

No cracking was observed in the antioxidant-based PCMs after the heating, but two commercial PCMs (T-pcm FSF52 and PCM 1052, with residual weight below 78 wt.% after heating, Table II) showed cracks after the heating. The loss of vehicle upon heating generates cracks when the vehicle has been mixed with a solid component.¹⁴ A high volume fraction of the solid component enhances the tendency for cracking,¹⁴ though the solid component volume fractions of commercial PCMs are proprietary.

Lifetime Evaluation Based on TGA

Lifetime evaluation by weight loss measurement in isothermal TGA was conducted for the PCMs. Figure 3 shows the Arrhenius plots of $\ln \sigma$ versus

Table II. Thermal Stability of Various PCMs, as Indicated by Weight Loss Measurements after Heating at 150°C for 24 h (Heating Rate 3 °C/min)

Vehicle	Solid Component	Residual Weight (%)		Cracking Tendency	Phase Change
		Excluding the Solid Component	Including the Solid Component		
2.0 wt.% GA80 + 98.0 wt.% TP-D	BN 16 vol.%	99.8 ± 0.0	99.9 ± 0.0	No	Yes
2.0 wt.% GA80 + 98.0 wt.% TP-D	CB 4.0 vol.%	99.5 ± 0.1	99.5 ± 0.1	No	Yes
2.0 wt.% GA80 + 98.0 wt.% TPM	BN 16 vol.%	97.5 ± 0.0	98.3 ± 0.0	No	Yes
2.0 wt.% GA80 + 98.0 wt.% TPM	CB 4.0 vol.%	96.3 ± 0.1	96.6 ± 0.1	No	Yes
Paraffin wax	—	50.7 ± 5.3	—	No	Yes
2.0 wt.% GA80 + 48.0 wt.% TP-D + 50.0 wt.% wax	—	83.8 ± 2.3	—	No	Yes
T-pcm 583	†	—	97.8 ± 0.2	No	No ^a
T-pcm HP105	†	—	90.9 ± 2.0	No	No ^a
T-pcm FSF 52	†	—	78.2 ± 2.4	Yes	No ^b
HeatPath PCM 1052 A011	†	—	77.7 ± 0.1	Yes	No ^b

BN = boron nitride, CB = carbon black; † the amounts and types of the solid components are proprietary; ^a softening rather than melting upon heating; ^b remaining solid upon heating.

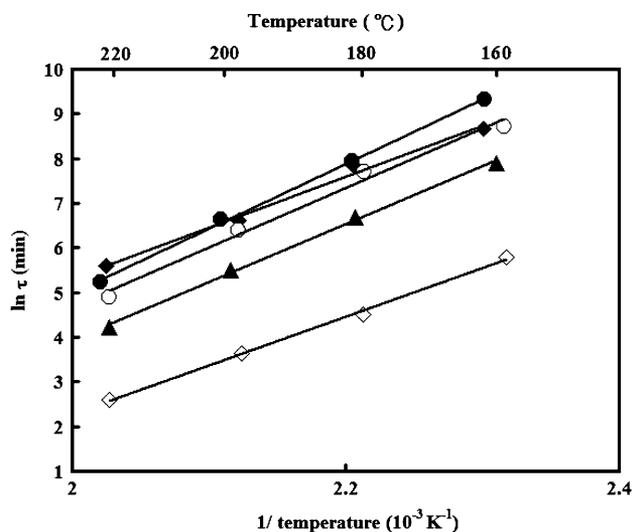


Fig. 3. Thermal stability of TIMs at 160 ± 2 , 180 ± 2 , 200 ± 2 , and $220 \pm 2^\circ\text{C}$, studied by using the isothermal method of TGA. ●: 2.0 wt.% GA 80 and 98.0 wt.% TP-D with 16 vol.% BN, ○: 2.0 wt.% GA 80 and 98.0 wt.% TP-D, ▲: 2.0 wt.% GA 80 and 98.0 wt.% TPM with 16 vol.% BN, ◆: commercial PCM (T pcm 583), ◇: commercial PCM (T pcm HP 105).

$1/T$, where σ is the lifetime indicator and T is the temperature in K. The commercial PCMs T-pcm 583 and T-pcm HP 105 were chosen for comparison with the antioxidant-based BN PCM, since these commercial PCMs show high thermal stability, as indicated by oven-aging testing at 150°C for 24 h (Table II). Extrapolation of the plot to the temperature of 100°C ($1/T = 2.7 \times 10^{-3} \text{K}^{-1}$, which is outside the horizontal scale in Fig. 3) gives the lifetime indicator for 100°C , which is a typical maximum operation temperature of a thermal paste used in computers. All data points essentially fall on a straight line in Fig. 3. The antioxidant-based PCM containing TP-D, GA80, and BN was more thermally stable than both of these commercial PCMs. It is superior to T-pcm 583 below 180°C and is superior to T-pcm HP 105 at all temperatures. This result is consistent with the relative values of the residual weight after heating at 150°C , as shown in Table II. The thermal stability of the antioxidant combination GA 80 (2.0 wt.%) and TPM (98.0 wt.%) filled with BN was worse than that of T-pcm 583, as shown by the relatively small values of τ (Fig. 3). This result is not consistent with that in Table II, which shows lower thermal stability for T-pcm 583. This difference between Table II and Fig. 3 is probably due to the difference in the extent of convection in the two experimental conditions. Figure 4 shows the residual weight percentage of the antioxidant-based PCMs. At the beginning of the isothermal heating, this antioxidant combination filled with BN showed a small degree of abrupt weight loss (Fig. 4). After this initial drop in weight, the residual weight decreases slightly faster than the TP-D-based PCM.

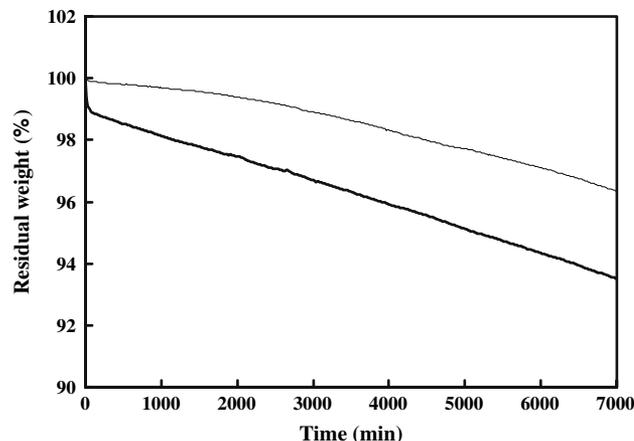


Fig. 4. Thermal stability of TIMs at $160 \pm 2^\circ\text{C}$, studied by using the isothermal method of TGA. Solid thin line: 2.0 wt.% GA 80 and 98.0 wt.% TP-D with 16 vol.% BN. Solid thick line: 2.0 wt.% GA 80 and 98.0 wt.% TPM with 16 vol.% BN.

The lifetime evaluation was performed by using an open aluminum pan (without a lid). The real situation in microelectronic application is similar to this open situation for the exposed edge of the TIM layer, but is different from this open situation for the part of the TIM that is covered by one or more of the adjoining surfaces. The exposed edge tends to be more severely decomposed than the interior. Therefore, the real lifetime at 100°C should be longer than the value reported here.

Table III shows the activation energy for each PCM, as obtained from the slope of the corresponding curve in Fig. 3. The antioxidant-based PCM (2.0 wt.% of GA 80 and 98.0 wt.% of TP-D, filled with BN) (line 1, Table III) shows the highest activation energy among the tested materials. The antioxidant TPM has a lower activation energy, though it is higher than the values for the commercial PCMs. Addition of BN enhances the activation energy. Table III also shows the 100°C lifetime indicator, as obtained by extrapolation of the curves in Fig. 3. A longer lifetime at 100°C is associated with a higher activation energy, in agreement with prior results,¹⁴ except that the antioxidant TPM exhibits a higher activation energy than the commercial PCM T pcm 583, though it has a shorter lifetime than T pcm 583. The longest lifetime of 5.3 years is attained for the antioxidant-based PCM containing BN. By changing the type of filler from BN to another solid component or by increasing the solid component loading, it may be possible to improve the thermal stability beyond 5.3 years.

Viscosity Testing

Table IV shows the viscosities at two different shear rates. Paraffin wax has a relatively low viscosity, due to its low molecular weight. However, due to the higher molecular weight of TP-D compared to paraffin wax, TP-D shows a higher

Table III. The Activation Energy (E) and Lifetime Indicator of Each of Five PCMs

Line No.	Material	E (kJ/mol)		100°C Lifetime Indicator (Year)	
		Excluding the Solid Component	Including the Solid Component	Excluding the Solid Component	Including the Solid Component
1	2.0 wt.% GA 80 and 98.0 wt.% TP-D with 16 vol.% BN	118	120	3.4	5.3
2	2.0 wt.% GA 80 and 98.0 wt.% TP-D	111	–	1.7	–
3	2.0 wt.% GA 80 and 98.0 wt.% TPM with 16 vol. % BN	98	108	0.21	0.63
4	T pcm 583	–	95	–	0.95
5	T pcm HP 105	–	91	–	0.1

Table IV. The Viscosity (cP) of Each of Three PCMs at Two Shear Rates

Matrix	Shear Rate	
	16 s ⁻¹	40 s ⁻¹
Paraffin wax ^a	6.5	5.9
TP-D	40	41
98.0 wt.% TP-D + 2.0 wt.% GA 80	45	43

^a Ref. 16.

viscosity. Addition of the primary antioxidant GA80 to TP-D increases the viscosity slightly. Low viscosity may cause the seepage problem. In order to significantly increase the viscosity at the operating temperature, a polymeric antioxidant may be used, but this is not addressed in this work.

Table V shows the effect of heating on the viscosity of PCMs. The effect is small, although it is larger for paraffin wax than the antioxidant PCM. Polyol-ester-based TIMs reported previously¹⁴ exhibited increased viscosity after heating at 200°C, in the case when antioxidants were not used.

Thermal Contact Conductance and Bond-Line Thickness

The thermal contact conductance and bond-line thickness for PCMs sandwiched by rough copper

surfaces are shown in Table VI. The thermal contact conductance depends on the volume fraction of solid component, the type of solid component, and other factors such as the surface roughness of the copper blocks. At a low volume fraction of the solid component, the particles of the solid component do not contact each other and do not fill the valleys in the surface topography, thus resulting in a low thermal contact conductance. The addition of a high volume fraction of the solid component increases the bond-line thickness, thereby lowering the thermal contact conductance. The dependence of the thermal contact conductance on this volume fraction depends on the type and shape of the solid component. CB and commercial PCMs show lower thermal contact conductance than BN, at least in the case of rough surfaces, in spite of the lower values of the bond-line thickness. Although, for the same solid component, a small bond-line thickness helps improve the thermal contact conductance, the BN PCM shows a high thermal contact conductance when the bond-line thickness is substantial. This is presumably due to the high thermal conductivity of the BN.

The thermal contact conductance for PCMs sandwiched by smooth copper surfaces is shown in Table VII. T-pcm FSF 52 exhibits a melting point, whereas T-pcm 583 merely exhibits a softening point. This difference suggests that the former can give a lower bond-line thickness. Indeed, the former gives a higher thermal contact conductance. The

Table V. Comparison of Viscosity (cP) after Heating at 150°C for Various Lengths of Time

Matrix	Shear Rate		
	16 s ⁻¹	40 s ⁻¹	79 s ⁻¹
Paraffin wax (heated for 1 h)	–	5.6 ± 0.4	6.4 ± 0.0
Paraffin wax (heated for 3 h)	–	8.1 ± 0.8	6.3 ± 0.2
98.0 wt.% TP-D + 2.0 wt.% GA 80 (heated for 12 h)	41 ± 0	42 ± 1	42 ± 0
98.0 wt.% TP-D + 2.0 wt.% GA 80 (heated for 24 h)	43 ± 0	43 ± 1	43 ± 0
98.0 wt.% TP-D + 2.0 wt.% GA 80 (heated for 3 days)	42 ± 0	43 ± 0	44 ± 2

Table VI. Thermal Contact Conductance and Bond-Line Thickness for Various PCMs Sandwiched by Rough Copper Surfaces at Different Pressures

Vehicle	Carbon Black	Boron Nitride	Thermal Contact Conductance ($10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$)			Bond-Line Thickness (μm)
			0.46 MPa	0.69 MPa	0.92 MPa	
Wax cs-2032 ^b	–	–	9.8 ± 0.5	10.4 ± 0.3	10.5 ± 0.1	–
Wax cs-2032 ^b	2.4 vol.%	–	5.5 ± 0.1	5.8 ± 0.1	6.1 ± 0.2	–
Wax cs-2032 ^b	–	4.0 vol.%	7.6 ± 0.2	7.7 ± 0.3	7.9 ± 0.1	–
TP-D ^b	–	–	11.8 ± 0.4	11.9 ± 0.1	12.8 ± 0.4	–
TP-D ^b	2.4 vol.%	–	5.4 ± 0.3	5.6 ± 0.1	5.8 ± 0.1	–
TP-D ^b	4.0 vol.%	–	7.3 ± 0.2	8.1 ± 0.2	9.2 ± 0.1	–
TP-D ^b	6.0 vol.%	–	2.0 ± 0.0	2.1 ± 0.0	2.1 ± 0.0	–
TP-D ^b	–	4.0 vol.%	8.9 ± 0.4	9.4 ± 0.5	10.9 ± 0.5	–
TP-D ^b	–	16 vol.%	11.8 ± 0.3	12.4 ± 0.2	11.5 ± 0.2	–
98.0 wt.% TP-D + 2.0 wt.% GA80 ^b	4.0 vol.%	–	8.7 ± 0.2	10.4 ± 0.1	11.1 ± 0.1	0.2 ± 0.3
98.0 wt.% TP-D + 2.0 wt.% GA80 ^b	–	16 vol.%	10.6 ± 0.3	12.2 ± 0.2	12.6 ± 0.2	4.3 ± 0.6
T-pcm FSF 52 ^b	a	a	9.1 ± 0.6	11.8 ± 0.4	11.9 ± 0.5	–
T-pcm 583 ^c	a	a	9.1 ± 0.2	9.6 ± 0.1	10.4 ± 0.1	2.7 ± 0.5
T-pcm FSF 52 ^c	a	a	8.4 ± 0.0	9.4 ± 0.2	9.5 ± 0.1	1.8 ± 0.3

^a The amounts and types of the solid components are proprietary; ^b conductance measured under condition A of alignment of the copper mating surfaces; ^c conductance measured under condition B of alignment of the copper mating surfaces.

Table VII. Thermal Contact Conductance for Various PCMs Sandwiched by Smooth Copper Surfaces at Different Pressures

Vehicle	Carbon Black	Boron Nitride	Thermal Contact Conductance ($10^4 \text{ W/m}^2 \text{ }^\circ\text{C}$)	
			0.46 MPa	0.69 MPa
98.0 wt.% TP-D + 2.0 wt.% GA80	4.0 vol.%	–	11.9 ± 0.2	16.1 ± 0.0
98.0 wt.% TP-D + 2.0 wt.% GA80	–	16 vol.%	12.7 ± 0.2	14.7 ± 0.1
T-pcm FSF 52	†	†	23.0 ± 1.6	24.0 ± 0.5
T-pcm 583	†	†	13.6 ± 0.2	13.7 ± 0.1

† Proportion proprietary.

antioxidant-based BN PCMs give higher thermal contact conductance than the commercial PCMs in the case of rough surfaces (Table VI), but are inferior in the case of smooth surfaces (Table VII). The origin of these differences is not completely clear, due to the proprietary nature of the components in the commercial PCMs.

Phase-Change Characteristics

Table VIII shows that the various PCMs (with or without a solid component) without any prior heating differ considerably in terms of supercooling (ΔT) and the heat of fusion (ΔH). The heat of fusion is zero for the commercial PCMs T-pcm HP105 and T-pcm 583, due to the fact that these materials soften rather than melt upon heating (Table II). Paraffin wax has a relatively high melting temperature. Paraffin wax and the commercial PCMs

exhibit less supercooling than the thiopropionate (LTDP, TPM or TP-D). The heat of fusion is relatively high for wax and thiopropionates. The values for TPM and LTDP exceed that of wax (Table VIII). The value is particularly high for TPM. However, the value for TP-D is below that of wax (Table VIII). The heat of fusion is higher for the antioxidant (TP-D or TPM)-based PCMs than the commercial PCMs.

TPM showed the highest heat of fusion and the smallest supercooling among the investigated thiopropionates. In contrast to TPM, TP-D exhibits a branched molecular structure, which may cause a reduction of the heat of fusion and increase of the supercooling, due to the lesser degree of alignment of the branched molecules compared to non-branched molecules. Due to the high heat of fusion of TPM, even in the presence of a solid component, the material still exhibits values of the heat of

Table VIII. Phase-Change Properties Observed by DSC for PCMs Without Prior Heating

Phase-Change Material	Solid Component	T_s (°C)		T_p (°C)		ΔH (J/g)	
		Heating	Cooling	Heating	Cooling	Heating	Cooling
Paraffin wax	-	47.2 ± 0.1	52.8 ± 0.2	47.2 ± 0.1	52.8 ± 0.2	-5.6 ± 0.3	148 ± 2
Paraffin wax	BN 4.0 vol.%	47.3 ± 0.1	53.4 ± 0.1	53.2 ± 0.0	51.1 ± 0.1	-6.1 ± 0.2	135 ± 0
Paraffin wax	CB 4.0 vol.%	47.6 ± 0.3	52.7 ± 0.2	53.7 ± 0.0	50.9 ± 0.0	-5.1 ± 0.5	136 ± 1
LTDP	-	36.5 ± 0.9	34.2 ± 0.2	39.9 ± 0.1	32.9 ± 0.1	2.3 ± 1.1	155 ± 2
TPM	-	45.4 ± 0.4	45.9 ± 0.2	50.3 ± 0.1	44.4 ± 0.2	-0.4 ± 0.7	196 ± 16
2.0 wt.% GA80 + 98.0 wt.% TPM	-	45.6 ± 0.1	45.9 ± 0.1	50.1 ± 0.1	44.3 ± 0.1	-0.3 ± 0.2	177 ± 0
2.0 wt.% GA80 + 98.0 wt.% TPM	BN 16 vol.%	45.8 ± 0.1	46.9 ± 0.1	49.8 ± 0.1	45.9 ± 0.0	-1.1 ± 0.2	120 ± 0
2.0 wt.% GA80 + 98.0 wt.% TPM	CB 4.0 vol.%	45.6 ± 0.1	46.1 ± 0.1	49.7 ± 0.2	44.8 ± 0.0	-0.5 ± 0.2	162 ± 1
TP-D	-	47.4 ± 0.1	42.2 ± 0.1	50.0 ± 0.0	40.0 ± 0.3	5.2 ± 0.2	128 ± 1
TP-D	BN 4.0 vol.%	48.0 ± 0.6	46.3 ± 0.2	50.3 ± 0.6	45.5 ± 0.6	1.7 ± 0.8	117 ± 1
TP-D	CB 4.0 vol.%	48.2 ± 0.8	44.4 ± 0.2	50.3 ± 0.6	43.0 ± 0.2	3.8 ± 1.0	117 ± 2
2.0 wt.% CYA 1790 + 98.0 wt.% TP-D	-	45.0 ± 1.1	39.0 ± 1.7	49.6 ± 0.0	34.9 ± 0.4	6.0 ± 2.8	123 ± 1
2.0 wt.% GA80 + 98.0 wt.% TP-D	-	46.9 ± 0.6	42.2 ± 0.8	49.7 ± 0.1	39.7 ± 1.0	4.7 ± 1.4	129 ± 0
5.0 wt.% GA80 + 95.0 wt.% TP-D	-	46.0 ± 0.3	41.5 ± 0.0	49.5 ± 0.2	38.9 ± 0.3	4.5 ± 0.3	126 ± 9
2.0 wt.% GA80 + 98.0 wt.% TP-D	BN 16 vol.%	46.5 ± 0.1	46.2 ± 0.2	49.3 ± 0.1	45.1 ± 0.2	0.3 ± 0.3	87.1 ± 1.9
2.0 wt.% GA80 + 98.0 wt.% TP-D	CB 4.0 vol.%	46.6 ± 0.4	44.0 ± 0.4	49.5 ± 0.3	42.8 ± 0.5	2.6 ± 0.8	115 ± 3
T-pcm FSF 52	†	42.4 ± 0.4	49.4 ± 0.3	50.1 ± 0.1	48.3 ± 0.1	-7.0 ± 0.7	29.1 ± 0.4
HeatPath PCM 1052 A011	†	45.6 ± 0.3	48.8 ± 0.1	51.0 ± 0.2	48.2 ± 0.2	-3.2 ± 0.4	29.3 ± 1.5
T-pcm HP105	†	-	-	-	-	-	0
T-pcm 583	†	-	-	-	-	-	0

BN = boron nitride, CB = carbon black; † proportion proprietary.

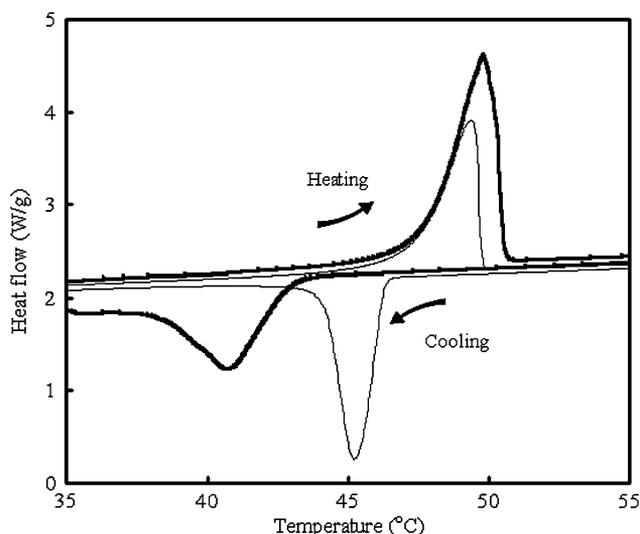


Fig. 5. DSC thermogram during heating and subsequent cooling for the antioxidant-based (2.0 wt.% of GA80, 98.0 wt.% of TP-D) PCM without prior heating. Thin line: with BN (16 vol.%). Bold line: without a solid component.

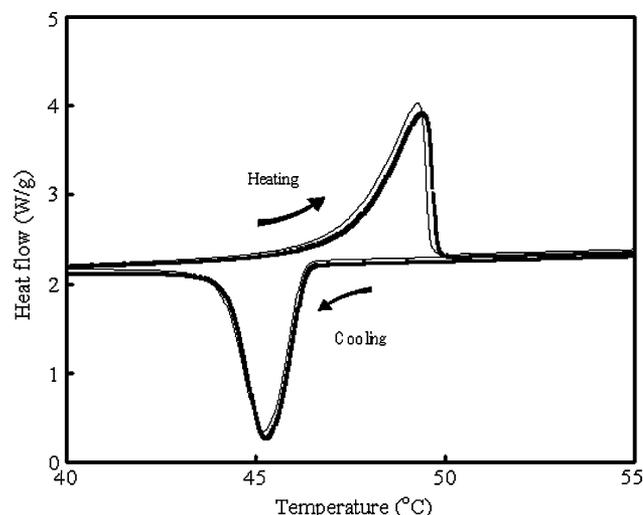


Fig. 6. DSC thermogram during heating and subsequent cooling for the antioxidant-based (2.0 wt.% of GA80, 98.0 wt.% of TP-D) BN (16 vol.%) PCM. Thin line: after heating at 150°C for 24 h. Bold line: before heating.

fusion that are higher than those of the commercial materials.

Although TPM shows a higher heat of fusion than TP-D, it is less thermally stable than TP-D. As a consequence, TP-D-based PCMs are more attractive for use as TIMs than TPM-based PCMs. The addition of a primary antioxidant (GA80 or CYA 1790) to the secondary antioxidant (TPM or TP-D) did not affect the phase-change characteristics, as shown in Table VIII.

The presence of a solid component tends to diminish the supercooling, except for 4.0 vol.% of CB with paraffin wax (Table VIII). BN is more effective than CB for diminishing the supercooling, as shown for any of the vehicles tested in this work at the same volume percentage of the solid component. On the other hand, for the same matrix, the

heat of fusion showed similar values at the same volume fraction of different solid components (Table VIII). Figure 5 shows DSC curves which compare the antioxidant-based (2.0 wt.% of GA80, 98.0 wt.% of TP-D) PCM with and without 16 vol.% of BN. Although the heat of fusion is decreased by the presence of BN, the supercooling is reduced by the presence of BN. BN may work as nuclei of the growing crystal of the phase-change matrix.

In the case that PCMs are used as TIMs in microelectronics, the amount of PCM involved is small. Therefore, the effect of their heat of fusion is not significant. However, the heat of fusion is important when a PCM is used for heat storage, which relates to heat removal from the electronics. The solid component and its composition affect the phase-change characteristics. The heat of fusion (latent heat per gram, absorbed during melting) is

Table IX. Phase-Change Properties after Heating at 150°C for 24 h (Heating/Cooling Rate 3 °C/min)

Phase-Change Material	Solid Component	T_s (°C)		T_p (°C)		ΔT (°C)	ΔH (J/g)	
		Heating	Cooling	Heating	Cooling		Heating	Cooling
Paraffin wax	—	36.1 ± 3.5	44.7 ± 1.3	43.8 ± 1.8	43.3 ± 0.6	-8.6 ± 4.8	9.5 ± 1.4	-11.0 ± 2.0
2.0 wt.% GA 80 + 98.0 wt.% TPM	BN 16 vol.%	46.9 ± 0.2	47.3 ± 0.0	50.2 ± 0.0	46.2 ± 0.0	-0.4 ± 0.2	127 ± 2	-123 ± 2
2.0 wt.% GA 80 + 98.0 wt.% TPM	CB 4.0 vol.%	46.0 ± 0.1	46.1 ± 0.1	50.0 ± 0.1	44.6 ± 0.0	-0.1 ± 0.2	162 ± 1	-157 ± 1
2.0 wt.% GA 80 + 98.0 wt.% TP-D	BN 16 vol.%	46.3 ± 0.1	46.2 ± 0.0	49.3 ± 0.1	45.2 ± 0.1	0.1 ± 0.1	85.6 ± 1.2	-85.6 ± 1.2
2.0 wt.% GA 80 + 98.0 wt.% TP-D	CB 4.0 vol.%	41.2 ± 0.1	42.1 ± 0.5	48.2 ± 0.3	39.4 ± 0.2	-0.9 ± 0.6	103 ± 2	-101 ± 0
T-pcm FSF 52	†	—	—	—	—	—	0	0
HeatPath PCM 1052 A011	†	—	—	—	—	—	0	0

BN = boron nitride, CB = carbon black; † proportion proprietary.

Table X. Phase-Change Properties after Heating at 200°C for 24 h (Heating/Cooling Rate 3 °C/min)

Phase-Change Material	Solid Component	T_s (°C)		T_p (°C)		ΔT (°C)	ΔH (J/g)	
		Heating	Cooling	Heating	Cooling		Heating	Cooling
2.0 wt.% GA 80 + 98.0 wt.% TP-D	BN 16 vol.%	33.1 ± 1.1	40.5 ± 0.4	41.6 ± 0.6	39.1 ± 0.1	-7.4 ± 1.5	33.0 ± 2.5	-24.7 ± 8.2
2.0 wt.% GA 80 + 98.0 wt.% TP-D	CB 4.0 vol.%	-	-	-	-	-	0	0
T-pcm FSF 52	†	-	-	-	-	-	0	0

BN = boron nitride, CB = carbon black; † proportion proprietary.

Table XI. Phase-Change Cyclability of the Commercial Phase-Change Material Thermagon T-pcm FSF 52

Cycle No.	ΔH (J/g)	
	Heating	Cooling
1	30	-33
2	33	-33
3	33	-32
4	32	-30
5	30	-29
6	27	-29

Table XII. Phase-Change Cyclability of the Antioxidant Phase-Change Material (98 wt.% TP-D, 2 wt.% GA80, 16 vol.% BN)

Cycle No.	ΔH (J/g)	
	Heating	Cooling
1	88	-86
2	89	-86
3	89	-86
4	88	-86
5	88	-86
6	85	-86
7	90	-86
8	89	-86
9	89	-85
10	88	-85
11	88	-85

decreased by the addition of a solid component, since the solid component does not melt and takes up a part of the mass.

Heating at 150°C for 24 h greatly degrades the phase-change properties of commercial PCMs (Table IX). This is mainly because of the poor thermal stability of the matrices in these commercial PCMs (Table II). Moreover, this degradation of the phase-change properties relates to the change in the chemical structure of the matrices of commercial

PCMs upon heating. Although the commercial materials T-pcm 583 and T-pcm HP105 show relatively high thermal stability (Table II), they merely soften upon heating and do not show clear phase-change behavior. This is probably because of the noncrystalline polymers involved. On the other hand, the antioxidant (98.0% of TP-D and 2.0% of GA 80)-based BN PCM showed relatively little effect of heating on the phase-change properties (Table IX and Fig. 6). Even after heating at 200°C for 24 h (Table X), it showed clear phase-change behavior (Table IX). In contrast, the phase-change behavior of the commercial PCMs ceases to exist after heating at 150°C (Table IX) or 200°C (Table X). The ability of the antioxidant (98.0% of TP-D and 2.0% of GA 80)-based BN PCM to retain its phase-change behavior after heating relates to the thermal stability of this material (Tables II and III).

Phase-Change Cyclability

Tables XI and XII show the effect of phase-change cycling on the heat of fusion for a commercial PCM (Thermagon T-pcm FSF 52) and an antioxidant-based PCM (98 wt.% TP-D, 2 wt.% GA80, 16 vol.% BN), respectively. Melting tends to remove the effect of thermal history on the molecular conformation of a PCM, so the values of the heat of fusion (ΔH) obtained during cooling (after melting) are more reliable than those obtained during prior heating. Based on the values obtained during cooling, ΔH is reduced by 12% after six cycles for the commercial PCM and is reduced by only 1% after 11 cycles for the antioxidant-based PCM. The superior phase-change cyclability of the antioxidant-based PCM is consistent with the results in Tables IX and X.

CONCLUSION

Antioxidant-based PCMs, with the antioxidants serving as the matrix and consisting mainly of hydrocarbons with linear segments, are effective as TIMs with high thermal stability. The thermal stability is superior to paraffin wax and commercial PCMs (Laird T-pcm 583, Thermagon T-pcm HP105, Thermagon T-pcm FSF 52, and HeatPath PCM 1052 A011). The combined use of 98.0 wt.% of a

thiopropionate secondary antioxidant (SUMILIZER TP-D) and 2.0 wt.% of a half-hindered phenolic primary antioxidant (GA80) as the matrix and the use of 16 vol.% BN particles as the solid component give a PCM with a 100°C lifetime indicator of 5.3 years, as shown by thermogravimetric analysis, in contrast to 0.95 year or less for the commercial PCMs. This PCM does not crack after heating at 150°C, in contrast to the cracking for some commercial PCMs. The phase-change properties are degraded by heating at 150°C to much smaller degrees than those of the commercial PCMs. The stability of the heat of fusion upon phase-change cycling is also superior.

The heat of fusion of an antioxidant-based PCM is much higher than those of commercial PCMs. The values for the branched antioxidant TP-D tended to be slightly lower than that of wax, but the values for the nonbranched antioxidants TPM and LTDP exceeded that of wax. The undercooling of an antioxidant-based PCM is larger than that of wax or commercial PCMs, in spite of the decrease of the undercooling due to the presence of a solid component. The viscosity of an antioxidant-based PCM is essentially unaffected by heating at 150°C; it is higher than that of wax. The thermal contact conductance of an antioxidant-based PCM is higher than those for the commercial PCMs in the case of rough (12 μm) copper mating surfaces, although it is lower than those for the commercial PCMs in the case of smooth (0.009 μm) copper surfaces.

The use of CB (4.0 vol.% or less) in place of BN gives slightly lower thermal stability and slightly lower thermal contact conductance for the rough case. The lower thermal contact conductance occurs in spite of the lower bond-line thickness for CB.

Compared to the BN antioxidant-based PCM, commercial PCMs give slightly lower values of the thermal contact conductance for the rough case, in spite of the lower values of the bond-line thickness. Commercial PCMs give higher values of the thermal contact conductance for the smooth case, presumably due to the lower values of the bond-line thickness.

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nitride were provided by GE Advanced Ceramics Corporation, Cleveland, OH (Polartherm 180). Commercial phase-change TIMs were provided by Thermagon, Inc.

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