Presented at IPC Printed Circuits Expo® 2002
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Low Transmission Loss Cyanate Ester Materials with Loose Cross-Linked Structure

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Abstract
A new thermosetting resin system with modified cyanate ester resins having a loose cross-linked structure and alloyed with polymers was developed to provide low dielectric constant (Dk) and low dissipation factor (Df) materials for high-frequency PCBs. The laminates with this resin and glass fabrics demonstrated low transmission losses at high frequencies up to 30 GHz. Those with inorganic filled resin and glass fabrics were almost comparable in Dk and Df to the conventional PTFE laminates. These new materials have a high Tg, low moisture absorption, and excellent mechanical performance. They showed the same processability and reliability as the conventional FR-4 materials. They will be suited to the multilayer PCBs for high-speed communications as well as the low loss circuit boards for telecommunications.

Introduction

In the sophisticated information-oriented society, large-volume and high-speed data transmission is imperative for the network systems and the related electronic equipment. The printed circuit boards (PCBs) used in these applications are required to transmit various kinds of high quality data at higher speed, for which reason the frequency on the electric circuits have become higher. However, the higher the frequency is, the more easily the electric signal on a circuit board will attenuate. To reduce transmission loss is one of the crucial problems of the high-frequency PCBs. Consequently, the development of the PCB materials is focused on low dielectric constant (Dk) and low dissipation factor (Df) materials for high frequency PCB use.

Cyanate ester (CE) resin is well known as one of the thermosetting network polymers with high heat performance and excellent dielectric properties. CE resin itself was developed back in 1967, and the application in the electronic industries has been studied from the start. Some materials, such as the blend materials with imide compounds or epoxy resins, were developed in order to improve the toughness and moisture resistance[1]. In the 1990's, CE resin drew attention again as a low Dk material suited to high-speed communication,[2] however, its dielectric properties could not satisfy the demands for high frequency PCBs.

It was found that some novel modified CE resins exhibit more desirable dielectric properties than the conventional resins. This paper reports on a new low Dk and low Df resin system and introduces low transmission loss PCB materials preferable for high-speed communications.

Experimental

Preparation of Cured Resin and Laminate

Aryl cyanate ester was allowed to react with modifying compounds in organic solvent to produce the modified CE resin, and then catalysts are added. The cured resin was prepared by casting the resin solution onto PET film, rubbing it into resin powder, and then pressing the powder into 1.0-mm-thick specimen using a PTFE spacer. The copper clad laminate was made by impregnating the resin solution into glass fabric, drying it to get prepregs, and pressing them with copper foils. The pressing was for 90 minutes at 175°C and the curing was for two hours at 230°C.

Properties of the Cured Resin

The molecular weight of the cross-links (Mc) was calculated based on the specific gravity and the storage elastic modulus at the rubber-like region measured with a dynamic visco-elastic analyzer (DVE). The functional groups in the cured resin were identified by infrared absorption spectra (FT-IR).

The dielectric properties of the cured resins in the range of 1MHz to 1GHz were measured by an impedance material analyzer based on IPC-TM-650. The transmission loss of the laminates up to 30 GHz at 25°C was evaluated by the triplate line resonator method on the wiring board specimens (dielectric thickness: 0.8mm, copper foil: 18μm thick, signal line width: 1mm, characteristic impedance: approx.50Ω) using a vector-type network analyzer. The Dk and Df were calculated based on the attenuation curves (S21) of the transmission lines.

Dielectric Properties of Conventional CE Resin

Dielectric properties of polymeric materials, especially Df, relate to the polarization and mobility of their chemical structure.[3] Cyanate esters have been known as the thermosetting resin curing through cyclotrimerization of reactive cyanato functional groups into a symmetric and rigid triazine structure, which is thermally stable and low in polarity. In thermosetting resins, the reactive functional groups are highly polarized and may keep polarity even after curing. To reduce the polarity of cured resins, the resin systems should react as much as possible so as to decrease the content of the reactive functional groups remained after curing.

Figure 1 shows the dielectric properties of the cured conventional CE resin. The Df of the conventional resin rises extremely as the frequency increases. This is caused by the remaining not-reacted cyanato groups, which have high polarity and high mobility.

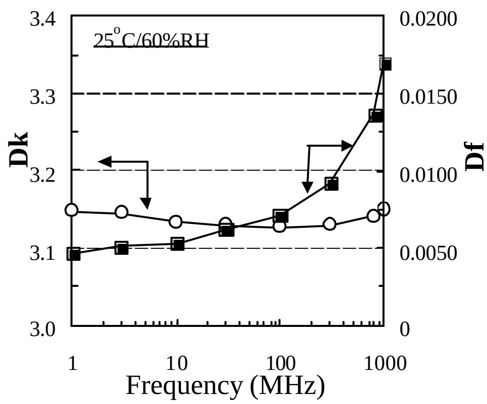

Figure 1 - Dielectric Property of CE Resin

The conventional CE resin has a very rigidly cross-linked structure. Therefore, the resin system loses its fluidity as the hardening progresses, and because of the increase in viscosity the mobility of the cyanato groups and molecular chains decreases rapidly. It is difficult for the cyanato groups of the CE resin to react completely and form the triazine structures, so that some not-reacted cyanato groups remain within the resin. Consequently, the conventional CE resin could hardly achieve its ideal dielectric properties, particularly Df in high frequency bands.

Cross-Linked Structure of Modified CE Resin

A new technique to modify the densely cross-linked structure of the cured resin was developed as a method of improving the dielectric properties. It is a technique to form a loose cross-linked structure by modifying CE resin with some compound, which will be incorporated into the cross-linked structures.[4] This technique results in a lower increase in viscosity during curing, and delays the time of losing fluidity. This feature will increase the reaction rate of cyanato groups; consequently, the quantity of the not-reacted cyanato groups will decrease. Also, the cured resins become more flexible and less brittle.

It has previously been reported[5] that the trimer obtained by combining cyanate esters with some compound shows an unusual triazine ring structure in which the modifying compound is incorporated in a triazine ring (Figure 2; left). And as shown in Figure 3, the molecular weight of cross-links (Mc), calculated from the visco-elastic properties and the specific gravity, becomes larger as the modification amount increases.[6]

Considering that the modified trimers preferentially have a structure of bifunctional. It was concluded that the modified cured resins would alter the usual three-dimensional rigid structure by building a unique loose cross-linked structure having a lower cross-linking density, as shown in Figure 2.

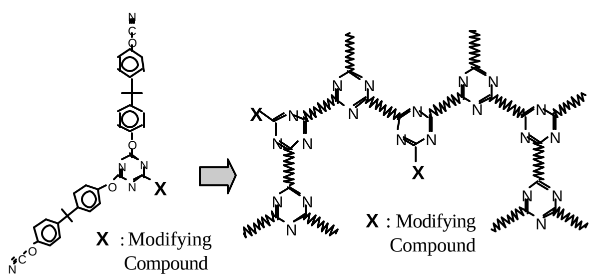

Figure 2 - Modified Trimer and Cross-Linked Structure

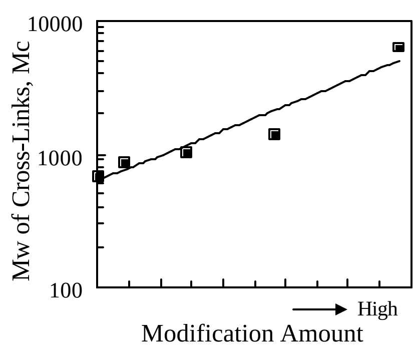

Figure 3 - Molecular Weight of Cross-Links (Mc)

Polarity of Cured Modified CE Resin

From the infrared absorption spectra of the modified CE resins, it was found that the not-reacted cyanato groups diminishes and eventually disappears as the modification amount increases (Figure 4). At the same time, cyclotrimerization increases. Thus, the resins with a higher modification amount will exhibit a higher reaction rate of the cyanato groups and more formation of triazine structures. These features of the resin systems seem to have improved their dielectric properties.

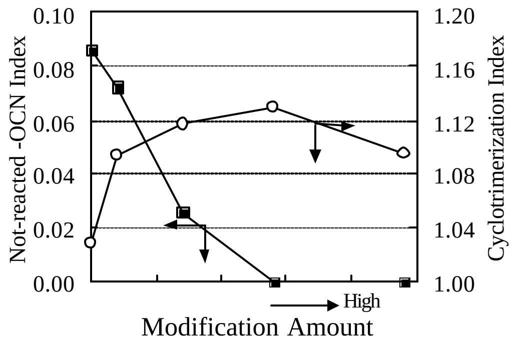

Figure 4 - Functional Group in Resin

Dielectric Properties of Modified CE Resin

Figures 5 and 6 show the dielectric properties of the cured resin of both modified and conventional resins. The modified CE resins achieved lower Dk and Df, particularly much lower Df in high-frequency bands, than the conventional resins. The results confirmed that the modified CE resin has more desirable dielectric properties than the conventional cured resins.

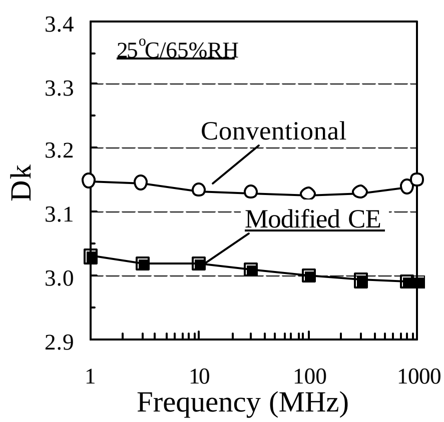

Figure 5 - Dk of Modified Resin

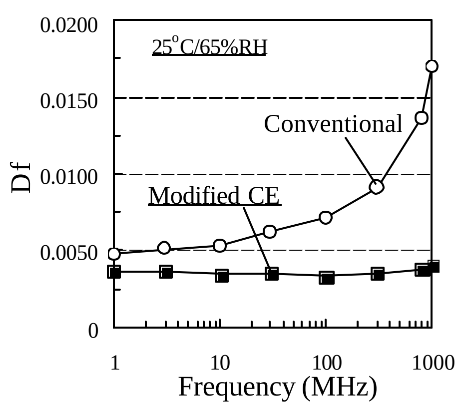

Figure 6 - Df of Modified Resin

The improvement of the dielectric properties of the modified CE resin was thought to be brought by its unique resin structure that is a loose cross-linked structure. From these results, it was realized that the technique of decreasing the cross-linking density of the cured resin by modifying the network structure with some compounds was effective in decreasing Dk and Df, because the reaction rate of the polarized reactive functional group would increase.[7]

In this technique, it is significant to minimize the degradation of thermal and physical properties of the resin, by adopting the method of decreasing the density of the reactive group, while maintaining the symmetry and rigidity of the original molecules although the cross-linking density decreases.

Lower Df by Alloying with Polymers

To improve the dielectric properties further, the alloying with some low-polarity and rigid-structure polymers was considered to be effective. But these kinds of polymers are incompatible; it is difficult to produce a homogeneous material. However, it was revealed that the modified CE resins of appropriately low cross-linking densities could be easily alloyed with the polymers that are conventionally incompatible.

The longer molecular chain in its cross-links enables the modified CE resin to tangle easily with polymers to produce a "semi-IPN" polymer. On the contrary, in the conventional resin a triazine ring will play as a knot in the cross-links, which makes it relatively difficult for the resin to tangle with polymers.

Thus, a new thermosetting resin system, an alloy of modified CE resin and low-polarity polymers has been developed, which features Dk <2.8 and Df <0.003 at 1GHz.

Lower Df with High Filler Content

New filler composite materials have been developed by efficiently loading a high content of inorganic fillers to achieve much lower Df characteristics, which was accomplished with the aid of an original surface treatment, called the Filler Interphase Control System (FICS).[8]

FICS is a treatment technology, which controls the properties of the interphase between fillers and matrix resin, to achieve high dispersion of fillers and good adhesion at the interface of fillers. By preventing the aggregation of fillers, FICS makes it possible to increase the filler content without bringing such disadvantages as moisture problem, low insulation reliability, and poor heat resistance.

Figures 7 and 8 show the effects of FICS treatment. The cured resin with FICS shows lower water absorption than that with untreated or typical coupling agent treated fillers, under a condition of pressure cooker test (PCT): 120°C/0.22MPa, 0 to 5 hours (Figure 7).

The cured resin with FICS treatment had a low Df of 0.0015 at 1GHz before the PCT. Even after 5 hours of the PCT, the Df was maintained below 0.005 whereas, those of the other resins increased linearly with PCT treating time (Figure 8).

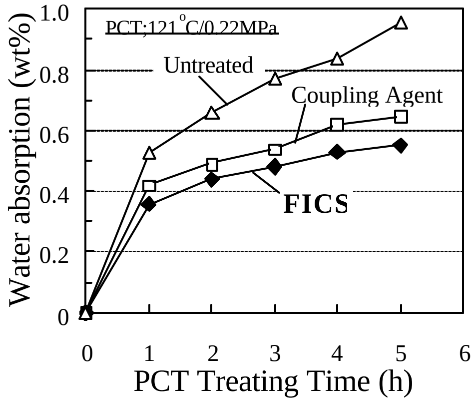

Figure 7 - Water Absorption of Resin with Filler

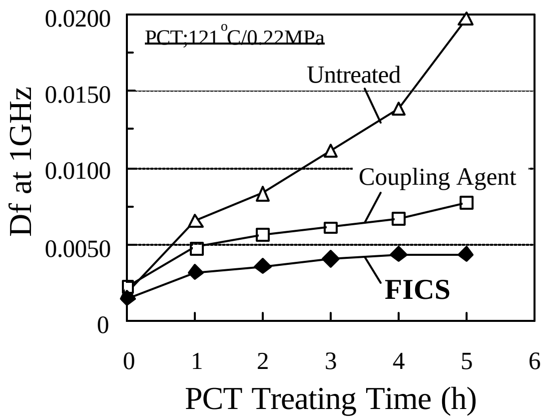

Figure 8 - Effect of Moisture on Df

General Properties of New Materials
Table 1 shows the general properties of the laminates made with the new thermosetting resin system compared with those of the conventional FR-4 and PTFE laminates. Two types of new materials were developed for multilayer PCB applications[9]. One was the modified CE resin material and the other was the filled modified CE resin material. The latter materials were applied to both E-glass fabric and special low-Dk glass fabric.

The Dk and Df of these laminates were calculated[10] from the transmission loss. The unfilled modified-cyanate/E-glass laminates demonstrated Dk: 3.44, Df:0.0043 at 1GHz; Df is about one-fifth of that of the conventional FR-4. The laminates with filled modified-cyanate had Dk: 3.50-3.70, Df:0.0027-0.0032 at 1GHz; the value of Df:0.0027 is almost comparable to that of the conventional PTFE laminate.

These new laminates are characterized by the Tg, as high as 185°C for the modified CE material and 170°C for the filled materials. These laminates had a good copper peel strength of more than 1.1 kN/m and a low water absorption less than a half that of FR-4. They showed the same levels of solder resistance, flammability (UL94V-0), and drilling processability as FR-4.

The laminates with the filled material showed a low coefficient of thermal expansion (CTE) in the z-direction, about one-fourth that of FR-4. The lower CTE will be effective in preserving an excellent through-hole reliability during the reflow process and the heat cycle evaluation.

Table 1 - General Properties of Laminates Made with New Materials

Properties		Unit	New Materials			PTFE	FR-4
Resin system			Modified -cyanate	Modified-cyanate [Filled composite]		PTFE	Epoxy
Glass fabric			E	E	Low Dk	E	E
Dielectric constant (Dk)*1	1GHz 3GHz	-	3.44 3.43	3.70 3.69	3.50 3.49	2.62 2.62	4.20 4.10
Dissipation factor (Df)*1	1GHz 3GHz	-	0.0043 0.0056	0.0032 0.0042	0.0027 0.0035	0.0026 0.0032	0.0215 0.0230
Copper foil peel strength	t:18μm	kN/m	1.30	1.10	1.10	1.90	1.50
Glass transition temp. (Tg)	TMA	°C	185	170	170	20	130
Coefficient of thermal expansion (CTE)	x-y(<Tg) z1(<Tg) z2(>Tg)	ppm/K	14 50 285	14 14 63	14 15 68	17 107 291	16 60 282
Flexural modulus	R.T. 200°C	GPa	18 15	23 15	21 10	11 7	20 4
Flexural strength	R.T. 200°C	MPa	526 468	395 303	332 257	202 59	500 85
Solder resist. (260°C-20s)	PCT*2	h	4	>4	>4	-	3
Water absorption	PCT-5h C-168/40/90	wt%	0.50 0.27	0.48 0.23	0.48 0.22	0.02 0.02	1.10 0.43
Surface flatness		μm	4.0-6.0	2.0-3.0	2.0-3.0	10.0-15.0	6.0-10.0
CAF durability*3		h	>1000	>1000	>1000	-	>1000
TH wall roughness after Drilling*4		μm	10 - 20	5 - 10	5 - 10	-	15 - 25
Flammability	UL-94	-	V-0	V-0	V-0	V-0	V-0

*1: Triplate-line resonator by Network Analyzer(25°C) *2: PCT: 121°C/0.22MPa
*3: TH-TH distance:0.3mm, 85°C/85%RH, 100Vdc *4: ϕ0.4, 80,000rpm, 2,400mm/min, 10,000hits

Dielectric Properties of the New Materials

Properties at High Frequency

Figure 9 shows the transmission loss of the laminates up to 30 GHz, measured by the triplate-line resonator method (dielectric thickness: 0.8mm, copper foil thickness: 18μm, signal line width: 1mm, characteristic impedance: approx.50Ω, temperature: 25°C). The new laminates showed low transmission losses up to 30GHz. For example, the loss at 2.5GHz was 3.5dB/m for the modified CE material and was 2.8-3.0dB/m for the filled. These new laminates could reduce transmission loss by 7.0-7.7dB/m compared with the conventional FR-4.

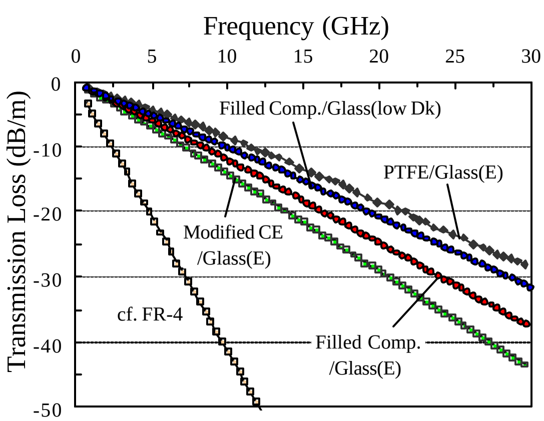

Figure 9 - Transmission Loss up to 30GHz

Figure 10 is the calculated results of Df. The Df of the modified CE material was 0.0073 at 15 GHz. The filled/low-Dk glass combination achieved the lowest Df value of 0.0047 at 15GHz, almost comparable to 0.0042 for the PTFE laminate.

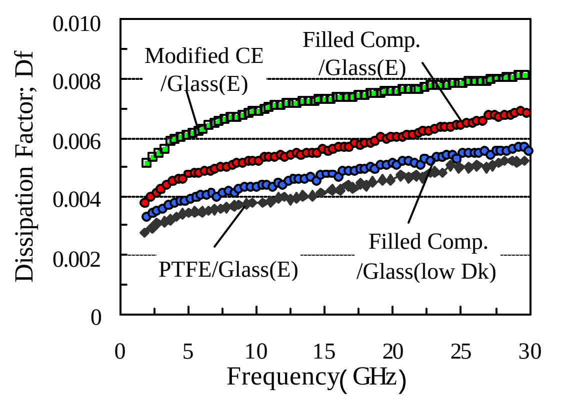

Figure 10 - Dissipation Factor up to 30GHz

Thermal Stability

Figure 11 shows the effect of temperature on the Df at 1GHz. The new laminates exhibited stable quality in the wide temperature range from -30°C to 90°C, while the Df of the PTFE laminate increased slightly with temperature.

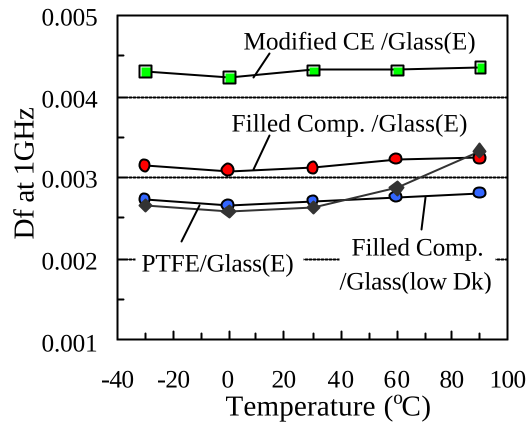

Figure 11 - Effect of Temperature on Df

Effect of Moisture

Figure 12 shows the effect of moisture on the Df at 1GHz. The Df of the new laminates showed smaller drift with moisture change under the PCT treatment up to 5 hours than that of the conventional FR-4, because of their lower moisture absorption characteristics.

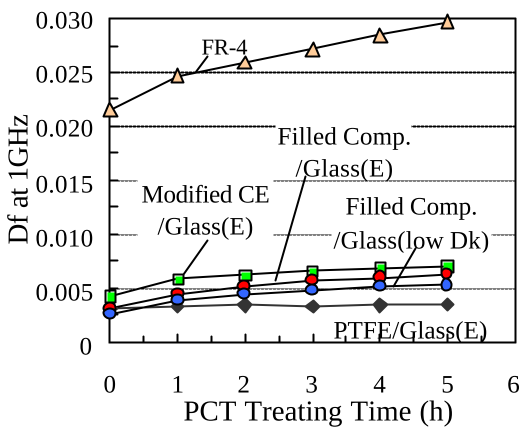

Figure 12 - Effect of Moisture on Df

The new laminates showed excellent dielectric properties at high frequency, and good stability against frequency, temperature, and moisture absorption.

Mechanical Properties

The flexural modulus of the modified CE laminate and the filled laminate were almost equal to (at room temperature) and 3.7 times (at 200°C) that of the conventional FR-4 laminate. They were almost 2 times (at both the temperatures) that of the PTFE laminate (Table 1). Because of their high elastic modulus, the new laminates will be effective in reducing the warpage in assembling ICs, and thickness of PCBs could be thinner with these new materials. Also, these new laminates will be applicable to large-size antenna boards in place of the PTFE laminate.

Processability of Multilayer Lamination

The processability for multilayer lamination of the unfilled modified CE resin prepreg was almost the same as that of the FR-4 prepreg. In the rheological viscosity-temperature profile, the modified CE resin showed a slightly higher melting viscosity than the FR-4, but it rose relatively slowly to the curing. Therefore, the modified CE resin prepreg showed the same ability as FR-4 in filling into inner layer patterns, and demonstrated a better accuracy of the dielectric thickness.

Drilling Processability

The drilling processability of the new laminates was very good. The roughness of the through-hole wall was measured from the cross-sectional photos of the through-holes. The wall roughness of the modified CE laminate and the filled laminate was respectively 70-80% and 30-40% of that of the FR-4 (Table 1).

Insulation Reliability

The ability to withstand the ionic migration was evaluated on the resistance against conductive anodic filaments (CAF) defects, in which the insulation resistance between through-holes 0.3mm apart at each wall was monitored under 100Vdc application in 85°C/85%RH atmosphere. The new laminates were free of the breakdown in resistance at least until 1000 hours, exhibiting excellent endurance against ionic migration (Table 1). On the other hand, the laminate with untreated fillers showed poor reliability.

Surface Flatness

Furthermore, these new laminates showed an excellent surface flatness. In general, the surface of the conventional FR-4 or PTFE laminate is not smooth, reflecting the roughness from the woven fabric and the thermal shrinkage of the resin. The modified CE resin laminate showed a smaller roughness of 4 to 6 micrometers than FR-4 because of its smaller thermal shrinkage. The laminate with filled resin showed much smaller roughness of 2 to 3 micrometers, because of the higher filler content or lower resin content resulting in smaller thermal shrinkage. This feature will be advantageous in manufacturing high-frequency PCBs of the finer lines/space and of the excellent precision of characteristic impedance.

We are now studying to apply the newly developed resin system to the HDI multilayer materials and the environment-friendly materials in the field of high-speed communications.

Conclusion

A new low Dk and Df thermosetting resin system was developed using a modification technique of CE resin and alloying with polymers. The laminates with this resin system (both inorganic filled and unfilled) showed excellent dielectric properties effective in decreasing the transmission loss on PCBs at high frequency bands. The new laminates also showed excellent heat resistance, mechanical properties, and reliability. It was confirmed that they have the same processability of multilayer lamination and mechanical drilling as the conventional FR-4. Such materials will be suited to antenna boards or the multilayer PCBs for base stations, and also to the higher multilayer PCBs for high-end servers and routers.

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