

The Search for an IDEAL LEAD-FREE LAMINATE

To make a wise decision, you'll have to understand the fundamental thermal properties of materials.

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Concerns arising from the proposed use of lead-free solder systems have resulted in a flurry of activity devoted to defining and promoting the optimum material for use at higher solder and reflow temperatures. Some propose developing an IPC slash sheet that defines a material in terms of its Tg, Td and T288 and T300 test results; the material would be a good candidate for "green solderability" if it met those criteria.

To date no one set of proposed material specifications has been accepted as adequately defining a lead-free compatible material, and for good reason – there is no assurance that a set of properties that characterize one or more materials that prove acceptable will necessarily be inclusive of other materials with very different properties.

We will try to define some of the important thermal characteristics of laminate materials and show how they do or don't relate to one another and to lead-free solder. Perhaps by pointing to some hard science we can give our readers a basis on which to start selecting materials appropriate not only for processing with lead-free solders, but that are also right for their intended end-use application.

There is considerable confusion about what determines the suitability of a given laminate material for its manufacture and application in terms of its thermal properties. We will look at several commonly considered thermal material

characteristics:

1. Tg – Glass transition temperature (°C)
2. Td – Thermal decomposition temperature (°C)
3. Continuous operating temperature (°C), (Underwriters Laboratories' RTI, or relative thermal index, is an example.)

Of these, glass transition temperature and thermal decomposition temperature are at least reasonably easily defined and explained in terms of hard science. But continuous operating temperature is as much a function of the application and use conditions as of any specific properties of the laminate material (and specifically the resin system), despite the ability to define a relative thermal index for each material.

To serve as examples of Tg vs. decomposition temperature, let me cite several examples in **TABLE 1**.

The Tg is related to the molecular free volume of a polymer system and, in simple terms, it is a relative measure of the ability of the atoms within the system to move relative to one another when heated. There is a point during the heating process at which the energy is such that the amount of molecular movement increases significantly, resulting in changes in physical properties of the material. In the case of Tg measured by thermomechanical analysis (TMA), it is the point at which there is an increase in Z-direction coefficient of thermal expansion (expressed in ppm/°C). See **FIGURE 1**. This measure of Tg relates to the reliability of plated through-holes on a PCB. The higher the Tg, all other things being equal, the lower the total Z-direction expansion during each thermal cycle it goes through, whether in fabrication or in use.

The use of differential scanning calorimetry (DSC) to determine Tg is based on precision measurement of heat flow in the material (see **FIGURE 2**). When a material goes through its Tg, the curve will show a deflection as the rate of heat absorbed by the material changes. This curve is from a high-Tg epoxy system with a Tg by DSC of about 174°C. Purists will say that DSC is the most accurate way to determine Tg because change in heat flow is a direct indication of a change in free molecular volume, which is the actual change in the material that affects secondary properties such as expansion coefficients and flexural strength. It is normal for a Tg taken by DSC to be about 5°C higher than it would be if taken by TMA. Other measurement methods such as dynamic mechanical analysis (DMA), which measures the stiffness of

TABLE 1. Typical properties of various resin systems

PRODUCT	Tg (TMA)	DECOMP.	TOTAL TMA EXPANSION ¹
FR-4 (tetrafunctional mod)	140°C	295°C ²	2.7%
Multifunctional epoxy	170°C	295°C	2.2%
Polyimide (UL 94 V1)	250°C	361°C	1.1%
Polyimide (UL 94 HB)	250°C	385°C	1.1%
Crosslinked styrene/diene	100°C	395°C	3.0%
Triazine modified epoxy	220°C	310°C	1.7%
Polytetrafluoroethylene	Subambient	>440°C	3.4%
"Green" epoxy (UL 94 V0)	160°C	310°C	2.0%

¹From room temperature 25°C to 250°C, assumes CTEz is 50-55 ppm/°C below the Tg and about 175 ppm/°C above Tg for all resin systems (which is within +/- 5 ppm/°C)

²Decomposition temperatures listed are based on the onset of thermal decomposition and not the 5% weight loss determination commonly referenced elsewhere, for reasons explained later.

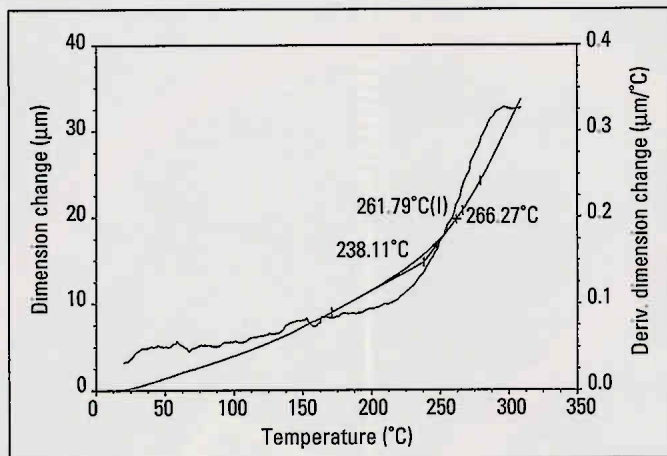


FIGURE 1. Tg by thermomechanical analysis (TMA).

a material in torsion, have also been used to determine Tg. In each case a slightly different derivative mechanical property is used to make the determination.

The decomposition temperature is related to the chemistry of the system. Every chemical bond in a molecule has an associated activation energy at which point it will break, or “cleave.” Thermal decomposition will occur when the temperature reaches the point at which this decomposition proceeds at a significant rate. This is determined by thermogravimetric analysis (TGA) and looks at the change (loss) of weight of the material as the temperature is increased (see FIGURE 3).

An important consideration must be mentioned here: how we determine the Td from Table 1. We select a point in the beginning of the deflection in the curve indicating sustained thermal decomposition. There is a widespread tendency to use as the Td the point at which a material has already lost 5% of its weight by thermal decomposition, and while this will add anywhere from 25 to 40°C to the apparent Td value, it is deceptive when trying to apply the value in a practical setting. By the time a material decomposes to that extent the PCB will be badly blistered or charred and will be well beyond the point of functioning. The values indicated in this paper reflect Arlon’s historically more conservative approach to Td.

Note that multifunctional epoxy has a decomposition temperature of 295°C (563°F) and polyimide materials, with much more stable molecular structures, have decomposition temper-

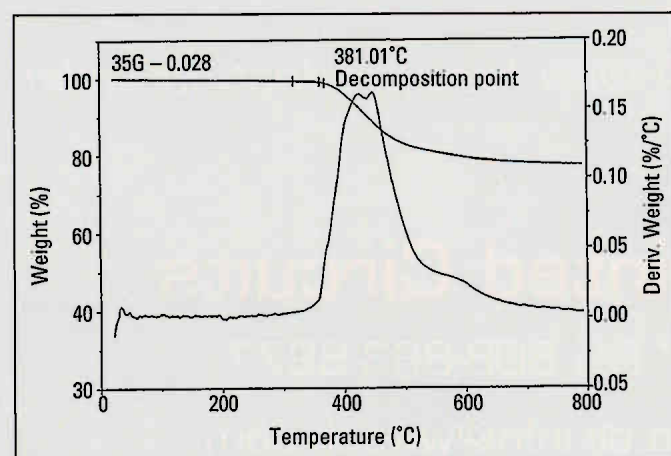


FIGURE 3. Td by thermogravimetric analysis (TGA).

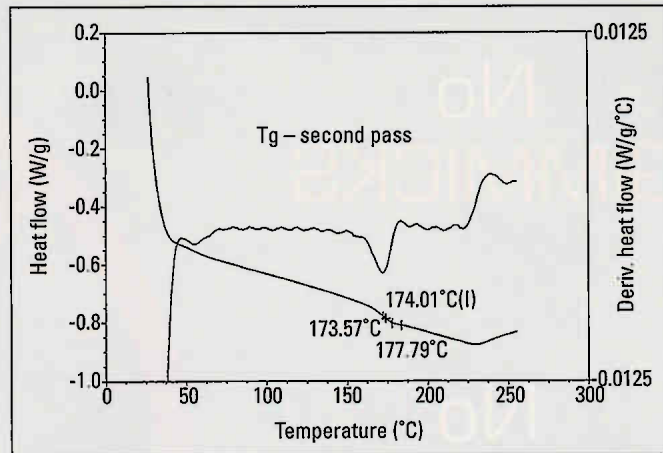


FIGURE 2. Tg by differential scanning calorimeter (DSC).

atures of 361°C and 385°C respectively, while the much lower Tg crosslinked olefin product has a decomposition temperature of 395°C. The assumption has always been that Tg and decomposition temperature more or less track one another. So what explains these somewhat unexpected differences?

The epoxy product is a conventional multifunctional system with a flame-retardant system based on bromine atoms included in the molecular structure of the system. The carbon-bromine bond in an epoxy molecule is relatively weak and determines the decomposition temperature of the system. The polyimide materials listed in Table 1 differ in that one of them contains a flame-retardant system (a much more stable bromine-containing system than the epoxy) and one does not. In addition, the aromatic structure of the polyimide provides more rigidity (less molecular motion) and better thermal stability since energy delocalizes somewhat in an aromatic ring structure. The flame-retardant polyimide system has the lower decomposition temperature (361°C), while the system with no flame-retardant additive has the higher decomposition temperature (385°C) because the flame retardant decomposes more readily than the polyimide polymer itself.

But despite this, their Tgs are the same. The crosslinked styrene/diene copolymer product cited is also non-flame-retardant, but has an inherently stable molecular chemistry brought about by its linear hydrocarbon chains, even though it does have a high molecular free volume that results in a lower Tg.

More complicated is trying to establish a so-called continuous operating temperature, which is not a definable material property. Rather it depends on the continuous operating temperature of the system, the rate of surface oxidation of the polymer (a chemical reaction not necessarily related to Tg or decomposition temperature) and the number of thermal cycles the material sees in its service life. Plated through-holes are gradually work-hardened by physical expansion and contraction, and can embrittle and fail even if the polymeric material itself is not damaged by the temperature extremes.

UL tests physical properties of laminate materials and has established a guideline temperature (see FIGURE 4) called the relative thermal index. Separate indices are established for physical and electrical properties since different failure mechanisms are involved. These represent an estimate of the temperature at which a material could operate 100,000 hours

and only lose 50% of the original value of the measured property (i.e., tensile strength as a physical property and voltage breakdown as an electrical property). Typically the failure rate doubles for every 10°C, since in most instances the failure mechanism is related to oxidation. Figure 4 shows how that index is derived, and how someone could interpolate to estimate relative service life at various temperatures.

It is difficult to say precisely what temperatures materials must withstand during lead-free soldering and reflow. But by looking at the melt point (more accurately the melt range for some alloys) and reflow temperatures of conventional tin-lead solder compared to some of the “solution set” of solder alloys that are in use or proposed, we can see where the different laminate materials fit. **TABLE 2** lists some of the common lead-free solder alloys comparing them to conventional tin-lead.

The most immediate and intuitively obvious observation is that at Arlon’s conservatively determined Td of 295°C, even a standard tetrafunctional modified or multifunctional epoxy system will not normally be exposed to its decomposition temperature during soldering and reflow operations, while other higher Td materials will be even further out of range. That will inevitably lead to the question, “Why not just use cheap FR-4?” Beside the concern that repeated exposure to high temperatures above the Tg may result in pad lifting and even board warpage due to softening of the epoxy system, there is a real concern that the higher temperatures of lead-free solders, which will result in an increase in the overall Z-direction expansion, will increase the risk of plated through-hole copper cracking or the development of latent defects in hole plating which will fail in subsequent service.

Although some end-users (in particular military houses) require materials to withstand a brief solder simulation test as high as 350°C to simulate field conditions with an out-of-control soldering iron, this would have been a test of seconds rather than minutes. It is notable that polyimide with a Td of 361°C, right at the edge of decomposition temperature, so to speak, always passed that test repeatedly and without report-

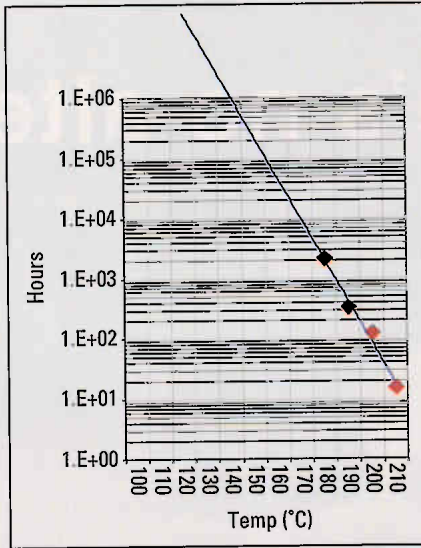


FIGURE 4. Determining relative thermal index (UL method).

a scramble to get that done as quickly as possible.

Conclusions

Tg and Td are not necessarily directly related or even correlated to one another. For instance PTFE, whose Tg, if it even exists is at a subambient temperature, has a Td of over 440°C. But a crosslinked styrene/diene copolymer with a Tg of just over 100°C has a Td of 395°C – higher than polyimides with Tg of 250°C and Td of 361-385°C.

The impact of thermal decomposition temperature is largely going to relate to the effect of sustained exposure to high temperature in use. In virtually all cases soldering temperatures will be below the Td and not be sustained long enough to cause significant decomposition.

Multifunctional epoxy systems with Tg of 160-170°C and Td of almost 300°C will be suitable for most “low-temperature” lead-free solder systems. For larger and thicker PCBs, or if higher-temperature lead-free solders are used, where there may be concern about stress on plated through-holes, polyimide (with its Tg of 250°C) is a proven commodity for both manufacturability and application use-temperature survivability, and a modified epoxy with a high Tg (200°C or more) can also be considered as a cost-performance compromise.

The selection of the right material for any application is not just a matter of “reading the data sheets” and picking materials with the highest (or “best”) values of a predetermined set of variables. It necessitates defining the requirements of the material for the application, then establishing what additional stresses are generated by the manufacturing process and narrowing the material choices accordingly and in that order. Our advice to designers is to always work with your material suppliers and with knowledgeable PCB fabricators at the earliest stages of design so that the material is an integral part of the design process. **PCDEM**

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TABLE 2. Commonly used lead-free solder alloys vs. standard tin-lead

SOLDER ALLOY	MELT TEMP.	REFLOW RANGE	INDUSTRY/APPLICATION
Tin-Lead	183°C	200-235°C	Historic standard
Tin-Silver-Copper	217°C	230-250°C	Telecom, automotive
Tin-Silver-Bismuth	206-213°C	225-240°C	Military, aerospace
Tin-Copper	227°C	230-260°C	Telecon, consumer
Tin-Zinc	198.5°C	215-230°C	Consumer

Data courtesy of IPC Lead-Free forum at http://leadfree.ips.org/LF_4-1-1.htm. Reflow Ranges estimated.