Ultra-low-modulus Polyazomethines and Their FPC Application

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Abstract: This work proposes ultra-low-modulus polyazomethines (PAzMs) aiming at applications as novel coating-type protective (cover) layer materials in flexible printed circuit boards (FPC). PAzMs were polycondensed from dialdehydes containing long alkylene chains and an ether-containing common diamine. An increase in the alkylene chain length (m) of the aldehydes resulted in a gradual decrease in the modulus of the PAzMs films and a prominent increase in the adhesion strength with the smooth side (S-side) of electro-deposited copper foil, which reached 0.85 kgf/cm at $m = 12$. The results are probably due to a combined effect of the anchoring effect based on the enhanced thermoplasticity of the PAzMs and the Cu–imine attractive interaction. The PAzM ($m = 12$) was further modified with an additional diamine containing polybutylene oxide units. The PAzM copolymer achieved the target properties established in this work; i.e., ultra-low tensile modulus (< 0.3 GPa) and very high peel strength (> 0.80 kgf/cm) with the S-side of copper foil and the cover layer material.
Keywords: Ultra-low-modulus polyazomethines / Cover layer materials for FPC /peel strength

1. Introduction

Flexible printed circuit board (FPC), which is fabricated by patterned etching of copper layer in copper clad laminates (CCL) and subsequent protection of the printed circuits with a cover layer, is a very important component in microelectronic devices such as liquid crystal display (LCD) modules for personal digital assistants. One of the target properties in FPCs for LCD modules is lower stiffness. FPCs possessing lower stiffness (lower spring-back property) are desirable for the assembly processes with bending of FPCs at a lower curvature radius in very narrower spaces of portable electronic devices. The simplest approach to weaken the spring-back property of FPCs is to design thinner FPCs, namely, to decrease the thickness of each layer (the cover films, copper layer, and dielectric film). One of the conventional cover films consists of adhesive-coated commercially available aromatic polyimide (PI) films. This type of the cover films possesses excellent properties, i.e., considerably high resistance to repeated bending, excellent Cu-adhesion strength, and resistant to Ni/Au-plating processes for the wiring- and the solder bonding. However, an intrinsically high modulus of aromatic PI cover films and the presence of the relatively thick adhesion layers (> 15 μm) are disadvantageous for reducing the spring-back property of FPCs.

Siloxane-containing PI systems are also known as another type of cover layer material possessing lower stiffness [**1–4**]. In this case, the cover layers can be directly formed on the printed circuits without adhesive layers by a simple coating process of the PI solutions. We observed that no appreciable curing of the FPCs occurred when the siloxane-containing PIs were used as cover layers. This results from an extremely low modulus (< 0.2 GPa) of the PIs themselves. However, the use of the siloxane-containing PIs caused another serious problem, i.e., interpenetration of an acidic solution during a subsequent Ni/Au plating process into the interface between the smooth surface (S-side) of electro-deposited copper foil and the cover layer. The effective strategy for avoiding this problem is to drastically improve the adhesion strength at the interface. In this work, we propose low-modulus polyazomethines (PAzMs) as promising candidates of novel coating-type cover layer materials which are expected to show adhesion-promoting ability on the basis of attractive interactions between

the imine groups (–CH=N–) in the PAzM main chains and the copper foil surface (S-side).

2. Experimental Section

2.1. Monomer Synthesis and polycondensation for PAzMs

(a) Alkylene-containing dialdehyde

4,4′-diformyl–α,ω–diphenoxydodecane (m = 12; the number (m) of the methylene group ($-CH_2-$) in the dialdehyde) was prepared according to the reaction scheme shown in Figure 1. The detailed procedure is as follows: in a 100 mL three-necked flask, 4-hydroxybenzaldehyde (2.48 g, 20.3 mmol) was dissolved in 5 mL of *N*,*N*-dimethylformamide (DMF) at room temperature. To this solution, 1,12-dibromododecane (1.67 g, 9.91 mmol) and Na_2CO_3 (2.17 g, 26.1 mmol) were added. The reaction mixture was stirred at 120 °C for 6 h in a nitrogen atmosphere and poured into a large amount of water to obtain precipitate. The crude product was collected by filtration and repeatedly washed with water, then purified by recrystallization from methanol, and finally vacuum-dried at 50 °C for 12 h. The overall yield of the white product was 33%. The product was confirmed to be the desired compound from ^{1}H-NMR, FT-IR spectra, and elemental analysis. ^{1}H-NMR (400 MHz, DMSO-d_6) δ(ppm): 9.86 (s, 1H), 7.85 (d, 2H, J = 8.7 Hz), 7.11 (d, 2H, J = 8.7 Hz), 4.08 (t, 2H, J = 12 Hz), 1.74 (quint, 2H), 1.41–1.27 (m, 8H). FT-IR (KBr, cm^{-1}): 3078 (ν_{CH}), 2924 (ν_{CH}), 1689 ($\nu_{C=O}$), 1263 (ν_{COC}). Elemental analysis: calculated for $C_{26}H_{34}O_4$; C, 76.06%; H, 8.35%; found C, 75.87%; H, 8.37%. Melting point: 76 °C. Other alkylene-containing dialdehydes (m = 2–10) were also synthesized carried out in a similar manner.

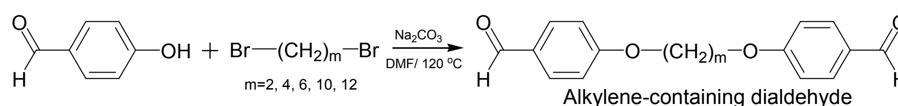


Figure 1. Reaction scheme for synthesis of alkylene-containing dialdehydes.

(b) Polymerization and film preparation

PAzMs were polymerized according to the reaction scheme shown in Figure 2. A typical polymerization procedure using dialdehydes [alkylene-containing dialdehydes or terephthalaldehyde; (TPAL)] and diamines (2,2-bis[4-(4-aminophenoxy)phenyl]propane; BAPP) or polybutylene oxide -containing diamine; PO-DA) as follows: in a 100 mL-flask, diamines (10 mmol) were dissolved in anhydrous *N*-methyl-2-pyrrolidone (NMP). Powder of 10 mmol dialdehydes (vacuum-dried at 40–50 °C for 12 h) was added to this solution. The reaction mixture with a total solute content of 18–45 wt% was stirred at room temperature for several days to obtain a turbid/viscous solution. PAzM films were prepared for mechanical property evaluation as follows; the homogenous solutions of PAzM heated at 100 °C were coated on a glass substrate and dried at 80 °C for 3 h in an air-convection oven. The PAzM films formed on the substrate were heat-treated at 120 °C/1 h + 250 °C/1 h in a vacuum oven. The PAzM films obtained were removed from the substrate.

PI precursor, poly(amic acid) (PAA), was prepared from pyromellitic dianhydride (PMDA) and diamines as follows: in a 70 mL-flask, diamine(e.g., BAPP, 3 mmol) was dissolved in anhydrous NMP. Tetracarboxylic dianhydride powder (3 mmol) (e.g., PMDA vacuum-dried at 160 °C for 12 h) was added to this solution. The reaction mixture with a total solute content of 30 wt% was stirred at room temperature for 72 h to form a viscous/homogeneous PAA solution. The PAA solution was coated on a glass substrate and dried at 80 °C for 3 h in an air-convection oven. The PAA film obtained was thermally imidized at 250 °C/1 h + 350 °C/1 h in vacuum. The PMDA-based PI film obtained was

removed from the substrate.

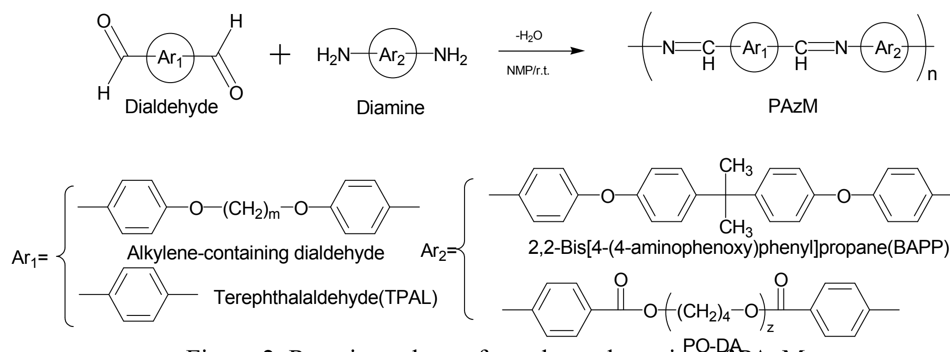


Figure 2. Reaction scheme for polycondensation of PAzMs.

2.2. Evaluation of Adhesion strength

The CCL specimens for the peel test were prepared as follows; the homogenous PAzM solution heated at 100 °C was coated on an electro-deposited copper foil (S-side), which was treated by chemical polishing agent (Mitsubishi gas chemical, CPE-750), then dried at 80 °C for 3 h. The laminates were heat-treated at 120 °C/1 h + 250 °C/1 h in vacuum. After the specimens were cut out from the central area of the CCL, a glass cloth–epoxy resin molding plate was attached onto the PAzM surface of the CCL specimens through an epoxy-type adhesive. Finally, the copper foil with patterned masking tapes was etched by immersing it in a $FeCl_3$ aqueous solution to form 3 mm-wide CCL specimens. The peel test was conducted on a mechanical testing machine (A & D, Tensilon UTM-II) at a cross head speed of 8 mm/min. The geometry of the 180° peel test is schematically depicted in Figure 3. The CCL specimens consisting of PMDA-based PIs, which were imidized at 250 °C/1 h + 350 °C/1 h in vacuum, were also prepared in a similar manner.

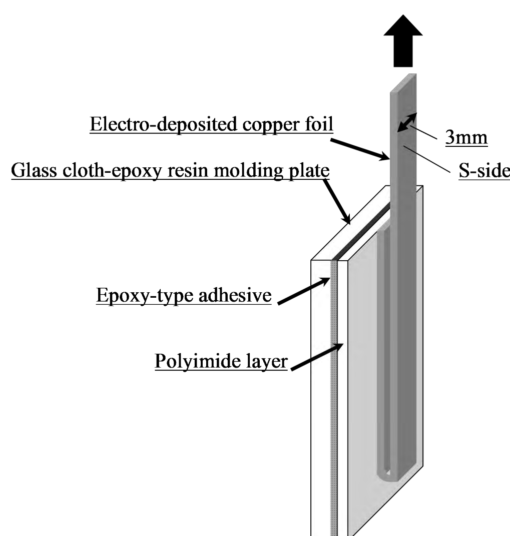


Figure 3. Schematic illustration of the 180° peel test.

2.3. Other Measurements

The mechanical properties [tensile modulus (E) and elongation at break (ε_b)] of PAzM (or PI) films (20 mm wide, 40 mm long, 10–12 μm thick) were measured using a mechanical testing machine (A & D, Tensilon UTM-II) at a cross head speed of 8 mm/min. Thermogravimetric analysis (Bruker-AXS,TG-DTA 2000S) was conducted to evaluate the thermal stability of PAzM (or PI) films from the 5% weight loss temperatures (T_d^5) at a heating rate of 10 °C/min in a nitrogen atmosphere. The reduced viscosities (η_{red}) of PAzMs (or PAA) were measured at 30 °C in NMP at a concentration of 0.5 wt% using an Ostwald viscometer. The storage- (E') and the loss modulus (E'') of the PAzM (or PI) specimens (30 mm long, 5 mm wide, and typically 15 μm thick) were measured in a temperature

range of r.t. to 500 °C at a heating rate of 5 °C/min with a frequency of 0.1 Hz to determine glass transition temperatures (T_g) from the peak temperatures in the E'' curve by the dynamic mechanical analysis (DMA) on TA Instruments, DMA-Q800.

3. Results and Discussion

3.1. Effect of imine bonds in PAzM main chains

Table 1 summarizes the film properties of the TPAL-based PAzM and PMDA-based PI films (Figure 4). The reaction between TPAL and BAPP led to a relatively low molecular weight of PAzM with a very low η_{red} of 0.15 dL/g. Nonetheless, the PAzM film was highly tough as illustrated from a high ε_b value of 99% as well as the corresponding PMDA-based PI film. The results probably arise from a toughening effect of BAPP and a chain extension based on a solid phase polymerization in PAzM films heat-treated at 250 °C. The PAzM film also showed a much lower T_g (190 °C) than the PI counterpart. This can be explained from easier internal rotation of the TPAL-based 1,4-phenylene unit than that of the PMDA-based diimide unit. In addition, it is most likely that no prominent intermolecular forces are expected in the PAzM whereas the corresponding PI gives rise to strong intermolecular forces such as charge–transfer (CT) and dipole–dipole interactions. Figure 5 shows the DMA curves for these systems. For the PAzM film, an abrupt decrease in E' above the T_g was observed without an appreciable rubbery plateau region in contrast to the E' curve of the corresponding PI film. Another feature was also observed in the PAzM film; i.e., an appreciably higher peel strength than that of the PI film. This may be related to the excellent thermoplasticity of the PAzM film, by which an anchoring effect becomes active in many cases. However, in the present situation (adhesion with the S-side of copper foil), the anchoring effect is probably not so effective. Alternatively, an effect of Cu–imine attractive interaction on the peel strength should be considered.

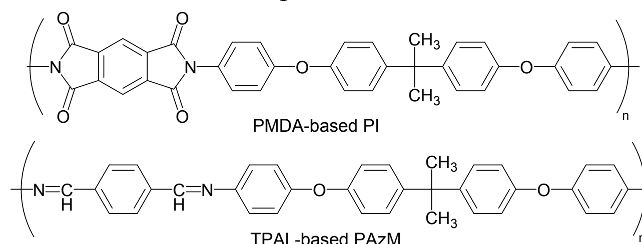


Figure 4. Structures of PMDA-based PI and TPAL-based PAzM.

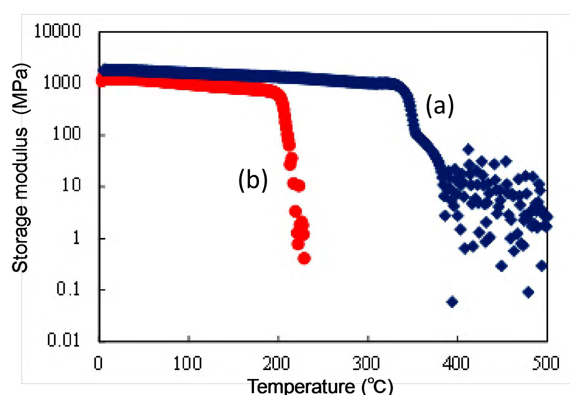


Figure 5. DMA curves of PMDA-based PI (a) and TPAL-based PAzM (b) films.

Table 1. Properties of TPAL-based PAzM and PMDA-based PI.

System	η_{red} (dL/g)	T_g (°C)	$T_d^5(N_2)$ (°C)	ε_b (%)	E (GPa)	Peel strength (kgf/cm)
PI (PMDA/BAPP)	0.60 (PAA)	308	513	133	2.08	0.14
PAzM (TPAL/BAPP)	0.15 (PAzM)	190	453	99	1.78	0.29

3.2. Film properties of PAzMs containing long alkylene chains

3.2.1. PAzMs derived from alkylene-containing dialdehydes

The properties of PAzMs derived from BAPP and alkylene-containing dialdehydes (m = 2–12) are

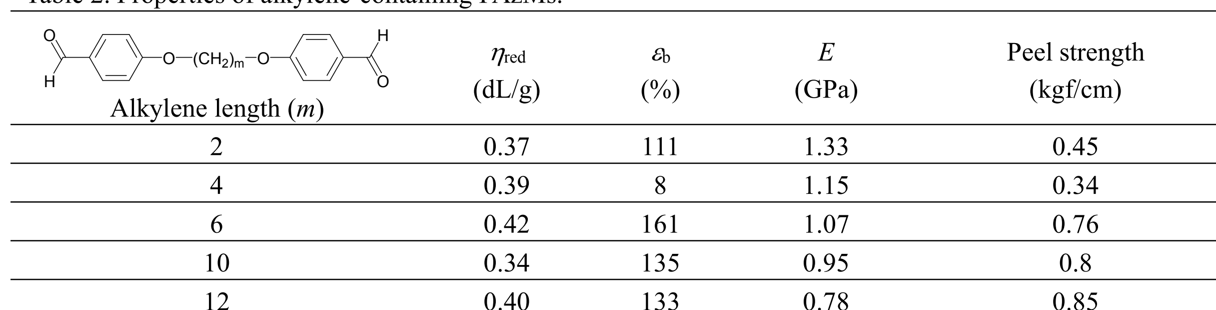
listed in Table 2. The PAzM films were basically highly tough with very high ε_b values (> 100%) except for the system with m = 4. No clear trend was observed against our initial prediction that ε_b enhances with an increase in the alkylene chain length (m). On the other hand, as shown in Figure 6(a), the tensile modulus of the PAzMs monotonously decreased with increasing m, consequently we obtained a relatively low modulus of 0.78 GPa at m = 12. It should be noted that the increase in the alkylene chain length also caused a prominent improvement of the adhesion strength as shown in Figure 6(b). This level of the S-side peel strength at m = 12 (0.85 kgf/cm) is usually difficult to achieve even if extremely flexible polymers were coated onto the S-side of copper foils (e.g., even for a siloxane-containing PI with a considerably low modulus of 0.2 GPa, its peel strength does not exceed 0.7 kgf/cm.[**2**]). Thus, the strikingly enhanced adhesion strength probably results from a combined effect of the excellent thermoplasticity for the alkylene-containing PAzMs and the Cu–imine attractive interaction.

An additional important subject in FPCs is to suppress curing of the laminates. Curling in CCLs occurs by thermal stress ($\Delta\sigma$) arising during the solution-casting/drying processes for the formation of cover films. The thermal stress is expressed as a definite integral from a drying temperature (T_{dry}) to room temperature (T_{rt}) as Eq. (I):

$$\Delta\sigma = \int [E_f/(1-\nu_f)](\alpha_s - \alpha_f)\mathrm{d}T \qquad \text{(I)}$$

where E_f and ν_f are Young′s moduli and Poisson′s ratio for the cover films, respectively. α_s and α_f are the in-plane coefficient of thermal expansion (CTE) of the substrate (copper foil in the present case) and the cover films, respectively [**5–7**]. Accordingly, thermal stress can be suppressed by significantly reducing Young′s modulus of the cover films or the CTE mismatch ($\alpha_s - \alpha_f$). The average tensile modulus of the alkylene-containing PAzM films (m = 2–12) ranged from 0.78 to 1.33 GPa as listed in Table 2. Unfortunately, curling was observed even at m = 12. This is attributed to the still high modulus of the PAzM films, suggesting that a further refined strategy should be considered.

Table 2. Properties of alkylene-containing PAzMs.



Alkylene length (m)	η_{red} (dL/g)	ε_b (%)	E (GPa)	Peel strength (kgf/cm)
2	0.37	111	1.33	0.45
4	0.39	8	1.15	0.34
6	0.42	161	1.07	0.76
10	0.34	135	0.95	0.8
12	0.40	133	0.78	0.85

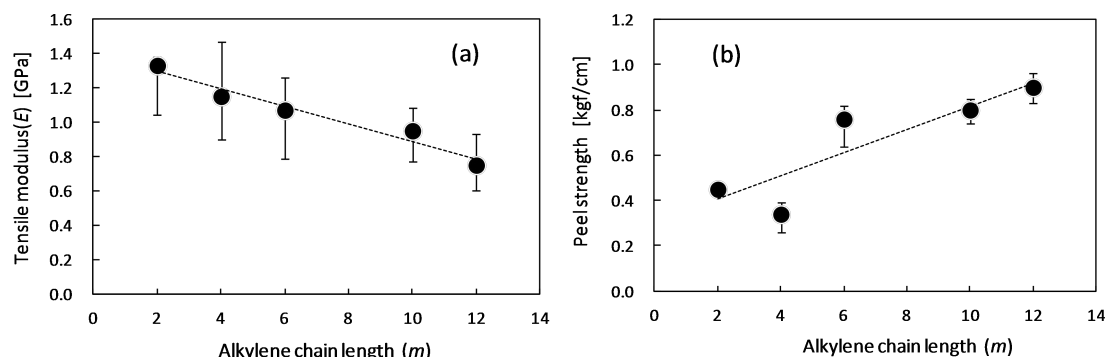


Figure 6. Film properties of alkylene-containing PAzMs as a function of alkylene chain length (m): (a) tensile modulus and (b) peel strength between copper surface (S-side) and PAzMs.

3.2.2. Attempts of modification by polybutylene oxide-containing diamines (PO-DA)

To further decrease the modulus of the PAzMs derived from alkylene-containing dialdehyde (m = 12) and BAPP, polybutylene oxide-containing diamine (PO-DA) was used as a comonomer of BAPP. Table 3 summarizes the properties of the PAzM copolymer derived from alkylene-containing dialdehyde (m = 12) with BAPP (100 – x) and PO-DA (x). The partial use of the PO-DA was effective for decreasing the modulus and reached 0.2 GPa at a PO-DA content of 25 mol%. It should be noted that this approach also enhanced the peel strength up to 1.00 kgf/cm at the PO-DA = 25 mol%. No curling behavior was observed for the CCL prepared using this copolymer with an extremely low modulus of 0.2 GPa. This can be interpreted as the result that the contribution of the low modulus overcame that of the CTE mismatch. Figure 7 shows the relationship between the tensile modulus and the peel strength for the present PAzMs and the PAzM copolymer systems. The results of siloxane-containing PIs are also plotted in this figure for a comparison. A good correlation between the peel strength and the modulus is observed for the PAzM systems in Figure 7. However, the peel strength–modulus curve for siloxane-containing PI systems is obviously located downward compared to that for the PAzMs. This probably reflects a positive contribution of the Cu–imine attractive interaction in the PAzM/Cu laminates to the adhesion strength.

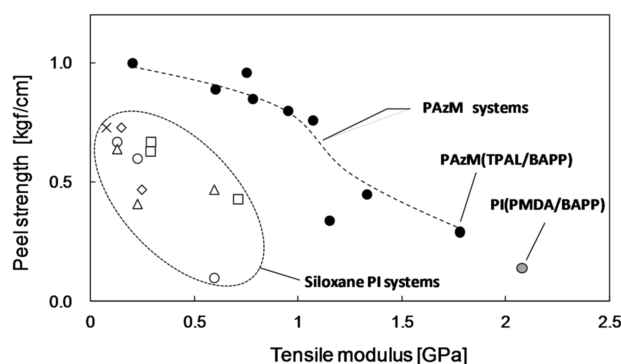


Figure 7. Relationship between the tensile modulus and the peel strength for various siloxane PIs and PAzMs.

Table 3. Properties of PAzM [dialdehyde (m = 12) /BAPP (100 – x) : PO-DA (x)] copolymer.

PO-DA x (mol%)	η_{red} (dL/g)	T_g (°C)	$T_d^5(N_2)$ (°C)	ε_b (%)	E (GPa)	Peel strength (kgf/cm)
0	0.40	85	423	133	0.78	0.85
10	0.21	55	415	175	0.60	0.89
25	0.22	40	400	13	0.20	1.00

3. Conclusions

Ultra-low-modulus PAzMs were studied to apply as novel cover layer materials in FPCs. PAzMs were polycondensed from alkylene-containing dialdehydes and BAPP. An increase in the alkylene chain length (m) resulted in a gradual decrease in the modulus and a prominent increase in the adhesion strength with the S-side of copper foil, which reached 0.85 kgf/cm at m = 12. The results are probably due to a combined effect of the anchoring effect based on the enhanced thermoplasticity of the PAzMs and the Cu–imine attractive interaction. The PAzM (m = 12) was modified with PO-DA as a comonomer of BAPP. The PAzM copolymer displayed an extremely low modulus of 0.2 GPa, as a result, curling of the CCL specimens was completely suppressed. Thus, the present PAzM systems can be promising candidates as novel coating-type cover layer materials.

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