Novel Applications Involving Transparent Polyimides ~ White PI coatings and Transparent FPCs ~

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Introduction

Display substrates for either LCs or OLEDs, solar-cell substrates, flexible copper clad laminates (FCCLs), transparent polyimides (PIs) have attracted a lot of attention recently.[1,2] In our work at Mitsui Chemicals, we have developed three types of transparent PIs having a characteristic polymer backbone. The difference in polymer structures results in different film characteristics, namely, optical, thermal, and mechanical properties, although they keep sufficient transparency and electric stability. These transparent PIs have novel applications for white PI coatings and transparent flexible printed circuits (FPCs), and this will have a great impact on the industry because their excellent thermal properties will boost the development of next-generation materials.

Results and Discussion

As shown in Table 1, a series of transparent PIs, from type A to C, posess a high transparency reaching 90% of light transmittance, and a relatively high T_g of 260 ˚C or higher as well as a good electric stability higher than 10^{16} Ω·cm. A thermal stability higher than 260 ˚C meets the requirements for the Pb-free soldering processes. Thermal and mechanical properties depend on polymer structures. In particular, CTE is decreased drastically when making the polyimide chemical structure firmer. Type A and B consist of relatively flexible linkages in the polymer chain, while type C is likely to have a rigid structure due to the absence of such a soft hinge. A low CTE of 17 ppm/K for type C is critical for FCCLs given the same CTE of copper (17 ppm/K) so that dimensional deterioration can be suppressed. A mismatch of CTE between copper and polymer substrate may cause undesired curling or peeling. The structural hardness of type C also affects the high tensile strength at 190 MPa, much higher than that of type A (90 MPa). The toughest type B film has a bending durability of more than 2 million bends which is attritutable to the structural symmetry of the polyimide.

Table 1. Properties of transparent PIs, type A, B and C.

Transparent PI	Light transmittance [%]	T_g a) [˚C]	CTE a) [10^{-6}/K]	Tensile strength b) [MPa]	Elongation at break b) [%]	MIT c) @ 4.9 N [times]	Volume resistivity [Ω·cm]
Type A	90	290	50	90	8	3000	$>10^{16}$
Type B	90	260	46	130	18	$>1\times10^{6}$	$>10^{16}$
Type C	88	280	17	190	15	$>1\times10^{5}$	$>10^{16}$

a) Measured by TMA in air. CTE was determined in the range of 100-200 ˚C.
b) Tensile test at 30 mm/min.
c) Folding angle of 270˚, curvature radius of 0.38 mm, and load of 4.9 N

Based on the fundamentals mentioned above, the transparent PIs were applied as white PI coatings for thermally stable reflectors and transparent FPCs. The white PI was prepared from a mixture of poly(amic acid) varnish as PI precursor using type B as well as white inorganic filler, which was coated on a substrate (*e.g.,*. Kapton®) and baked as imidization proceeded. Figure 1 shows the clear varnish of type B, the white PI varnish, and the white PI coating. A high reflectivity of 85% was demonstrated even after thermal treatment at 260 ˚C. As another potential application, transparent FPCs were developed with type C which met the thermal property of Cu foil. The varnish of type C was first coated on Cu foil and baked to convert the corresponding PI, followed by formation of a thin adhesive layer on the transparent PI layer and laminated to make a 3-layered FCCL (Cu-PI-Cu). Figure 2 depicts an example of a transparent FPC with fine copper patterns (line width: 75 μm) on the both sides of the transparent PI substrate, demonstrating a clear through-viewing of the background scenery even with the existence of Cu lines. This clear view can not be accomplished with traditional colored-PI FPCs as can be seen in Figure 2. Table 2 shows the properties of FCCLs for duplex-patternable transparent FPCs regarding peel strength, tensile test, dimensional stability, dielectric constant, volume resistivity, and chemical resistance toward IPA, MEK, HClaq, and NaOHaq. These results suggest comparable utilization vis-a-vis the traditional colored FPCs, which will undoubtable contribute to the novel applications as transparent FPCs.

Table 2. Properties of transparent 3-layered FCCLs (Cu-PI-Cu).

FCCL based on type C	Peel strength [kN/m]				Tensile test		
	R.T.	@ 85 ˚C /85%RH		Soldering	Strength	Modulus	Elongation
		500 hr	1000 hr	(260 ^{o}C 5 sec)	[MPa]	[GPa]	[%]
MD	0.66	0.63	0.62	0.66	210	8.5	6.8
TD	0.66	0.64	0.62	0.67	220	8.9	7.4

FCCL based on type C	Dimensional change [%]		Dielectric constant @ 1 MHz	Volume resistivity [Ω·cm]	Chemical resistance			
	After etching	After heating			IPA	MEK	HClaq. @ 2N	NaOHaq. @ 2N
MD	-0.08	-0.17	2.95	1.2×10^{16}	OK (No delamination)			
TD	-0.09	-0.18						

Conclusion

As a result of the development of a series of transparent polyimides, type A to C, we have successfully demonstrated the existence of two promising applications: white PI coatings and transparent FPCs.

Non-color and transparency of the PI substrate enables us to add desired color to it. Thus, we have made white PI coatings in conjunction with white inorganic filler, which has resulted in 85% reflectivity and durability to the Pb-free soldering process at 260 ˚C. Highly transparent polyimide having a low CTE comparable to copper has revealed itself to have great potential for transparent FPCs albeit with moderate FCCL properties.

References

1. M. -C. Choi, Y. Kim, C.-S. Ha, *Prog. Polym. Sci.*, **33**, 581-630 (2008).
2. M.-J. Yu, Y.-H. Yeh, C.-C. Cheng, C.-Y. Lin, G.-T. Ho, B. C.-M. Lai, C.-M. Leu, T.-H. Hou, Y.-J. Chan, *IEEE Electron Device Lett.*, **33**, 47-49 (2011).

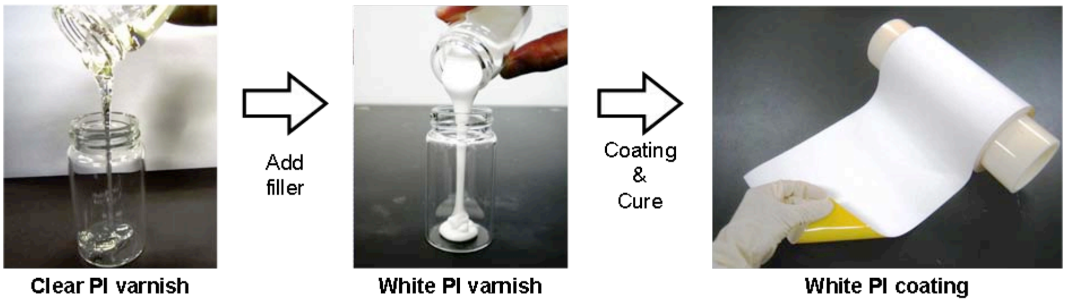

Figure 1. Example of white PI coating prepared from clear PI varnish through to white PI varnish. The reflectivity of the white PI coating is 85%.

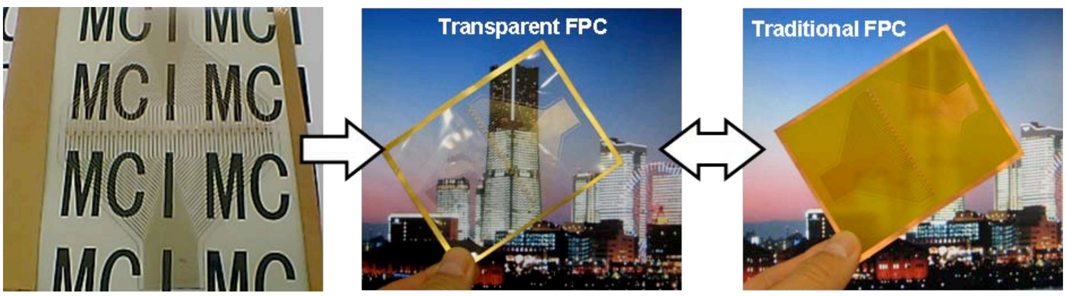

Figure 2. Example of a transparent FPC and a traditional FPC. The Cu line width is 75 μm.