Technical Report

Adhesiveless Polyimide Copper Clad Laminates "ESPANEX™ (M,F series)"

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Abstract

Since the 1980s, Nippon Steel Chemical & Material Co., Ltd. has been developing flexible copper clad laminates (FCCL) and polyimide resins used in flexible printed circuits (FPC). The ESPANEX™ M series, launched in the early 2000s, has been well received in the market for its high dimensional stability and continues to be mass-produced. In order to meet the demand for low transmission loss materials with the spread of 5G, we have developed and launched the low dielectric type ESPANEX™ F series. We have developed polyimide technology with low dielectric properties and a low coefficient of thermal expansion for future high-frequency transmission substrates.

1. Introduction

Mobile phones began to spread in the mid-1990s, went through the feature phone era, and continued to become more sophisticated and equipped with a variety of functions beyond just calling functions until the appearance of smartphones in the late 2000s. Flexible printed circuits (hereinafter referred to as FPCs) were already being used in consumer devices such as cameras, printers, and hard disks due to their thinness and flexibility. They began to attract attention to meet the demand for greater density and downsizing to improve the portability associated with the increased functionality of these mobile electronic devices.

1.1 High-performance requirements for FPCs

Flexible copper-clad laminates (hereinafter referred to as FCCLs) had been used as FPC materials until then. They were three-layer FCCLs (polyimide, adhesive, and copper foil) made by bonding polyimide film and copper foil with a low heat-resistant epoxy or acrylic adhesive. As mobile electronic devices have become more sophisticated, there have been increasing demands for multilayering and finer wiring, adaptability to the high-temperature LSI mounting process on the FPCs, thinning, flexibility, and resistance to repeated bending.

1.2 Overview and features of ESPANEX™ M series

Nippon Steel Chemical & Material Co., Ltd. launched ESPANEX™, a two-layer FCCL (polyimide and copper foil) with polyimide alone used for the insulating layers in the late 1980s to solve the problems of three-layer FCCLs. Generally, the manufacturing methods of two-layer FCCLs are roughly divided into the lamination method, in which a polyimide film prepared in advance by a tenter method or the like is laminated to copper foil, and the casting method, in which a polyimide precursor solution (hereinafter, polyamic acid varnish) is directly applied to copper foil and cured on the copper foil to form a polyimide layer.[1] The manufacturing concepts of the respective methods are shown in **Fig. 1**.

With the tenter method (left in Fig. 1) polyamic acid varnish is applied to a heated drum. The applied film is dried to form a gel film, peeled off from the drum, clamped at the ends with tenter clips, and heat treated at high temperatures while they are tensioned in the line and width directions by a biaxial stretching method. Since the heat-treated gel film is transported while being stretched in the line and width directions, the residual stress from the heat treatment remains in the cured polyimide film. It tends to cause anisotropy and variation in the coefficient of thermal expansion (CTE) in the line and width directions.

On the other hand, in the casting method (right in Fig. 1), polyamic acid varnish is dried and cured on a support such as copper foil, so the support constrains the polyimide film (polyimide layer), and the anisotropy of stress in the line and width directions is unlikely to occur. Therefore, polyimide films produced by the casting method generally have little anisotropy of the CTE and excellent dimensional stability. In the early 2000s, Nippon Steel Chemical & Material developed and marketed the "ESPANEX™" M series, which combines its unique polyimide design technology and pro-

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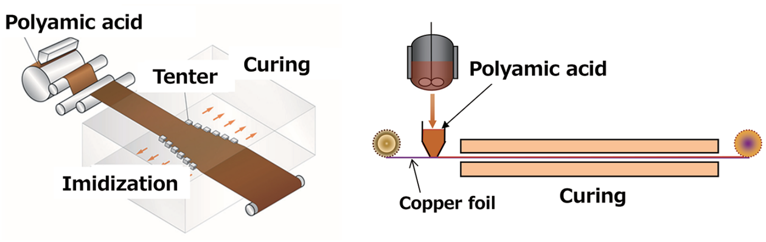

Fig. 1 Conceptual diagram of polyimide film forming method

cess technology. The ESPANEX™ M series, the main product line in Nippon Steel Chemical & Material's ESPANEX™ business, achieves high dimensional stability by suppressing the expansion and contraction of materials due to heat and moisture absorption, thanks to the small CTE variation of the polyimide layer, which is also a feature of the casting method, and the low moisture absorption rate. Consequently, it suppresses the problem of misalignment caused by the miniaturization and multilayering of FPC wiring and has been highly evaluated in the market.

2. Development of Low Dielectric Polyimide

Since then, various technological innovations have progressed in mobile phones and smartphones. The signals used inside these devices have gradually become higher in frequency. In Japan, the fifth generation (5G) commercial service of mobile communication systems was launched in March 2020. Consequently, there has been an increasing demand for low transmission loss and low dielectric constant substrate materials to accommodate further increases in frequency, especially for substrates around antennas.

In order to meet these market needs, Nippon Steel Chemical & Material has developed and launched the low dielectric type ESPANEX™ F series. In addition, for 6G communication, which is expected to start in 2030, development is actively underway to expand communication areas (ultra-wide coverage), achieve ultra-low power consumption and low cost, and accomplish ultra-high reliability. The realization of 6G requires the establishment of ultra-high speed and large-capacity communication technology. Even higher frequency bands are expected to be adopted for transmission signals in addition to the frequencies applied in 5G. To support this high-frequency transmission, resins for circuit boards are required to reduce transmission loss further. Therefore, Nippon Steel Chemical & Material has worked on the development of a new ultra-low dielectric polyimide that achieves a low dielectric constant, which is effective for further reducing transmission loss, based on the polyimide technology for FCCLs that it has cultivated for many years.

2.1 Transmission loss

Transmission loss increases as the frequency of the signal passing through the wiring increases. As the frequency increases, the transmission loss becomes an important characteristic. The transmission loss is the sum of dielectric loss (D) and conductor loss. The dielectric loss is derived from the dielectric constant (Dk) and dielectric loss tangent (Df) of the dielectric material. As shown by Eq. (1), reducing the dielectric loss tangent is more effective than reducing the dielectric constant in reducing the dielectric loss.[2] Low moisture absorption is also important to prevent the transmission loss from changing depending on the operating environment.

$$D = b \times f \div C \times \sqrt{Dk} \times Df \quad (1)$$

where b is a constant, f is frequency, and C is the speed of light.

The conductor loss is an item related to the conductor and increases as the resistance value of the conductor deteriorates. In high-frequency signals, a phenomenon called the skin effect occurs in which the current concentrates on the surface of the conductor, so the surface shape of the conductor (surface roughness or roughened shape) becomes important. For these reasons, low transmission loss materials are required not only to have a low dielectric loss tangent, but also to use copper foil with a smooth surface shape.

2.2 Low transmission loss materials

A typical example of a low transmission loss material is a liquid crystal polymer (LCP). The LCP has a small molecular dipole and rigidity, which results in low mobility in an electric field, leading to excellent dielectric properties and low moisture absorption.[3] On the other hand, because it is thermoplastic, the material softens during high-temperature lamination pressing and high-temperature reflow soldering in multilayering. This softening can distort the wiring layer and pattern shape and cause mounting defects. The FPC manufacturers must have unprecedented manufacturing expertise. In addition, it is difficult for the LCP to bond chemically to the copper foil interface, complicating its adhesion to smooth copper foil.

On the other hand, polyimide has a long history of usage as an FPC material. It has excellent properties not found in other resins, such as heat resistance, flexibility, dimensional stability, and adhesion to copper foils and bonding sheets during multilayer FPC production. For this reason, there has been a strong demand for FCCLs using polyimide that can support high-speed transmission.

To meet the growing need for high-frequency materials in such markets, Nippon Steel Chemical & Material has developed low-dielectric loss tangent polyimides and a new polyimide FCCL that achieves the low transmission loss required for high-frequency signal FPCs in combination with smooth copper foils.

2.3 Development of low dielectric F series

In general, reducing the polar group concentration is an effective way to reduce the dielectric constant of resins. However, when the polar group concentration is reduced in polyimide, there are concerns that the heat resistance may decrease due to the reduction of the glass transition temperature (Tg) and that the dimensional stability may deteriorate due to an increase in the CTE. Therefore, there is a limit to how much the polar group concentration can be reduced to reduce the dielectric constant of polyimide while still maintaining the soldering heat resistance and dimensional stability required for polyimide FCCLs.

Meanwhile, Nippon Steel Chemical & Material has various dimensional control technologies for polyimide FCCLs using the casting method that it has developed over many years. By making the most of these dimensional control technologies, we have succeeded in developing the low dielectric F series, which ensures dimensional stability as a polyimide FCCL while reducing the polar group concentration as much as possible. **Table 1** shows a comparison of the

Table 1 Properties of ESPANEX™ F, M series, LCP-FCCL

		F series	M series	LCP-FCCL
Dielectric constant	10 GHz	3.3	3.4	3.4
Dissipation tangent	10 GHz	0.003	0.005	0.002
Peel strength [kN/m]	Cast side	1.2	1.1	–
	Laminate side	1.7	1.6	1.0
Water absorption [wt%]		0.8	1.1	<0.1
Dimensional stability [%]	After etching (MD/TD)	0 / −0.04	0.05 / −0.04	0.03 / −0.02
	After heating (MD/TD)	−0.04 / −0.02	−0.04 / −0.06	−0.03 / 0.09
Solder heatproof [°C]	105°C, 1 h	380	380	270
	40°C, 90%RH, 8 day	320	320	270

insulating layer characteristics of the F series, M series, and LCP-FCCL. The insulating layer of the LCP-FCCL used for comparison uses a commercially available LCP film.

The F series has superior dielectric and moisture absorption properties compared to the conventional M series. The dielectric loss tangent is 0.003, and the moisture absorption rate is kept low at 0.8%, demonstrating unprecedented polyimide properties. Generally, when the polar group concentration of polyimide is reduced in polyimide FCCLs, there is a concern that the heat resistance may decrease. However, the F series displays a sufficient heat resistance of over 320°C in the soldering heat resistance test after moisture absorption, which is one of the harshest heat resistance tests for FCCLs.

The peel strength was evaluated in combination with finely roughened copper foils (surface roughness Rzjis of 1.0 μm) used in high-frequency applications. Both the cast surface (coated surface) and the laminated surface (pressure-bonded surface) had a peel strength of 1.0 kN/m or more. They were confirmed to adhere sufficiently to copper foils for high-frequency applications.

2.4 Transmission loss measurement results of low dielectric F series

Table 1 shows that the dielectric constant and dielectric loss tangent are 3.4 and 0.002 for the LCPs and 3.3 and 0.003 for the F series. The LCPs have a smaller dielectric loss than the F series. On the other hand, the F series is more likely to exhibit a better adhesion to metals than the LCPs, so it can use smoother copper foils suitable for high-frequency transmission and reduce the conductor loss. The samples used for the transmission loss measurement had an insulation layer thickness of 25 μm, a circuit width of 50 μm, and a line length of 100 mm. The samples were conditioned for 24 h in an environment of 23°C and 50% RH. The transmission loss was calculated by measuring the S parameters using a network analyzer. **Figure 2** shows a comparison of the transmission loss in the microstrip line structure of the respective polyimides and LCPs.

The F series takes full advantage of being able to use smooth copper foils and is a polyimide FCCL that can be adapted to high-frequency signal applications by reducing both dielectric loss and conductor loss.

2.5 Proposal of materials for high-frequency transmission boards in the 6G field

As mentioned above, Nippon Steel Chemical & Material has developed and marketed the low dielectric F series, which ensures dimensional stability (low CTE) while reducing the polar group concentration as much as possible. Although the specific characteristics

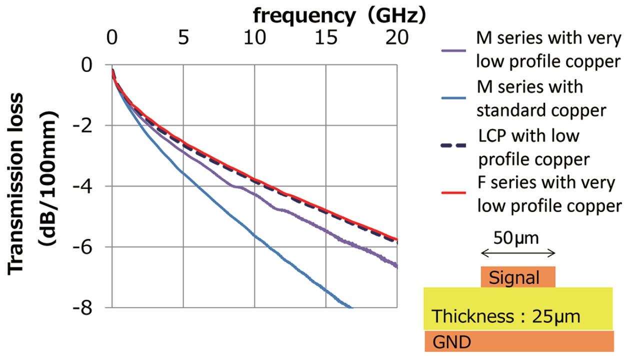

Fig. 2 Transmission loss in microstrip line

Table 2 Properties of new ultra-low dielectric polyimide

		Target	New ultra-low dielectric polyimide
Dielectric constant	10 GHz	≤3.0	2.8
Dissipation tangent	10 GHz	≤0.001	0.0014
CTE [ppm/K]		≤20	≤20
Water absorption [wt%]		≤0.2	≤0.2

required for substrate materials for 6G applications have not yet been clarified, we provisionally have set the development targets shown in **Table 2**. We have begun the development of a new ultra-low dielectric polyimide. To achieve an even lower dielectric constant, designs other than the reduction of the polar group concentration are necessary. Therefore, a technology for suppressing movement at the polyimide molecular level was devised and reflected in our polyimide resin design.

As a result, although it is still a product under development, we achieved a dielectric constant of 2.8, dielectric loss tangent of 0.0014, and CTE of 20 ppm/K or less, as shown in Table 2. We have confirmed the possibility of a new ultra-low dielectric polyimide that combines excellent low dielectric properties and low CTE, which could not be achieved with conventional designs. Currently, we are optimizing the resin composition based on this concept, aiming to achieve a dielectric loss tangent of 0.001 or less.

Considering that substrates will continue to become denser and more highly integrated in the future, we expect that the need for materials that combine low dielectric constant and low CTE will increase not only for FCCLs, but also for various other applications.

To respond to such needs flexibly, we will advance our technology and expand it into various products, not just for FCCL applications.

3. Conclusions

The ESPANEX™ F series achieves a low dielectric constant while maintaining the same workability, soldering heat resistance, dimensional stability, and wiring adhesion as the M series does. It is already being mass-produced and adopted for some items. In addition, we are developing even lower dielectric constant resins in anticipation of 6G.

Nippon Steel Chemical & Material has cultivated a variety of technologies over the years as a manufacturer of two-layer FCCLs and polyimide materials. We plan to utilize these technologies to develop new technologies and not only respond to future trends toward higher frequencies, but also to provide polyimide materials with various characteristics for a wide range of applications.

References

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