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A Novel Halogen-Free Material for High Speed PCB

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Abstract
The mobile communication devices such as cell phones require high speed transmission of large volume data as well as reduction in size and weight. When signal is transmitted in high speed and frequency on PCB, signal integrity becomes a problem. This problem is getting worse as the transmission becomes faster and larger. Therefore, materials with low Dk/Df are need for high frequency board.

Another requirement for current communication board is environmental friendliness, which is lead and halogen free. As for laminates, there are some low Dk/Df ones and many halogen free ones. However, material with both is hard to find, quite expensive and difficult to process. Therefore, communication industry is looking for new materials.
To meet this demand, a novel halogen free material with low Dk/Df, DS-7402D, has been developed. A hydrophobic epoxy resin was used as base resin to improve the dielectric properties. In addition, a phosphorus containing resin was applied as a hardener and halogen free flame retardant. The resulting material has better dielectric properties, Dk of 3.9 and Df of 0.01, than those of conventional FR-4. It also shows an excellent thermal stability, Td higher than 380C, which makes it suitable for lead-free process. The other properties of this material, such as copper adhesion, modulus and water absorption will be presented.

Introduction
The amount and speed of information processing is increasing as daily life becomes more information dependent. In computing side, small computers like laptop have the processing power which was only possible for the super computer in the past. Now, the clock speed of personal computer approaches 3GHz, and is expected to reach tens of GHz range in the near future. In addition, the communication frequency will be very high as the information technology progresses. One area expected to benefit from this development is automobile electronics. Electronic devices such as navigation system and Electronic Toll Collection (ETC) system have adopted high performance boards. And the technology will more widely migrate to low-end cars from premium cars. The boards drive the development of materials for high speed and frequency application. While high speed printed circuit boards (PCBs) need materials with low dielectric constant (Dk), high frequency PCBs require materials with low dissipation factor (Df).

On the other hand, as most industries are interested in "Green Technology", environmentally friendly materials are developed for electronic applications. While the potential for environmental legislation is lessening in Europe, primarily because Tetrabromo-Bisphenol A (TBBA) is not on the banned list, polybrominated aromatic compounds are still considered undesirable. Plastic materials that contain polybrominated biphenyls or polybrominated diphenyl ethers can be converted to dioxin and furan, respectively. While these specific flame retardants are not typically used in PCBs, the vision is that PCBs will produce dioxin and furan derivatives upon thermal degradation. Conventional materials already have been using halogen free products and the categories will widen.

Thus, PCB companies need to develop materials of low Dk, Df for high frequency PCB as well as good flammability. CCL companies have also developed new resin systems which have low dielectric properties and good flame retardants which keep up performances of CCL. The typically used resins are modified epoxy, Polyphenylene ether (PPE) or oxide (PPO), Cyanate esters (C.E), Hydrocarbons, and Teflons. These polymers are quite different in terms of structure, properties, processibilities and cost except one thing in common; that is, better dielectric properties than Epoxy resins. (Table1) Since their electric properties are also different, one has to choose the right material considering its applications, strong and weak points.

Table1 Effects of low dielectric base materials on laminate properties

Base Materials	Effects on				Comments
	PCB Processibility	Thermal Properties	Mechanical properties	Cost	
Modified Epoxy	**No effect**	**No effect**	**No effect**	**Some increase**	**A small improvement of Dk & Df**
PPO or PPE	**Somewhat negative**	**No effect**	**No effect**	**Some increase**	**Hard to deal with**
Cyanate Esters	**Somewhat negative**	**Somewhat positive**	**No effect**	**High increase**	**Short prepreg shelf life**
Hydrocarbons	**Somewhat negative**	**Somewhat positive**	**Somewhat negative**	**High increase**	**Limited supply**
Teflon	**Highly negative**	**Highly positive**	**Somewhat negative**	**High increase**	**Huge improvement of Dk & Df**
Modified E-glass	**Somewhat negative**	**No effect**	**No effect**	**Some increase**	
Organic reinforcements	**Highly negative**	**No effect**	**Somewhat negative**	**High increase**	**Very expensive**

On the other hand, there are non-halogenated flame retardants which are applicable to Halogen free CCL. They are phosphorous compounds, nitrogen compounds (including polyamides and polyamines), oxy-acid compounds and inorganic fillers.

As far as phosphorus compounds are concerned, there are two types, an additive and a reactive. The former is economical and easy to apply. However, it is possible that plating baths can be poisoned if the additive phosphorous flame retardant is used. The low molecular weight phosphorous compound not reacted into the resin matrix could potentially leak out the plating bath and could reduce Tg. On the other hand, the latter can react with epoxy resin and be incorporated into the polymer backbone. Therefore, there is little performance degradation with the reactive phosphorous flame retardant application. However, it is expensive and hard to apply. Nitrogen and oxy-acid based flame retardants could reduce thermal reliability and also have poor dielectric property. Inorganic filler could increase dielectric constant and have an adverse effect on manufacturing processibility. (Table2) Thus, we adopted reactive phosphorous flame retardant including hardener function. It has provided high flame retardancy as well as better dielectric properties than conventional halogen free FR-4.

Table2 Non- Halogenated Flame retardants

Non-halogenated flame retardants	Advantages	Disadvantages
Reactive phosphorous compound	**- Widely available**	**- Leak out in plating process,** **- Reduce Tg**
Additive phosphorous compound	**- Good thermal reliability**	**- High water absorption**
Nitrogen type & Oxy-acid based type	**- Can be used as hardener**	**- Reduce thermal reliability** **- Poor electrical property**
Inorganic filler type	**- Decrease dielectric loss**	**- Increase dielectric constant**

Strategy of New materials

As mentioned earlier, there is no problem for epoxy based resin to be processed in PCB fabrication. In order to have lead-free solder compatibility, the material should have high thermal stability, reflected on high glass transition temperature (Tg) and longer time to delamination. The commom way to improve thermal stability is to increase cross-linking density of cured resin by adding multifunctional resins. High thermal stability makes laminate not only suitable for lead-free soldering but also stable for the through hole expansion. However, increasing cross-linking density has adverse effects on peel strength, dielectric properties and drillability. Therefore, usage of rigid backbone instead of increasing cross-linking density has been adapted. Through this approach it was possible to maintain the strong points of epoxy properties as well as to improve dielectric properties. In addition, we adopted the hardener which can be synthesized with reactive phosphorous. It has high mole volume and low functional group content, and this structure of hardener has dual function such as to boost the electric properties and satisfy the flammability V-0 without halogen flame retardant. This resin system fulfills three requirements for high speed boards, which are good dielectric properties, high thermal stability and FR-4 compatibility. It also has proper operation window in treating and pressing processes due to the slow curing compared with fast reaction of multifunctional system.

Properties of New materials

a. Dielectric properties

Dielectric constant and dissipation factors were calculated from Q values at resonating frequencies. Studies showed that new material resulted in lower Dk values than conventional halogen free FR-4 as shown in fig.1 Conventional Halogen free FR-4s have dielectric constant (Dk) that are >4.6.The dissipation factors (Df) on these same products are generally >0.020 at 1GHz. The other hand, new material has Dk 4.0, Df 0.020 at 2GHz and Dk 3.9, Df 0.013 at 8GHz respectively.

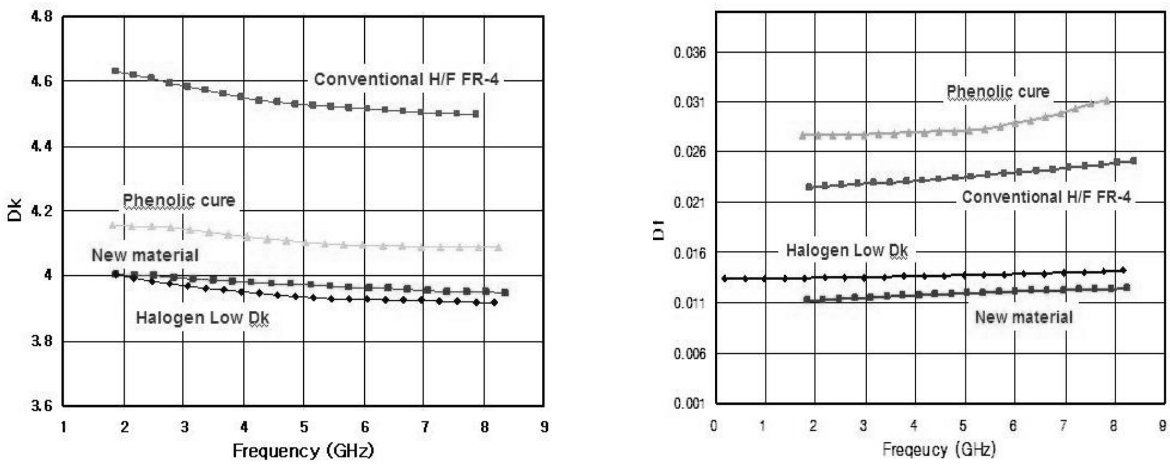

Fig.1 Measurement of Dk and Df

In order to compare the transmission properties with materials, we analyzed *S parameter* and *eye diagram* as the frequency using micro-stripline type coupon. Fig.2 shows the results of measured S_{21} on stirpline of 50cm length. New material has 6.6dB and conventional H/F or phenolic materials have 9.9dB at 3GHz. The results mean new material has lower loss value than others. In addition, even though two patterns are almost identical at 1Gbps, the difference was evident at 5Gbps, open eye for a new material compared with closed eye for FR-4 (Fig.3). Therefore, new material can keep signal integrity at high frequency, which makes it suitable for high speed applications.

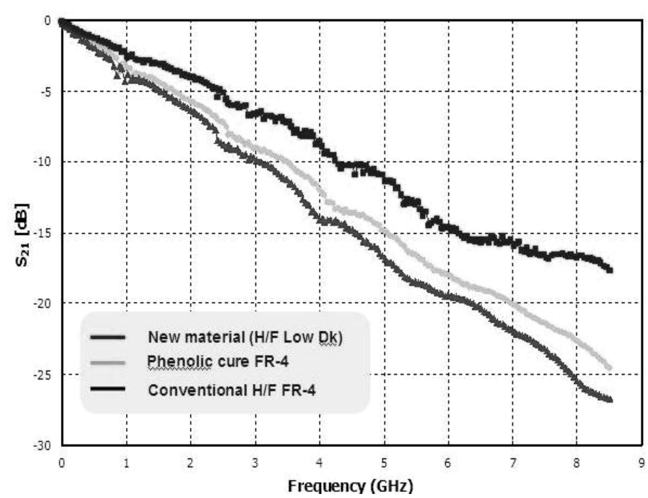

Fig.2 Measured S_{21} of Stripline

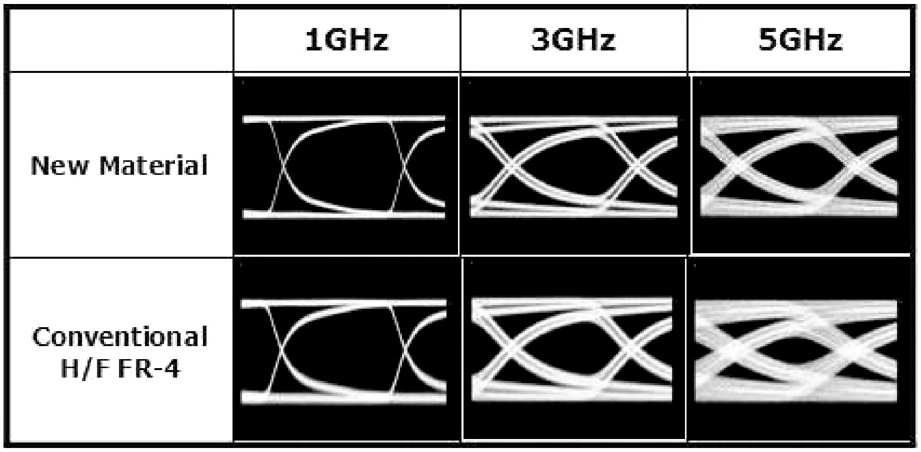

Fig.3 Result of Eye diagram

b. Thermal resistance for Lead-free Requirements

There are numerous work groups and industry organizations involved in a "lead-free solder initiative", including IPC, NEMI, and HPD. Thermally stable materials that can tolerate high temperature (260℃) during the IR flow process have become necessary. In order to measure thermal stability, time to delaminate at high temperature such as 260℃ (T-260) or 288℃ (T-288) is widely used together with Tg due to the limitation of Tg as a sole indicator of thermal stability.

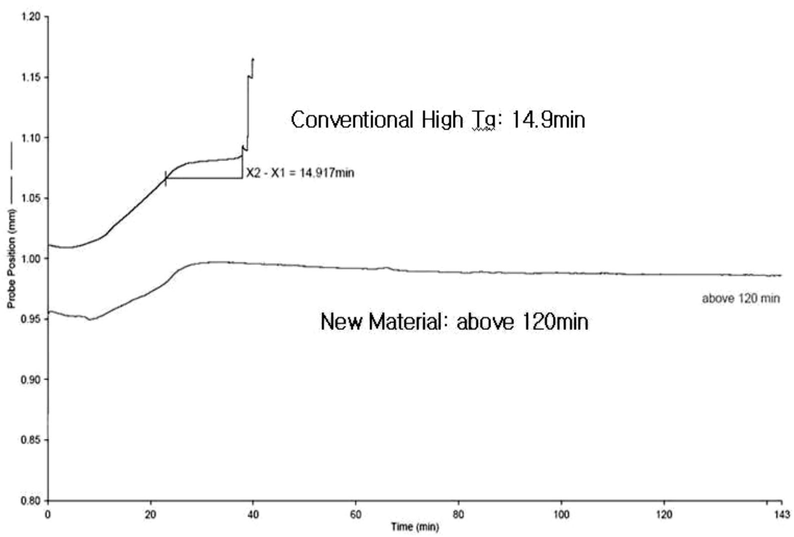

Fig.4 T-260 data of new material

New material has excellent thermal resistance as listed in Table 3. Decomposition temperature (Td) by thermal gravimetric analysis (TGA) is one of the most important properties for lead-free process. The mass change of the sample is measured as temperature rises. At the beginning of heating, the water and the non-volatile ingredients evaporates (within 5%) and the gas is released as the high temperature makes chemical bonds of resin broken. The temperature where the mass of sample is reduced by 5% is called the decomposition temperature. The importance of Td was recently recognized because the PCB process will be greatly influenced by emitted gas at high temperature as the lead free solder is processed at higher temperature. The TGA results of new material and high Tg material are shown in Fig.5. It shows that new material is more than suitable for lead-free process because its Td is more than 40 degrees higher than that of the conventional.

Table3. Times to delamination of various materials (min)

	Low Tg FR-4	High Tg FR-4	New material
Temperature (□)	**Tg 140**	**Tg 170**	**Tg 175**
260	**20**	**14.9**	**>120**
288	**< 2**	**< 2**	**25**
300	**< 1**	**< 1**	**2**

c. General properties of new material

New materials with low Dk and Df have been developed for high speed and frequency applications. Their properties are better than those of high Tg material as listed in below in Table4. In addition, they are compatible with lead free process, which requires high thermal stability.

Table4. General Properties of new material

Properties	Condition / Method	Unit	Value
Mechanical			
Peel Strength (1oz Cu)	IPC-TM-650.2.4.8	kgf/cm	1.2
z-CTE (before Tg / after Tg)	IPC-TM-650.2.4.41	ppm/℃	43/ 243
z-axis Expansion	50℃-260℃	%	2.7
Flexural Modulus	IPC-TM-650.2.4.4	GPa	23~27
Flexural Strength	IPC-TM-650.2.4.4	MPa	460~560
Electrical	R/C=50%		
Dk @1GHz (DS-7402D)	IPC-TM-650.2.5.5.1		4.0
Df @1GHz (DS-7402D)	IPC-TM-650.2.5.5.1		0.010
Volume Resistivity	IPC-TM-650.2.5.17.1	ohm-cm	-
Surface Resistivity	IPC-TM-650.2.5.17.1	ohm	-
Thermal			
Tg (DSC)	IPC-TM-650.2.4.25c	℃	170 ~ 175
Pressure Cooker	IPC-TM-650.2.6.16		Pass
Chemical / Physical			
Water Absorption	E-24/50 + D-24/23	%	0.1
Flammability	UL94		V-0

Reliability of new material

a. Anti-migration property

The movement of metallic ion from anode to cathode under fixed voltage at high humidity is called electrochemical migration and the most typical migration is called the conductive anodic filament (CAF). CAF is a significant and potentially dangerous source of electrical failure in the PCB and, thus, the overall system of which it is a part. Especially, as PCB's circuit density gets higher and line space between patterns become narrower, the CAF resistance becomes much more important among the reliability properties. The 18 layer test coupon was prepared and preconditioned by similar treatment as the actual PCB process through reflow. As shown in figure 5, the CAF didn't occur even after 700 hours.

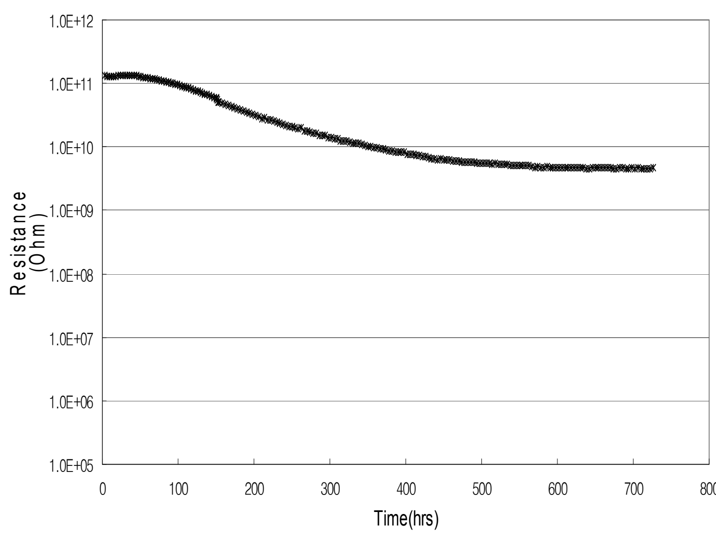

Fig.5 CAF test data of new material

b. Interconnect Stress Testing (IST)

The most challenging experience for a PCB is the survival of the assembly process. Double sided reflow and a small amount of rework is undoubtedly the toughest environment that most PCBs ever encounter in their service life. Add to this the higher temperatures encountered as boards transition to lead free and it becomes essential that you know that boards will survive assembly. This IST testing and data analysis method gives insight into the consumption of plated through via life during assembly and rework, the impact of lead-free processing versus eutectic solder, and potentially the ability to predict the remaining life of products in the field. The 24 layer test coupon was prepared and tested IST by IPC method. As shown in Table5, the coupon of new material passed 1000cycles.

Table5. Result of IST

	Test pre-condition	Power/sensor circuit	
		P post @150℃	S PTH @150℃
#1	x6 @ 230 ℃	1000 (Pass)	1000 (Pass)
#2	x6 @ 260 ℃	1000 (Pass)	1000 (Pass)

- Φ0.25(10mil), Pitch 0.8mm(32mil), PTH 24L, thickness 3.2t

c. Thermal stress test

The PCB reliability test was performed at same temperature (255℃~265℃) as the actual lead-free process after preparing 20 layer test coupon and preconditioning them at fixed temperature and humidity. The coupons were micro-sectioned and checked to see if there is any defect in the inner layer. There were no cracks or delaminations in the board under microscope regardless of the degree of conditioning as shown in Fig.6. The boards are clean even after the thermal cycling while defects were detected for the coupons with conventional FR-4.

Treatment condition	Time	Reflow Condition	Result
85℃,85%RH	168hr	Peak 260℃ x 3cycle	OK

After Reflow

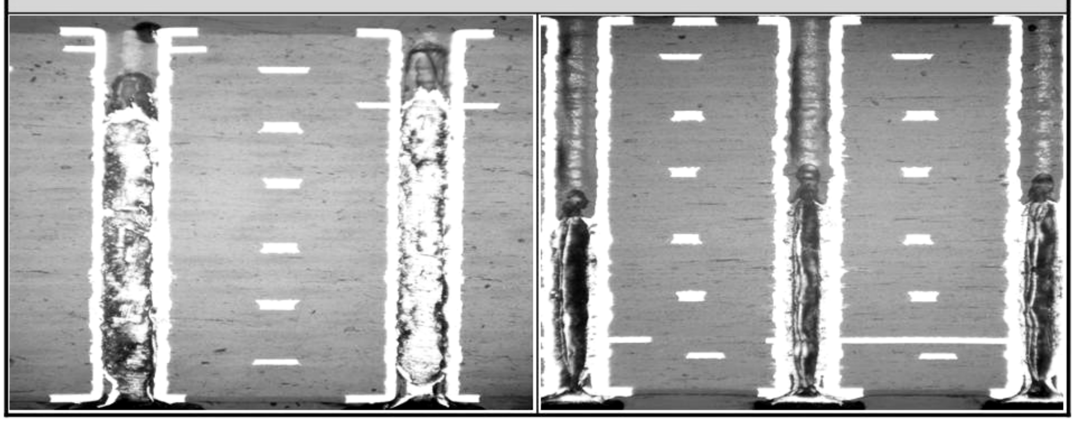

Fig.6 Micro-section after harsh conditioning and following reflow

Conclusion

New material technology gives performance advantages over the currently available non-halogenated FR-4 resin system. New material has lower Dk and Df as compared to most non-halogen offerings. In addition, this new resin system provides more thermal resistance than conventional high Tg materials. Thus, this halogen free low Dk material is a viable candidate for high speed PCB and lead-free solder applications.

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