Novel Low Dk/Df Materials for High Speed PWB

Duksang Han, Tim (Minsu) Lee* and DongKi Nam Doosan Cooperation, Electro-Materials BG Yongin, S. KOREA

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 PWB, signal integrity becomes a big problem. One of the most widely used methods to tackle the problem is to apply low Dk/Df materials. Even though various materials are available for that purpose, they tend to be quite expensive and require special care during the fabrication process. Therefore, PWB fabricators have been looking for more affordable and easily processable low Dk/Df material. To meet these demands, a novel PWB material has been developed. The special epoxy resin with rigid backbone was used, which does decrease Dk level but not significantly for the application. Therefore, hydrophobic hardener was adopted to compensate the difference in dielectric properties. The resulting material has Dk of 3.8 at 1 GHz, which is 10% lower than that of conventional FR-4. In addition, its Tg is higher than 170 C. It also shows an excellent thermal stability, withstanding longer than 30 minutes at T-288. The further development of material toward better dielectric properties was made possible with application of NE glass instead of conventional E glass. The resulting laminate has Dk of 3.5 as well as a Df of less than 0.01. The other properties of these materials, such as migration property, Td and reliability will be presented.

Introduction

The amount and speed of the information processing is increasing as daily life becomes information dependent. On the computing side, small computers like laptops have a processing power which was only possible for the super computers in the past. Now, the clock speed of personal computer approaches 3 GHz, reaching tens of GHz range in the near future. In addition, communication frequency will be very high as the information technology progresses. One area expected to benefit from this development is automobile electronics. Already, electronic devices such as navigation system and Electronic Toll Collection (ETC) system have adopted high performance boards. And the technology will be widely migrated to low-end cars from premium cars. The boards drive the development of materials for high speed and frequency application. While high speed printed wiring boards (PWBs) need materials with low dielectric constant (Dk), high frequency PWBs require materials with low dissipation factor (Df). In order to develop these materials, the CCL industry uses two different approaches. The one is to adapt polymers with low Dk and Df instead of conventional epoxy resins.

Table1. Effects of low dielectric base materials on laminate properties

Base Materials	PWB	Thermal	Mechanical	Cost	Comments	
	Processibility	Properties	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	

The other is to use different reinforcements or glasses other than typical E-glass. The former is widely used and adapted resins are modified epoxy, Polyphenylene Ether (PPE) or Oxide (PPO), Cyanate Esters (CE), Hydrocarbons, and Teflon. These polymers are quite different in terms of structure, properties, processibility and cost except one thing in common, that is better dielectric properties than Epoxy resins. Since their electric properties are also different, one has to choose the right material considering its application's strong and weak points. In addition to the properties listed in Table 1, reliability and lead free process compatibility are other important properties as high layer count boards are widely used and concern for the environment increases. Therefore, the development target is a new laminate with good dielectric properties, high reliability, PWB processibility and lead free process compatibility. And we started with a search for the proper epoxy resin since some epoxy resin can satisfy all of above at reasonable cost.

Strategy of low Dk/Df 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 by high glass transition temperature (Tg) and longer time to delamination. The common way to improve thermal stability is to increase cross-linking density of cured resin by adding multifunctional resins. High thermal stability makes a 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, introducing a rigid backbone instead of increasing cross-linking density has been adapted. Through this approach it was possible to maintain copper adhesion as well as to improve dielectric properties. In addition, the adoption of a hardener with high

mole volume and low functional group content boosted the electric properties. The resin system fulfills three requirements for high speed boards: good dielectric properties, high thermal stability and FR-4 compatibility. It also has a proper operation window in treating and pressing processes due to the slow curing reaction compared with fast reaction of multifunctional system.

Properties of new materials

a. Dielectric Properties

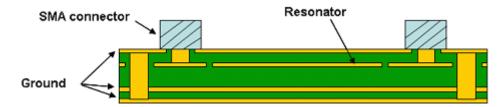


Figure 1. Test coupon structure

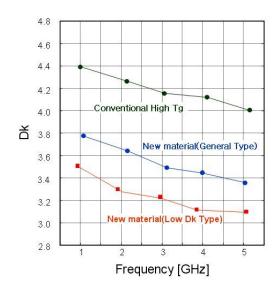


Figure 2. Dielectric property of new materials

However, its reliability, especially through hole reliability, was found to be unsatisfactory because of relatively high coefficient of thermal expansion (CTE). The proper filler was chosen after testing of various fillers. The CTE was properly adjusted with the addition of the filler. The resulting material, DS-7409D, has all the necessary properties for high speed application. However, the dielectric properties of the material are not good enough for more advanced application at higher than 5 GHz transmission. Therefore, the low Dk version of the material for high end application, DS-7409DS, was subsequently developed by applying new reinforcement with same resin system. The dielectric property of the material at 50% resin content was measured using a series of gap resonator and a network analyzer. A stripline type test coupon was chosen over the micro-stripline design because of high accuracy as shown in Fig.1.

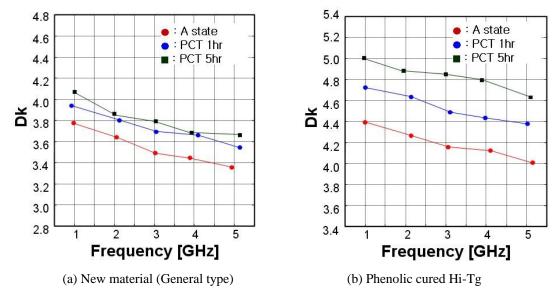


Figure 3. Effects of water absorption on dielectric property

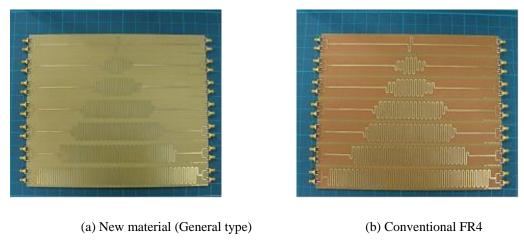
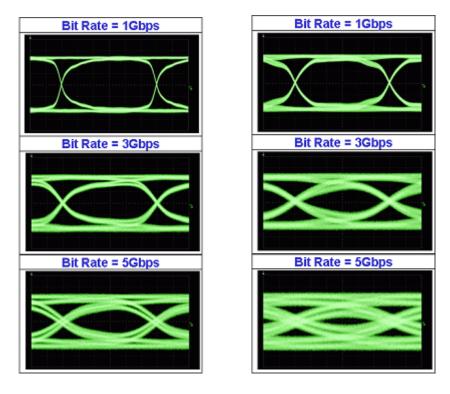


Figure 4. Test coupons for Eye diagram analysis

Furthermore Dk and Df values were calculated from Q values at resonating frequencies. Studies showed the new material was in lower Dk values than conventional high Tg material as shown in Fig 2. A low Dk type has even better dielectric properties. For example, the Dk values of conventional high Tg, general type and Low Dk type materials at 1Ghz are 4.4, 3.8 and 3.5 respectively. And the values are lower as the frequency is higher for all three materials. In order to test the effects of water absorption on materials' Dk, the laminates were forced to take water in a pressure cooker. The results clearly showed negative effect of water absorption on Dk (Fig.3). The adverse effect was higher for the conventional high Tg than for the newly developed materials reflecting a higher dielectric stability of the new material. On the other hand the transmission properties were analyzed using an "eye" diagram. Coupons with 100 OHM differential pair micro-stripline circuit were prepared in house as shown in Fig. 4. The resulting pattern confirms good dielectric properties of developed material. Even though two patterns are almost identical at 1G bps, the difference was evident at 5 Gbps where the "eye" is open for the new material compared with a closed "eye" for FR-4 (Fig. 5). Therefore, the new material can maintain signal integrity at high frequency which makes it suitable for high speed applications.

b. Lead free process compatibility



(a) New material (General type)

(b) Conventional FR4

Figure 5. Eye diagrams

The use of lead in solder, the main joint material in board technology, is regulated with the enactment of RoHS in Europe. Thermally stable materials that can tolerate high temperature $(260\,^{\circ}\text{C})$ during the IR flow process have become necessary. In order to measure thermal stability, times to delaminate at high temperature such as $260\,^{\circ}\text{C}$ (T-260) or $288\,^{\circ}\text{C}$ (T-288) are widely used together with Tg due to the limitation of Tg as a sole indicator of thermal stability.

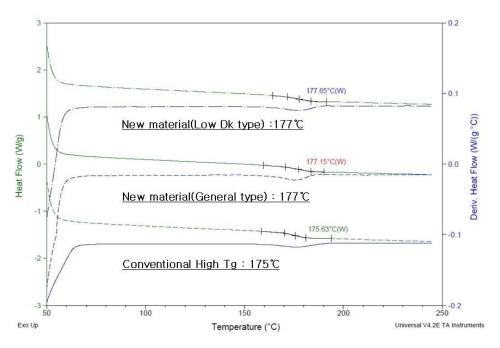


Figure 6. DSC data of various materials

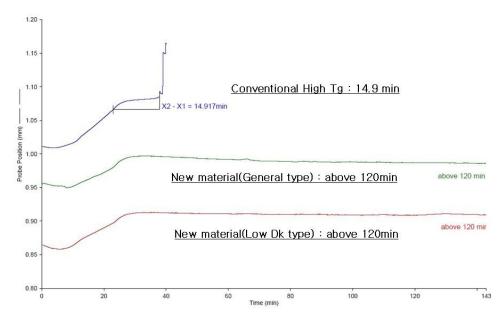


Figure 7. T-260 data of new materials

Tg and T-260 data of conventional high Tg material and new materials are shown on Fig. 6 and Fig. 7. Although the Tgs of new materials are almost the same as that of high Tg FR-4, their T-260s are longer than 2 hours, which is 8 times longer than that of high Tg material. New materials have excellent thermal resistance as listed in Table 2. In fact, they can stand almost 3 minutes at 300°C while the high Tg material delaminates during heating. 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 volatile ingredients evaporate (within 0.5%) and then gas is released as the high temperature breaks the chemical bonds of the resin. The temperature where the mass of sample is reduced 5% is called the decomposition temperature. The importance of Td is recently recognized because the PWB 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.8. 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 material.

Table 2. Times to delamination of various materials (min)

	Low Tg FR-4	High Tg FR-4	New material
Temperature ($^{\circ}$ C)	Tg 140	Tg 170	Tg 175
260	20	14.9	>120
288	< 2	< 2	30.7
300	< 1	< 1	2.7

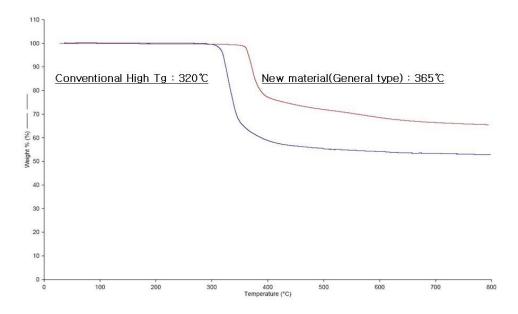


Figure 8. TGA data of laminates

c. General properties of new materials

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 table 3. In addition, they are compatible with lead free process, which requires high thermal stability.

Reliability of new materials

a. Anti-migration property

A metallic ion moving 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 PWB and thus, the overall system of which it is a part.

Table3. General Properties of new materials

Decoration	Constitution (Markets I	TT 24	High Tg	New material	
Properties	Condition/Method	Unit	Material	General	Low Dk
Mechanical					
Peel Strength (1oz Cu)	IPC-TM-650.2.4.8	kgf/cm	1.6	1.4	1.4
z-CTE (before Tg /after Tg)	IPC-TM-650.2.4.41	ppm/℃	55/260	45 / 257	45 / 257
z-axis Expansion	50℃-260℃	%	3.4-3.5	3.0	3.0
Flexural Modulus	IPC-TM-650.2.4.4	GPa	23-27	23 ~ 27	23 ~ 27
Flexural Strength	IPC-TM-650.2.4.4	MPa	460-560	460 ~ 560	460 ~ 560
Electrical	R/C=50%				
Dk/Df @1GHz	IPC-TM-650.2.5.5.1		4.2/0.015	3.8/0.013	3.5/0.011
Volume Resistivity	IPC-TM-650.2.5.17.1	ohm-cm	5.0E+13 ~ 5.0E+14	5.0E+13 ~ 5.0E+14	5.0E+13 ~ 5.0E+14
Surface Resistivity	IPC-TM-650.2.5.17.1	ohm	1.0E+13 ~ 1.0E+14	1.0E+13 ~ 1.0E+14	1.0E+13 ~ 1.0E+14
Thermal & Chemical					
Tg (DSC)	IPC-TM-650.2.4.25c	$^{\circ}$	170 ~ 175	170 ~ 175	170 ~ 175
T-260			15 min	> 120 min	> 120 min
Water Absorption	E-24/50 + D-24/23	%	0.15-0.20	0.1	0.1

As PWB's circuit density gets higher and line and space between patterns become narrower, the CAF resistance becomes much more important among the reliability properties. The 4 layer test coupon was prepared and preconditioned by a treatment similar to the actual PWB process through reflow. As shown in figure 9 CAF did not occur even after 700 hours.

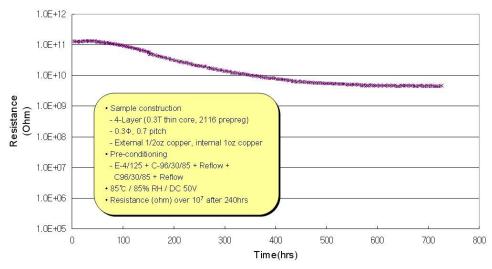


Figure 9. CAF test data of new material (General type)

Pre-Treatment Condition	Reflow Condition	1 st Result	Thermal Cycling Condition	2 nd Result
30℃, 60% RH, 168hr	Peak 260℃ x 3 Cycles	ок	-65 ℃, 30min ⇔ RT, 15min ⇔ 125 ℃, 30min x 175 Cycles	ок

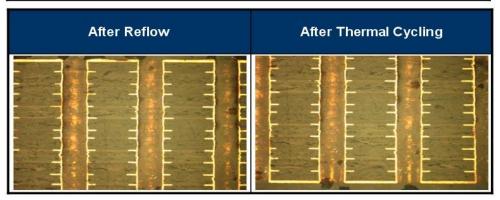


Figure 10. Micro Section after mild conditioning and following reflow

b. Thermal stress tests

The PWB reliability test was performed at same reflow temperature $(255\,^{\circ}\text{C} \sim 265\,^{\circ}\text{C})$ as the actual lead-free process after preparing 14 layer test coupons and preconditioning them at fixed temperature and humidity. The coupons were microsectioned and checked to see if there is any defect in the inner layers. There were no cracks or delamination in the board by the microscope regardless of the degree of conditioning as shown in Figs. 10 and 11. The boards are clean even after the thermal cycling while defects were detected for the coupons with conventional FR-4.



Figure 11. Micro Section after harsh conditioning and following reflow

PWB Processibility of new materials

One of the processes which can be influenced by resin with rigid backbone and high hydrophobicity is the desmear process because the new material's smear can not be removed as easily as FR-4's can. If that happens the hole wall will not be clean. As a result the plated through hole reliability will suffer. When the hole wall was treated according to Shipley's recommended condition the desmear rate of new material is exactly same as that of high Tg Fr-4, which is much higher than that of the CE system as listed in Table 4. The new materials do not need special processes for desmear just like high Tg material.

Conclusion

A new material for high speed PWB has been developed. This material has low Dk and Df values. Its thermal stability has outstanding compatibility for the lead free soldering process. In order to develop such material, the new epoxy resin with rigid backbone was selected. By carefully applying hydrophobic hardener and filler, an FR-4 laminate satisfying required dielectric properties could be made.

Table4. Desmear rates of various

	Water	Sweller	213B	213A-1	216-3	Temp.	Time
Sweller	80%	20%	25	50	-	80℃	2min
Oxidizer	75%	.=	15%	10%	-	70℃	7min
Neutralizer	80%		=	-	20%	45℃	5min

- Shipley Recommended Condition

Tg 150℃ Phenolic Cured	Tg 170℃ Phenolic Cured	Tg 200℃ Cyanate Ester with Epoxy Blend	New material (General Type)	
0.7 mic	0.6 mic	0.2 mic	0.6 mic	

materials

- Test Specimen: 0.4T Declad (7628 X 2 Plies)

The development of low Dk version of it was possible by substituting E-glass with NE-glass. The materials obtained demonstrated lead free process compatibility as well as good reliability. In addition, the desmear process ability was comparable with that of conventional high Tg FR-4.

Acknowledgement

Authors thank Mr. Kwangsuk Park and other members of R&D center for not only technical support but also discussions and encouragements.

References

- 1. S. Ehler, Reliability Investigations of Printed Circuit Boards, IEMT/IMC Symposium, (1998)
- 2. K. Sauter, Evaluating PWB Design, Manufacturing Process and Laminate Material, Impacts on CAF Resistance, CircuiTree, July, 10 (2002)
- 3. L. Tubini, The Real Cost of Lead-Free Soldering, IPC International Conference on Lead-Free Electronic

Components and Assemblies, (2002)

- 4. M. Kakimoto and A. Takahashi, High Performance Materials for Electronics Package Substrate, CMC Press, Tokyo (2005)
- 5. Electronic Application of Epoxy Resin, Gijutu Press, Tokyo (2005)
- 6. M. Ochi and S. Numata, The Latest Technology of Epoxy Resin for Electronic Devices, CMC Press, Tokyo (2006)
- 7. Toray Research Center, Trends in Advanced Packaging Technology, TRC R&D Library, Tokyo (2007)