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Solution-processable CF_3-substituted ductile polyimides with low coefficients of thermal expansion as novel coating-type protective layers in flexible printed circuit boards

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ABSTRACT

This work proposes practically useful novel coating-type cover layer materials. A copolyimide (PI) system derived from pyromellitic dianhydride (PMDA, 50 mol%), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (s-BPDA, 50 mol%) with 2,2′-bis(trifluoromethyl)benzidine (TFMB) showed a low coefficient of thermal expansion (CTE) by thermal imidization. However, this system was not compatible to chemical imidization process because of gelation. A structural modification of this copolymer by 4,4′-(hexafluoroisopropylidene)dianiline (HFIDA) significantly improved the solubility, as a result, allowed for chemical imidization in a homogeneous state and the formation of a stable PI solution from less hygroscopic solvents such as triglyme (TriGL). The TriGL-cast PI film at an HFIDA content of 25 mol% displayed excellent combined properties; a low CTE (22.9 ppm K^{-1}), a very high T_g (327 °C), and a common level of tensile properties [modulus (E) = 3.6 GPa and the elongation at break ($\varepsilon_b{}^{max}$) = 10.4%]. The PMDA(50);s-BPDA(50)/TFMB copolymer system was also modified with other ether-linked fluorinated diamines; i.e., 2-trifluoromethyl-4,4′-diaminodiphenylether (3FODA) and 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (6FBAPB). At a 3FODA content of 25 mol%, the NMP-cast PI film displayed the lowest CTE (20.7 ppm K^{-1}) among the PIs examined in this work. The modification using 6FBAPB was most effective to enhance the solubility. Thus, the structural modifications of PMDA(50);s-BPDA(50)/TFMB copolymer by these fluorinated diamines (HFIDA, 3FODA, and 6FBAPB) were an effective way to obtain almost satisfying target properties except for a high level of ε_b. A mechanism was proposed for explaining why the effect of the CF_3-substituted ether-linked diamines on the toughness improvement was not so prominent. The approach simultaneously using some CF_3-free ether-linked monomers enabled us to significantly enhance the film toughness ($\varepsilon_b{}^{max}$ > 50%) while maintaining low CTE characteristics and good solution-processability. Thus, some of the PI systems can be promising candidates as novel coating-type cover layer materials.

1. Introduction

Flexible printed circuit board (FPC) components have been used in various electronic devices such as cellular phones, hard disc drives (HDD), and tablet computers because FPCs can be mounted in narrow spaces of portable electronic devices by freely folding them. This feature greatly contributes to down-sizing and lightening of the devices [1]. FPCs also allow for excellent interconnections between fixed circuits and moving electronic parts such as a foldable cellular phone and HDD suspensions. Polyimides (PIs) are indispensable polymeric materials as dielectric layers in FPCs for their distinctive features, i.e., outstanding heat resistance, electric insulation reliability based on an extremely high purity (practically no ionic/metallic contaminations), good mechanical properties, and simple manufacturing processes [2–7]. In FPCs, PIs are primary used as dielectric substrates (12–50 μm thick) on which printed circuits are formed. Recently, the dielectric substrates (called "base films") are needed to possess high dimensional stability against both of heating/cooling cycles and water/moisture absorption in the FPC fabrication processes. For this purpose, we have so far proposed a molecular design for simultaneously controlling the coefficients of thermal expansion (CTE) and the humidity expansion (CHE) while keeping excellent properties inherent to conventional PIs [8–10]. In conventional FPCs, PIs are also used as protective films (cover layers) for the printed circuits as depicted in Fig. 1(a). In this case, the printed circuits are covered by

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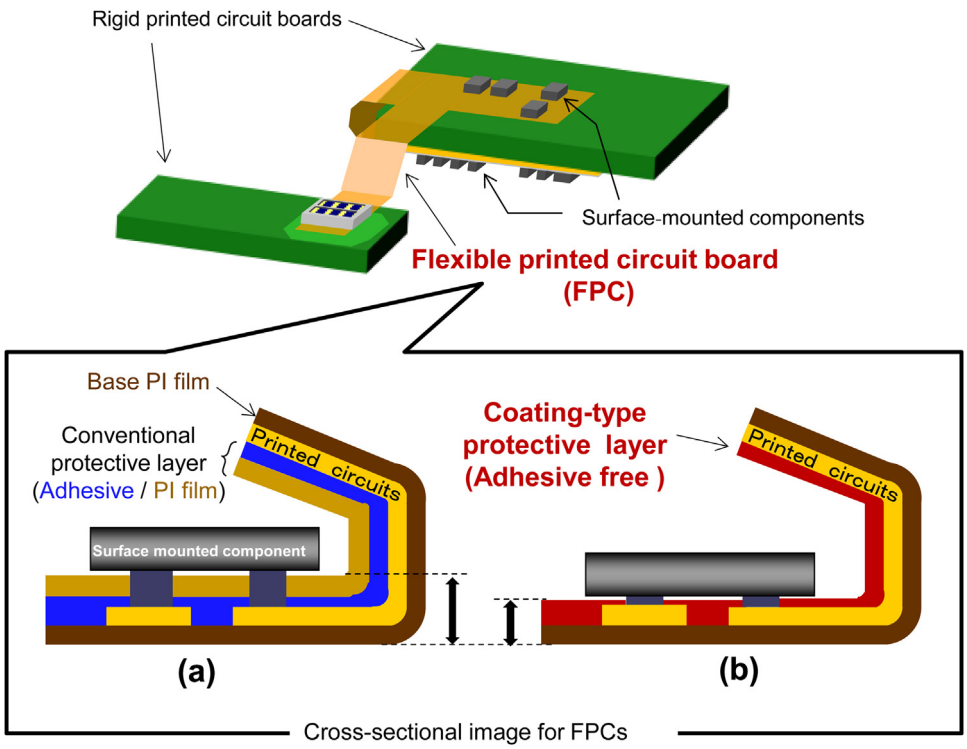

Fig. 1. Schematic illustration for FPCs: (a) conventional type and (b) coating type.

thermo-compressing the protective films (12–50 μm thick) precoated with a thermo-setting adhesive layer (15–35 μm thick) on the single face. More recently, a problem is pointed out in the conventional FPCs; i.e., a spring-back property arising when they are mounted in narrow spaces by three-dimensionally folding with a low curvature radius. The intensive restoring forces against bending can be responsible for a decrease in the reliability of electric connection with other electronic components.

One of the effective strategies for reducing the spring-back property is to replace the conventional (laminate-type) protective films by the coating-type ones [Fig. 1(b)], thereby the "stiffness" (consequently, the restoring forces) of the FPCs can be minimized by a decrease in the total FPC thickness. If stable PI solutions are available, adhesive-free protective layers can be directly formed on the printed circuits via simple solution casting (coating and drying) by means of a screen-printing technique without subsequent thermal imidization process. However, as long as common aromatic PI systems are used as the coating materials, significant curing of the FPCs is unavoidable. To solve this problem, we have studied coating-type ultra-low-modulus cover layer materials [11–13]. However, they are inferior to the conventional laminate-type cover films in the circuit break down resistance against repeated bending, although the former is sufficiently resistant to single bending. This is probably related to a very low modulus of the cover layer itself, thereby the conductive layers suffer stress concentration. The present work proposes novel coating-type overcoat materials for solving the crucial problems mentioned above (curling and bending stress resistance).

2. Experimental

2.1. Materials

2.1.1. Monomer synthesis

2-Trifluoromethyl-4,4′-diaminodiphenylether (3FODA) was synthesized according to the reaction scheme shown in Fig. 2; 2-chloro-5-nitrobenzotrifluoride (44.6 mmol) and 4-nitrophenol (58.0 mmol) were dissolved in 50 mL of dry *N,N*-dimethylformamide (DMF), and K_2CO_3 (53.3 mmol) was added in it. The reaction mixture was stirred at 60 °C for 4 h in a nitrogen atmosphere, and it was poured into a large amount of a NaOH aqueous solution (20 wt%). The precipitate was collected by filtration and repeatedly washed with water, and vacuum-dried at 50 °C for 12 h (yield: 84.6%); ^{1}H NMR [400 MHz, dimethyl sulfoxide (DMSO)-d_6, δ (ppm)]: 8.54–8.58 (m, 2H; ArH), 8.36 (d, J = 8.8 Hz, 2H; ArH), 7.44–7.46 (m, 3H; ArH); FT-IR (KBr, cm^{-1}): 3086 (C_{arom}–H), 1520 (NO_2), 1346 (NO_2), 1246 (COC); melting point: 83 °C [endothermic peak temperature in the differential scanning calorimetry (DSC) thermogram].

The dinitro compound obtained (3.0 mmol) was dissolved in ethyl acetate at room temperature, and Pd/C (Pd: 10%, 0.1 g) was added as a catalyst. The reaction mixture was stirred at 35 °C for 4 h in a hydrogen atmosphere. After the catalyst was filtered off, the solvent was removed by an evaporator, purified by recrystallization from ethanol, and vacuum-dried at 80 °C for 12 h (yield: 87.2%); ^{1}H NMR [400 MHz, DMSO-d_6, δ (ppm)]: 6.54–6.88 (m, 7H; ArH), 5.26 (s, 2H; NH_2), 4.88 (s, 2H; NH_2); FT-IR (KBr, cm^{-1}): 3420/3400 (NH_2), 3077 (C_{arom}–H), 1228 (COC); elemental analysis (%): calculated for $C_{13}H_{11}F_3N_2O$; C, 58.21; H, 4.13; N, 10.44, found C, 57.93; H, 4.25; N, 10.19; melting point: 113 °C.

4,4′-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl (6FBAPB) was also synthesized in a similar manner (Fig. 2)[14]. The dinitro compound obtained (yield: 71.6%) was characterized as follows; ^{1}H NMR [(400 MHz, DMSO-d_6) δ (ppm)]: 8.55–8.48 (m, 4H; ArH), 7.86 (d, J = 8.7 Hz, 4H; ArH), 7.36 (d, J = 8.7 Hz, 4H; ArH), 7.22 (d, J = 9.2 Hz, 2H; ArH); FT-IR (KBr, cm^{-1}): 3109 (C_{arom}–H), 1530/1351 (NO_2), 1243 (COC); melting point: 211 °C. The corresponding diamine was obtained by catalytic reduction of the nitro compound and recrystallization from ethanol (yield: 92.4%); ^{1}H NMR [400 MHz, DMSO-d_6, δ (ppm)]: 7.56 (d, J = 8.7 Hz, 4H; ArH), 6.94–6.82 (m, 10H; ArH), 5.49 (s, 4H; NH_2); FT-IR (KBr, cm^{-1}):