Thermal Conductivity Measurements of Conductive Epoxy Adhesives by MDSC®

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ABSTRACT

Determination of a material's thermal conductivity is important in evaluating its utility for a specific application. A variety of techniques are available to determine thermal conductivity including Modulated DSC®. MDSC® has the advantage of widespread availability due to its use in the study of the glass transition, melting temperature, crystallization, etc. of materials. This study extends the working range of MDSC for the thermal conductivity measurement by a factor of 4 to 4.0 W/(K m) enabling it to be used for conductive epoxy based adhesives.

INTRODUCTION

In the electronics industry epoxy based adhesives or encapsulates are often used to mount devices or protect them from excessive heat buildup. The thermal conductivity of these adhesives is an important characteristic aiding device design to avoid premature failure. Often the desired thermal conductivity is in the range 0.7 to 3.5 W/(K m).

ASTM Method E1952 (1) describes the measurement of thermal conductivity by Modulated DSC®. It is applicable to homogeneous, non-porous solid materials with a thermal conductivity in the limited range of 0.10 to 1.0 W/(K m) and a temperature range from 0 to 90 °C.

In this test, the heat capacities of a thin and thick sample are measured with Modulated DSC (2, 3, 4). When the thin sample is encapsulated in a pan of high thermal conductivity and subjected to a temperature modulation with long period, the sample has a uniform temperature distribution, and the measured specific heat capacity is the thermodynamic heat capacity of the sample. When the thick sample is exposed to a temperature modulation at one end, the measured apparent heat capacity is lower in comparison with the thin sample, because of the non-uniform temperature distribution across the height of the sample. The apparent heat capacity is proportional to the square root of the thermal conductivity of the sample, as shown by equation 1.

$$K = (8\ L\ C^2) / (C_p\ M\ d^2\ P) \quad (1)$$

K is the observed thermal conductivity in W/(K m), C is the apparent heat capacity in mJ/K for the thick sample, C_p is the specific heat capacity in J/(g K) for the thin sample, L is the sample height in mm for the thick sample, M is the thick sample mass in mg, d is the thick sample diameter in mm, and P is the modulation period in s.

Using equation 1 the thermal conductivity of a sample is derived from the heat capacity measured on a thin and thick sample and some geometric and experimental factors. If the thermal conductivity of the sample is low and approaches that of the surrounding purge gas, a correction to the observed thermal conductivity is necessary to compensate for heat loss through the sample side (4).

To obtain a reliable thermal conductivity measurement, the thickness for the thick sample must be sufficiently large that the temperature wave does not penetrate the full length of the sample. To increase the upper thermal conductivity limit, either the sample thickness must be increased or the penetration depth decreased. Typically the sample thickness is limited by the size of the DSC furnace to 3-4 mm (4). The penetration depth is given by (5):

$$d_p = (2\ D / \omega)^{1/2} \quad (2)$$

where d_p is the penetration depth, D is the thermal diffusivity [$= K / (C_p\ \rho)$], ρ is density and ω is angular frequency ($= 2\ \Pi / P$).

According to equation 2 decreasing the period of the modulated measurement decreases the penetration depth. Typically a period of 60-100 s is used (1). The upper thermal conductivity limit of about 1.0 W/(K m) is reached for a sample like Pyrex® glass. For Pyrex the ratio between apparent heat capacity and specific heat capacity, measured with an 80 s modulation period, is about 0.80 (4). For lower thermal conductivity materials like polystyrene this ratio is only about 0.45 (4). This ratio is an indication of the ease with which temperature uniformity is achieved across the sample. Above a ratio of 0.80 the apparent heat capacity approaches too close the specific heat capacity, resulting in an unreliable thermal conductivity determination. By reducing the period from 80 to 20 s the limiting ratio of 0.80 is expected to be reached only at conductivity higher than 1.0 W/(K m), and so the upper thermal conductivity limit is extended.

Recently a new heat flow measurement technique, known as Tzero™ technology, was developed, that greatly improves the modulated measurement (6, 7, 8, 9). This approach is based on a new DSC sensor and the use of a pan corrected four-term heat flow equation. Modulation periods as short as 20 s can readily be used. This DSC technique is explored to extend the range of thermal conductivity currently assessed by Modulated DSC, and to study the thermal conductivity of conductive epoxy based adhesives.

EXPERIMENTAL

The two necessary heat capacity measurements are performed on a TA Instruments Q1000 DSC, equipped with Modulated DSC™ and using the four-term heat flow equation (6). Nitrogen is used as a purge gas. The temperature and enthalpy calibration are performed using indium. The heat capacity calibration is performed with sapphire. The measurements are done at 25 °C, with modulation amplitude of 0.5 °C.

The modulation period is 20 s and the measurements are compared to measurements at 100 and 40 s period.

The specific heat capacity measurements are performed on thin disks, with a thickness of 0.5-0.8 mm and a diameter of 5.20 mm ± 0.05 mm. These samples are placed directly on the DSC sensor, after moistening with silicone oil used to improve the thermal contact between sensor and sample. The sensor on the reference side is moistened as well with the silicone oil. This procedure differs from the original procedure described in (4), where the thin sample is encapsulated in a crimped sample pan.

The apparent heat capacity measurements are performed on right circular cylinders, with smooth and parallel faces. The thickness is between 3.0 and 4.0 mm and the diameter is 5.20 mm ± 0.05 mm. These samples are placed directly on the DSC sensor, after moistening the sample sensor lightly with silicone oil. The reference sensor is equally moistened. This procedure differs from the procedure described in (4), where in between sample and wetted sensor, a thin aluminum disk is placed to ensure a uniform temperature distribution.

RESULTS AND DISCUSSION

Five different conductive epoxy resins are investigated. Heat capacity of a thin and thick sample is measured with MDSC and the thermal conductivity is calculated using equation 1. The results are summarized in Table 1. The influence of different modulation periods is illustrated in Figures 1 and 2.

For the most conductive samples (1 and 2) good agreement is found between the MDSC measurement at 20 s period and other techniques. For these samples at a period of 70-100 s the ratio between apparent and specific heat capacity equals unity; at 20 s it is below 0.80, which seems to be the critical upper limit.

For the intermediate conductive samples (3 and 4) the MDSC result at 20 s period is lower than expected. The ratio between apparent heat capacity and specific heat capacity is in this case about 0.42. This is possibly around a critical lower limit, below which the modulation becomes too fast for the sample to follow. The result at 100 s period is also too low. However in this case C/C_p is far above 0.80 and the result no longer accurate. A 40 s period (C/C_p= 0.65) seems to be a good compromise, and thermal conductivity in good agreement with the other techniques is found.

As expected, low thermal conductivity value is found at 20 s for low conductivity material sample 5. At 100 s the value is higher than measured with other techniques. It should be noted, however, that the correction for heat loss through the sample side, as described in (4), is not taken into account in this study. For the high and intermediate conductive samples this correction is negligible, while for this low conductivity material it is necessary to consider this “shunting” heat flow.

For sample 1 the mean thermal conductivity result from 5 measurements is 3.96 W/(K m) with a standard deviation of 0.32 W/(K m) or 8 %. The relative standard deviation is in good agreement with reference (10), where for lower conductivity materials like PS and PMMA a within laboratory relative standard deviation of 12 % is found.

The thick samples are placed directly on the wetted sensor, without using an aluminum foil in between. In reference (4) aluminum foil is recommended to distribute the heat more evenly over the sample area, since the sample diameter is somewhat larger than the sensor diameter. In the present study, where better conducting samples are

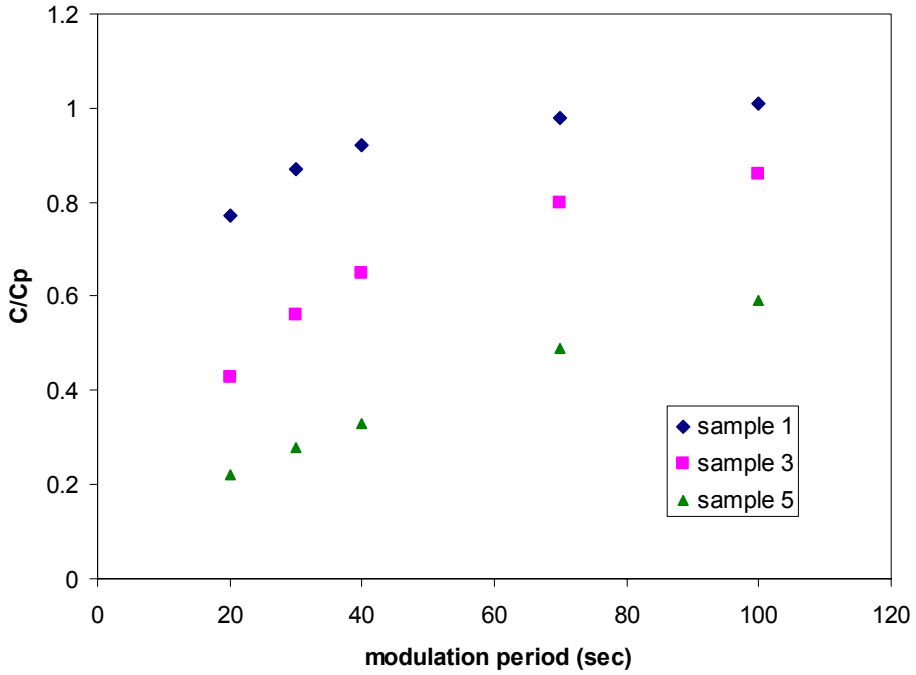

Figure 1 – Ratio of the Apparent heat Capacity © to the Specific Heat capacity (C_p) Versus Modulation Period for Different Samples

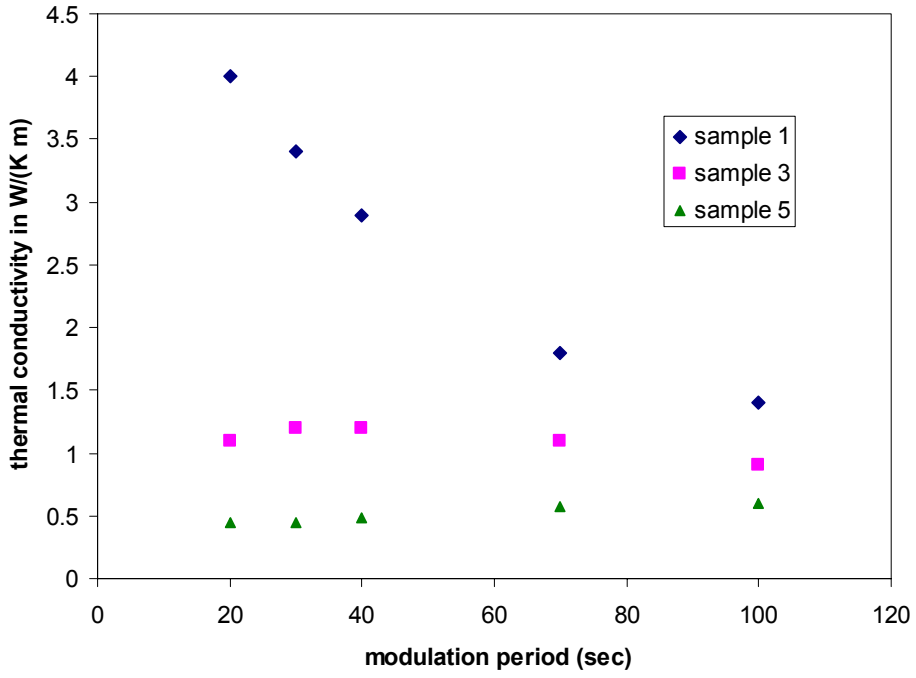

Figure 2 – Thermal Conductivity Versus Modulation Period for Different Samples

Table 1 -Thermal Conductivity of Various Conductive Epoxy Resins Measured with MDSC®. Influence of modulation period on the result. Comparison with results obtained by other techniques (laser flash technique, hot disk method). C_p is the specific heat capacity measured on the thin sample, C is the apparent heat capacity measured on the thick sample.

				Thermal conductivity in W/(K m)	
Sample	Period in s	C_p in J/(g K)	Ratio C/C_p	MDSC	Other techniques
1	20	0.42	0.77	4.0	3.8-3.9
	30		0.87	3.4	
	40		0.92	2.9	
	70		1.0	1.8	
	100		1.0	1.4	
2	20	0.48	0.67	2.6	2.5-2.7
3	20	0.95	0.43	1.1	1.2-1.4
	30		0.56	1.2	
	40		0.65	1.2	
	70		0.80	1.1	
	100		0.86	0.88	
4	20	0.92	0.42	0.98	1.2-1.4
	40		0.65	1.2	
	100		0.91	0.95	
5	20	1.10	0.21	0.44	0.5
	30		0.28	0.45	
	40		0.33	0.48	
	70		0.49	0.57	
	100		0.60	0.60	

investigated, it is found that the use of the aluminum disk is superfluous. Moreover, omitting it increases the reproducibility of the results. Similarly, the heat capacity measurements on these better conducting samples are done without pans. The silicone oil contributes almost nothing to the specific heat capacity measurement of the thin samples. assuming an imbalance of 0.1 mg silicone oil on sample versus reference side, would lead to a contribution to the sample C_p of less than 1 % (C_p of the silicone oil is 1.64 J/(g K)). Not using the silicone oil reduces the reproducibility of the results far more. The specific heat capacity measured in this way is almost independent of the modulation period. The largest difference on C_p found for the various samples using a modulation period of 100 s versus 20 s is less than 3 %.

CONCLUSION

By decreasing the period of the modulation to 20 s, the upper limit for the thermal conductivity measured is extended to 4 W/(m K), a fourfold increase over earlier uses. Using this method it is possible to measure accurately the thermal conductivity of conductive epoxy based adhesives for the electronic industry.

REFERENCES

1. E1952, "Method for Thermal Conductivity and Thermal Diffusivity by Modulated Temperature Differential Scanning Calorimetry", ASTM International, West Conshohocken, PA.
2. S.M. Marcus and R.L. Blaine, "Thermal Conductivity of Polymers, Glasses and Ceramics by Modulated DSC", *Thermochimica Acta*, **1994**, 243, pp. 231-239.
3. R.L. Blaine and S.M. Marcus, "Derivation of Temperature Modulated DSC Thermal Conductivity Equations", *Journal of Thermal Analysis*, **1998**, 54, pp. 467-476.
4. S.M. Marcus and R.L. Blaine, "Thermal Conductivity of Polymers, Glasses and Ceramics by Modulated DSC", TA Instruments TA086.
5. Kittel and Kroemer, *Thermal Physics*, 2nd Edition, pp. 424-427.
6. R.L. Danley, "New Modulated DSC Measurement Technique", *Thermochimica Acta*, **2003**, 402/1-2, pp. 91-98.
7. R.L. Danley and P.A. Caulfield, "DSC Baseline Improvements Obtained by a New Heat Flow Measurement Technique", *Proceedings of the 29th Conference of the North American Thermal Analysis Society,* **2001**, pp. 667-672.
8. R.L. Danley and P.A. Caulfield, "DSC Resolution and Dynamic Response Improvement Obtained by a New Heat Flow Measurement Technique". *Proceedings 29th Conference of the North American Thermal Analysis Society,* **2001**, pp. 673-678.
9. L.C. Thomas, "Practical Benefits of Using Heat Capacity Versus Heat Flow Signals", *Proceedings of the 29th Conference of the North American Thermal Analysis Society,* **2001**, pp. 818-823.
10. R.L. Blaine and R.B. Cassel, "Precision and Bias of the ASTM Test E1952 for Thermal Conductivity by Modulated Temperature DSC", TA Instruments TA265.

KEYWORDS

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