Novel Thermoplastic Polyimide Adhesives; KANEKA PIXEO™

-Use for High Temperature Resistant Circuits.-

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Abstract
Printed Wiring Boards (PWB) have been increasing their thermal resistance and electrical reliability during the past two decades. For these increased demands in PWB applications, higher heat resistance and lower ionic impurities containing adhesives have been strongly needed. It has been recognized that polyimide adhesives meet the needs of this on-going trend. KANEKA PIXEO™ has been successfully developed as thermoplastic polyimide hot-melt adhesives aimed at the heat resistant usage of PWB's. In this presentation, molecular design, properties of PIXEO™ TP-D(Tg of 151℃), TP-T(Tg of 190℃), and TP-E(Tg of 225℃) adhesives, and characteristics of Flexible Copper Clad Laminate (FCCL) as one of their application, will be discussed.

1. Introduction

The polyimide are well known as one of the outstanding super engineering plastics which has excellent heat resistance, good dielectric behavior, and excellent physical properties. It has been widely used as film, molding materials, and varnish. It is chosen as the primary dielectric substrates for flexible printed circuit (FPC) applications. For example, FCCL is often prepared from polyimide film using a variety of non-polyimide thermosetting adhesives, such as acrylics, epoxies, and phenolics. Recently, the demand for polyimide adhesives which have good processability and adhesive properties while maintaining good flexibility is strongly increasing because of the lack of thermal and electrical reliability of conventional low temperature adhesives.
In this presentation, newly developed polyimide adhesives; PIXEO™ thermoplastic polyimide adhesive will be discussed along with properties of the FCCL.

2. Discussion

Polyimides have been synthesized by the polycondensation reaction of dianhydride and diamines. Thermoplastic polyimides can be prepared introducing a thermoplastic segment into its polymer backbone. The glass transition temperature (Tg) can be controlled while maintaining its high temperature resistance by varying amount of the thermoplastic segment.

2.1 Novel Thermoplastic Polyimide PIXEO™

Generally, thermoplastic polyimide films are prepared by curing polyamic acid film formed after coating polyamic acid varnish on PET film. PIXEO™ has been successfully prepared by chemical or thermal imidization and can be provided as a film with a thickness of 0.5mil to 4mil. It has controlled bulk physical, chemical, and mechanical properties. Multiple layer construction film, combinations of core/base layers with thermoplastic layers made by a thermal lamination technique are also available. This allows control of properties such as thermal expansion coefficient (CTE) and high dimensional stability

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Table 1 Summary of KANEKA PIXEO™ Properties.

Items	Units	KANEKA PIXEO™ Grades			Conditions	Methods
		TP-D	TP-T	TP-E		
Tg	°C	151	190	225		DMA
Td	°C	460	490	500	in N_2	TGA
CTE	ppm	51 78	51 70	49 65	20 to 100°C 100°C to Tg	TMA
Thermal Conductivity	cal/cms°C	6×10^{-4}	6×10^{-4}	6×10^{-4}		
Water Absorption	%	0.5	0.3	0.4		ASTM D570
Ionic Impurities Na^+ K^+ Cl^-	mg/l	0.2 0.1 0.1	0.2 0.2 0.1	0.2 0.1 0.1	Sample10g Water100g PCT-96/121	ICP ICP Ion chromato.
Tensile Strength	MPa	93	102	121	20°C	ASTM D882
Tensile Modulus	GPa	2.1	2.2	2.3	20°C	ASTM D882
Elongation at a break	%	62	83	60	20°C	ASTM D882
Volume Resistively	Ω -cm	$>10^{15}$	$>10^{15}$	$>10^{15}$	20°C	ASTM D257
ε	-	2.9	2.9	2.9	20°C, 1MHz	IPC-TM-650
tan δ	-	0.008	0.008	0.008	20°C, 1MHz	IPC-TM-650

2.2 Properties of PIXEO™

PIXEO™ shows excellent properties as a thermoplastic polyimide film. Table 1 summarizes various properties of PIXEO™. PIXEO™ has three Tg variations of TP-D, TP-T, and TP-E with 151°C, 190°C, and 225°C, respectively. Each variant shows softening behavior around Tg+100°C, but film integrity is well maintained over 400°C, well above Tg. In addition, PIXEO™ maintains high initial polymer decomposition temperature of 460°C to 500°C, tensile modulus of 2GPa, tensile strength of 93 to 121MPa, elongation at a break of 60 to 83%, and CTE of 49ppm to 51ppm(20°C to 100°C). Electrical properties such as volume resistance and dielectric constant are almost the same as those of conventional polyimide films(i.e., APICAL™, KAPTON™, and UPILEX™). PIXEO™, however, shows very low water absorption of 0.4 to 0.5% 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 molecular design of the polymer chemical structure, which will be briefly discussed in this presentation.

2.3 Adhesive Properties

PIXEO™ adheres with various materials such as copper, steel, silicon wafer, aluminum, and polyimide film. The adhesive strength at different temperature by using copper foil and each of three PIXEO™ films as an adhesive layer was evaluated. Figure 1 showed the temperature dependence of adhesive behavior. PIXEO™ showed good adhesive strength with copper foil (electrodeposited; ED, roughened side). Adhesive behavior with other metals will be also mentioned in this presentation.

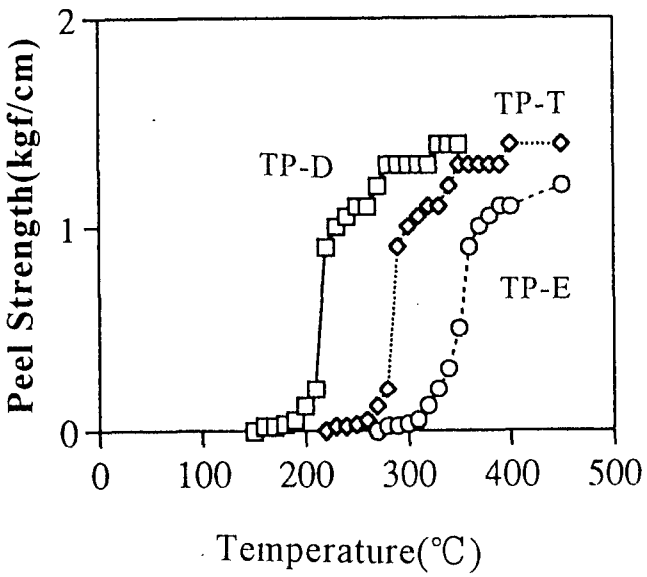

Figure 1 PIXEO Adhesive Strength with Copper.

3. Application

It is well known that polyimide is widely used as a dielectric base/core film of PWB. PWB have been increasing their thermal resistance and electrical reliability during the past two decade. Depending on these demands, high temperature resistant adhesives were widely introduced. However, these laminates required higher temperature and pressures for curing than conventional adhesives. Additionally, copper foil of PWB 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.

PIXEO™ is one of the good candidates for a high temperature resistant adhesive for FCCL.

3.1 Properties of FCCL

Adhesiveless FCCL consisting of copper foil (ED) and PIXEO™ TP-T film will be shown in this presentation and was prepared by a Roll-to-Roll type continuous lamination method using a Double Belt Press (DBP) lamination process.

Table 2 summarizes various properties of FCCL. Electrical properties are excellent such as insulation resistance of $>10^9$ Ω , surface resistance of $>10^{15}$ Ω , volume resistance of $>10^{14}$ Ω under various conditions. Thermal shock at 260 ℃ , ≧ 180sec solder had not produced any visual defects or delamination in the FCCL. The adhesive retains good peel strength at elevated temperatures up to 180℃ and solder float at 260℃. Flexural endurance with different diameters is also good.

3.2 Aging Studies

Excellent adhesion stability of FCCL after accelerated aging has been examined with different conditions of aging shown Figure 2, 3.

Table 2 Summary of FCCL Properties.

Items	Units	Treatment		Conditions	Methods
Insulation Resistance	Ω		$>10^9$	20° C	JIS Z3197
Surface Resistance	Ω	Initial	$>10^{15}$	20° C	JIS C6481
		C-25/40/90	$>10^{15}$		
		C-50/40/90	$>10^{15}$		
		C-100/40/90	$>10^{15}$		
Volume Resistance	Ω /cm	Initial	$>10^{14}$	20° C	
		C-25/40/90	$>10^{14}$		
		C-50/40/90	$>10^{14}$		
		C-100/40/90	$>10^{14}$		
Solder Float		Condition A	Pass	20° C	JIS Z3197
		C-96/20/60	Pass		
		C-96/40/90	Pass		
Flammability			V-0		UL-94
Peel Strength	kgf/cm	20° C	1.8/2.2	90° Peel Single/Double	JIS C6471
		20° C	1.6	180° Peel Double-Sided	
		150° C	1.3		
		180° C	1.3		
		After Solder Float			
		260℃ 1sec.	1.4	180° Peel Double-sided	
		3sec.	1.4		
		5sec.	1.4		
Flexural Endurance	Cycles	R=0.38	80		
		R=0.80	230		
		R=0.20	1550		

Figure 4 shows the result of insulation resistance changing by PCT condition of 130° C. 85% relative humidity with DC100V bias. It was assumed that low ionic impurity and low water absorption can result in an excellent retention of insulation resistance even after exposure of 200hrs.

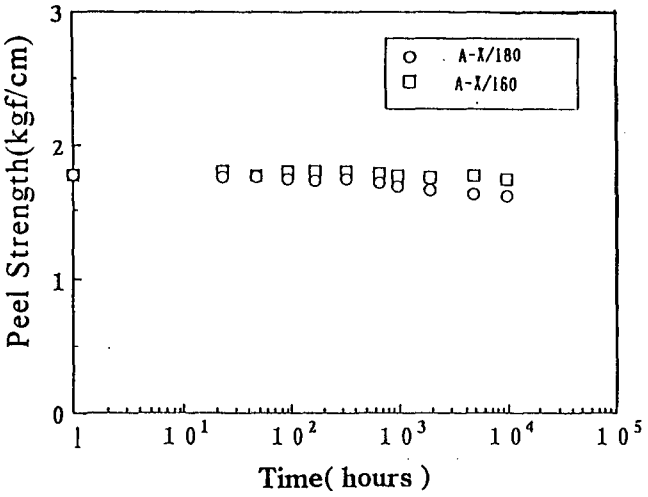

Figure 2 Peel Strength vs. Treatment Temperature and Time.

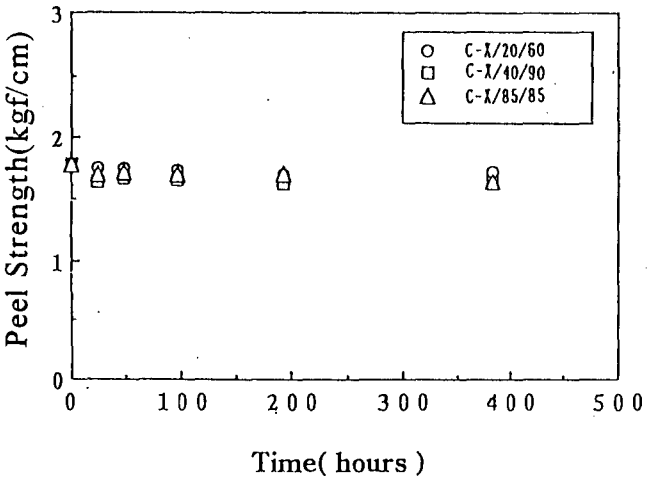

Figure 3 Peel Strength vs. Humidity and Time.

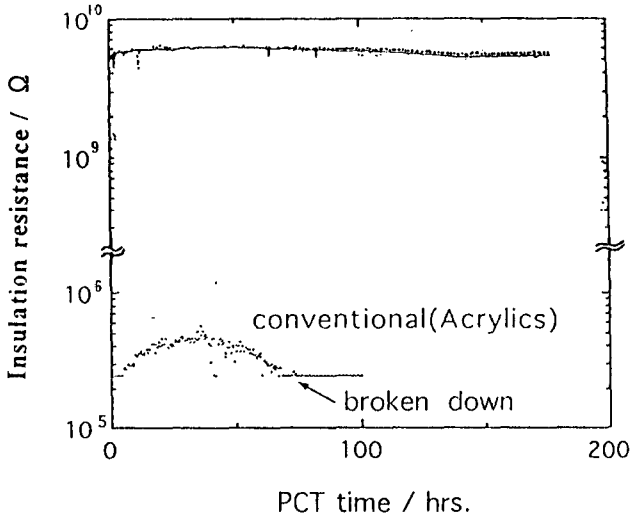

Figure 4 Insulation resistance change by PCB Test

4. Future Work

PIXEO™ shows high solubility in various organic solvents such as dimethylformamide (DMF) and N-methylpyrolidone (NMP). It can be used as a solution type adhesive which can be applied by spin coating and/or screen imaging. These results will be presented in future.

5. Conclusion

PIXEO™ thermoplastic polyimide adhesive film was successfully developed with various characteristics mentioned below.

(1)PIXEO™ showed combinations of properties such as very low water absorption and good mechanical properties.

(2)PIXEO™ can be chosen based on the required the lamination temperature due to having of Tg variation of between 150° C to 225° C.

(3)Adhesiveless FCCL prepared by copper foil and PIXEO™ TP-T film, showed high temperature resistance and good adhesive properties even under high humidity condition.

6. Acknowledgment

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