Extremely low loss halogen-free substrate materials

Laibao Zhang, Kevin Bivona, Tomoaki Nakanishi, Qiang Wei, Yoji Nakajima
AGC Multi Material America
1555 W 10th Pl, Tempe, AZ 85281 USA
Phone: (480) 392-3153
Email: Laibao.Zhang@agc.com

Abstract
To meet the increasing demands of high-speed/high-frequency computing and communication systems, further reduction in the dielectric loss (Df) of substrate material is needed. However, this must be balanced with environmental concerns of halogenated flame retardants, leading to the need for halogen-free resin compositions. Current low loss resin systems have limitations in meeting both low Df and good flame retardancy with halogen-free resin compositions. This paper highlights a recent breakthrough in the trade-off relationship between low Df and flame retardancy while maintaining good copper peel strength and thermal properties. The development of high-speed/high-frequency laminates and prepregs, with Dk being adjustable through low Dk filler, is discussed. The use of multiple glass cloths to control the cost and overall material properties is also discussed. The potential of these materials for high-speed/high-frequency chip packaging applications is discussed. The developments from this work will help to create more sustainable and high-speed/high-frequency materials for PCB and chip packaging applications.

Key words
chip packaging, halogen-free, low loss, substrate material

I. Introduction

The post-modern world is undergoing a rapid transformation, becoming a tightly interconnected network where communication plays a crucial role. As we look ahead, the volume of communication data is expected to soar, calling for faster and more efficient signal processing solutions. At the same time, the urgency to address power consumption concerns has become a pressing societal issue, compelling researchers and engineers to seek innovative ways to tackle this challenge.

One of the driving forces behind this data revolution is the emergence of high-speed wireless networks, with 5G technology poised to take center stage. However, to ensure optimal performance and signal integrity in 5G networks, low loss substrates have become essential, particularly when utilizing higher frequencies. This is because as operating frequencies increase, the dielectric loss of substrates becomes more pronounced. For example, in antenna-in-packages for RF front end, low loss materials that transmit high frequencies are required for substrate materials. Antenna-in-package is expected not only for smartphone applications, but also for autonomous vehicle radar applications. Additionally, the expansion of high-speed wired networks such as 112/224 Gbps systems for high-speed AI servers adds further need for low loss technology development.

In response to these challenges, we have developed extremely low loss substrate materials tailored to meet the demands of cutting-edge applications, such as 5G, 112/224 Gbps systems, and autonomous vehicle radar applications.

II. Extremely low loss halogen-free material

A. Extremely low loss substrate material

Initially, extremely low loss substrate material was developed as lowest loss level substrate materials (CCL and prepreg) for especially high-speed digital PCB applications such as for 112/224 Gbps systems. The key properties of an extremely low loss substrate material are presented in Table 1, with Df and Dk being the two most significant parameters under consideration.

Table 1 Dielectric Properties of extremely low loss laminates with various glass cloths

	BCDR		
Extremely low loss laminate with NE glass	Freq. / GHz	Dk	
	14	3.07	0
	28	3.07	0
	40	3.07	0
Extremely low loss laminate with NER glass	Freq. / GHz	Dk	
	14	3.05	0
	28	3.05	0
	40	3.05	0
Extremely low loss laminate with L2 glass	Freq. / GHz	Dk	
	14	3.01	0
	28	3.01	0
	40	3.01	0

1078 2ply, 5.5 mil

Figure 1 illustrates the insertion loss characteristics of the extremely low loss laminate at various frequencies. These results demonstrate that the extremely low loss laminate outperforms existing low loss laminate in terms of signal integrity. The microvia structure of a 20 layer PCB using extremely low loss laminate is depicted in Figure 2, demonstrating the excellent laser processability of the laminate. Table 2 presents the D-coupon test results, which are indicative of excellent thermal reliability of the extremely low loss laminate. The extremely low loss laminate successfully passed 6 reflow cycles and 100 heat cycles ranging from -55°C to 170°C, demonstrating its superior microvia reliability.

The development of extremely low loss substrate materials has seen PCB substrate materials leading the way, as conventional chip packaging substrate materials did not require such low loss materials. Traditionally, polar materials with high loss, such as epoxy, imide, and BT resins, have been used as chip packaging substrate materials. However, as signals become higher in frequency and speed, and the technological convergence of chip packaging and PCB progresses, extremely low loss substrate materials would also be required for chip packaging substrates.

In this work, we have made full use of material design technology for the development of extremely low loss substrate materials for not only PCB substrates but also chip packaging materials.

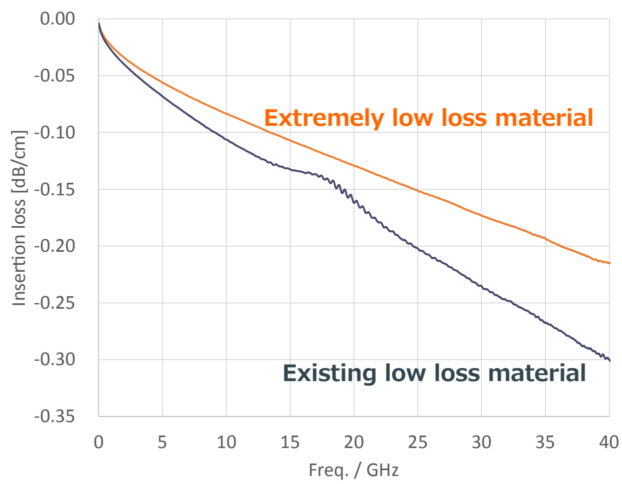

Figure 1. Insertion loss characteristics at different frequency

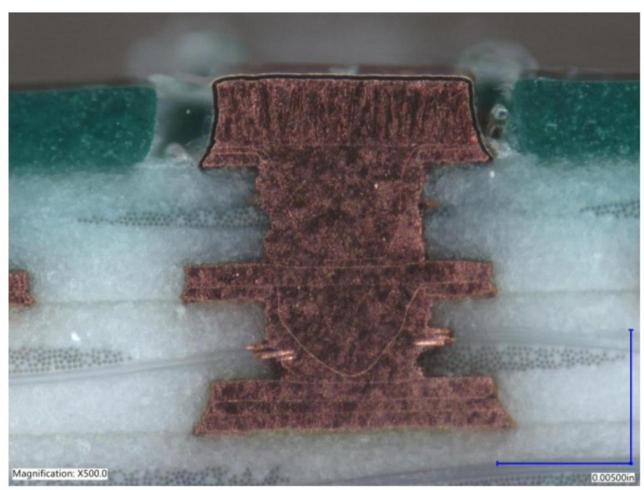

Figure 2. Cross-sectional view of stacked microvia

Table 2 Reflow test and 170°C heat cycle test results of D-coupon

Coupon	Reflow test				170 deg C cy		
	Net1	Net2	Net1	Net2	Net1	Net2	Net
1	>6	>6	-0.1	-0.2	>100	>100	1.7
2	>6	>6	0.0	-0.2	>100	>100	1.6
3	>6	>6	0.1	0.0	>100	>100	1.3
4	>6	>6	0.2	0.1	>100	>100	1.6
5	>6	>6	-0.1	-0.2	>100	>100	1.0
6	>6	>6	-0.0	-0.3	>100	>100	1.6
7	>6	>6	0.1	-0.2	>100	>100	2.1
8	>6	>6	0.1	-0.2	>100	>100	1.7

B. Extremely low loss halogen free substrate material development

Most chip packaging applications require halogen-free substrate materials. High Df and high polarity resins such as epoxy, imide, and BT resins often have a certain degree of inherent flame retardant properties. On the other hand, resins with low Df and low polarity tend to be flammable, making a halogen-free substrate material harder to achieve. Despite these challenges, we have successfully developed a halogen-free substrate material with Df=0.0014. The typical properties of the material as laminate are shown in Table 3.

Table 3 Properties of extremely low loss halogen-free laminates

Property	Item	Typical value	U
Thermal	Tg	200	°
	CTE, Z-axis	40	ppm
	Td (5% weight loss)	430	°
	T300	120+	m
Electrical	Dk (IPC)	3.4	-
	Df (IPC)	0.0014	-
Physical	Peel Strength	0.74	N/
	Flame Resistance	V-0	-

It is also crucial to address potential challenges posed by unreacted functional groups in thermoset materials after curing. In certain cases, these functional groups may cause an increase in Df and Dk over time. For example, the presence of a 1,4-butadiene structure in SBS (styrene-butadiene-styrene) has been reported to undergo oxidation, generating polar hydroxyl groups that can negatively affect electrical properties. However, we found our material exhibited excellent stability after aging at 125°C, showing no noticeable changes in Df and Dk. This demonstrates the material's reliability and potential suitability for high-frequency applications where consistent electrical performance in high temperature environments is essential.

In addition to low loss, certain applications also require low Dk, aiming for values of 3.0 and below. The advantage of low Dk dielectric material lies in its ability to reduce the dielectric thickness for a given trace width, influencing the signal propagation of the device. In recent years, significant advancements have led to the development of low Dk fillers. By incorporating low Dk fillers in combination with conventional silica fillers, it becomes possible to lower the Dk of the material, achieving Dk even slightly under 2.9. Figure 3 shows Dk decreases with the increasing amount of low Dk filler. This approach would empower designers to tailor the material's Dk to meet the precise requirements of various applications, enhancing signal performance and overall functionality.

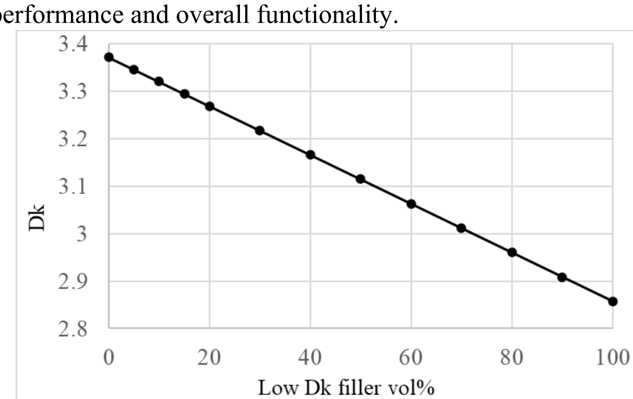

Figure 3. Dk can be adjusted by using low Dk filler

To enhance the miniaturization of electronic devices, it is also essential to achieve excellent adhesion of the material to copper foils. The adhesion to foil is influenced by factors such as chemical structure, curing density, and Cu foil surface roughness. But due to the distinctive chemical structure of our resins, we can achieve a Cu peel strength higher than 0.7 N/mm, even when dealing with low-profile copper (Rz=1.0 um). Moreover, our resins demonstrate stability in mechanical properties, even after prolonged aging. As shown in Figure 4, when subjected to an extraordinary amount of aging at 190°C for 16 weeks, the flexural strength remains at 65% of its original value.

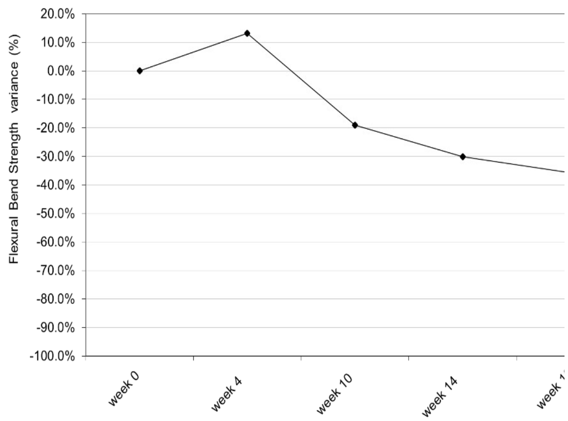

Figure 4. Plot of flexural strength vs time at 190°C

Lamination is affected by a variety of factors, including processing parameters, intrinsic material properties, and environmental conditions. The layers must adhere strongly to one another and to the copper foil surface. Otherwise, defects such as delamination or misalignment of fabric layers may occur. The elastic deformation of the fiber network is prohibited by curing the matrix material under compression.

Proper resin flow and curing rate are required to form interpenetrating polymer networks between fiber networks during compaction, to avoid fiber-fiber and fiber-copper contacts. We characterized the rheological properties of the new material and measured the squeeze flow of the slurry under pressure. Figure 5 illustrates the use of a typical laminate with the new material, employing a 12-ply construction. No resin rivers or voids were observed, indicating a defect-free lamination process. These findings indicate that this new material exhibits favorable lamination properties, enabling its effective use in various applications where strong adhesion between layers and minimal defects are crucial for optimal performance.

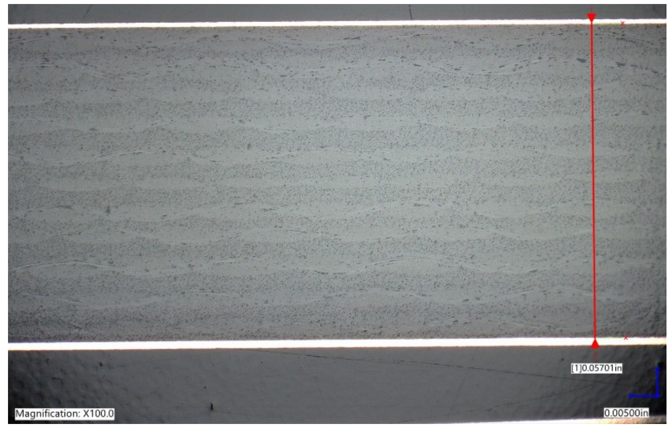

Figure 5. Cross-sectional view of 12-ply laminate

It is critical for high-frequency materials to have superior heat resistance. The thermal properties were evaluated by thermo-gravimetry (TG), dynamic mechanical thermal analysis and thermomechanical analysis. During the curing process, crosslinking mechanism effectively constrained the movement of polymer chains, reinforcing the material's resistance to thermal expansion. The TG results demonstrated commendable thermal stability, as indicated by the 5% weight-loss temperature of 430°C. The Tg of this material was observed at 200°C.

The utilization of appropriate glass cloths enables precise control over material properties while maintaining cost-effectiveness. Recent advances in fiberglass weaving have led to more isotropic glass distribution, resulting in reduced skew from local variation. This improvement also enhances surface smoothness, dimensional stability, and facilitates both laser and mechanical drilling processes. The X-Y CTE is also dictated by the glass cloth used. We have achieved X-Y CTE values below 12 and 4 ppm/°C for $\alpha 1$ and $\alpha 2$, respectively with a low-cost E glass cloth. These results demonstrate the superior thermal expansion properties of this new material.

III. Conclusion

Our new material technology presents remarkable performance advantages over current low loss materials. A notable feature of the extremely low loss halogen-free material is its significantly low Df. Moreover, this material technology offers a range of other important benefits, including adjustable Dk to below 2.9, improved thermal, environmental, chemical, mechanical reliability, as well as ease of processing. We are continuing to develop chip packaging substrate materials that balances lower CTE and even lower loss. Its attributes of reduced signal loss and enhanced stability make it an excellent choice for cutting-edge, high-speed, high frequency electronic designs, such as antenna-in-package and autonomous vehicle radar applications, and as a material to facilitate the realization of 112/224 Gbps systems.

Acknowledgment

Our deepest gratitude to Greg Almen and Doug Leys for their invaluable support and discussions. Thanks to Toshifumi Kakiuchi of KTC and Taiki Kuroda of AGC YTC, Japan, for assisting with analytical characterizations. Special appreciation to the AGC PD team, Bob Gosliak of BD team, Ty Ilercil of BA team for making this project a reality.

References

[1] M. Lewin, E.D. Weil, “Mechanisms and Modes of Action in Flame Retardancy of Polymers”. In: A.R. Horrocks, D. Price, editors. Fire Retardant Materials. Woodhead Publishing Limited; Cambridge, UK: 2001. pp. 31–68. Chapter 2

[2] J. Green, “Mechanisms for Flame Retardancy and Smoke Suppression—A Review”. J. Fire Sci. 1996, 14:426–442. doi: 10.1177/073490419601400602

[3] Shui-Yu Lu, Ian Hamerton, “Recent developments in the chemistry of halogen-free flame retardant polymers, Progress in Polymer Science”, Volume 27, Issue 8, 2002, Pages 1661-1712.

[4] E. Westberg, J. Staudinger, J. Annes, and V. Shilimkar, “5G Infrastructure RF Solutions: Challenges and Opportunities,” IEEE Microwave Magazine, vol. 20, no. 12, pp. 51–58, 2019.

[5] Preeya Kuray, Thomas McCarthy, Caleb Ancharski, and Yoji Nakajima, “Properties of low dielectric constant buildup materials containing micron sized hollow silica”, 2024 IEEE 74th Electronic Components and Technology Conference

[6] A. O. Watanabe, M. Ali, S. Y. B. Sayeed, R. R. Tummala and M. R. Pulugurtha, "A Review of 5G Front-End Systems Package Integration," in IEEE Transactions on Components, Packaging and Manufacturing Technology, vol. 11, no. 1, pp. 118-133, Jan. 2021, doi: 10.1109/TCPMT.2020.3041412.