Highly Dimensionally Stable Polyimide Film APICAL™ HP and its application.

*Hirosaku Nagano, Kiyokazu Akahori, Hiroyuki Furutani

KANEKA Corporation
Electronic Materials R&D Department
Otsu, SHIGA 520-0104, JAPAN.

Abstract: Flexible Printed Circuits(FPC) have been subject to increasingly demanding processing reliability and thermal resistance during over the past three decade. For these stringent demands of FPC application, highly dimensionally stable base film and higher heat resistant adhesives have been strongly needed. Novel polyimide film; APICAL™ HP which has a tensile modulus of 6GPa and coefficient of thermal expansion(CTE) of 12ppm, has been successfully developed as the appropriate base film for this on-going trend. In addition, it is used as the base film for all polyimide bond-ply PIXEO™ BP consisting of thermoplastic hot-melt type polyimide adhesives and APICAL™ HP for adhesiveless flexible copper clad laminate(FCCL). The composite design concept and characteristics of PIXEO™ BP are also studied. Dimensional changing percentage of FCCL made of PIXEO™ BP of 0.02% after etching of a copper foil, peel strength of 10N/cm after aging for 1000hrs at 180° C, and no "Pop-corn" delamination after solder float test at 300° C, were also observed.

1. Introduction

It has been well recognized that wholly aromatic polyimide materials have been extensively used in electric and electrical device applications due to their excellent mechanical and electrical properties and thermal stability[1]. The application of FPC has been changing during the last three decades. In the 1970's, FPC was mainly used for parts of cameras and during 1980's, used for parts of video camcorders. Nowadays, in 1990's, application for computers are noticeably increasing.

Arising from this change in FPC applications, the demands for fine pattern FPC are increasing. Therefore, the demands on polyimides films have been also changing. Recently, the dimensional stability has became one of most important characteristics of polyimide films for fine line circuitry. Even though KANEKA had introduced APICAL™ NP[2] with low thermal expansion coefficients compared with conventional APICAL™ AV, the development of precise circuits with quite high dimensional stability and high heat resistance have been more focused for *i.e.* Plasma Display or Multi-layered FPC applications as the next generation.

In this presentation, properties of novel APICAL™ HP and PIXEO™ BP developed to meet the demand for fine pattern applications, will be discussed.

Corresponding to; Hirosaku Nagano.
e-mail; hirosaku.Nagano@kaneka.ne.jp

2. Discussion

Generally, polyimide films are prepared by curing polyamic acid films formed after coating polyamic acid varnish synthesized by the polycondensation reaction of dianhydrides and diamines, on either PET film or an endless metal belt or drum. APICAL™ HP was successfully developed using the same technique *via* the strong demands from our customers.

2.1 The market activities of polyimide films

In the US market and Europe markets, main application of polyimide films are insulation for motor or magnet wire cable. In the Japanese and Asian market, FPC is a main application of polyimide film.

The application of FPC has been changing in these 20~30years, in 1970's FPC is mainly used for parts of cameras, in 1980's used for parts of video cameras, and 1990's application for computer is noticeably increasing.

According to this change of application of FPC, the demands for fine pattern FPC is increasing. The demands to polyimides films have been changing, too. Recently, the dimensional stability becomes an important character for polyimide films.

2.2 Novel High Dimensionally Stable Polyimide Film

To achieve low CTE and high modulus, APICAL™ HP was prepared by a copolymerization method. Properties are summarized in Table 1. APICAL™ HP is characterized as an excellent candidate film for FPC with properties combining not only high tensile modulus and low CTE, but also low coefficient of humidity expansion(CHE) and low water absorption.

3. Application

3.1 All Polyimide Hot-melt Adhesive type Bond-ply

FCCL is often prepared from polyimide film and copper foil using a variety of non-polyimide thermosetting adhesives, such as acrylics, epoxies, and phenolics. Recently, the demand for adhesiveless FCCL using an all polyimide bond-ply which has good processability and adhesive properties while maintaining high dimensional stability is strongly increasing because of the lack of thermal and electrical reliability of conventional low temperature adhesives. In this presentation, to achieve both a good dimensional stability and a high thermal resistance, newly developed PIXEO™ BP will be discussed along with properties of the FCCL.

Table 1 - Summary of KANEKA APICAL™ HP Properties.

Items	Units	Values	Conditions	Methods
CTE[1)]	ppm	12	100 to 200° C	TMA
CHE[2)]	ppm	5	50° C	HMA
Water Uptake	%	1.2	D-24/20	ASTM D570
Moisture Uptake	%	1.0	C-96/40/90	ASTM D570
Tensile Strength	MPa	280	20° C	ASTM D882
Tensile Modulus	GPa	6.0	20° C	ASTM D882
Elongation at break	%	40	20° C	ASTM D882
Volume Resistivity	Ω-cm	$>10^{15}$	20° C	ASTM D257

1)CTE; coefficient of thermal expansion
2)CHE; coefficient of hygroscopic expansion

3.1.1 Composite Design Study

3.1.1.1 Dimensional Stability of FPC

Figure 1 and 2 showed an example of the FPC manufacturing process and the dimensional change during the process, respectively. Polyimide film and copper foil are exposed to the high temperature and the humidity condition. In a continuous process, polyimide film and copper foil are exposed to the high tensions, too. During this process, polyimide film undergoes dimensional changes like elongation and/or shrinkage, so that the copper foil pattern will be slipped out of position as shown on Figure 2. Highly dimensionally stable polyimide film is thus strongly needed to avoid this difficulty.

It was said that conventional polyimide films such as APICAL™ and KAPTON™ have higher CTE compared with metals and ceramics; so they don't have sufficient dimensional stability for fine pattern applications. However, there are many previous studies identifying poyimides having very low CTE. It has been reported that some aromatic polyimide with rigid segments in the polymer backbone have achieved low CTE[4)].

3.1.1.2 Mechanism of Dimensional Change in Process

Figure 3 shows an assumped mechanism of dimensional change of FCCL. According to Figure 3, the internal strain generated in polyimide film(*i.e.* PIXEO™) during lamination with copper foils had remained in it, because of having a higher CTE than copper foils. On the other hand, the internal stress was also generated polyimide film by tension and pressure during lamination, due to the low tensile modulus compared with copper foil. Therefore, polyimide film shrunk more than copper foils after etching. To avoid possibilities, it is necessary that polyimide films have CTE as low as copper foil coupled with a high tensile modulus.

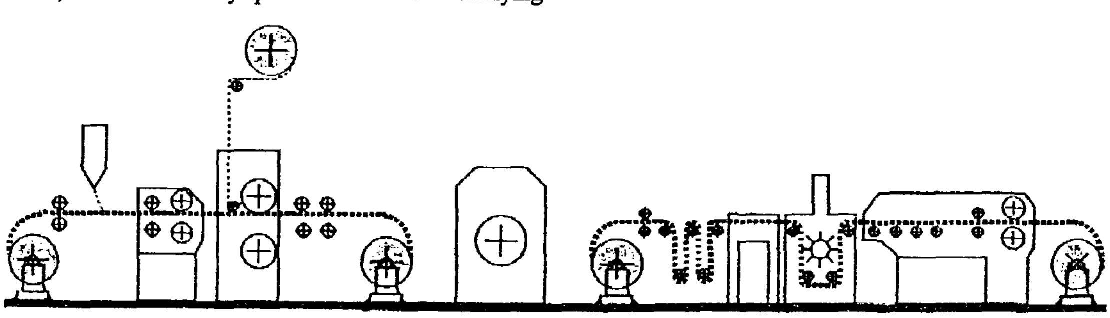

Figure 1 - Schematic FPC Manufacturing Process.

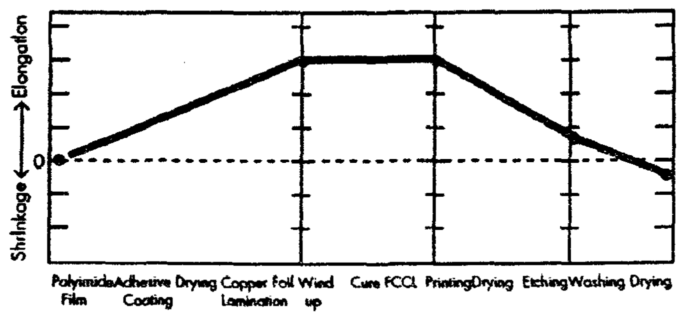

Figure 2 - Dimensional Changes during the FPC Process.

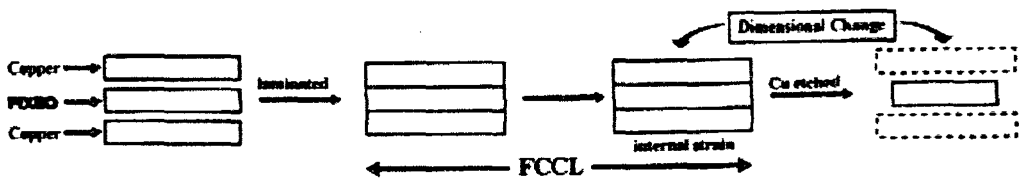

Figure 3 - Assumpted Mechanism of Dimension Change of FCCL.

3.1.1.3 Composite Design Study

According to the assumption of section 3.1.1.2, CTE and tensile modulus possibly related to the cause of dimensional change during FCCL preparation process, *i.e.* lamination, etching, and drying. It was said that the dimensional change(%) of FCCL: ΔL_{FCCL}, was expressed by temperature change: ΔT and CTE of bond-ply: $\Delta \alpha_{BP}$.

$$\Delta L_{FCCL}(\%) = \mathrm{A} \times \Delta T \times \Delta \alpha_{BP} \times 100 \quad \cdots \quad eq.\ ①$$

On the other hand, with the three layered composite model of Hoock's law, it was found that $\Delta \alpha_{BP}$, should be calculated from properties of each layer with a thickness: t, tensile modulus: E, and α, respectively. The composite design of bond-ply for FCCL as thickness of 25 μ m(1 mil) was studied in detail. In this presentation, it will be explained how PIXEO™ BP was designed with a base film; APICAL™ HP of 17 μ m and thermoplastic polyimide adhesive; PIXEO™ TP-T[3](Tg of 190°C) of 4 μ m on the both sides.

3.2 Properties of PIXEO™ BP

PIXEO™ BP shows excellent properties as polyimide adhesives for FPC application. Properties are summarized in Table 1. PIXEO™ BP has Tg of 190°C. It shows softening behavior around Tg+100°C, but film integrity is well maintained over 400°C, well above Tg. Proposed press conditions will be mentioned in this presentation. In addition, PIXEO™ BP maintains high initial polymer decomposition temperature of 490°C, tensile modulus of 6.5GPa, tensile strength of 320MPa, elongation at a break of 30%, and CTE of 22ppm(100°C to Tg). PIXEO™ BP, however, shows very low water absorption of 1.0% and very low ionic impurity levels of 0.1 to 0.2mg/l, respectively. It is assumed that these typical properties are caused by the very unique three layered structure mentioned in section 3.1.1.3 and the polymer structure of thermoplastic polyimide adhesive; PIXEO™ TP-T[3].

3.3 FCCL Study

FPC made from FCCL have been increasing their thermal resistance and electrical reliability during the past three decades. Depending on these demands, high temperature resistant adhesives were widely introduced. However, these laminates required higher temperature and pressures for curing compared with conventional adhesives. Additionally, copper foil has a tendency to oxidize and/or degrade. Even when using these high temperature adhesives, it was difficult to provide high temperature resistance and accelerated aging with high temperature (above 150°C) and humidity conditions. So both processability and high thermal resistance were required by adhesives at the same time. PIXEO™ BP is one of the good candidates for these demands. FCCL made of only PIXEO™ BP and copper foil was studied as one of the application examples of APICAL™ HP.

Table 2 - Summary of KANEKA PIXEO™ BP-HP 4/17/4 Properties.

Items	Units	Values	Conditions	Methods
Tg	°C	190		DMA
Td	°C	490	in N_2	TGA
CTE	ppm	22	100°C to Tg	TMA
Water Uptake	%	1.0	D-24/20	ASTM D570
Ionic Impurities Na^+	mg/l	0.2	Sample10g	ICP
K^+		0.1	Water100g	ICP
Cl^-		0.1	PCT-96/121	Ion chromato.
Tensile Strength	MPa	320	20°C	ASTM D882
Tensile Modulus	GPa	6.5	20°C	ASTM D882
Elongation at a break	%	30	20°C	ASTM D882
Volume Resistively	Ω-cm	$>10^{15}$	20°C	ASTM D257

Table 3 - Summary of Double-sided Adhesiveless FCCL(BP-HP4/17/4 and 1/2oz rolled copper) Properties.

Items	Units	Treatment	Values	Conditions	Methods
Insulation Resistance	Ω	C-24/20/60	$>10^{12}$	100V, 20°C	JIS Z3197
Surface Resistance	Ω	C-24/20/60	$>10^{15}$	20°C	JIS C6481
Volume Resistance	Ω/cm	C-24/20/60	$>10^{15}$	20°C	
Solder Float	-	C-24/20/60, 300°C/60sec. C-96/40/90, 280°C/10sec.	Pass Pass		JIS Z3197
Flammability	-		V-0		UL-94
Through-hole reliability	-		good		JIS C6471 10.2
Dimensional Change	%	After etching	0.03	20°C	IPC TM-650
		After etching+150°C/30min.	0.01		
Peel Strength	N/cm	Initial E-1000/180 C-1000/85/85	12 11 11 11	20°C 150°C 20°C 20°C	JIS C6471
Flexural Endurance	Cycles	R=0.38, 500g	>500	20°C	JIS C5016

3.3.1 Properties of FCCL

Adhesiveless FCCL consisting of rolled copper foil(double sided) and PIXEO™ BP was prepared by a Roll-to-Roll type continuous lamination method using a Double Belt Press(DBP) process. Properties of FCCL are summarized in Table 3. Electrical properties are excellent such as insulation resistance of $>10^{12}$ Ω, surface resistance of $>10^{15}$ Ω, and volume resistance of $>10^{15}$ Ω, respectively. The adhesive retains good peel strength at elevated temperatures up to 150℃. Flexural endurance is also good. Flammability showed V-0 class by UL-94 method.

3.3.2 Aging Study

Thermal stability of FCCL after accelerated aging has been examined. It will be shown during the presentation.

3.3.3 Solder Float Resistance Study

By thermal shock either at 300℃ for 60second with the condition of C-24/20/60 or at 280℃ for 10second with the condition of C-96/40/90, the solder float test has not produced any visual defects or "Pop-corn" type delamination on the FCCL, respectively.

4. Conclusion

Novel polyimide film; APICAL™ HP was successfully developed with various characteristics mentioned below.

(1)APICAL™ HP showed combinations of properties such as very low water absorption, high tensile modulus, and low CTE & CHE.

(2)APICAL™ HP can be chosen, not only as a base film for high dimensional stability use, but also as a base film of all polyimide hot-melt type bond-ply PIXEO™ BP requiring both high dimensional stability and high temperature resistance, for the next generation's precise FPC application.

(3)Adhesiveless FCCL using copper foils and PIXEO™ BP-HP 4/17/4, showed high temperature resistance, good humidity resistance, good processability, and excellent dimensional stability.

5. References

1)C. E. Sroog, *J. Polym. Sci., Macromol. Rev.*, 1976, 11, 161.

2)H. Nagano *et al.*, *Proceedings of PME'89*, 1989(Tokyo), 102.

3)H. Furutani, *Proceedings of IPC National Conference, Flexible Circuits'98*, 1998(San Jose, CA), *Vol. II*, 56.

4)S. Numata and N. Kinjo, *J. Appl. Polym. Sci.*, 1986, 31, 101.

October/30-31/2000.