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Synthesis and Characterization of Polyurethane Acrylate Oligomers for Electrodes Protection Adhesives of Plasma Display Panel (PDP)

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A series of polyurethane acrylate oligomers having different molar ratio of diol and diisocyanate has been synthesized from isophorone diisocyanate (IPDI), mixture of poly(ethylene-co-1,2-butylene)diol (PEBD) and 2-butyl-2-ethyl-1,3-propanediol (BEPD) and 2-hydroxyethyl methacrylate (HEMA) using dibutyl tin dilaurate (DBTL) as a catalyst. Then, the UV curable adhesives were fabricated by mixing the prepared oligomers, acrylate monomers, photo initiators, and other additives. Subsequently, the physical and mechanical properties such as coefficient of thermal expansion (CTE), elastic modulus (E'), glass transition temperature (Tg), adhesion strength and water absorption were measured. Electrochemical migration of Ag electrodes, which was resulted in the degradation of surface insulation resistance, was also investigated by measuring insulation resistance during 100 hours of 50°C, 90%RH storage test.

Keywords: electrochemical migration; electrodes protection; plasma display panel; polyurethane acrylate; UV curable adhesive

INTRODUCTION

Recent years, UV curing technologies have been widely used in the fields of protective coatings, electronic devices, adhesives and inks due to their high curing speed, energy conservation, pollution reduction, and cost effectiveness [1]. Therefore, UV curable adhesive

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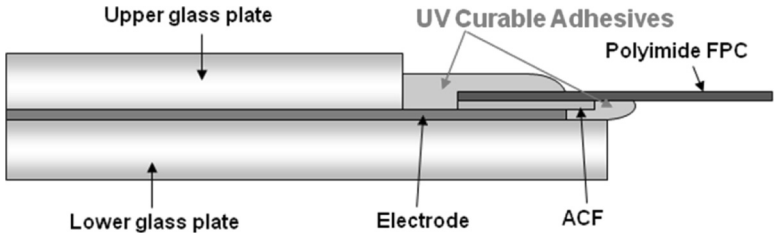


FIGURE 1 Application of UV curable adhesive for PDP.

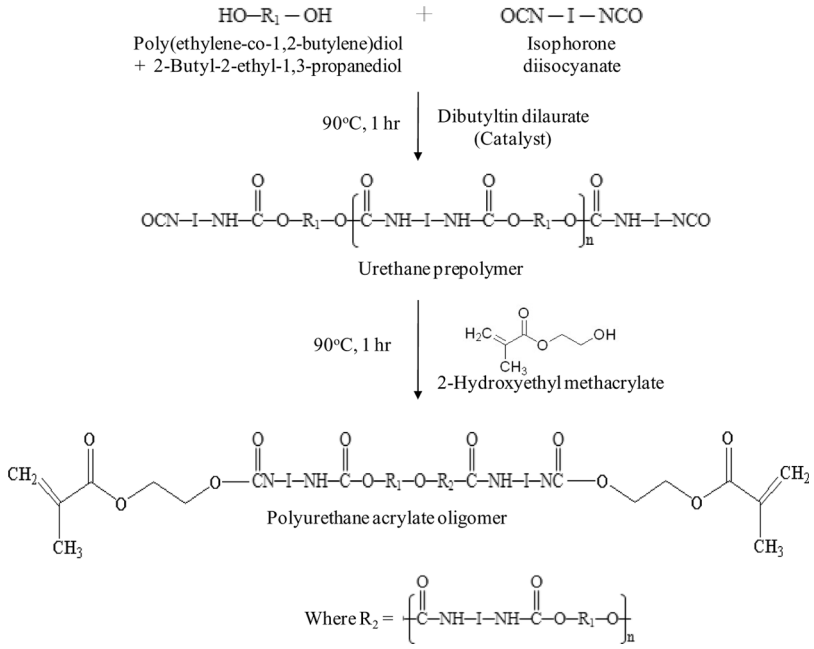
materials are gaining consideration as an alternative candidate to silicone RTV which was currently used electrodes protective adhesive for PDP application. The main purpose of applying the electrodes protective layer on the PDPs is to reduce the electrochemical migration of silver electrodes, which was resulted in the degradation of surface insulation resistance (Fig. 1). It is well known that under the influence of direct current (DC) bias, the silver ions move from anode to cathode through the absorbed water layer on an insulating surface. Then, the metallic silver accumulates at the cathode, subsequently results in silver bridges between the electrodes [2,3]. Minimum required conditions to occur the Ag migration are elevated relative humidity and voltage bias between a positive and negative electrodes [4]. Therefore, interface adhesion and water absorption property are the most important properties for the purpose of the PDP application. In this study, a series of polyurethane acrylate oligomers having different molar ratio of OH and NCO have been synthesized. Then, the physical and mechanical properties and electrochemical migration reliability were investigated as a function of the molar ratio of diol (OH) and diisocyanate (NCO).

EXPERIMENTAL

Synthesis

Synthesis of Polyurethane Acrylate Oligomers

The polyurethane acrylate oligomers were synthesized according to a procedure described elsewhere [5,6]. Mixture of PEBD, BEPD and DBTL was added into three-necked flask with Di-tert-butyl-4-methylphenol (BHT) as a thermal stabilizer. IPDI was slowly dropped into the reactor at 60°C for 20 min. and then, stirred for an additional 1 hr at 90°C. A calculated amount of HEMA was gradually added into the reaction mixture and stirred for an hour to terminate the NCO group. Finally, four different oligomers were prepared with a ratio



SCHEME 1 Synthesis of polyurethane acrylate oligomers.

of equivalents of OH/NCO as 0.67, 0.75, 0.80, and 0.83 (Scheme 1). Obtained oligomers were monitored by FT-IR to confirm the extinction of NCO ($\sim 2270\,cm^{-1}$). Mw and PDI of the oligomers were also measured using GPC.

Fabrication and Characterization of UV Adhesive

Four different UV curable adhesives were fabricated by mixing the prepared oligomers with different OH/NCO molar ratio (70 wt%), 4-hydrobutyl acrylate (15 wt%), photo initiators (~5 wt%), and other additives such as silane coupling agents and adhesion promoters (10 wt%). For the adhesion and the Ag migration test, the prepared adhesives were dispensed on the Ag patterned glass or the PI substrate and cured by using a metal halide lamp ($300\,mW/cm^2$, wave length range is 265~420 nm) with dose of $1800\,mJ/cm^2$. For the materials properties test, adhesives were coated on the separator film using the applicator and cured with same conditions.

Electrochemical migration test was also carried out using the test structure and the set-up as shown in Figure 2. The UV curable adhesive was applied on the Ag electrodes and cure with UV dose of

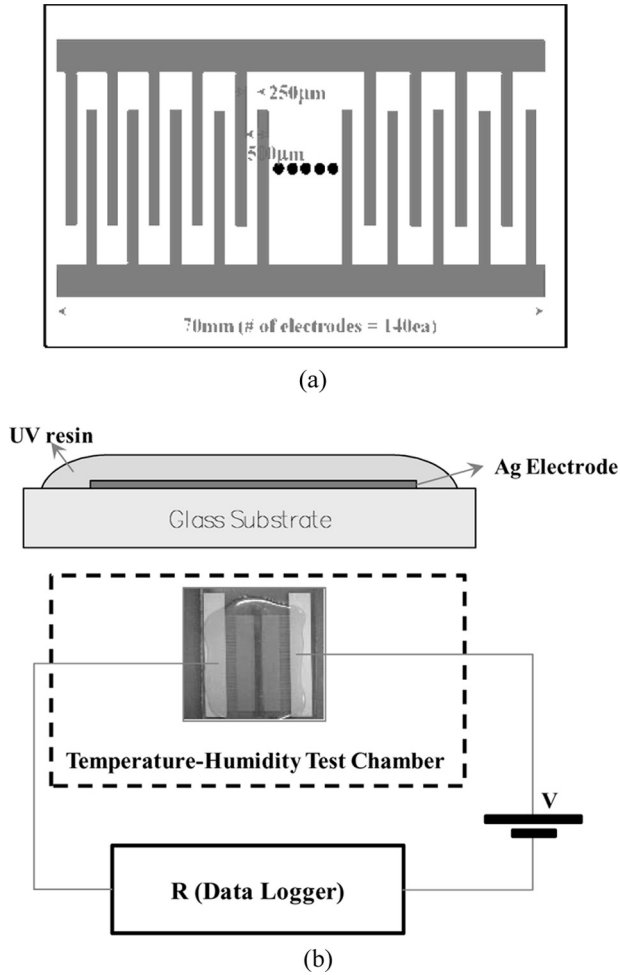


FIGURE 2 Test structure (a) and set-up (b) for Ag electrochemical migration.

1800 mJ/cm^2. Then, 100 V of DC current was applied during 100 hours of high temperature and humidity condition (50°C, 90%RH) and insulation resistance was monitored through the test.

MEASUREMENTS

FT-IR spectrometer (GX series, Perkin-Elmer) was employed to check the NCO termination of oligomers. GPC experiments were also carried out to determine the molecular weight (Mn) and polydispersity index

(PDI) of prepared oligomers. Characterization of the UV curing behavior of prepared adhesives was done using a photocalorimeter (PCA) from TA Instrument. Coefficient of thermal expansion (CTE), modulus (E′) and glass transition temperature (Tg) of cured adhesives were measured by using thermo-mechanical analyzer (TMA/SS 6100, Seiko).

RESULTS AND DISCUSSION

The physical and mechanical properties of oligomers and cured adhesives were shown in Table 1. The viscosity and number-average molecular weight (Mn) of the oligomers increased as the OH/NCO ratio increased. Because higher OH/NCO molar ratio leads the more soft (alcohol) – rigid (isocyanate) repeating unit in the oligomer structure, and as results, the viscosity and Mn increased.

Figure 3 shows the results of PCA measurements of UV adhesives prepared with different OH/NCO ratio. There's no remarkable difference in cure peak temperature, but the heat of reaction was reduced from 210.5 J/g to 148.9 J/g as the OH/NCO ratio of the oligomers increased. Because the oligomers with a lower OH/NCO ratio showed lower Mn (Table 1), the UV adhesives using oligomers with a lower OH/NCO ratio have more reactive sites than oligomer with a higher OH/NCO ratio. Thus, the heat of reaction was reduced as the OH/NCO NCO ratio of the oligomers increased.

Deterioration of cured adhesive properties such as CTE, modulus, Tg and adhesion strength were observed as the OH/NCO molar ratio increased. These are mainly due to the decrease of crosslink density which was originated from the increase of molecular weight

TABLE 1 Materials Properties of Oligomers and Cured UV Adhesives

Diol/Diisocyanate ratio			0.67	0.75	0.80	0.83
Oligomer	Viscosity (poise, 25°C)		266	2040	9450	29500
	Mn		3719	4930	5858	6329
	PDI		2.88	2.69	2.62	2.63
Cured UV adhesive	CTE (ppm)	1	156	174	176	188
		2	10950	11237	14244	15710
	Tg^{TMA} (°C)		31.7	24.5	23.0	22.6
	Modulus (Pa) at 20°C		1.8E8	5.5E6	2.0E6	1.7E6
	Tg^{DMA} (°C)		27.5	18.6	16.1	14.8
	Water absorption (%)		0.195	0.102	0.037	−0.007
	Adhesion to Glass (gf/mm)		196	156	145	114
	Adhesion to PI (gf/mm)		119	100	103	74

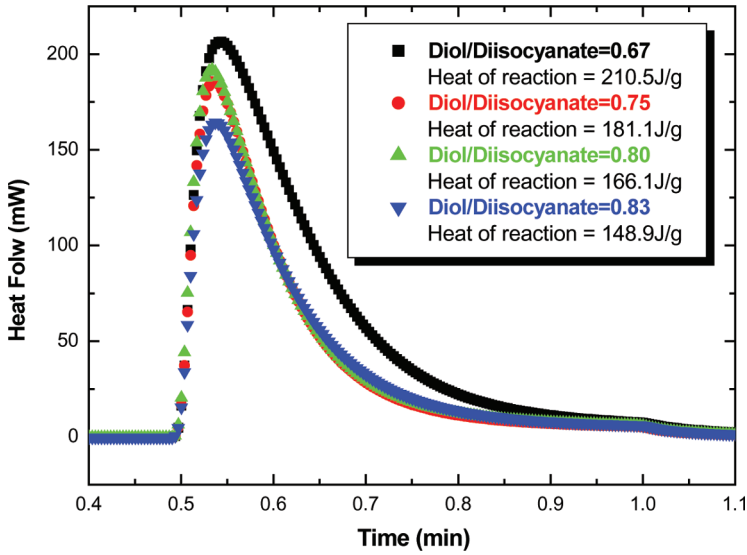


FIGURE 3 Photocalorimeter (PCA) curves of UV curable adhesives with different OH/NCO molar ratio.

of oligomers. Crosslink density can be estimated from the rubber elasticity theory modified by Nielsen [7].

$$\nu = \frac{\mathrm{Er}}{3\mathrm{RT}}$$

where ν represents the crosslink density (number of moles of chains per cm^3), R is the gas constant (8.314 J/K mole), T is the temperature, and Er is the elastic modulus. The estimation results of crosslink density were 4.13×10^{-3} (OH/NCO = 0.67), 7.55×10^{-4} (OH/NCO = 0.75), 2.79×10^{-4} (OH/NCO = 0.80), and 2.45×10^{-4} moles/cm^3 (OH/NCO = 0.67). But the amount of water absorption decreased with OH/NCO molar ratio. Because the intermolecular forces between hard (NCO) and soft (OH) domains increase with the OH/NCO molar ratio increased, and as a result, the water absorption decreased [8].

Electrochemical migration test was carried out and test set-up and results were shown in Figure 4. 100 V of DC current was applied during a temperature and humidity test (50°C, 90%RH for 100 hours) and insulation resistance was monitored throughout the test. As shown in Figure 4, the insulation resistances of samples with OH/NCO ratio of 0.67 and 0.75 decreased sharply around the aging time of 30 to 50 hrs. This is mainly due to the higher amount of water absorption which

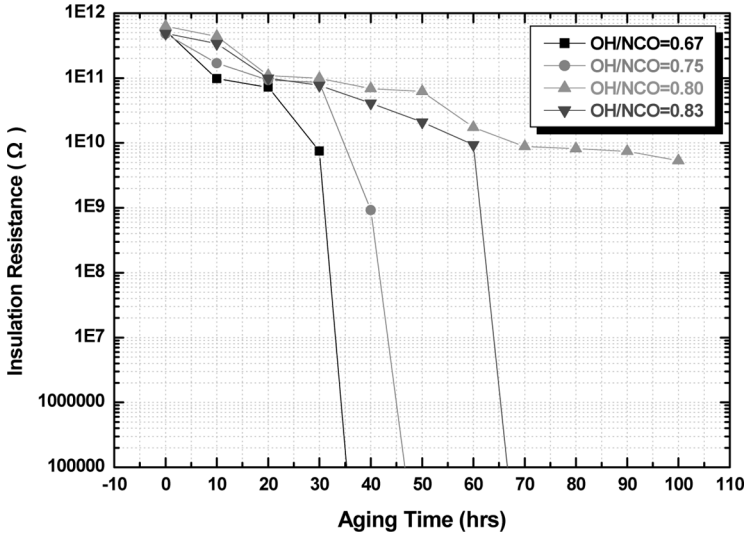


FIGURE 4 Changes of insulation resistance during electrochemical migration test.

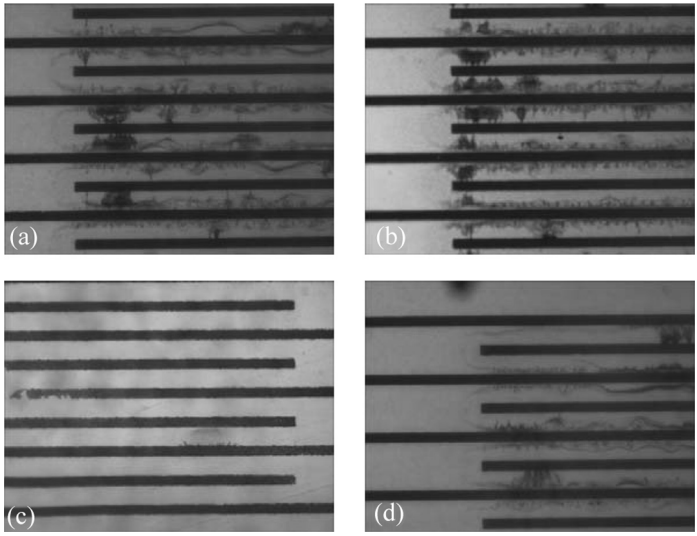


FIGURE 5 Optical microscope images of test substrates after electrochemical migration test. OH/NCO molar ratios of samples are (a) 0.67, (b) 0.75, (c) 0.80, and (d) 0.83.

is critical to the migration. The insulation resistance of sample with OH/NCO ratio of 0.83 also showed remarkable decrease around 70 hrs of aging time and this is originated from the weaker adhesion to the polyimide substrate. Only the sample with OH/NCO ratio of 0.80 showed good resistance to the electrochemical migration test. After completion of electrochemical migration test, all samples were observed by optical microscope to confirm the Ag dendrite growth. As shown in Figure 5, all the samples except the sample with OH/NCO molar ratio of 0.80, showed severe Ag dendrite formation from anodes (+) to cathodes (−). And the results are well accordance with the Figure 4.

CONCLUSIONS

A series of polyurethane acrylate oligomers having different ratio of diol and diisocyanate has been synthesized. Subsequently, UV curable adhesives using prepared oligomers were prepared for electrodes protection application. The Mn and viscosity of prepared oligomers increased, the materials properties of cured adhesives decreased, and water absorption properties of cured adhesives improved as the OH/NCO molar ratio increased. The results of electrochemical migration test showed that the amount of water absorption and the adhesion strength are critical to the resistance of Ag migration. Conclusively, the optimum performances of the UV curable adhesive for electrodes protection of PDP were observed with OH/NCO ratio of 0.80.

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