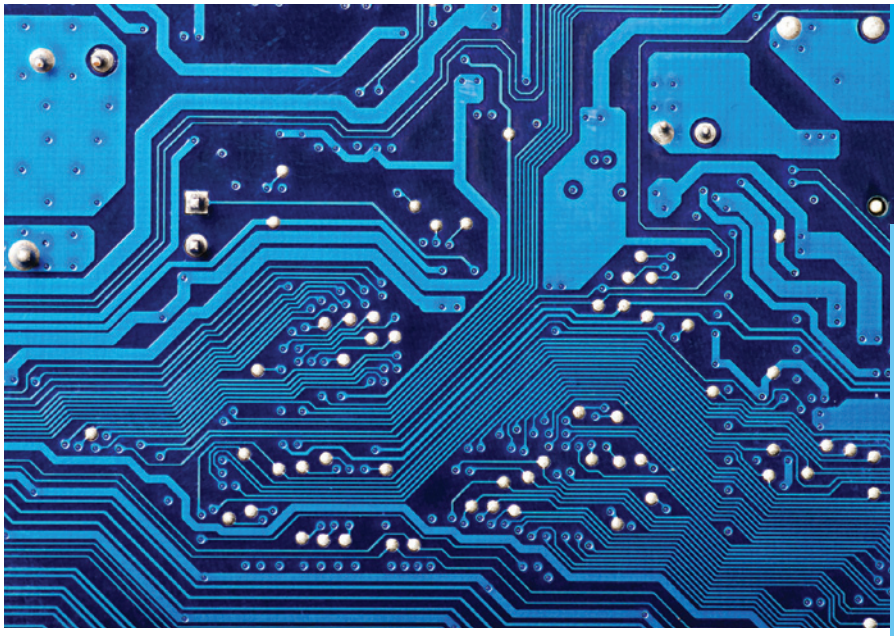

APPLICATION NOTE

Thermal Analysis

Characterization of Electronic Materials Using Thermal Analysis

Thermal analysis comprises a series of powerful techniques for the characterization of the thermal, physical, mechanical and degradation properties of materials. One valuable application of thermal analysis is for the characterization of electronic materials and components, including printed circuit boards (PCB) and encapsulants.

Thermal analysis can help address the following key properties of electronic materials:

- Softening temperature or Tg
- Heats of cure
- Degree of cure
- Onset of cure
- Maximum rate of cure
- Completion of cure
- Compositional analysis (thermoset and fiberglass)
- Onset of degradation
- Dimensional stabilities
- Coefficients of thermal expansion
- Stress relief
- Modulus (stiffness) properties
- Damping or energy absorbing characteristics

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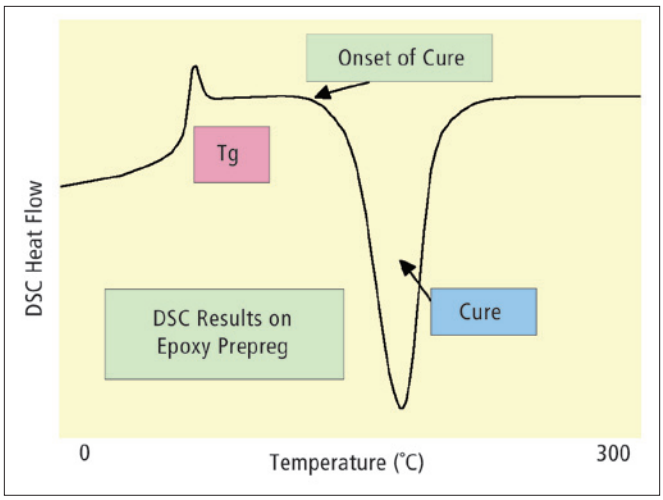
In the manufacture of printed circuit boards or flip-chip packaging, the issue of cure of the epoxy matrix and the dimensional characteristics of the epoxy-based materials becomes critical. It is essential to ensure that the degree of cure obtained by the epoxy materials is sufficiently high enough to ensure good stability and that the cure times are sufficiently rapid so that the processing time can be significantly reduced, thus providing a cost-savings.

DSC

Differential scanning calorimetry (DSC) measures heat flow into or from a sample under heating, cooling or isothermal conditions. The following DSC scan shows the results obtained from an epoxy-fiberglass prepreg used to produce PCB's.



The DSC results, obtained at a heating rate of 20 °C/min, show that the Tg or softening of the epoxy prepreg material occurs at 60 °C. With further heating, the epoxy resin undergoes cure and crosslinking and this is observed as a large exothermic peak with a peak temperature of 160 °C. The peak temperature is equivalent to the point at which the resin achieves its maximum rate of cure.

DSC can be used to establish the degree of cure achieved by an epoxy resin or a PCB using the following two means:

- Tg
- Residual heat of cure

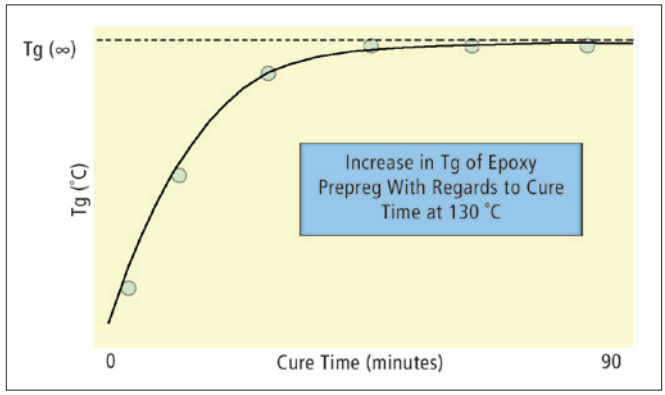
As an epoxy resin goes to a higher crosslink density or greater degree of cure, its Tg increases to a maximum value, Tg(∞). The following figure shows the increase in Tg of an epoxy resin with regards to degree of cure. The values of the glass transition temperature reach a plateau, which is Tg(∞), indicative of nearly complete crosslinking.

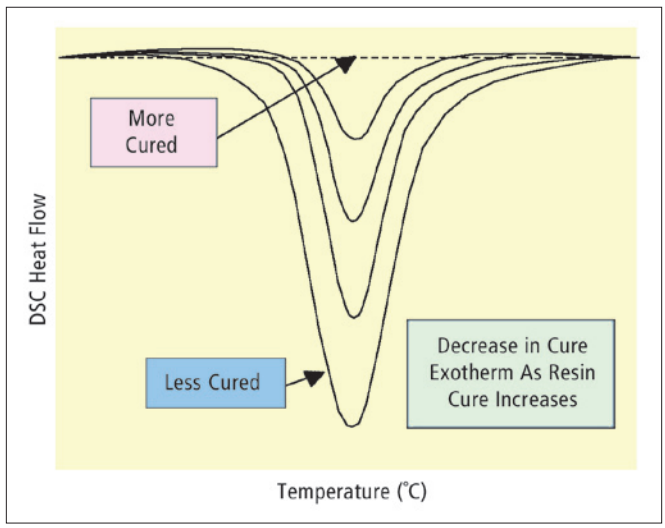
DSC can also be used to examine epoxy materials for completion of cure based upon the occurrence of a residual curing exothermic peak. If no peak is observed, then the resin system is nearly completely cured or crosslinked. The following DSC curves show how the cure exothermic peak of an epoxy resin becomes smaller as the degree of cure increases. At high levels of cure, the exothermic peak can no longer be detected.

The heat of cure measured on epoxy material can be used to assess the percent cure. The following simple equation provides this information:

$$\% \text{ Cure} = [\Delta H \text{ uncured} - \Delta H \text{ sample}] / [\Delta H \text{ uncured}] \bullet 100\%$$

In this equation, ΔH uncured is the heat of cure (J/g) of the unreacted resin or prepreg and ΔH sample is that of the actual test specimen or material.



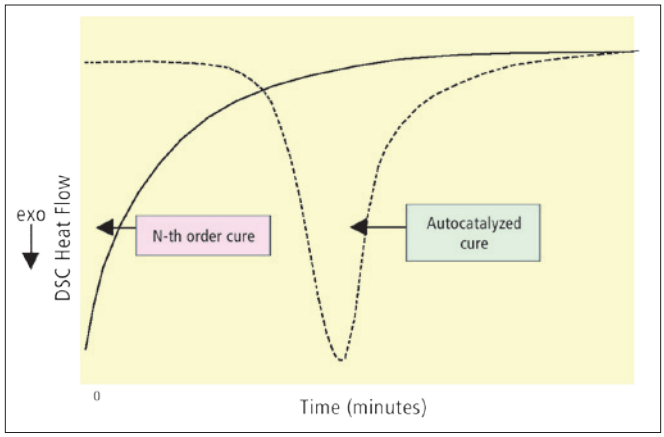


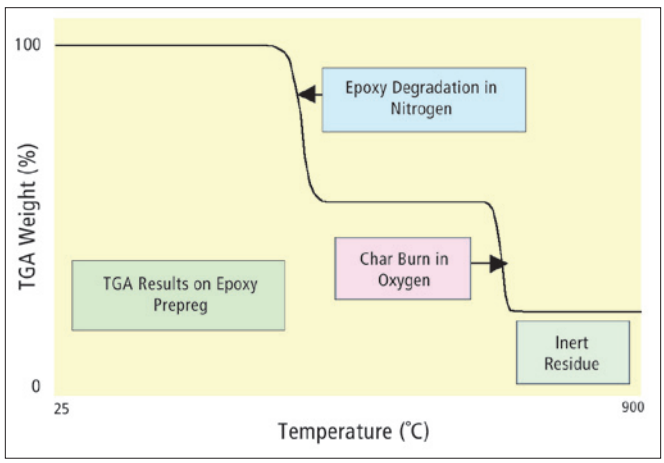
For electronic materials, the cure associated with an epoxy thermosetting resin may follow two distinctly different reaction mechanisms:

- N-th order
- Autocatalyzed

Autocatalyzed epoxy resins require the development or build-up of an intermediate component which then catalyzes the main curing reaction. N-th order epoxy resins will react immediately when the temperature is suitably high enough to allow the curing reaction to proceed. It is important to know which of the two reaction mechanisms an epoxy resin will follow, as this will affect the cure and processing conditions. Generally, standard heating DSC experiments will not be able to make obvious distinctions between epoxy resins as to whether they follow n-th order or autocatalyzed reaction kinetics. However, an isothermal DSC experiment will be able to conclusively make this determination between n-th order or autocatalyzed kinetics.

The following DSC results represent the isothermal curing of two epoxy resins one of which follows an n-th order reaction and one which follows an autocatalyzed mechanism.

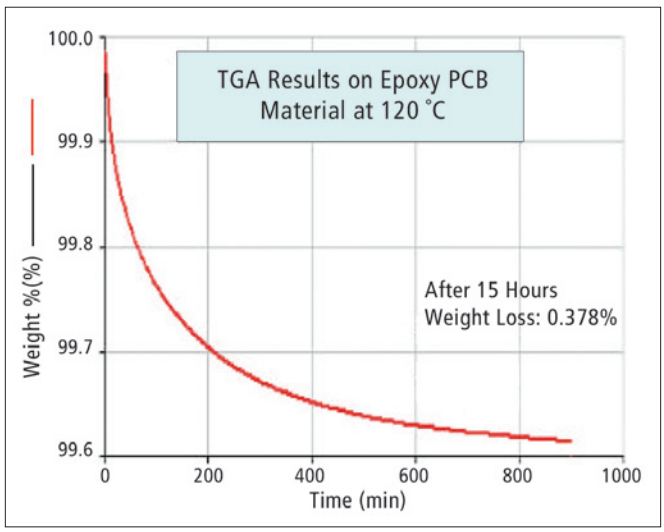




These results show that the autocatalyzed resin achieves its peak maximum at several minutes into the isothermal hold period. This reflects the time required to develop the internal catalyst to allow the main cure reaction to proceed. In contrast, the n-th order epoxy resin has its peak maximum at time = 0. This means that the maximum rate of cure, for n-th order epoxy resins, reaches its maximum rate right at the start of the isothermal holding period.

In order to best establish the isothermal cure of epoxy resins used for electronic purposes, and make the clear distinction between resins following n-th order or autocatalyzed reaction, it is absolutely essential to have a DSC instrument which can heat the resin very quickly (i.e., 500 °C/min) and equilibrate rapidly at the desired isothermal temperature. The PerkinElmer power compensated DSC meets both of these criteria with the use of very low mass (1 g) and separate furnaces for the sample and reference sides. This DSC is able to heat the uncured resin or prepreg sample from room temperature to the desired isothermal cure temperature at a controlled heating rate of 500 °C/min. The instrument then quickly equilibrates once the isothermal target temperature is reached and the peak maximum, even for n-th order resins, is obtained.

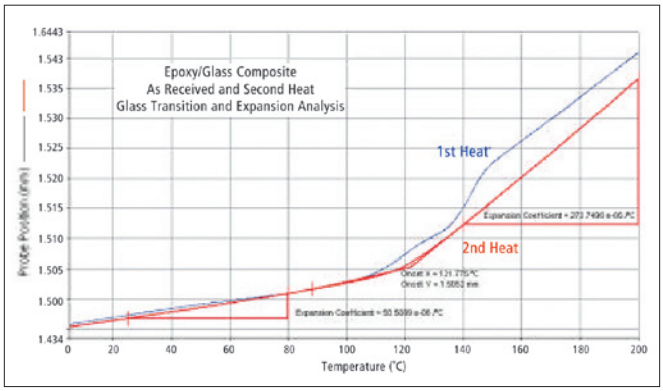
In contrast, the large mass heat flux DSC instruments (furnace mass of 200 g), cannot heat or thermally equilibrate quickly. With these thermally sluggish DSC devices, the only way that isothermal cure studies can be performed is to pre-heat the DSC cell to the target temperature, manually open the hot cell, and then drop the sample into the DSC, close the cell and then allow the DSC to reequilibrate before data is acquired. This results in lost data when attempting to study isothermal cures of epoxy resins or prepregs by heat flux DSC instruments. No valuable data is lost with the power compensated DSC.

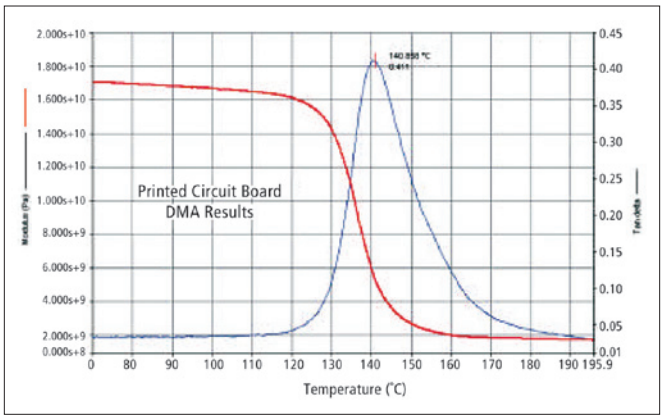


TGA

Thermogravimetric analysis (TGA) is used to measure sample mass losses and decomposition temperatures under heating or isothermal conditions. To control and/or reduce the expansion rates of PCB's or encapsulants, inert materials, such as fiberglass or silica, is added to the epoxy resins. It is essential to know the level of epoxy and filler in a prepreg or compound as this compositional information will have a major effect on the end-use characteristics of the material.

The following TGA results are those obtained on an epoxy – fiberglass prepreg material used to generate printed circuit boards. The sample was analyzed in nitrogen up to 700 ˚C and then in oxygen to burn off any carbon char to leave behind the inert residue (fiberglass).





From these results, the total epoxy content (weight losses in nitrogen and oxygen) are found to be 67.0% and the inert fiberglass residue content is 33.0%. The onset temperature of epoxy degradation gives an indication as to its thermal stability. Higher decomposition temperatures generally translate into better stabilities.

The high sensitivity PerkinElmer TGA instrument can be used to assess the very small weight losses associated with the epoxy prepregs used to generate PCB's. It is desired to have a low volatiles loss during cure to reduced the occurrence of voiding in PCB's as well as encapsulants. The following results show the TGA mass loss at 120 ˚C for an epoxy resin under isothermal conditions.

The TGA results show that the epoxy material loses only 0.367% of its mass. The low generation of volatiles indicates that the resin will have a low propensity for voiding during processing. The outstanding performance of the PerkinElmer TGA permits the high sensitivity measurements to be performed.

TMA

Thermomechanical analysis (TMA) measures the dimensional properties (expansion, penetration, coefficients of thermal expansion) of materials while heating, cooling or under isothermal conditions. TMA is particularly useful for the electronics industry as it helps to ensure that individual components can be produced which have nearly identical coefficients of thermal expansion. This helps to reduce the occurrence of thermal stresses, which can adversely affect the integrity of the printed circuit board or flip-chip packaging. The build-up of significant thermal stresses and significantly shorten the lifetime of the component.

The figure below shows TMA results in the expansion mode obtained on an epoxy PCB. The plot shows the % length (expansion) versus temperature. The sample was analyzed as received (1st heat), cooled back to the starting temperature, and then reheated (2nd heat).

During the 1st heating segment, the PCB exhibits stress relief as the temperature reaches the Tg of the epoxy matrix. The stresses are a result of processing and are frozen into the material as it cools down below its Tg. The stress relief is manifested as a non-linear response in the sample's expansion response above Tg. During the first heating, the stress factors are dissipated and are no longer observed during the second heating segment. A simple change in the expansion rate is observed during the 2nd heat and the onset temperature reflects the Tg of the epoxy matrix. For this PCB, the Tg is found to be 121.7 ˚C.

From the TMA expansion results, the coefficient of thermal expansion (CTE) can be assessed below and above Tg. The coefficient of thermal expansion is defined as:

$$CTE = \Delta L / [\Delta T \bullet Lo]$$

where $\Delta L/\Delta T$ is the measured change in expansion over a temperature interval (mm/˚C) and Lo is the sample's original thickness (mm).

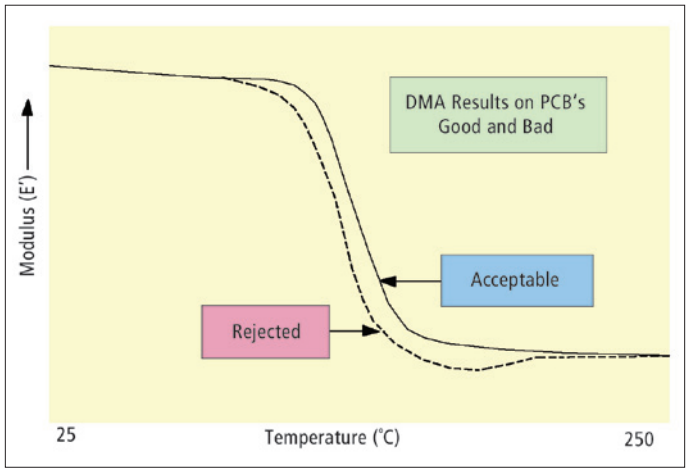
In the TMA results for the epoxy fiberglass PCB, it was found that the value of the CTE below Tg was 5.05 10^{-5}/° while above the glass transition, it was significantly higher with a value of 2.71 10^{-4}/°. The values of the CTE are critical for electronic applications to ensure that the PCB or the components in the PCB or in flip-chip packaging have proper and matching expansion levels. If there is a mismatch between CTE's, thermal stresses can result during operation and this can significantly decrease the integrity of the electronic component.

DMA

Dynamic mechanical analysis (DMA) measures the viscoelastic properties of materials as a function of temperature (heating, cooling or isothermal) and as a function of frequency. DMA is used to measure a material's storage modulus (stiffness) and loss modulus (energy absorption or damping) over a temperature range. In terms of assessing a sample's Tg and the completeness of cure, DMA is the most sensitive of the thermal analysis techniques.

For electronic components, it is desired to know the values of the storage modulus, E', over the temperature range of operation. For PCB's and underfill materials, it is generally desired to have a high value of the modulus as this helps to effectively distribute thermal stresses.

Shown in the example below are the DMA results obtained on an epoxy-fiberglass PCB. The plot shows the storage modulus (E') and tan delta (E"/E') as a function of sample temperature at a frequency of 1.00 Hz using the 3-point bending mode of deformation.



The glass transition of the epoxy matrix is observed as a large drop in the storage modulus and a peak in the tan delta response at 141 °C. These results indicate that the PCB is fully cured as no increase is observed in the E' response above Tg. If the epoxy matrix was slightly under-cured, an increase would be obtained in the storage modulus response above Tg reflective of additional or residual crosslinking.

The residual crosslinking of an unacceptable PCB is displayed in the figure below showing DMA storage modulus results on 'good' and 'bad' epoxy-fiberglass composites.

The rejected PCB was slightly uncured and had a significantly lower Tg than the acceptable, more crosslinked material. Also, the undercured epoxy-fiberglass composite exhibited an increase in its modulus response above Tg, which indicates additional crosslinking.

Summary

Thermal analysis comprises a series of techniques (DSC, TGA, TMA and DMA) for the complete characterization of electronic materials. Valuable information can be obtained on such properties as: softening or Tg, completeness of cure, degree of cure, rate of cure, compositional analysis, degradation temperatures for stability assessment, expansivities, coefficients of thermal expansion, modulus (stiffness) and damping properties.

PerkinElmer offers a complete line of state-of-the-art thermal analysis instruments (DSC, TGA, TMA and DMA) for the analysis and characterization of the critical thermal, physical, degradation and mechanical properties of electronic materials. The results are highly useful for research and development as well as quality assurance applications.

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