Microelectronics Reliability 49 (2009) 517–522

Contents lists available at ScienceDirect

Microelectronics Reliability

journal homepage: www.elsevier.com/locate/microrel

Effects of soft segment mixtures with different molecular weight on the properties and reliability of UV curable adhesives for electrodes protection of plasma display panel (PDP)

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ARTICLE INFO

Article history:
Received 10 September 2008
Received in revised form 5 February 2009
Available online 26 March 2009

ABSTRACT

A series of urethane acrylate oligomers has been synthesized from isophorone diisocyanate (IPDI), mixture of soft segments with different M_w, i.e., poly(ethylene-co-1,2-butylene)diol (PEBD, M_w = 2400) and 2-butyl-2-ethyl-1,3-propanediol (BEPD, M_w = 160) and 2-hydroxyethyl methacrylate (HEMA) using dibutyl tin dilaurate (DBTL) as a catalyst. Subsequently, the UV curable adhesives were fabricated by mixing the prepared oligomers, reactive diluents (Isobonyl acrylate and 4-hydroxybutyl acrylate) and photo initiator (1-hydroxy-cyclohexyl-phenyl-ketone). The physical and mechanical properties of UV cured adhesives such as coefficient of thermal expansion (CTE), elastic modulus (E'), glass transition temperature (T_g), adhesion strength and water vapor transmission rate (WVTR) were measured. And electrochemical migration of Ag electrodes, which brings on the degradation of surface insulation resistance, was also investigated by monitoring insulation resistance during 100 h of 50 °C, 90%RH storage test.

1. Introduction

A UV curing system is generally consisted of reactive oligomers, reactive diluents, and photo initiators. The most critical component in determining the ultimate physical and mechanical properties is reactive oligomers [1,2]. Commonly used formulations for UV curable adhesives contain unsaturated acrylic oligomers and the main types of acrylic oligomers are epoxy acrylates, polyester acrylates, urethane acrylates and silicone acrylates. Among them, urethane acrylate oligomers offer wide range of excellent application properties, such as high impact and tensile strength, abrasion resistance, toughness, good adhesion to various substrates and excellent weathering resistance combined with excellent resistance to chemicals and solvents [3].

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 [4,5]. Thus, UV curable adhesive materials are gaining more consideration as an alternative candidate to silicone RTV which was currently used electrode protective adhesive for PDP application.

The main purpose of applying the electrode protective adhesive on the PDPs is to reduce the electrochemical migration of silver electrodes which brings on 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 [6,7]. Minimum required conditions to occur the Ag migration are elevated relative humidity and voltage bias between a positive and negative electrode [8]. 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 BEPD (low M_w diol) and PEBD (high M_w diol) was synthesized for the preparation of UV curable adhesives. Subsequently, the UV curable adhesives were fabricated by mixing the prepared oligomers, reactive diluents, and photo initiator. The physical and thermo-mechanical properties of cured adhesives and electrochemical migration stability of PDP modules were investigated as a function of molar ratio of BEPD (low M_w diol) and PEBD (high M_w diol).

2. Experiments

2.1. Synthesis of urethane acrylate oligomers

A series of urethane acrylate oligomer was synthesized according to a procedure described elsewhere [9,10]. Mixture of soft segments with different M_w (BEPD and PEBD) and catalyst (DBTL)

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doi:10.1016/j.microrel.2009.02.001

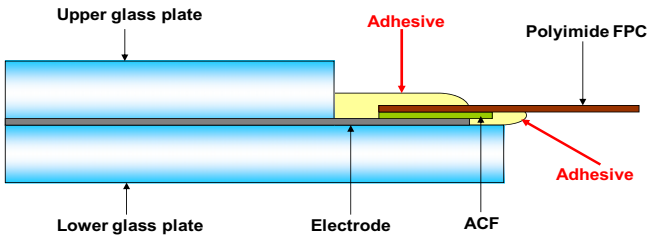


Fig. 1. Application of UV curable adhesive for PDP.

were added into three-necked flask with 2,6-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 h at 90 °C. A calculated amount of HEMA was gradually added into the reaction mixture and stirred for an hour at 90 °C to terminate the NCO group. Finally, five different oligomers were prepared with a ratio of equivalents of PEBD (high M_w soft segment, $M_w = 2400$) and BEPD (low M_w soft segment, $M_w = 160$) as 0/1, 0.11/0.89, 0.27/0.73, 0.43/0.57 and 0.67/0.33 (Scheme 1). Obtained oligomers were monitored by FT-IR spectrometer (GX series, Perkin–Elmer) to confirm the extinction of NCO group ($\sim$2270 cm^{-1}) and the relative weight average molecular weight (M_w) and PDI values of the oligomers were determined by GPC using polystyrene standards.

2.2. Fabrication and characterization of UV adhesives

Five different UV curable adhesives were fabricated by mixing the prepared oligomers with different PEBD/BEPD molar ratio (70 wt%), reactive diluents (11 wt% of isobonyl acrylate and 4 wt% of 4-hydroxybutyl acrylate), photo initiators (5 wt% of 1-hydroxy-cyclohexyl-phenyl-ketone), and other additives such as silane coupling agents and adhesion promoters (10 wt%).

Characterization of the UV curing behavior of obtained oligomers was done using photocalorimeter (PCA, TA instrument). For physical and thermo-mechanical properties tests, UV adhesives were coated on the separator film using the applicator 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. Water vapor transmission rate (WVTR) was measured by dry cup method according to the ASTM E 96-95. Coefficient of thermal expansion (CTE), storage modulus (E') and glass transition temperature (T_g) of cured adhesives were measured by using thermo-mechanical analyzer (TMA/SS 6100, Seiko).

For the adhesion strength and Ag migration test, 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. Adhesion strength test was performed with peel off conditions of 50 mm/min speed and 90° peel angle.

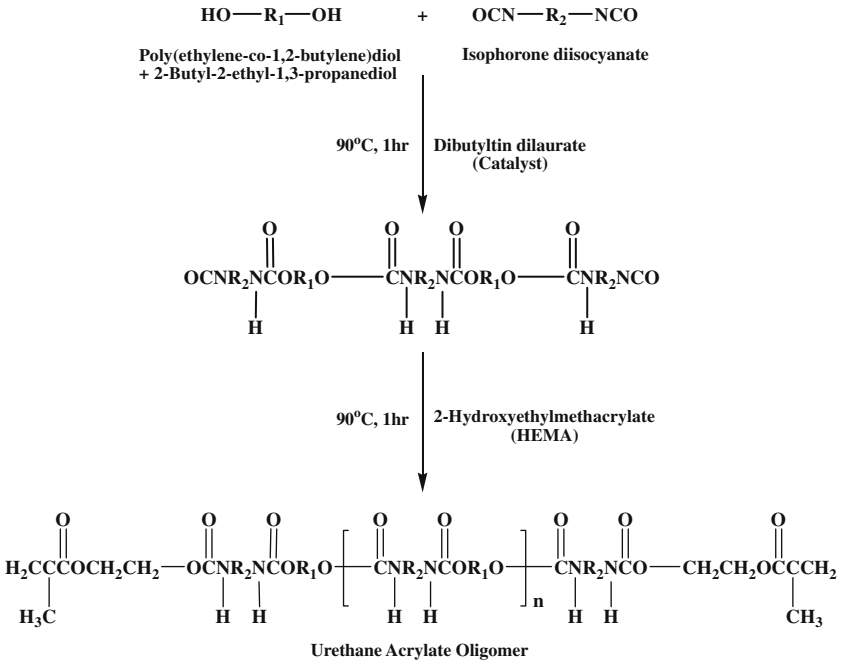
Electrochemical migration test was also carried out using the test structure and set-up as shown in Fig. 2. For substrate glass applied to PDP, high strain point and low thermal shrinkage are essential to ensure dimension stability during the firing process at high temperature (550–580 °C) [11]. Thus, PD-200 glass (Asahi glass company), which is widely employed in PDP manufacturing, was used for the test substrate. For Ag electrochemical migration test, 4-μm-thick, 500 μm pitch (250 μm wide Ag electrode and 250 μm gap between adjacent electrodes) Ag traces were formed on the glass substrate with thickness of 1.8 mm. UV curable adhesive was applied on the Ag patterned glass substrate and cure with UV dose of 1800 mJ/cm^2. Then, 100 V of DC current was applied during 100 h of high temperature and humidity condition (50 °C, 90%RH) and insulation resistance was monitored through the test.

3. Results and discussion

3.1. Material characterization

3.1.1. Analysis of oligomers

FT-IR spectra of oligomer synthesis process (0.43 mol% of PEBD content) were shown in Fig. 3. When the reaction was continued for an hour after HEMA added to the system, no absorption band was observed at 2270 cm^{-1}, indicating that the NCO groups have been completely reacted. The relative weight average molecular



Scheme 1. Preparation of urethane acrylate oligomer.

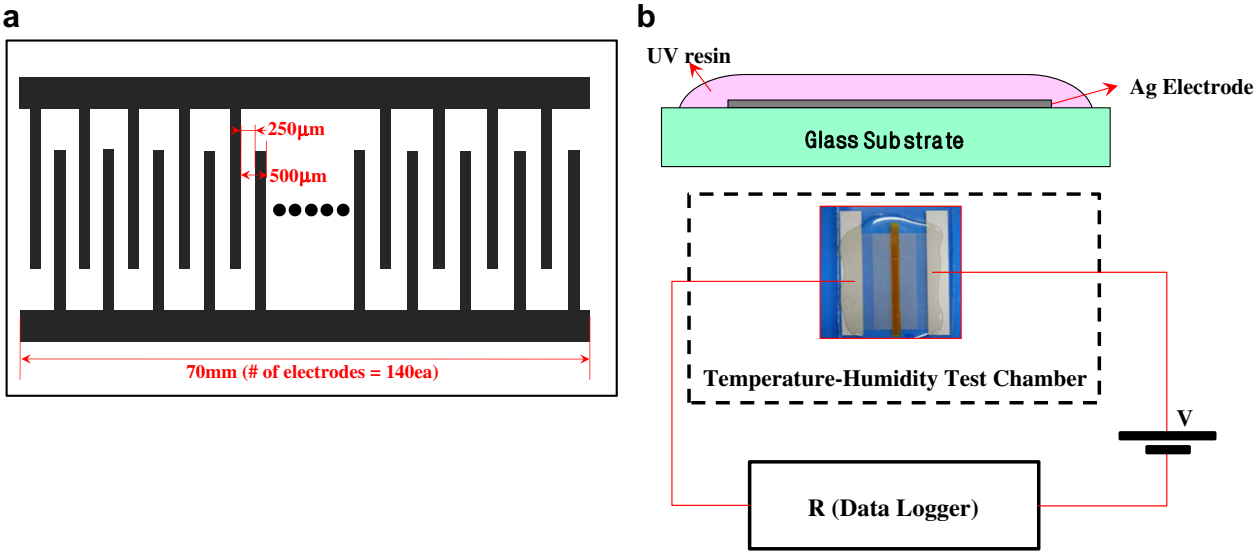


Fig. 2. Test structure (a) and set-up (b) for Ag electrochemical migration.

weight (M_w) and PDI values of the oligomers were determined by GPC using polystyrene standards. The determined M_w and PDI values of the oligomers are collected in Table 1. As the increase of the high M_w PEBD ratio, the M_w and the PDI of oligomer was increased due to the increment of high M_w soft segment portion in the oligomers.

3.1.2. Cure kinetics of UV adhesives

Fig. 4 shows the results of PCA measurements of UV adhesives which were prepared from oligomers with different PEBD and BEPD ratio. As shown in Fig. 4, there's no remarkable difference in cure peak temperature, but the completion time of cure was delayed in proportion to the high M_w PEBD ratio increased. Furthermore, the heat of reaction and degree of cure also decreased as the PEBD ratio increased (Fig. 5). Because the increase of high M_w PEBD ratio lead to the increment of M_w of oligomers (Table 1) and viscosity of UV adhesive system (Fig. 6), the reactivity of molecular chain was hindered and, as a result, curing speed, heat of reaction and degree of cure decreased.

3.1.3. Thermo-mechanical properties of cured adhesives

Deterioration of cured adhesive properties such as coefficient of thermal expansion (CTE), storage modulus (E') and glass transition temperature (T_g) were observed as the high M_w PEBD ratio increased (Table 1). These are mainly due to the reduction of crosslink density which was originated from the increase of high M_w soft segment (PEBD) ratio. As the high M_w PEBD ratio increased, number average molecular weight between crosslink (M_c) also increased. M_c can be determined using equation from rubber elasticity theory [12]:

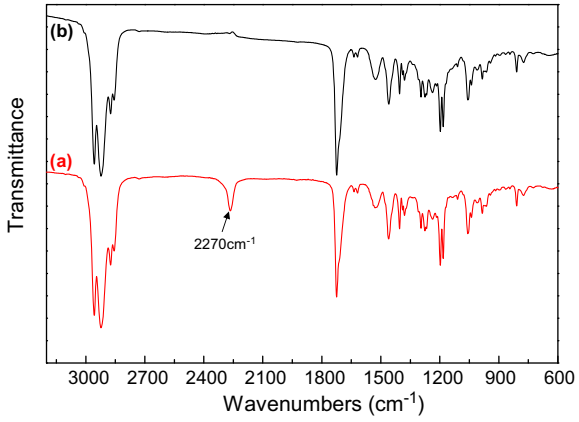


Fig. 3. Infrared spectra of oligomers containing 0.43 mol% of PEBD content; (a) before and (b) after terminated.

$$M_c = q\frac{d\mathrm{RT}}{\mathrm{Er}} \tag{1}$$

where q is the front factor (usually 1), d is the density (Table 1), R is the gas constant (8.314 J/K mol), T is the temperature in Kelvin at 40 °C above the glass transition temperature of samples and Er is the elastic modulus. In addition, crosslink density can be estimated from the rubber elasticity theory modified by Nielsen [13];

$$v = q\frac{\mathrm{Er}}{3\mathrm{RT}} \tag{2}$$

Table 1
Materials properties of oligomers and cured UV adhesives.

Molar ratio of PEBD/BEPD	Oligomers	Cured adhesives							
	M_w	PDI	Density (g/cm^3)	M_c (g/mole)	Crosslink density (moles/cm^3)	CTE (ppm/°c)		T_g (°C)	E'(Pa) @ T_g + 40 °C
						Below T_g	Above T_g		
0/1	5666	1.62	0.987	241	1.36×10^{-7}	167	7987	65	1286
0.11/0.89	9442	2.14	0.985	285	1.15×10^{-7}	234	13,457	55	1.058
0.27/0.73	11,095	2.33	0.979	336	0.97×10^{-7}	378	17,324	52	884
0.43/0.57	12,758	2.51	0.975	516	0.63×10^{-7}	453	18,934	51	572
0.67/0.33	18,418	2.72	0.961	875	0.37×10^{-7}	879	23,212	43	325

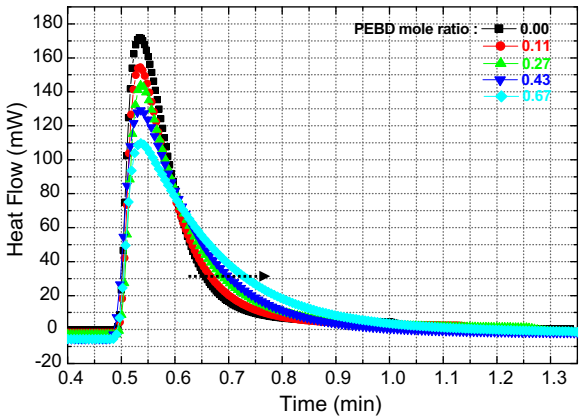


Fig. 4. Photocalorimeter (PCA) curves of UV curable adhesives with different PEBD ratio.

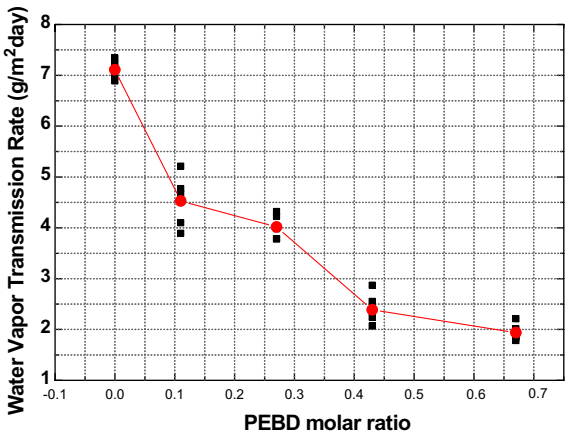


Fig. 7. The WVTR measurement of UV cured adhesives.

where ν represents the crosslink density (number of moles of chains per cm^3).

The calculated values for the M_c and crosslinking density are tabulated in Table 1. The crosslink density of adhesive network is in inverse proportion to the M_c. From the results of M_c and crosslink density estimation, the use of high M_w PEBD could be resulted in higher M_c and lower crosslink density. The decrease in the dynamic mechanical properties of cured adhesives was attributed to the more unrestricted motion of network chain segments due to the damping with increasing M_c. Therefore, the use of high M_w soft segment (PEBD) can deteriorate the thermo-mechanical properties of cured adhesives.

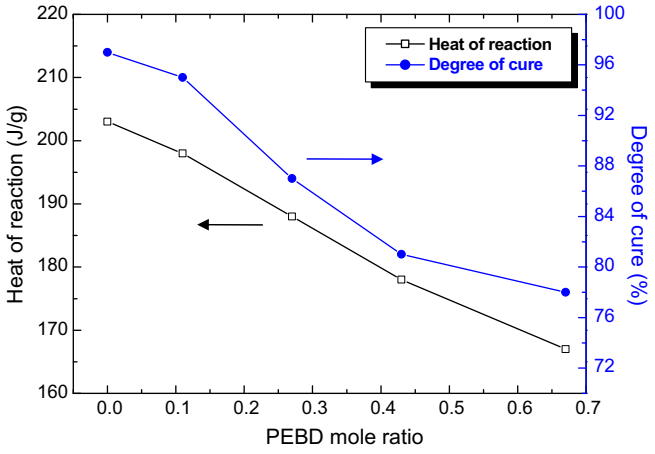


Fig. 5. Heat of reaction and degree of cure plots versus PEBD mole ratio in UV adhesives.

3.1.4. Water vapor transmission rate (WVTR) test

As mentioned above, the main purpose of applying the electrode protective adhesive on the PDPs is to reduce the electrochemical migration of silver electrodes which brings on the degradation of surface insulation resistance. And the main path of silver ions is the absorbed water layer on an insulating surface. Therefore, water vapor transmission rate is the most important properties for the purpose of the PDP application. The standard dry cup method (ASTM E 96-95) was used to measure the WVTR and anhydrous calcium chloride was used as a desiccant. The test conditions are 50 °C, 90%RH for 24 h. As shown in Fig. 7, the WVTR was decreased as the high M_w soft segment (PEBD) ratio increased. The partial dispersion of the hard segment (diisocyanate) to soft segment domain (diol) was hindered and the intermolecular forces between hard segment and soft segment domains increased as the high M_w soft segment portion increased. Therefore, arrangement of the soft segments was occurred easily and, as a result, the WVTR was decreased [14].

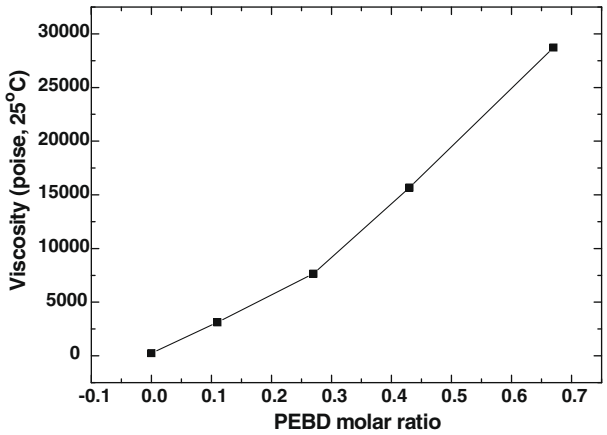


Fig. 6. Viscosity changes of UV adhesives according to the PEBD mole ratio.

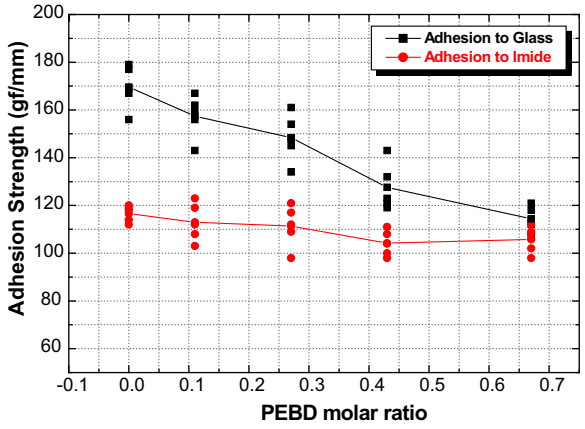


Fig. 8. Adhesion strength of cured adhesives to glass and imide substrates.

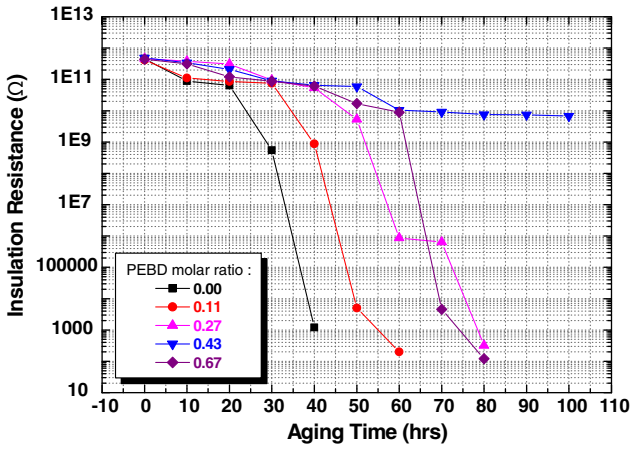


Fig. 9. Changes of insulation resistance during electrochemical migration test.

3.1.5. Adhesion strength of cured adhesives

Weak adhesion strength can lead the delamination between the adhesive and the substrate, which can offer the paths of water absorption. Thus, adhesion strength is also critical to the Ag migration stability as well as WVTR.

As shown in Fig. 1, UV adhesive is applied on the glass and imide substrates at the same time, it is important to maintain the adhesion to glass and imide substrate simultaneously. But the structural point of view, the adhesion to the glass substrate is more critical than that to the imide substrate due to the position of electrodes. The delamination between the glass and UV adhesive makes direct influence to the electrodes via water absorption. But the delamination between the imide and UV adhesive can not affects the electrode directly because there's no electrode between the imide and UV adhesive interface.

The test results of adhesion strength to the glass and the imide substrates were shown in Fig. 8. As the high M_w soft segment (PEBD) ratio increased, the molecular weight between crosslink (M_c) increased and crosslink density decreased (Table 1). Therefore, the adhesion strength was expected to decrease as the increase of PEBD ratio. From Fig. 8, the decrease of adhesion strength to glass substrate was observed with the increase of PEBD ratio, as might be expected.

But the adhesion strength to imide substrate showed no remarkable changes with the PEBD ratio. Generally, the imide group was always present in the aromatic ring plane and could not easily make strong intermolecular interactions with other molecules such as hydrogen bonding. Thus, internal stress is more important criterion than the other properties such as crosslink density to maintain the adhesion strength. Because the samples with higher PEBD ratio showed lower modulus than with lower ratio ones, the adhesion strength of higher PEBD ratio samples showed similar adhesion properties to the lower PEBD ratio samples.

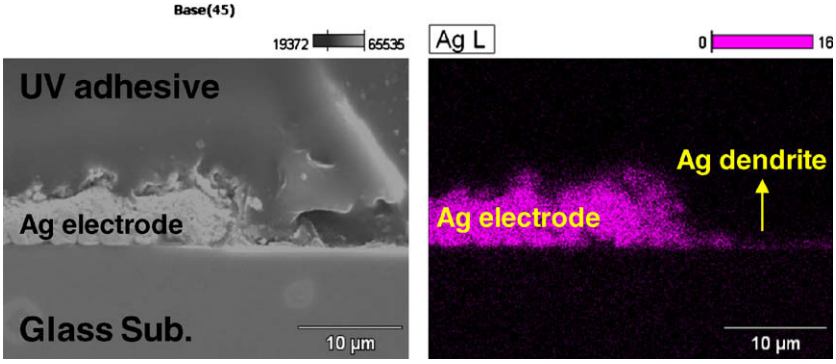


Fig. 10. EDS analysis result of test substrate after electrochemical migration test. The PEBD ratio of the sample is 0.67.

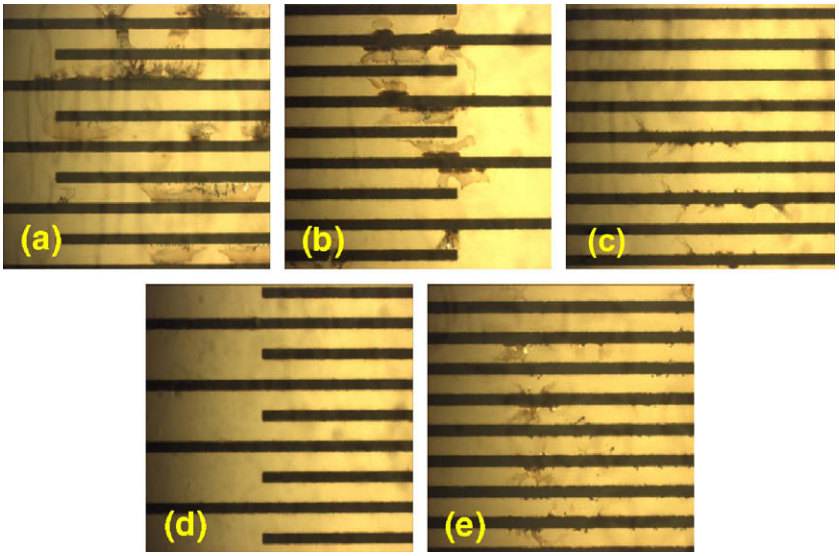


Fig. 11. Optical microscope images of test substrates after electrochemical migration test. PEBD ratio of samples are (a) 0, (b) 0.11, (c) 0.27, (d) 0.43 and (e) 0.67.

3.2. Electrochemical migration stability of silver electrodes

Electrochemical migration test was carried out and test set-up and the results were shown in Figs. 2 and 9, respectively. 100 V of DC current was applied during a temperature and humidity test (50 °C, 90%RH for 100 h) and insulation resistance changes were monitored throughout the test.

In case of UV adhesives with high M_w soft segment (PEBD) content of 0, 0.11 and 0.27, the insulation resistance decreased sharply at the aging time of 30, 40 and 50 h, respectively. This is mainly due to the high water vapor transmission rate (WVTR), which is critical to the migration stability. The sample with PEBD ratio of 0.43, which has the WVTR of 2.4 g/m^2·day, showed stable insulation resistance during the 100 h of the test.

In spite of low WVTR (1.9 g/m^2·day) property of sample with PEBD ratio of 0.67, the insulation resistance showed remarkable decrease around 70 h of aging time. The sharp decline of insulation resistance around the 70 h can be explained by the lower T_g values (43 °C) of the UV adhesives than the test temperature (50 °C) and the deterioration of the adhesion strength between the glass substrate and the UV adhesive. As shown in Fig. 10, it is clear that the electrochemical migration of Ag electrodes was occurred through the glass and UV adhesive interface. Therefore, there were some delaminations between the glass and UV adhesive, and severe water absorption was occurred through the delaminations, subsequently. And, as a result, the growth of Ag dendrites due to the electrochemical migration made the deterioration of insulation resistance.

After completion of Ag electrochemical migration test, all samples were observed by optical microscope to confirm the Ag dendrite growth. As shown in Fig. 11, all the samples except the sample with PEBD ratio of 0.43, showed severe Ag dendrite formation from anodes (+) to cathodes (−). And the results were well in accordance with the Fig. 9.

4. Conclusion

A series of urethane acrylate oligomers having different molar ratio of BEPD (low M_w diol) and PEBD (high M_w diol) were synthesized. Then, UV curable adhesives using prepared oligomers were manufactured for electrode protection of PDP module.

Because incorporation of high M_w PEBD lead to low crosslink density, materials properties such as coefficient of thermal expansion (CTE), elastic modulus (E'), and glass transition temperature (T_g) of the cured adhesives were deteriorated as the increase of high M_w PEBD ratio. The WVTR was decreased as the high M_w soft segment (PEBD) ratio increased due to the increase of the intermolecular interaction between the soft and hard segment domains. Adhesion strength of UV adhesive to glass substrate was decreased as the PEBD ratio increased due to the reduction of crosslink density. But, in case of imide substrate, there were little changes in adhesion strength regardless to the PEBD ratio. This is attributed to the low internal stress originated to the low modulus values.

It is clear that the WVTR, T_g and adhesion strength to glass substrate were critical criteria to determine the electrochemical migration stability. The samples with lower PEBD ratio (0, 0.11 and 0.27) showed the Ag dendrite growth due to their high WVTR, whereas sample with PEBD ratio of 0.67 was due to the T_g which was lower than the test temperature and poor adhesion strength to glass substrate. Conclusively, the optimum performances of UV curable adhesive for electrode protection of PDP were observed with PEBD ratio of 0.43.

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