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Polyurethane Modified Epoxy Adhesives for the Application to FCCL

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Summary: The peel strength of blends of epoxy resin/curing agent (diamino diphenyl sulfone, DDS)/ polyurethane was measured using INSTRON 4485 under normal, chemical and thermal treated states. Glass transition temperature was measured by using differential scanning calorimetry (DSC, Pyris1) according to the contents of polyurethane. Adhesive strength was, approximately, 1.3N/mm and there was no significant effect on the peel strength by the chemical and heat cycle treatments. Glass transition temperature of the adhesive increased from 0 °C to 74.76 °C by increasing the contents of polyurethane. The dimensional stability of epoxy adhesives which contain 30wt% of polyurethane was improved about 98% compared to that of neat epoxy adhesives.

Keywords: adhesive; curing; epoxy; FCCL; polyurethane

Introduction

FPCB (Flexible Printed Circuit Board) is a printed board which is composed of the thin plastic film and copper foil that are laminated. Many parts of equipments such as LCD monitor, main board, cellular phone, notebook computer and digital camera etc. require flexibility and higher density mounting of electronic components. As the tendency above mentioned, new type FPCB becomes to be employed.

FCCL (Flexible Copper Clad Laminate) that classified two types is the raw material for FPCB. One type of FCCL is 2-layer that is composed of polyimide film and copper foil and the other is 3-layer that is composed of polyimide film, epoxy or acrylate adhesives and copper foil. Generally, 3-layer FCCL shows easier processability and lower price but lower thermal and dimensional stabilities and worse flexibility than 2-layer FCCL. These problems of 3-layer FCCL can be settled by improving the thermal properties of adhesives. Figure 1

Epoxy resins are generally used as adhesives for the 3-layer FCCL. Also brominated epoxy resins are used to improve the flame retardancy.

Neat epoxy, in this study, is composed of the following raw materials: YD- 128 and YD-011 are selected as the base epoxy resins of the adhesives for the 3-layer FCCL, KR-208 to reduce brittleness of the epoxy resins, XNBR to get flexibility and YDB-400 to obtain the flame retardancy of the epoxy resins. These adhesives are cured with diamino diphenyl sulfone (DDS). In this study, XBNR was replaced by polyurethane to increase the low Tg of adhesives, as a result, to improve thermal resistance of the epoxy adhesives. Peel strength, chemical resistance and thermal resistance, and dimensional stability of adhesives which contain polyurethane were studied.

Experimental Part

Materials

The polyimide film used in this study was Taimide®(1mil thickness) manufactured by TAIMIDE TECH. INC., and copper

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Figure 1.
Classification of FCCL: (a) 2-layer type and (b) 3-layer type.

foil (1oz thickness) manufactured by Mitsui & Co., Ltd.

The epoxy system was based on the commercial grade DGEBA (Grade: YD-128, YD-011, KUKDO Chemical Co, Ltd., Korea) with an average epoxy equivalent of 189g/eq and 475g/eq, respectively. NBR modified epoxy resin (KR-208, KUKDO Chemical Co, Ltd., Korea) and brominated epoxy resin (YDB-400, KUKDO Chemical Co, Ltd., Korea) were used to obtain the flexibility and flame retardancy, respectively. XNBR (Nipol 1072, ZEON CHEMICAL), polyurethane (VYRON UR3500, TOYOBO CO., LTD.) were used without any treatments. Diamino diphenyl sulfone (DDS, Aldrich) used as a curing agent and methyl ethyl ketone was used as a solvent.

Preparation of Adhesives for the 3-Layer FCCL

The epoxy resins, such as YD-128, YD-011, YDB-400 and KR-208 were solved in methyl ethyl ketone in proportion to 20wt%, 20wt%, 30wt% and 10wt%, respectively. Also 20 wt% of XNBR was added. Epoxy/polyurethane blended resin mixtures with 20 and 30wt% of polyurethane were prepared. After adding DDS (17 phr) to the previous mixture, the blends continuously stirred for 24 hrs. The formulation of adhesives was shown in Table 1.

Preparation of 3-Layer FCCL

Adhesives were cast on the polyimide film, subsequently the cast polyimide film was dried at 80 °C for 5 min to remove solvent. After removing solvent, polyimide film was laminated with copper foil at 140 °C with the rate of 600mm/min. For the curing, it was heated in a vacuum oven at 160 °C for 3 hrs.

Adhesive Strength

The 180° peel strength (10mm width of a peel test specimen) of the adhesive joints between the copper foil and polyimide film was evaluated with a peel rate of 50mm/min using an Instron 4485 based on JIS C6471. Each value of peel strength was determined from the average values of 10 test specimens.

Chemical Resistance

The specimens were immersed in the chemicals at room temperature for 30 mins, and then examined the peel strength as the same method of the adhesive strength test. In this study, hydrochloric acid solution (2M), sodium hydroxide solution (2M), methyl ethyl ketone were used as an acid, a base and a solvent.

Heat Resistance

The specimens were put in an oven at a temperature 180 °C for 60 min (applied 4

Table 1.
Formulation of epoxy adhesives according to polyurethane contents.

Component	Solvent	Contents			
		Neat epoxy	Polyurethane 10wt%	Polyurethane 20wt%	Polyurethane 30wt%
Polyurethane	MEK+Toluene	–	10wt%	20wt%	30wt%
XNBR	MEK	20wt%	10wt%	–	–
YD-128		20wt%	20wt%	20wt%	20wt%
YD-011		20wt%	20wt%	20wt%	20wt%
YDB-400		30wt%	30wt%	30wt%	30wt%
KR-208		10wt%	10wt%	10wt%	–
DDS		17phr	17phr	17phr	17phr

cycles) and 250 °C for 60 sec (applied 4 cycles), respectively. After that the specimens were removed from the oven and examined the peel strength as the same method of the adhesive strength test.

Thermal Resistance

For measuring glass transition temperature, a differential scanning calorimetry (DSC, Pyris1) was used with the following experimental conditions; heating rate, 10 °C/min and temp. sweep, from −50°C to 250°C.

Dimensional Stability

Dimensional stability of FCCL due to thermal exposure was evaluated at standard condition based on IPC Test Method 2.2.4. Scribe lines at positions A, B,C and D in specimen at locations shown in Figure 2. Allow specimen to be stabilized at 23 °C ± 2 °C and 50% ± 5% relative humidity (RH) and measure separation of lines between corresponding positions (center of line). The test specimen was placed in an oven maintained at 150° for 30 minutes after that cooled to standard conditions of 23 °C ± 2 °C and 50% ± 5% RH for 24 hours. Finally remeasure separation of lines and record as final measurement after thermal exposure.

The dimensional change should be calculated using the equations as shown below.

$$MD = \frac{\frac{(A-B)_F-(A-B)_I}{(A-B)_I} + \frac{(C-D)_F-(C-D)_I}{(C-D)_I}}{2} * 100$$

$$TD = \frac{\frac{(A-C)_F-(A-C)_I}{(A-C)_I} + \frac{(B-D)_F-(B-D)_I}{(B-D)_I}}{2} * 100$$

Where, MD = % change in machine direction, TD = % change in transverse direction I = initial reading, F = final reading A–B = separation between points A and B, A–C = separation between points A and C C–D = separation between points C and D, B–D = separation between points B and D

Results and Discussion

Peel Strength

A peel test profile of polyurethane 30wt% epoxy adhesive is shown in Figure 3. The profile is very stable during the peel test. Adhesive strengths of epoxy-polyurethane matrix according to polyurethane contents of 0wt%, 10wt%, 20wt% and 30wt% are shown in Figure 4.

At the normal state, the peel strengths of neat epoxy and 30wt% polyurethane modified epoxy adhesives are 1.37N/mm and 1.36N/mm, respectively. Adhesive strengths of the specimens that are treated with HCl, NaOH, MEK and applied heat cycles are fluctuating around 1.3N/mm. Chemical treatments have no effect on the peel strength of the polyurethane modified epoxy adhesives. It is considered that

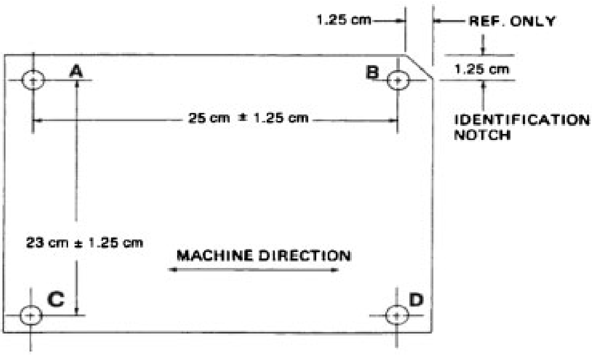

Figure 2.
Test pattern for dimensioal stability.

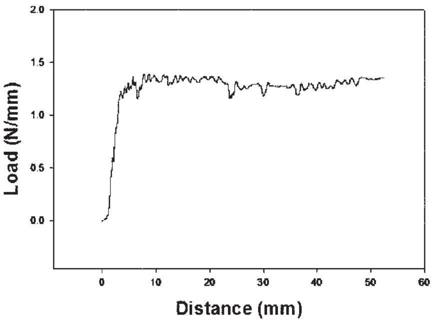

Figure 3.
Peel test profile of an epoxy/DDS/polyurethane (30wt%) system.

polyurethane can work like XNBR in aspect of adhesive strength.

Thermal Resistance

Neat epoxy which consists 20wt% of XNBR (Tg : –24.75°C) shows two glass transition temperatures (Tg) at 0°C and 111.12°C as shown in Figure 5 (a), which are originated from the glass transition of the XNBR phase and the epoxy phase, respectively. The low Tg, i.e. 0 °C, of the neat epoxy adhesive impairs the thermal stability of the 3 layer FCCL. As the contents of polyurethane (Tg : –2.95 °C) increase, the Tg of the polyurethane phase increase and that of epoxy phase decrease. 30wt% of polyurethane modified epoxy adhesive shows one Tg at 74.76°C as shown in Figure 5 (d), which may be due to the miscibility between polyurethane and epoxy resin.

In this system, low Tg of neat epoxy due to the XNBR phase increased as the contents of polyurethane increased. It means that thermal resistance of polyurethane modified epoxy adhesives is improved compared to that of the neat epoxy adhesives.

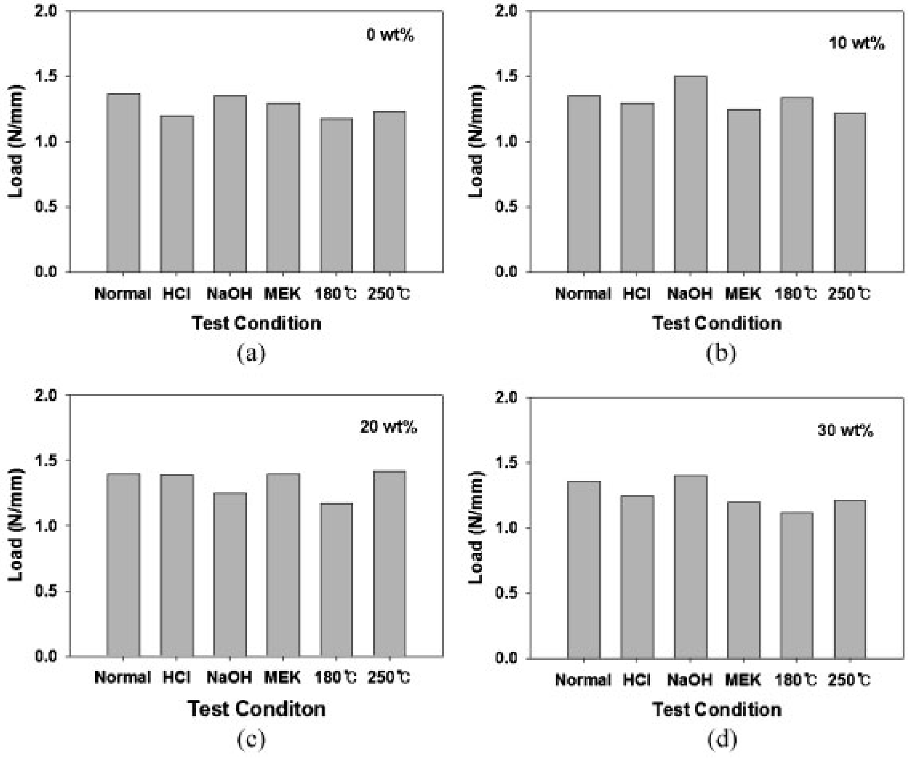

Figure 4.
Peel strength of FCCL at normal state and after heat and chemical treatments; (a) an epoxy/DDS/polyurethane (0wt%) system, (b) an epoxy/DDS/polyurethane (10wt%) system, (c) an epoxy/DDS/polyurethane (20wt%) system, and (d) an epoxy/DDS/polyurethane (30wt%) system.

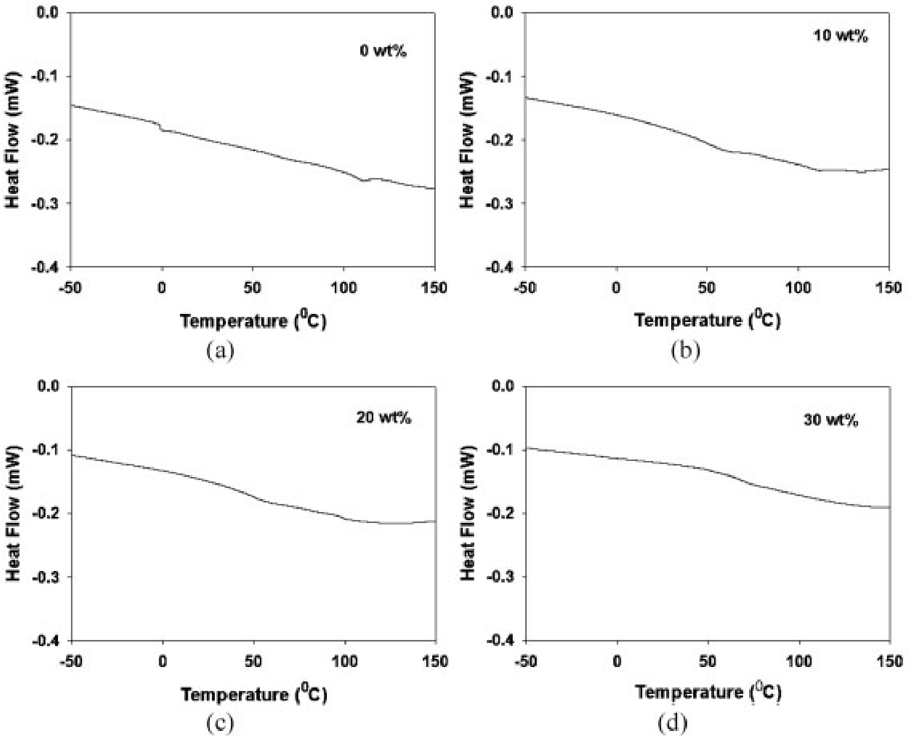

Figure 5.
DSC thermogram of epoxy adhesives: polyurethane contents; (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, and (d) 30 wt%.

Dimensional Stability

The dimensional change is shown in Table 2.

In Table 2, MD and TD of neat epoxy are 2.027% and 2.031%, respectively. As the polyurethane contents increase from 0wt% to 30wt%, the MD and TD are decreased to 0.055% and 0.021%, which means that the dimensional stability of polyurethane contents 30wt% epoxy adhesives was improved by about 98% compared to that of neat epoxy. This is attributed to that, as stated above, the thermal resistance (Tg) of polyurethane (Tg : $-2.95\,^{\circ}$C) in the epoxy adhesives is higher than that of XNBR (Tg : $-24.75\,^{\circ}$C). As the result, the epoxy adhesives can be maintained more stable at high temperature condition as the polyurethane contents increased.

Table 2.
Values of MD and TD of the dimensional stability test results.

		Neat epoxy	10wt%	20 wt%	30 wt%
A-B (cm)	I	24.923	24.929	24.967	25.019
	F	24.926	24.949	24.968	24.035
C-D (cm)	I	25.043	24.929	24.997	24.974
	F	25.025	24.921	24.996	24.994
A-C (cm)	I	22.968	23.026	22.987	22.953
	F	22.053	23.083	22.947	22.960
B-D (cm)	I	22.972	23.039	22.983	22.953
	F	22.954	23.052	22.992	22.956
MD (%)		2.027	0.107	0.089	0.055
TD (%)		2.031	0.151	0.067	0.021

Conclusion

Peel strength was evaluated for the epoxy/DDS/polyurethane adhesives by changing the contents of polyurethane. Adhesive strengths of the specimens that are treated by HCl, NaOH, MEK and applied heat cycles were fluctuated around 1.3N/mm. However, Tg of adhesives increased from 0 °C to 74.76 °C as the polyurethane contents increased from 0 wt% to 30wt%. The dimensional stability was improved significantlt, i.e., from 2.027% and 2.031% to 0.055% and 0.021% which represent MD and TD, respectively.Thermal resistance of epoxy adhesives was improved by introducing polyurethane instead of XNBR without sacrificing peel strength.

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