The Challenges of Higher Temperature Lead Free Process -- An Introduction to Laminates with Higher Heat Resistance and Reliability

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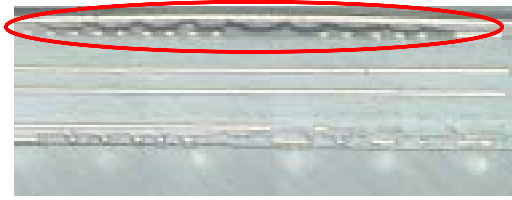
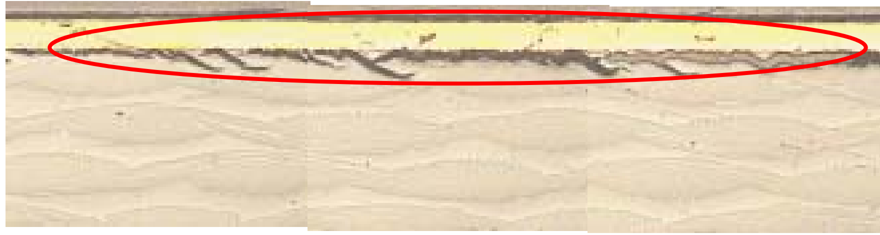
1. Preface

As the environmental consciousness in the world runs high, "Directive of the European Parliament and of the Council on the Restriction of the Use of Certain Hazardous Substasnces" (RoHS) of European Union has required to restrict the use of lead (Pb), cadmium (Cd), mercury (Hg), hexavalent-chromium (Cr^{+6}) compounds, polybrominated biphenyl (PBB), and polybrominated diphenyl ether (PBDE) from July 1st, 2006. Therefore the tin-lead (SnPb) in solders for assembly used in the past must be migrated to the lead-free alloy solders. The melting point, tin-solder temperature, and wave soldering temperature of lead-free solder are more than 20 ~ 30℃ higher than those of traditional tin-lead solder. In addition, the lead free solder is less adhesive to tin, most assembly houses may consider to raise the temperature in solder to improve manufacturability and improve the throughput. Higher operating temperature and longer cycle are serious impacts to the heat-resistance for traditional FR4 material. Hence, the back-end assemblers reported abnormal deleamination sporadically, undoubtedly, it claimed a new era of technology of high heat-resistance materials.

(1) Delamination

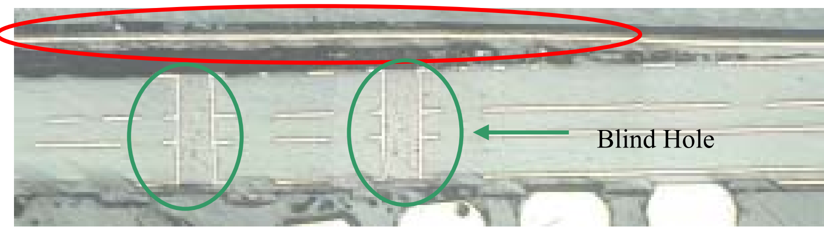


(2) Crack of thick copper clad



Crack happened under 3oz copper after HASL

(3) HDI crack



The old idea that high-Tg is equivalent to high heat-resistance is no longer true in a lead free era. Instead, characteristics such as the temperature of decomposition (Td), time to deleamination by TMA (T-260/T-288), coefficient of thermal expansion (CTE), etc., are major indices referenced by the PCB industry in choosing the high heat-resistance laminate materials. Among them PN-cured laminate materials is the most favorable, mainly because the resin of PN-cured laminate materials has more aromatic structure, which has relatively lower water absorption and better heat resistance: Td > 350℃、T-288 > 15min、and CTE value on total expansion <4%. In addition, consider from the cost, it can also be improved based on dicy-cured FR4 to make its price and manufacturability close to those of currently

used ordinary FR4, and it can be applied to 10LB↓ design, hence another option besides PN-cured laminate materials.

2. Impact of higher temperature lead free process on laminate

From the comparison of IR reflow temperature curve of the traditional SnPb solder and lead free solder of Fig. 1, most assembly houses raise the lead free process temperature by 20 ~ 30℃, and increase its process time. Higher temperature with heated for longer time impact on the laminate. Therefore the old idea that high-Tg is equivalent to high heat-resistance is challenged severely while plate warpage, and delamination happened almost everywhere. The following is a portrait of typical destruction model for laminate material in a higher temperature lead free process.

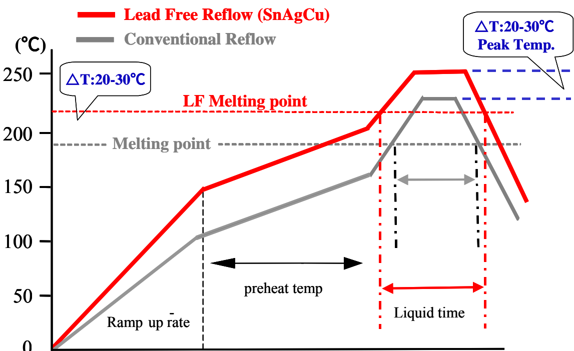
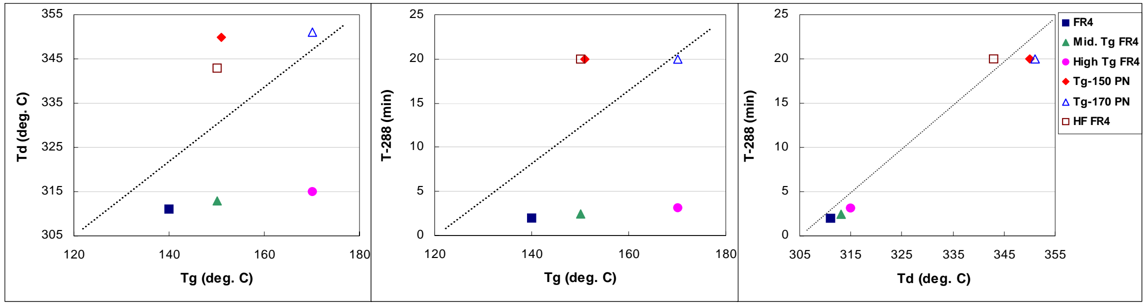


Figure 1 Comparison of IR Reflow Temp. Profile: traditional SnPb solder vs. lead free solder

3. Choosing the high heat-resistance, high-reliability laminate materials

For the traditional SnPb solder process, the industry benchmark of the laminate heat resistance is aligned to Tg of hardened resin laminates because high Tg material is superior to low Tg material in its heat-resistance, chemical resistance, and mechanical strength. While we are entering into the lead free solder era, are above-mentioned views still suitable? The following are clarification and discussion to these points. Fig. 2 shows comparison of Tg, Td and T-288 laminate heat resistance in the test. As is shown in the picture, when Tg increases, Td and T-288 do not increase linearly with it. In addition, we find from the picture that Td and T-288 tests are in consistence with each other. So in the era of high-temperature lead free process, Tg does not fully represent laminate heat-resistance instead, Td value is more representative in showing whether the laminate can stand the high heat.

In addition, the electronic product is getting lighter, thinner, shorter, and smaller, whereas PCB layer count is getting higher and higher, wires are getting thinner and denser in circuit, requirement in reliability is relative higher also. There was view that high Tg laminate had lower CTE in the past, but this is not all correct; as shown in Fig. 3, high Tg material has lower expanding rate, if the laminate itself has low CTE characteristic, its expanding rate is obviously lower than those of the same Tg. So, in higher layer count and higher density circuit design, the inflation rate of the laminate can't be ignored.



(a) Tg vs. Td- no linear relation (b) Tg vs. T-288- no linear relation (c) Td vs. T-288- linear relation

Figure 2 Relation between Tg、Td and T-288

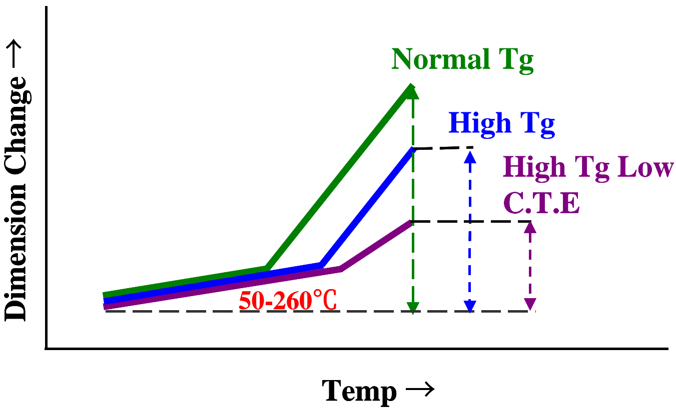


Figure 3 Impact of Tg and CTE values on the total expansion

In dealing with high layer count, high reliability, high-temperature lead free process, the substrate makers are also developing high heat resistance, high reliability laminate materials. In this article, we will introduce the high heat resistance and high reliability in particular.

4. High heat-resistance and high reliability laminate materials

(1) Heat resistance test

Among high temperature lead free processes, with PN-cured laminate materials being the most attractive, mainly because resin of PN-cured laminate materials has more aromatic structures, lower water absorption, and better heat resistance.

- Dicy

$H_2N-C(=NH)-N(H)-C\equiv N$

- Phenol Novolac

OH OH OH — phenol–CH_2–[phenol]–CH_2–phenol

From table 1, we see hard PN-cured laminate materials material has better heat resistance compared to dicy-cured laminate, where T-288 tests is longer than 20 minutes, and temperature of decomposition is greater than 350℃. PN resin has excellent heat resistance itself, but in order to deal with the required low Z-axis thermal expansion, one can also add filler and reduce laminate Z-axis CTE value to meet the reliability required in higher layer count application.

		Normal FR4 (DICY)	Tg-150 (PN)	Tg-170 (PN)	FR4 Modify (DICY)
Thickness (mm)		1.6	1.6	1.6	1.6
DSC Tg		140°C	150°C	170°C	135°C
1/2hr PCT moisture		0.23%	0.15%	0.147%	0.21%
1/2hr PCT+288°Csolder dipping		3′ ~ 4′	10′ ↑	10′ ↑	10′
Peel strength (1oz)		11 ~ 13	9 ~ 10	9 ~ 10	11 ~ 12
CTE (ppm/°C)	α_1	50-70	40-60	40-60	50-70
	α_2	250-350	270-300	270-300	250-300
CTE 50-260°C(%)		4.3	4.0 3.5(with filler)	3.5 3.0(with filler)	4.0
T-288 (min)		> 2	> 20	> 20	> 5
Td (5% Loss)		311°C	350°C	351°C	325°C

Table 1 Comparison of the characteristics of base materials

In order to test whether the laminates can sustain multiple assembly steps at 260℃, TMA method is used to simulate the thermal cycles. The test method is as in Fig. 4; ramp 20°C/min to 260°C from room temperature; stay at 260°C for 1.5 minutes then cool down to room temperature to complete one cycle. From Table 2, we carry out more than 20 cycles in Tg-150 and Tg-170 for PN-cured laminate materials. Normal FR4 and High Tg FR4 laminates can only pass 9~10 thermal cycles test. Also, we test finished PCB with 10 layers by the same method, and the results are shown in table 3. Both PN-cured materials can pass test over 15 cycles whether the layer contains copper or not, which shows better heat resistance than Normal FR4 laminate that passes test with 4~5 cycles. Therefore we can prove that heat resistance of PN is much higher than Normal FR4, and high enough to tolerate many cycles of lead free high temperature assembly process for many times.

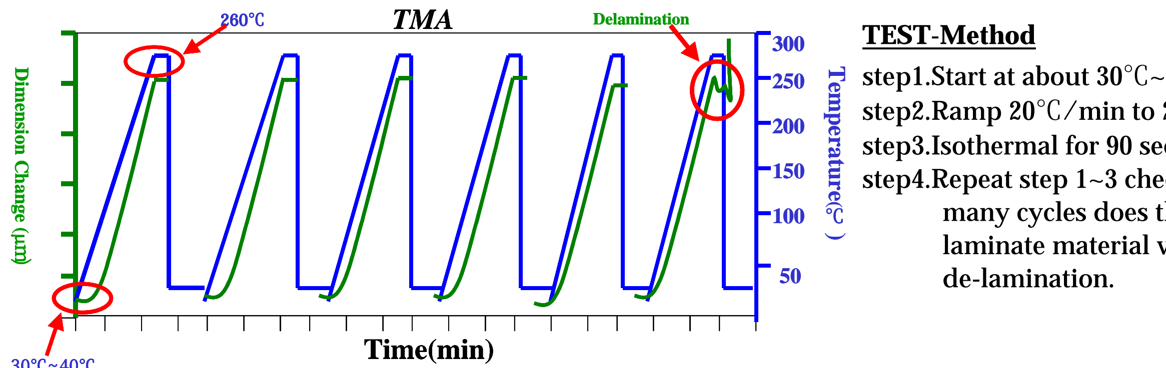


Figure 4 TMA thermal cycle test to simulate the high-temp lead free process

	Normal FR4 (DICY)	High Tg FR4 (DICY)	Tg-150 (PN)	Tg-170 (PN)
T-260°C Cycle	9	10	20↑	20↑

Table 2 Test Result by TMA cycling test (Test sample：1.6mm de-clad CCL)

	Normal FR4 (DICY)	Tg-150 (PN)	Tg-170 (PN)
With copper	4	15↑	15↑
Non copper	5	15↑	15↑

Table 3 Test Result by TMA cycling test (*Test sample：10 LB PCB*)

(2) Reliability test

① CAF reliability test

Comparing CAF characteristic of Normal FR-4 and PN material, uses 0.8mm laminate to make into CAF test coupons, pattern design shown in table 4. The first test conditions are, applied voltage at 24V, relative humidity at 85%, 85°C, and test voltage is 250V; PN-cured laminate and FR4 all can pass test after 2000 hours. Using the original test coupons, we increase the applied voltage to 250V, both PN-cured laminates pass the test after 2000hours, while resistance of Normal FR-4 decreases only after 47 hours stressing.

(a) CAF TEST => Test 2000 hrs

85°C 85% **Applied 24V** Test 250V	L/S (90/90)(80/80)μm	TH (0.35mm) 0.8/0.75/0.7mm	TH (0.3mm) 0.75/0.7/0.65mm	TH (0.25mm) 0.7/0.65/0.6mm
Normal FR4	PASS	PASS	PASS	PASS
Tg-150 PN	PASS	PASS	PASS	PASS
Tg-170 PN	PASS	PASS	PASS	PASS

(b) CAF TEST => Increase Applied Voltage to 250V

85°C 85% **Applied 250V** Test 250V	L/S (90/90)(80/80)μm	TH(0.35mm) 0.8/0.75/0.7mm	TH(0.3mm) 0.75/0.7/0.65mm	TH(0.25mm) 0.7/0.65/0.6mm
Normal FR-4	PASS	156	114	47
Tg-150 PN	PASS	PASS	PASS	PASS
Tg-170 PN	PASS	PASS	PASS	PASS

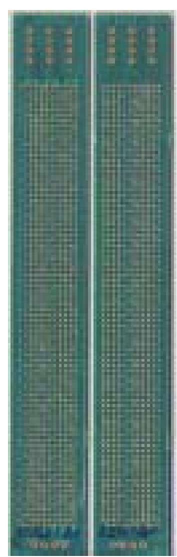
Table 4 CAF test results

② IST test

PN material is made into 18 layers and pretreated with 5X@230°C, IST test (25-150°C) can pass through 2000 cycles. In addition, accelerate the test with 5X@230°C pretreatment, 25-190°C IST test, Tg-170 PN-cured material can also pass through 470 cycles test. Cross-section is made to observe the hole wall quality, we found no crack in the PTH and buried via, and there is no delamination in the pad of the blind via.

Condition / Type	25-150°C	25-190°C
Tg-170 PN	2000 cycle	470 cycle
Tg-150 PN	2000 cycle	-

Layer count: 18LB; Pre-condition: 5X@230°C

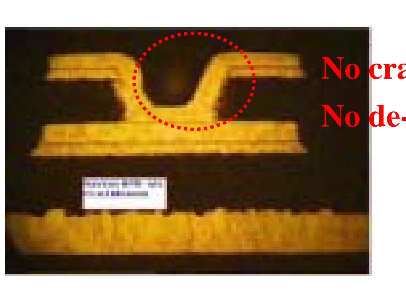


Material: Tg-170 PN

Layer count: 18LB

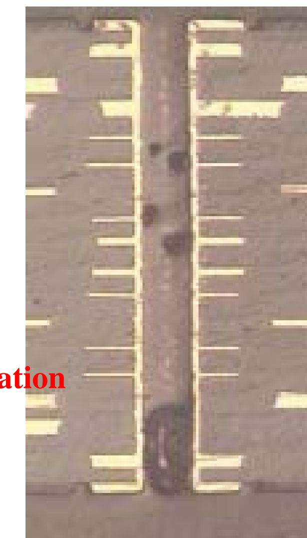
Pre-condition: 5X@230°C

Test result: Pass 470X@25-190°C



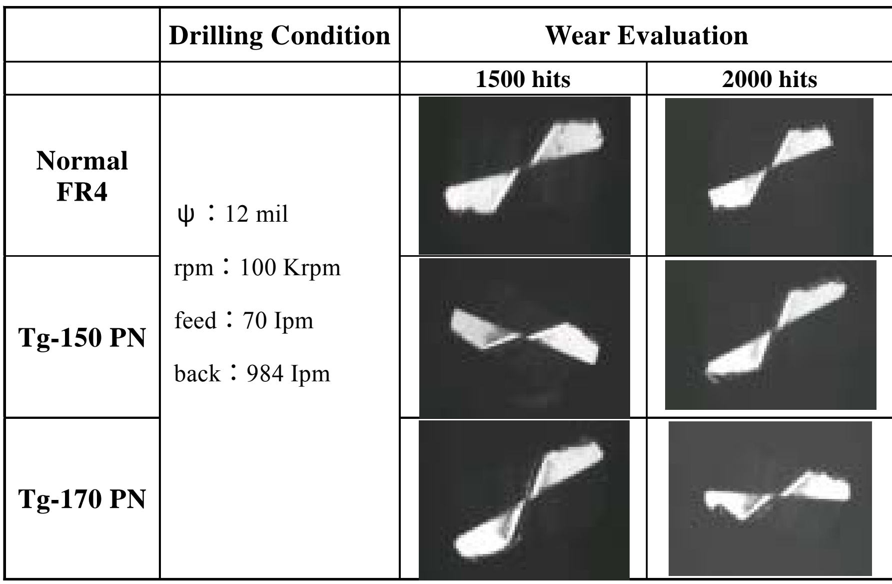
No crack

No de-lamination



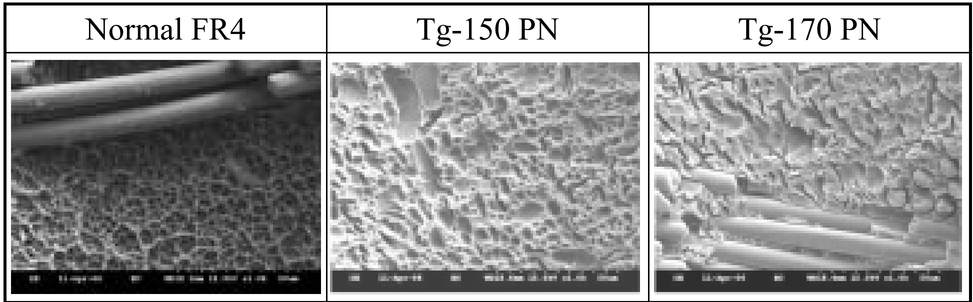
(3) Discussion of PCB processes condition

In choosing the base materials for PCB application, besides consideration in its characteristics, the more important thing is the characteristic of process; there are more than 20~30 process steps in dry and wet technology; the characteristics of material process not only affect the characteristics of the finished product, but also increase of the cost. (a) Comparison of the wear on drill bits: from Fig. 5, under the same drilling condition, PN-cured laminate material drills attrite faster, it starts to attrite after drilling 2000 hits, while FR4 can drill up to 3000 hits. (b) Desmear process: PN-cured laminate takes longer desmear processing and require use high polarity amide base chemical; FR4 system can desmear to honeycomb structure with glycol ether, such as Fig. 6. (c) Black and Brown Oxide process: PN-cured material has poorer bonding strength of black and brown oxide, as showed in Table 5. This is characteristic of PN-cured laminate materials with a harder cross-linking structure and their brittle nature.



	Drilling Condition	Wear Evaluation	
		1500 hits	2000 hits
Normal FR4	ψ：12 mil rpm：100 Krpm feed：70 Ipm back：984 Ipm		
Tg-150 PN			
Tg-170 PN			

Figure 5 Base on the evaluation of the wear on drill bits



Glycol ether for Normal FR4 and FR4 Modified; Amide for Tg-150 (PN)

Figure 6 Comparison of desmear process of base materials

	Black Oxidation	**Brown Oxidation**
Normal FR4	4.5 5.5	4.0 5.0
Tg-150 (PN)	3.5 4.5	2.5 3.5
Tg-170 (PN)	3.5 4.5	2.5 3.5

Table 5 Bonding strength of black and brown oxide process

It is unquestionable that PN-cured material has higher heat resistance and good reliability, but the setting and optimization of PCB processing condition takes a lot of manpower and time thus increases the cost. See table 6.

	DICY Type	PN Type
Laminate Price	1.0	1.05 ~ 1.15
Drilling Cost	1.0	1.5 ~ 2.0
Desmear Time	1.0	1.5 ~ 2.0
PCB Total Cost	**1.0**	**1.05 ~ 1.1**

Table 6 Comparison between DICY and PN laminate for PCB process cost

In order to reduce the cost of materials and minimize the impact of process changes, we have focused on the improvement of traditional FR4 dicy-cured laminate by increasing its heat resistance and temperature of decomposition, as well as reducing the water absorption. As table 1 shows, FR-4 modify has higher Td, heat resistance, and T-288 than traditional FR-4. Therefore, FR-4 modify material can stand tighter and severe high temperature lead free assembly process.

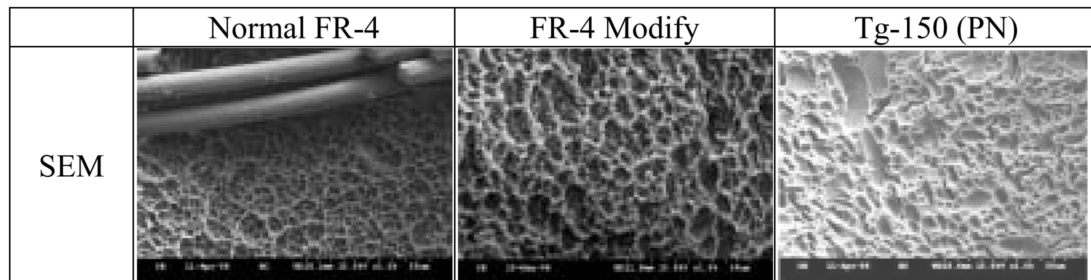
In addition, probe into PCB manufacturability of FR-4 Modify material. (a) With regards to processing, the wear of drill bits at 2500 hits to 3000 hits is the same with that of normal FR4 as in Fig. 7. (b) Desmear: In the desmear process; current glycol ethers can be employed to produce the same honeycomb structure without modifying the process conditions. It will have better results than PN-cured materials that require amide based chemicals such as Fig6. (c) FR-4 Modified materials also exhibit similar bonding strength to normal FR4 as showed in Table 7.

In terms of manufacturability, under the same operating condition FR-4 Modify laminate is very the same as traditional FR-4 and easier to process than PN-cured laminate materials. FR-4 Modify material makes improvement from traditional Dicy-cured FR4; its cost and manufacturability are similar to normal FR4, but heat resistance and reliability improve by a wide margin. So, it can be applied to 10LB↓ design as another option besides PN hard laminate.

	Drilling Condition	Wear Evaluation			
		1000 hits	2000hits	2500 hits	3000hits
Normal FR-4	ψ：12 mil rpm：160 Krpm feed：122 Ipm back：984 Ipm				
FR-4 Modify					

Figure 7 FR-4 Modify micro via drilling comparison

	Normal FR-4	FR-4 Modify	Tg-150 (PN)
SEM			



Glycol ether for Normal FR4 and FR4 Modified; Amide for Tg-150 (PN)

Figure 8 Comparison of desmear process of base materials

	Black Oxidation	Brown Oxidation
Normal FR-4	4.5 5.5	4.0 5.0
FR-4 Modify	4.5 5.5	4.0 5.0

Table 7 Bonding strength of black and brown oxide process

5. How to choose the suitable laminate materials

The better the laminate characteristics, the safer it is when applied to higher temperature process. However the laminate with better characteristics will increase the cost and is not conformation with the PCB cost-effectiveness. How to choose the laminate? We can consider the following factors to choose the material.

(1) Customer's actual IR Reflow Profile: You can choose the proper heat resistance material according to the range of process temperature. And the normal lead free IR Reflow process to fabricate the print circuit board, its actual board temperature is about 230℃-260℃.

(2) PCBs design and total thickness: With more layers, the internal interface combination will be more thus more defects inside the PCB are possible. In addition, thicker total PCBs design results in higher total Z-axis thermal expansion, therefore, it is the primary consideration to choose high heat-resistance material with lower CTE value on total expansion.

(3) PCB makers' manufacturability: PCB processes difference can influence heat resistance of finished products. Using black/brown oxide process as an example, different factory brand chemical solution have very great influence on adhesion of PCB, so one must also pay attention to the compatibility of the board and chemical solution while choosing the laminate materials.

According to our assessment and experience in the past, we suggest the PCB makers use the following flow chart as a reference in choosing laminate materials: