The Influence of Material Reactivity in Dk/Df Electrical Performance

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Abstract

Over the years, signal integrity performance and bandwidth gets more critical for today's higher signal transmission speeds and bandwidth demand in every field of applications such as computing, multimedia, communication infrastructure and a variety of communication bus and cable like PCI express, SATA II and AGP bus for computer system. Base material electrical performance especially for dielectric loss will dominate signal communication behavior while communication speeds push up to 5~10Gbps.

Because one labors under the hypothesis of lead-free process compatibility, high Tg demand and thermal reliability concerns, the base resin system candidates for print circuit boards is limited. Basically, bisphenol-A novolac construction resin has been the mainstream resin in the market for years. Unfortunately, its characteristic restricts its dielectric loss performance . How can one further improve dielectric loss and signal integrity performance? Besides post-remedial measures in manufacturing technology like oxide treatment roughness, laminate construction, resin content, fabric weaving density, etc., CCL resin system reactivity and the choice of catalyst system are two significant factors for electrical performance improvement beside the resin and hardener design. Our study shows that a resin system reactivity with and without optimization can make a difference of up to 20% gap in signal integrity performance.

Introduction

IPC international technology roadmap 2006-2007, included a quantitative summary of the expected changes and trends in PC board, component, material and assembly technology from 2006 to 2016 and ranks thse items by RCG (Revenue Center of Gravity) and SoA (State of the Art) for reference. It says that communication clock frequency will increase for all eight categories. Take consumer products and mid-range performance application for instance, clock frequency for RCG will increase from 130 MHz and 1000 MHz up to 1000Mhz and 3500MHz respectively in the near future, and the desired base materials type is CEM3 and shifting to high performance RoHS capable FR4 gradually. Material requirement and change will be severe for the PCB supply chain.

Commercial epoxy resins were made significantly around 1947 and started to be applied in electronics industry. The effect of epoxy chemistry is well-known for the reaction rates and mechanism of reactions with acids and bases, etc. The curing of epoxy resin for printed circuit board application is an addition reaction based on the reaction between the epoxy group and other kinds of curing agents with the help of a catalyst. Curing agents and catalysts can be divided into three classes: active hydrogen compounds; ionic initiators; crosslinkers.

The laminate resin recipe is composed of the epoxy part and the hardener part. In the market, a variety of basic resin systems have been commercialized as shown in Figure 1. Common polymer backbone constructions include bisphenol A, phenol novolac, cresol novolac, phenol aralkyl novolac, tetraphenylolethane, bisphenol-A novolac, allyl novolac, bisphenol F novolac and DCPD novolac, styrene copolymer and triazine and so on, with reactive site such as epoxy, polyamines, polyphenols, acid anhydride, ester and benzoxazine as end funtional group for the addition reaction. Unfortunately, for lead-free RoHS thermal performance trade-off consideration, the bisphenol A novolac resin system, which was considered as the mainstream resin system for the copper claded laminate industry, is inferior in dielectric loss electrical performance to conventional dicyanidamide cured FR4 material. We can find that the base resin system developing trend cannot help in the application requirement.

The type of flame retardant is another key consideration. Brominated epoxy derived from bisphenol A resin and tetrabromobisphenol A is the regular FR4 flame retardanant for CCL. Because of the latest tendency of halogen family compound restriction, people are using nitrogen and phosphrous organic compounds and/or inorganic fillers as flame retardant to meet UL V-0. Those including DOPO, DOPO-HQ, PMP, TGIC, TPP, TMP, TCPP, DMMP, ATN, biphenol novolac and further more, non-nitrogenous and non-phosphrous based materials that were developed for better environment protection.

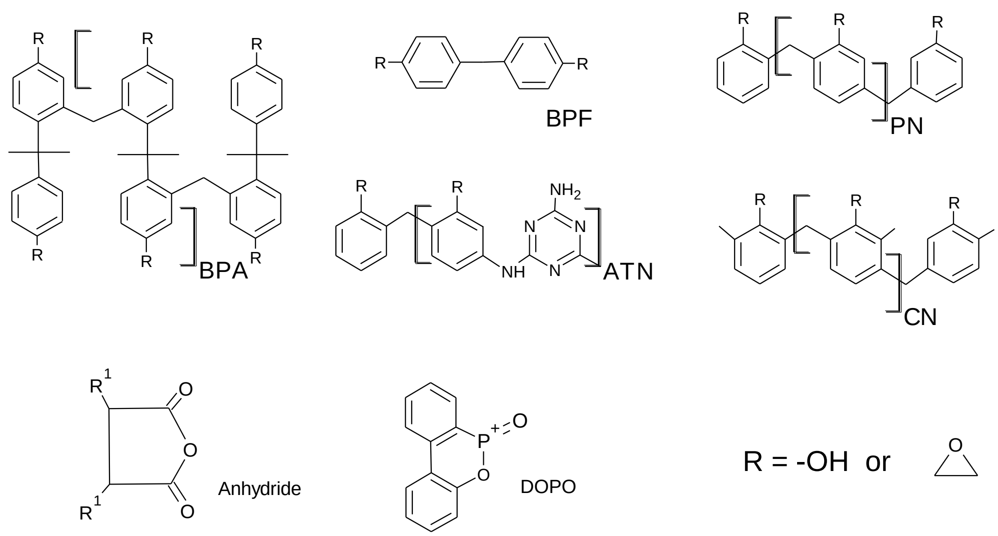

Figure 1: Common back-bone construction for epoxy and hardener

Generally, molecular polarizability can provide information about a materials dielectric properties, dielectric constant and dielectric loss as a function of frequency. Polarizability is the relative tendency of a charge distribution, like the electron cloud of a molecule, to be distorted from its normal shape by an external electric field. This global polarization ability consists of four different dielectric mechanisms which include electronic, atomic, orientation or dipolar and ionic polarization mechanisms. Each dielectric mechanism effect has a characteristic relaxation frequency. Molecular dipolar characteristic relaxation frequency is the most critical mechanism for printed circuit board material and the characteristic frequency is around $10^2 \sim 10^{10}$ Hz. The general principle in predicting and comparing molecular polarity is the comparison of similar regions of the molecule and taking Lewis structure lone pairs and/or single unpaired electrons into account. Our studies compare the coincidence between several kinds of common mature resin system using novolac curing agent , their dielectric properties and the expectation of the theory. Bromide resin construction and bisphenol A novolac resin construction, for instance, have more lone-pair electrons and unsymmetrical regions, and lead to inferior dielectric property performance compard to other construcions.

Beside molecular construction, latent catalyst is another important factor in the resin recipe for dielectric properties. Catalyst plays a role as an initiator to kick-off and speed-up polymer chain growing reactions. It dominates the reaction reactivity and reaction mechanism/route/order between varied epoxy resins in the recipe.

In general, a variety of latent catalyst types are available. The common chemical for copper clad laminate is imidazole and its derivatives, such as 2-ethyl imidazole, 2-benzyl-4-methyl imidazoline, 2-phenyl imidazole, 2-phenyl-4,5-dihydroxymethylidazole, etc. and some metal salts and their complexes, such as boron trifluoride, TBPAAc, zinc, manganese, cobalt, copper or acetylacetonates and peroxide for unique curing mechanism and resin systems.

Resin and Hardener Impact for Dielectric Properties

It's no doubt that resin types and hardener systems can decide the material's final dielectric property performance rank. Actually, dielectric constant and dielectric loss are the negative and positive proportions respectively as functions of CCL resin content. Test frequency is another key factor for dielectric properties. Here we use resin content around 55% and test frequency of 1GHz as a baseline to compare the resin and hardener impact. Figure 2 is a fundamental dielectric property study result. It's easy to figure out the significant factors and impact through ANOVA analysis.

Two-way ANOVA: Resin & Hardener Impact in Df

Source	DF	SS	MS	F	P
Resin	3	0.0000087	0.0000029	4.14	0.021
Hardener	2	0.0003189	0.0001594	228.28	0.000
Error	18	0.0000126	0.0000007		
Total	23	0.0003401			

Two-way ANOVA: Resin & Hardener Impact in Dk

Source	DF	SS	MS	F	P
Resin	3	0.046033	0.015344	3.44	0.039
Hardener	2	0.397908	0.198954	44.66	0.000
Error	18	0.080192	0.004455		
Total	23	0.524133			

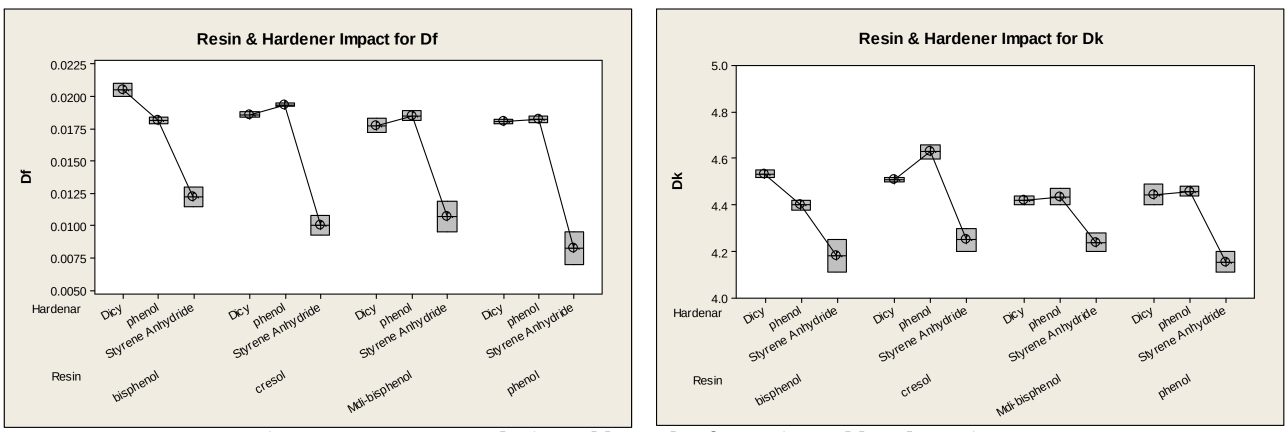

Figure 2: ANOVA analysis and box-plot for resin and hardener impact

Table 1 : Polarizability and density theoretical values over structures

Basic Construction	Polarizability (Å^3)	Density (g/cm^3)
Bisphenol-A Novolac	54	1.02
Cresol Novolac	39	1.01
Phenol Novolac	34	1.04
TBBPA	43	1.81
Bisphenol-F	22	1.00

Studied factors and levels include phenol novolac, cresol novolac, bisphenol-A novolac and TUC modified bisphenol-A novolac variables in epoxy part and arranged in pairs with dicy, phenol novolac and acid anhydride polymer variables in hardener part. Resin systems and hardener types are significant factors under 95% confidence levels. We can find out that anhydride hardener is a critical factor to reduce dielectric properties but it shows higher variance relative to other factors. In this study, we use common imidazole as a latent catalyst without screening and optimization measures, as it was considered as a critical factor in this high variance case.

The calculated molecular theoretical polarizability and density of the basic resin back-bone constructions are listed in Table 1. We could utilize the theoretical values to estimate resin system relative dielectric properties performance under identical hardener and catalyst curing mechanism. Lead-free capable mainstream bispehnol-A novolac type resin system shows inferior dielectric properties compared to others. Contrasting this with actual materials dielectric properties results, material theoretical polarizability order is matched with actual study results as is shown in the following model of a 4 layer board stripline pattern to get a clear picture of signal attenuation .(Figure 3.)

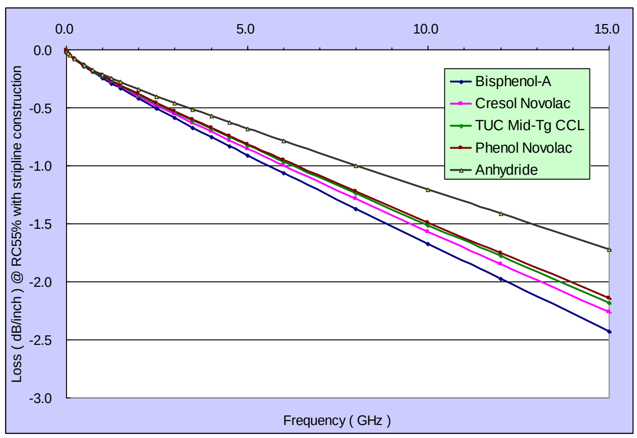

Figure 3: Signal attenuation over resin systems.

The model was configured with 4mil line width and different trace lengths for the pairs and for an average resin content of 55%. The circuitry is designed with 50 ohms impedance and following most of the high layer count and high speed applications. In order to minimize and eliminate the noise generated from the through holes, connectors and measurement, we reduced the through hole diameter size to 6 mil, used 26GHz frequency capable SMA connectors and 30GHz band width measuring equipment with noise filtering and applied comparative techniques to extract and benchmark neat material signal loss performance over the range of resin and hardener systems.

Signal attenuation tendency is identical with base materials dielectric properties. Take phenol novolac resin material as a baseline, the mainstream lead-free capable bisphenol-A novolac and advanced anhydride cured based materials have around 0.1 dB/inch higher and 0.2 dB/inch lower signal attenuation loss accordingly at a 5GHz working frequency. For a variety of lead-free capable FR4 materials in market, it’s easy to find an alternative material in thermal performance aspects, but it’s difficult to find out a FR4 material with superior dielectric properties when the signal attenuation performance is a critical concern in applications. Actually, choosing a suitable FR4 material can effectively extend the material design life cycle and/or reserve more bandwidth for bus and chip components.

Furthermore, phenol novolac resin has superior dielectric properties while Bisphenol-A resin has the inferior values. However, the resin construction of phenol novolac gets more brittle and has a lower decomposition temperature by nature and these characteristics lead to inferior lead-free capable capability. Generally, from the formulation point of view, the material’s dielectric properties and the PCB process friendly/lead-free performance go in opposite directions. Currently, EU RoHS restriction is a must and therefore bisphenol-A novolac base system is the mainstream solution in order to gain a higher Td, T288, toughness etc. performance to overcome lead-free and PCB process friendly barrier issues putting electric performance aside. Previously we have conducted a series of studies in lead-free includeing the base resin system, laminate basic properties and PCB processing. The final PC board thermal reliability like TCT and IST were also noted. We found that in order to have a good PCB process window for a range of RCG applications, a balanced and moderated laminate's basic physical performance is important. Selecting a suitable modified novolac-cured system instead of signal and regular resin has the balanced performance; like low alpha one coefficient of thermal expansion with moderate Td. The IPC suggested Td of the material needs to be at least 320°C for it to be classified under lead free category. However, higher Td implies that the PCB processing window is narrower. In order to balance the thermal and electrical properties, designed materials lead in a novel polymer construction as marked with modified bisphenol-A resin system in brominates mid-Tg low CTE product to cope with the thorny thermal problems with superior electrical properties.

Latent Catalyst and Temperature Impact for Reactivity

The common latent catalysts for copper clad laminate industry include imidazole and its derivatives, likes 2-ethyl imidazole, 2-phenyl imidazole, 2-benzyl-4-methyl imidazoline, 2-phenyl-4,5 -dihydroxymethylidazole, etc. as shown in Figure 4. Imidazoles have five membered rings containing two nitrogens. The latent catalyst cross-linking with epoxy is accomplished

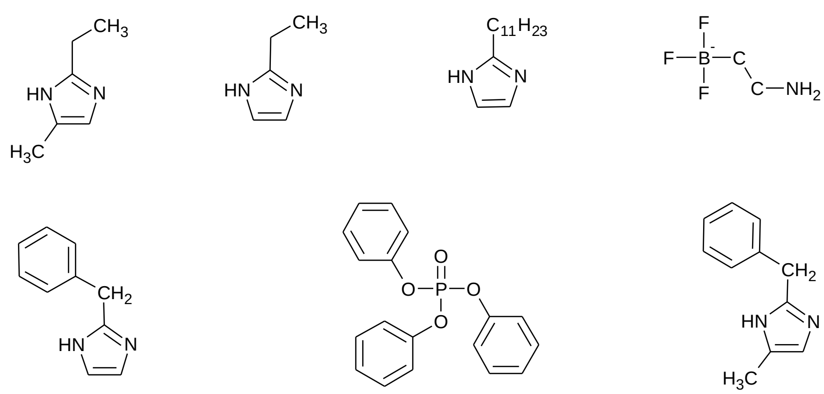

Figure 4: Common imidazole types, TPP and BF3.MEA latent catalysts

by the tertiary amine mechanism. Each catalyst has their own characteristic reactivity rates, active temperature start points, ranges, process windows and result in different physical and electrical properties. Beside the imidazole series catalyst, we also introduced ionic initiators, like BF_3.MEA and TPP in the study matrix to understand the impact and difference between catalyst types and reactivity in material performance.

In academic research, people establish reaction mechanistic equations and parameters by applying different temperature dynamic ramping rate scans, but this kind of theoretical approach is unsuitable for application in an actual material study and development application. In CCL practical applications, people use the measure resin gel time as an index to simplify and quantify overall resin reactivity using one factor and then adjust prepreg powder gel time to represent resin conversion for lamination process windows. In fact, it's suitable for process control but can't provide sufficient information to describe resin reactivity and process window behaviors. However, we can use it as a good indicator in a preliminary study.

One fundamental study selected four epoxy resins, five hardener types, four catalyst types and different reaction temperature conditions in the test matrix. Here we use concise gel time properties as a response to understand the behavior of the reaction. Figure 5 is an overall box-plot for the evaluation matrix. We can distinguish the influence and difference between catalyst, hardener and temperature in resin reactivity behaviors easily. Some of the catalyst types are more temperature sensitive than others and shows longer box bars in the chart. Some of the catalysts show selectivity in reaction mechanism with significant contrast activity in terms of hardener types in the chart. It's a simple method to present a clear relationship profile by changing the grouping order of variables between specific and interesting factors. Generally, imidazole series catalysts have higher reactivity in common resin systems, however ionic initiators, like BF3.MEA catalyst maybe more suitable to kick-off some unique phosphide hardener reactions.

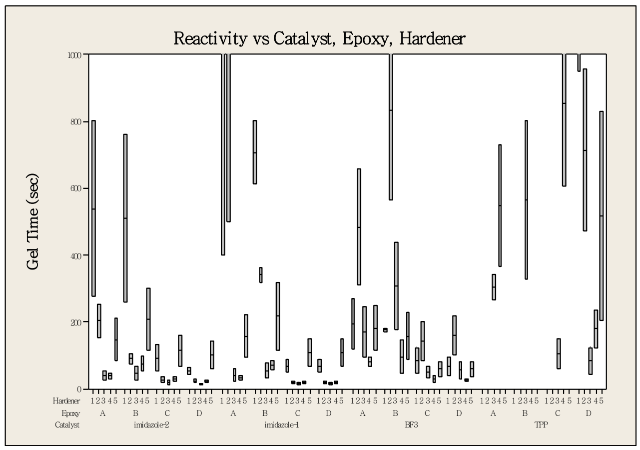

Figure 5: Reactivity in terms of epoxy, hardener and catalyst

Epoxy part:
(A) Basic BPA Epoxy
(B) Low Dk/Df Epoxy
(C) Phenol Novolac Epoxy
(D) BPA Novolac Epoxy

Hardener part:
(1) Phosphide-1
(2) DDS
(3) Dicy
(4) Acid Anhydride
(5) phosphide-2

Reactivity Impact for Signal Integrity

We would like to screen down the material factors to one lead-free capable FR4 material using a variety of imidazole derivative (branch) catalysts (#1~#4) and catalyst dosage quantity to further study and determine the desired reaction rate for dielectric loss performance comparison. According to a two-way ANOVA analysis and box-plot as shown in Figure 6, catalyst grade and reaction rate are all significant factors that show interactions and affect the dielectric loss property. Under similar imidazole series catalysts, they show dramatic changes in electrical performance trends and variance over reaction rates. Take catalyst #3 and #4 for instance, the reaction rate optimization directions are opposite. It's clear that latent catalysts play a critical role in material design.

Catalyst #4's structure connects a benzene ring and additional branch chains on imidazole. In theory, it was thought this would generate serious stereo hinderance in the reaction giving a low conversion reaction rate recipe and leading to a higher variance results compared to other catalysts.

Two-way ANOVA: Df versus Catalyst, Reaction Rate

Source	DF	SS	MS	F	P
Catalyst	3	0.0000176	0.0000059	15.00	0.000
Rate	2	0.0000030	0.0000015	3.820	0.036
Interaction	6	0.0000198	0.0000033	8.410	0.000
Error	24	0.0000094	0.0000004		
Total	35	0.0000498			

S = 0.0006262 R-Sq = 81.12% R-Sq(adj) = 2.46%

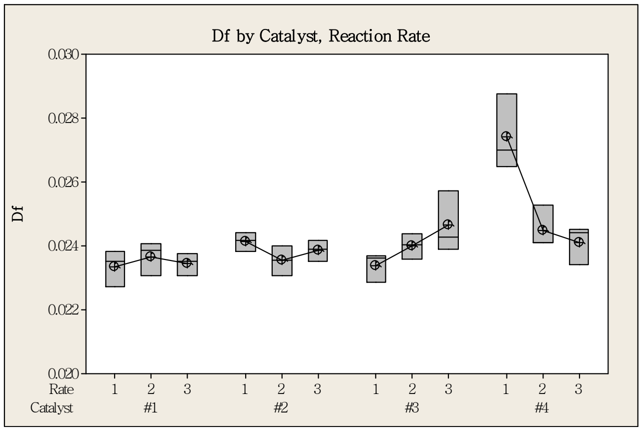

Figure 6: ANOVA analysis and box-plot for Df over catalyst types and reaction rate; Reaction rate level: 1 / low; 2 / moderate; 3: high

Case Study for Signal Integrity Optimization

Here we actually developed a novolac cured low CTE high Tg and a low Dk/Df high Tg FR4. We use these two materials as examples to discuss the impact on signal integrity and try to achieve lower dielectric constant and dielectric loss through the optimization measures in catalyst aspect instead of changing epoxy and/or hardener systems.

We built a stripline construction TV to measure and compare signal attenuation performance with 50 ohms target impedance and around 70-75% high resin content level as shown in Figure 7. We measured these two materials values before and after catalyst optimization measures. The extracted effective dielectric constant and effective dielectric loss value in terms of frequency is up to 20GHz which follows the IBM SPP technique. The dotted line pair, higher dielectric constant and dielectric loss, is the performance of the common catalyst without optimization.

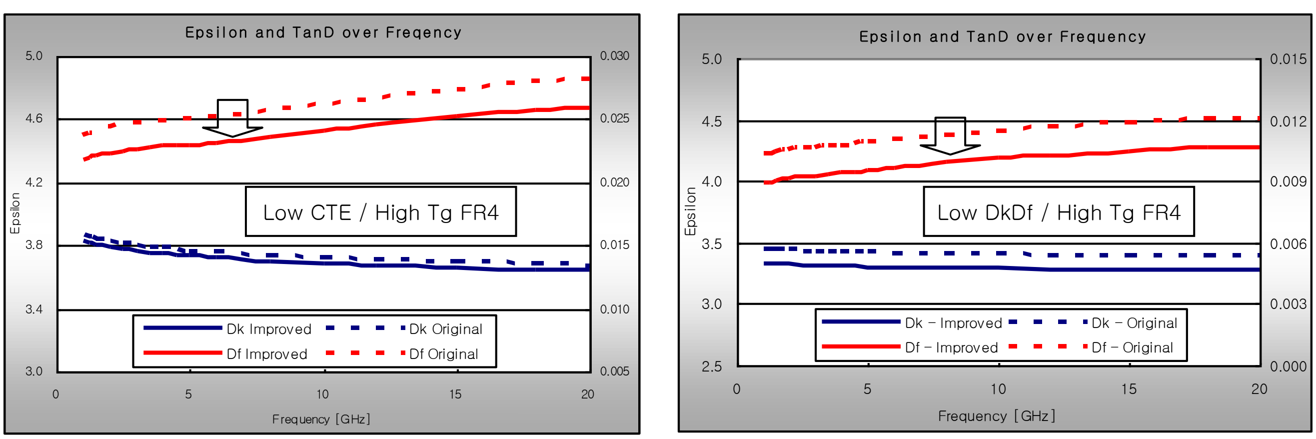

Figure 7: Dielectric constant and dielectric loss performance with/without catalyst optimization.

After testing a series of catalysts, and reaction rates in our matrix with trade-offs with process windows, we utilized multi-imidazole catalysts system for low CTE high Tg product and applied one unique catalyst for low Dk/Df high Tg product to improve the performance of dielectric properties. Basically, the change of dielectric constant is minor, i.e. around 5%, but the gap in dielectric loss is more significant. The catalyst improved the materials' dielectric loss around 10~20% depending on the frequency applied in these two materials case.

Conclusion

Signal integrity is a very complex question and demand is getting more and more critical. Material-wise, people used to amend resin and hardener types to improve dielectric properties. It's a simple and quick way to modify and improve materials relatively. Unfortunately, this kind of approach might suffer inform years of safety confirmation and qualification. Our study found that the catalyst system is a factor that can move us one step further in performance under identical resin system and hardener conditions. We can now utilize mature resin systems with better signal integrity. This means that material's thermal performance must be fully understood. This approach could minimize the change in basic properties and reduce time and cost consumption during redesign and qualification.