

# A study of UV-curable epoxide resins containing thermal accelerator – Tertiary amines

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## Abstract

The individuals of tertiary amines, including imidazole (1-amine), 1,2-dimethylimidazole (2-amine), 2,4,6-tris(dimethyl-amino-methyl)phenol (3-amine), 1-methylimidazole (4-amine), and 2-methylimidazole (5-amine), were added into UV-curable epoxide resins, respectively, and the effects on UV/thermal conversions, thermal properties and adhesion strengths for various types of substrates were investigated. According to the experimental results, the extent of effects of amines on physical properties was found in the order of: 3-amine > 4-amine > 1-amine > 2-amine > 5-amine. The resin with 3-amine exhibited the highest glass transition temperature ( $T_g = 72.3$  °C) value and the lowest coefficient of thermal expansion (CTE = 70.8 ppm/°C), which also exhibited the highest adhesion strengths on various substrates, on glass (greater than 199 kg/cm<sup>2</sup>), ITO (greater than 182 kg/cm<sup>2</sup>), PET (115 kg/cm<sup>2</sup>), and stainless steel (232 kg/cm<sup>2</sup>), and possesses great potentials for advanced opto-electronic applications.

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**Keywords:** Tertiary amines; UV-curable epoxide resin; Cationic polymerization; Conversion; Adhesion strength

## 1. Introduction

UV-curable resins have been widely used in many applications such as coatings, encapsulation, inks, adhesives, and in the preparation of assembly substrates due to its fast curing and solvent-free features [1]. One of the important UV-curable resins is epoxy compound, utilizing photo-initiated cationic ring-opening polymerization, because of its rapid polymerization rate and good physical prop-

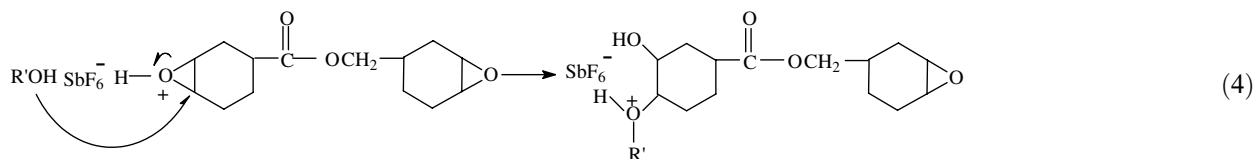
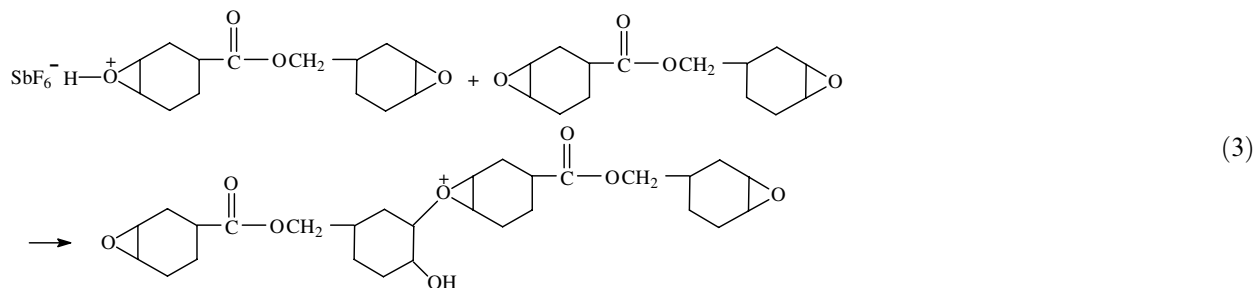
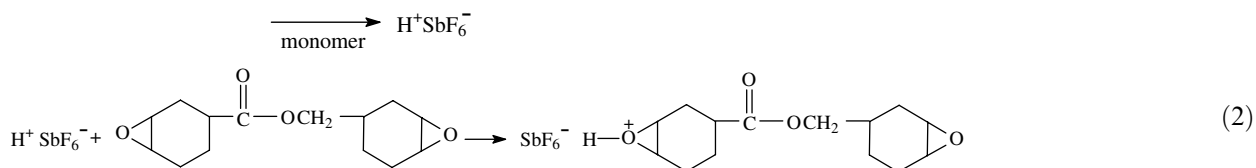
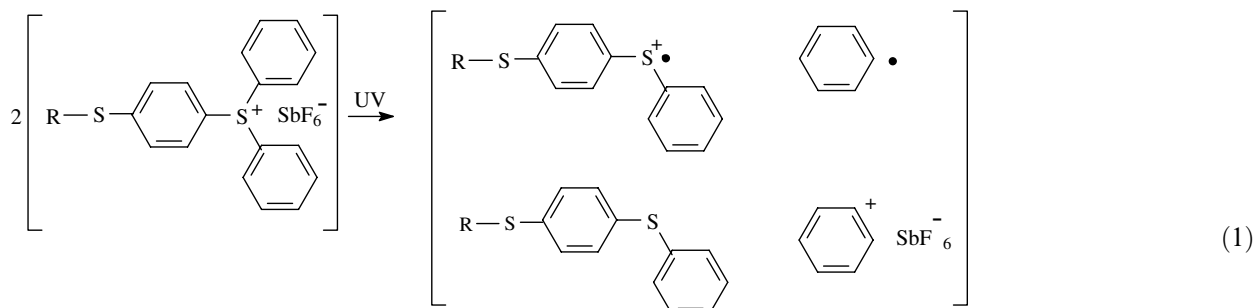
erties of the final products. There are many studies relating to the deterioration of OLEDs [2]. Most of them agreed that the primary degradation mechanism in un-encapsulated OLEDs is the exposure of the organic-cathode interface to ambient moisture and oxygen. This leads to the oxidation and delamination of the active cathode as well as the chemical reactions of the light-emitting layers during device operation [3]. In order to inhibit degradation, the packaging of OLEDs is commonly accomplished by dispersing the UV-cured sealing adhesive around the active part of the device. For applications of packaging applications, most of adhesive resins undergo cationic polymerization because of their excellent adhesion strength and good resistance to chemical/oxygen permeation [4].

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Triarylsulfonium salts are used as photoinitiators for possessing high thermal stability, which undergo rapid photolysis when they are irradiated by UV light with wavelengths ranging from 200 to 300 nm. Both homolytic and heterolytic cleavage mechanisms are involved in the photolysis of the triarylsulfonium salts, photoinitiator. In the homolytic process, the excited state first cleaves to release diphenylsulfinyl radical cation, phenyl radical and anion. Eq. (1) depicts the reactive species including aryl radicals, aryl cationic radicals, aryl cations and the Brønsted acid ( $\text{H}^+\text{SbF}_6^-$ ) generated by the photolysis of the photoinitiator [5,6]. And the reaction mechanisms of cationic photo-polymerization reactions of epoxide resin and polyol monomer are depicted in Eqs. (2)–(6) [7–9]

Regarding to epoxy resins, tertiary amines are common thermal accelerators to reduce curing temperatures and promote thermal conversions. One of the special features of tertiary amines is that they may react with carbonyl compounds, singlet oxygen and other species *via* an electron transfer process to improve the low ionization potential property [10]. The imidazole of tertiary amines, which is usually used as a thermal accelerator and could be thermally cured at 80–120 °C, not only reacts with epoxy through one or both of the nitrogens on the ring but also catalyzes the reactions. The other tertiary amine, 2,4,6-tris(dimethylamino-methyl)phenol, is a very effective room-temperature accelerator/co-curing agent for polyamine and polyamide-based coatings as well as other types of





adhesives [11]. Compare to UV-curable resins, the thermal-curable resins exhibit higher  $T_g$ , lower CTE and higher adhesion strengths, but they do not fit to OLED applications due to higher curing temperatures, longer curing times and solvent-contained. Therefore, how to improve the properties such as  $T_g$ , CTE and adhesion strength of UV-curable resins becomes a challenge for their applications to OLED packaging.

In the past, the tertiary amines such as acrylate monomers containing amine groups, *e.g.*, monoacrylate of a cyclic carbamate, monoacrylate of a cyclic urethane [10] and amine acrylate [12,13], may serve as oxygen inhibitors in UV-curable resins. Effects of imidazole and other tertiary amines on thermal polymerization of resins have been widely studied [14–17]. However, their addition to UV-curable resins and effects on key physical properties of resins are rarely reported. Thermal accelerator, tertiary amine, is applied to UV-curable resin, hence this work studies the addition of imidazole and tertiary amines to UV-curable epoxide resins and their effects on conversions of UV/thermal curing, thermal properties and adhesion strengths on various types of substrates. The types of tertiary amine and optimum content were identified so as to fabricate the UV-curable epoxide resins with satisfactory properties for the packaging of advanced opto-electronic devices.

## 2. Experimental

### 2.1. Materials and sample preparation

The cycloaliphatic epoxide oligomer resin, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate; the silane coupling agent, vinyltrimethox-

ysilane; the photoinitiator, triarylsulfonium hexafluoroantimonate salts; the monomer, tri(propylene glycol), were all purchased from Aldrich Co. Thermal initiator, benzoyl peroxide (BPO), was provided by Fluka Co. The five different types of tertiary amines, imidazole (1-amine), 1,2-dimethylimidazole (2-amine), 1-methylimidazole (4-amine) and 2-methylimidazole (5-amine) were supplied by Aldrich Co. and 2,4,6-tris(dimethylamino-methyl)phenol (3-amine) was bought from TCI Co.

The resin samples were prepared by mixing the cycloaliphatic epoxide and monomer at the weight ratio of 4:1 along with 1.0 wt.% of silane coupling agent by 1.5 h stir then about 1.5 g of photoinitiator and 0.2 wt.% BPO were added into with another 1.5 h stir and 1.0 wt.% tertiary amines was added into above mixture and stirred till completing the resin samples preparation.

### 2.2. UV conversions

The UV conversions of samples were carried out by first coating various types of resin samples on KBr discs then cured in an UV oven (C-SUN, UC-1000) with various time spans. The cured samples were sent to a Fourier-transform infrared spectrometer (Nicolet Protégé 460 FTIR) for structure analysis. The conversions of the samples were determined by the peak absorbance at  $910\text{ cm}^{-1}$  of FTIR spectra. An internal standard band method was chosen in order to compensate the change in sample thickness resulted from UV curing. The absorption band at  $1728\text{ cm}^{-1}$  for  $\text{C}=\text{O}$  of dicycloaliphatic epoxide was adopted as an internal standard band for calculation. The conversions of samples were calculated according to the following equation:

$$\text{UV Conversion (\%)} = \left( 1 - \frac{[A]_{\text{Et}}/[A]_{\text{rt}}}{[A]_{\text{E0}}/[A]_{\text{r0}}} \right) \times 100\% \quad (7)$$

where  $[A]_{\text{Et}}$  = peak intensity of epoxy group in the normalized spectrum of the sample subjected to UV curing,  $[A]_{\text{rt}}$  = peak intensity of C=O group in the normalized spectrum of the sample subjected to UV curing,  $[A]_{\text{E0}}$  = peak intensity of epoxy group in the normalized spectrum of the sample prior to UV curing and  $[A]_{\text{r0}}$  = peak intensity of C=O group in the normalized spectrum of the sample prior to UV curing.

### 2.3. NMR characterizations

Tertiary amines blended with BPO were further dissolved in  $\text{CDCl}_3$  then characterized by INOVA 500 MHz nuclear magnetic resonance (NMR) spectrometer to reveal their  $^1\text{H}$  NMR spectra after they were cured by UV radiation.

### 2.4. Kinetics of thermal curing

Kinetics of thermal curing of resin samples were determined by using a differential scanning calorimeter (DSC, Perkin Elmer, Diamond) at a heating rate of  $100\text{ }^\circ\text{C}/\text{min}$ . The samples were underwent 10 min irradiation, which were hermetically sealed in aluminum pans and isothermally scanned at  $80\text{ }^\circ\text{C}$  for 1 h in an ambient purged with nitrogen at gas flow rate of  $20\text{ cc}/\text{min}$ . The extent of the reaction or, the thermal conversion, as a function of time was determined by integrating the isothermal curves by using the relationship [18,19]

$$\text{Thermal Conversion (\%)} = \frac{100}{\Delta H_{\text{T}}} \int_0^t \frac{dH}{dt} dt \quad (8)$$

where  $\Delta H_{\text{T}}$  is total enthalpy change calculated from the integral of  $dH/dt$  from  $t = 0$  to  $t = \infty$ .

### 2.5. Thermal properties

Thermal properties including coefficient of thermal expansion (CTE) and glass transition temperature ( $T_{\text{g}}$ ) of resin samples were measured by using a TA 2940 thermal mechanical analyzer (TMA). The UV-curable resin were underwent 10 min irradiation and  $80\text{ }^\circ\text{C}$  post-curing. A tension probe was adopted to detect the expansion of sample with  $1\text{ mm} \times 4\text{ mm} \times 25\text{ mm}$  in sizes during heating from room-temperature to around  $150\text{ }^\circ\text{C}$  at a heat-

ing rate of  $5\text{ }^\circ\text{C}/\text{min}$ . The value of CTE was calculated from the plot of dimension change *versus* temperature. The point where a significant change of slope was also identified from the plot and the onset temperature corresponding to such a change was termed as the  $T_{\text{g}}$  of the resin sample.

### 2.6. Adhesion strengths

Adhesion strengths of resin samples on various types of substrates, namely, glass, ITO, PET, and stainless steel were evaluated according to ASTM D897 standard by using a pull tester (HT-8116, Hung Ta Instrument Co.). The glass plates coated with 200-nm thickness of ITO overlayer which were supplied by Merck Display Tech. Co., and adopted as the ITO substrates. The PET substrates were formed by firmly gluing the PET films on glass plate. As to the adhesion test of resins on stainless steel, 2-mm thickness plates were adopted as the substrates. The samples for adhesion strength measurement were prepared by first coating appropriate amount of resin sample on various substrates. A glass block with  $10\text{ mm} \times 10\text{ mm} \times 8\text{ mm}$  in dimensions was then attached onto the substrate and delivered to the ovens for UV curing followed by a post-baking. The UV curing was carried out in the UV oven for 10 min and the post-baking was performed at  $80\text{ }^\circ\text{C}$  for 1 h. After the completion of curing, two steel bars were attached onto the two ends of the sample and then delivered to the pull tester operating at pull rate of  $5\text{ mm}/\text{min}$  for adhesion strength measurement as shown in Fig. 1. For each type of resin samples, the

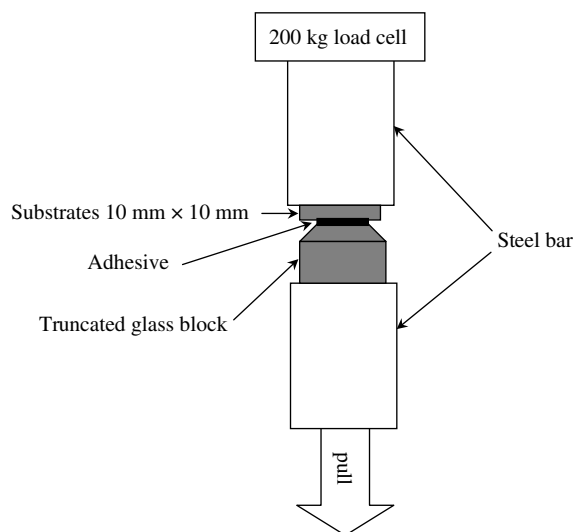


Fig. 1. The test scheme for adhesion strength measurement.

average value of pull strengths was taken from at least five samples and adopted as the adhesion strength of that sample. The fracture of adhesion sample also propagated along the resin matrix instead of occurring at the resin/substrate interface, in such case, the pull strength cannot represent the true adhesion strength of resin on a specific substrate. The mechanical strengths of resin samples, which were defined by the hardness of resin in this work, were thus measured in order to correlate with the results of adhesion test. The hardness of resins was measured by using a D scale Shore hardness meter (BAREISS, Germany) according to ISO R868 (ASTM D 2240) standard. The thickness of samples for hardness measurement was at least 6 mm.

### 3. Results and discussion

#### 3.1. Effect of tertiary amine on UV conversions

Varying times of UV irradiation and amount of 3-amine for different UV conversions in this study. Fig. 2 presents the UV conversions of resin samples containing various amounts of 3-amine, which were calculated based on the deviation of peak height at  $910\text{ cm}^{-1}$  of epoxy group FTIR by Eq. (7). During UV curing, the strong Brønsted acid ( $\text{HSbF}_6$ ), a derivative of photoinitiator, may induce cationic polymerization in epoxide resins to produce oxiranium ion. The cationic polymerization takes place by attacking the protonated epoxide on another epoxide resin. The peak height of absorption band at  $910$

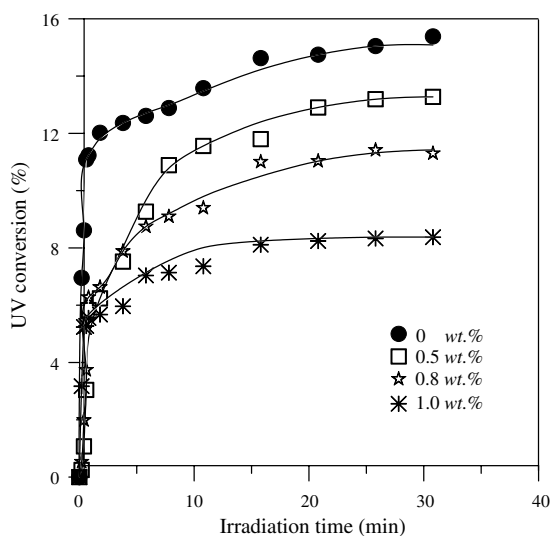


Fig. 2. UV conversion *versus* the irradiation time of resin samples containing various amounts of 3-amine.

$\text{cm}^{-1}$  corresponding the epoxy group hence changes with the UV irradiation time and amine amount. In Fig. 2 that the UV conversion decreases with the increasing of 3-amine content up to 1.0 wt.%. The resin sample could no longer be UV-cured when the amount of 3-amine exceeded 1.0 wt.% and similar results were observed in the resin samples containing the other four types of amines. The nitrogen atom of amines owning a lone pair of electrons may react with  $\text{HSbF}_6$  to produce ammonium salts [20] and consequently inhibit the photo-polymerization process of adhesive resins [21]. Therefore, the UV conversion decrease when tertiary amine content increase. The excess amount of imidazole or tertiary amines is hence not allowed in the UV-curable epoxide resins. There are same results of the other amines, such as 1-, 2-, 4 and 5-amine, in this study.

#### 3.2. The tertiary amine reacts with BPO under UV irradiation

Tertiary amines (1 wt.%) mixed with 2 wt.% BPO then underwent UV irradiation for 10 min. The result of reaction was described by FTIR spectroscopy for assessing. The 3-amine mixed with BPO which of the absorption intensity of  $\text{CH}_3\text{-N-}$  on 3-amine at the  $1232\text{ cm}^{-1}$  disappeared after UV irradiation as shown in Fig. 3. In addition, Fig. 4 is  $^1\text{H}$  NMRs of spectra of 3-amine mixed with

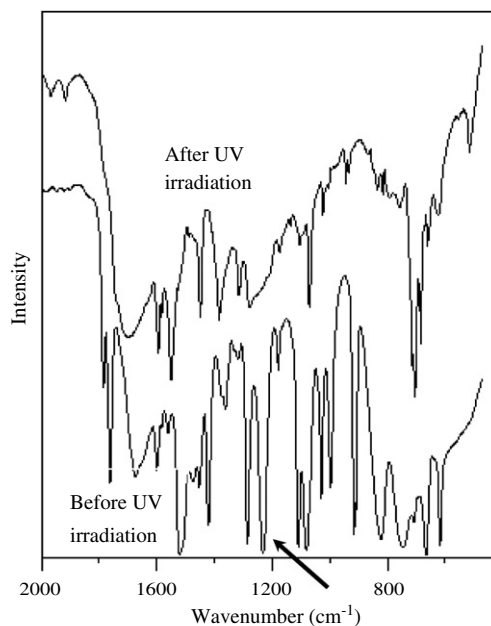


Fig. 3. 3-Amine mixed with BPO before and after UV irradiation.

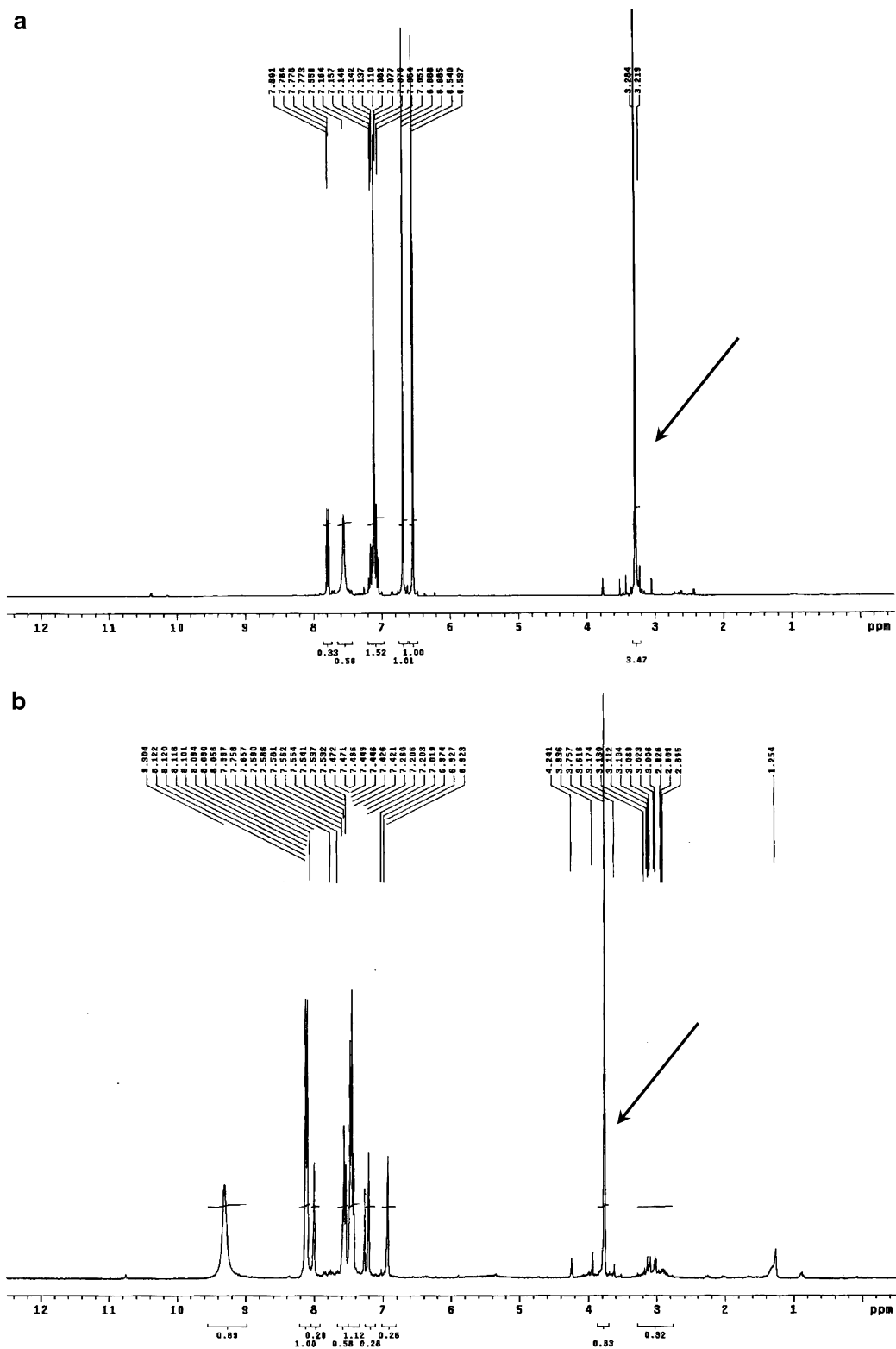
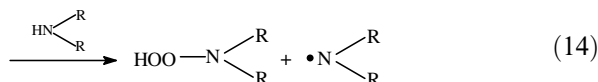
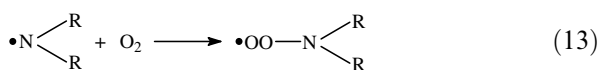
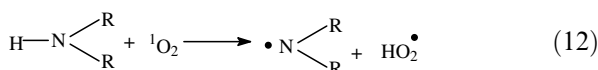
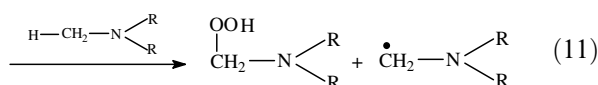
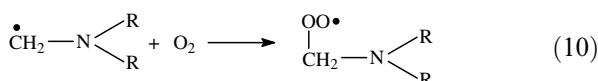
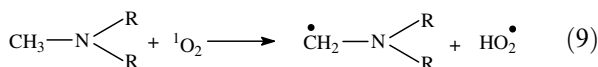


Fig. 4.  $^1\text{H}$  NMR spectra of 4-amine mixed with BPO: (a) before UV irradiation and (b) after irradiation.

BPO before UV irradiation and after irradiation. The  $\text{CH}_3\text{-N-}$  on 3-amine took place a chemical shift from  $\delta$  3.284 ppm of  $^1\text{H}$  NMR spectrum to  $\delta$  3.757 ppm after UV irradiation and there were same results as 2- and 4-amines were replaced by 3-amine. Due to singlet oxygen was produced by a triplet energy transfer from photosensitizer (*i.e.*, the free radical initiators such as BPO) to ground-state oxygen during UV irradiation [22]. The singlet oxygen may react with 2-, 3- and 4-amines *via* an electron transferring process to produce  $\alpha$ -aminoalkyl radicals in accordance with Eq. (9) [23] then react with oxygen to produce  $\alpha$ -hydroperoxyamine ( $\text{HOOCH}_2\text{NR}_2$ ) and  $\alpha$ -aminoalkyl radical *via* the reactions shown by Eqs. (10) and (11) [23,24].

As Fig. 5 presents, 1-amine reacted with BPO while the absorption intensity of  $\text{NH-}$  on 1-amine at the  $1136\text{ cm}^{-1}$  disappeared after UV irradiation and there was same result as 1-amine was replaced by 5-amine. The aminyl radicals of 1- and 5-amines, in reactions of singlet oxygen with 1- and 5-amines were shown in Eq. (12) which further reacted with oxygen to produce  $\text{HOONR}_2$  and aminyl radical *via* the reactions shown by Eqs. (13) and (14). The oxygen scavenging processes were depicted by Eqs. (9)–(14) are able to inhibit the oxidation in the backbone structure of resins [25]



### 3.3. Effect of amine in UV-curable resin on thermal conversions

Thermal conversion of the resin samples containing various types of amines which subjected to 10-min UV curing followed by post-curing at  $80\text{ }^\circ\text{C}$  for 1 h was studied by DSC isothermal scanning

method. As seen in Fig. 6, the blank resin has lowest thermal conversion and the resin sample containing 3-amine exhibits the fastest thermal conversion. Due to thermal polymerizations of all types of samples were resulted from the photolysis of photoinitiator that produced  $\text{HSbF}_6$  to attack epoxide resin and consequently induce the polymerization [26]. The cycloaliphatic epoxide resins are highly sensitive to acid-catalyzed cationic polymerization at

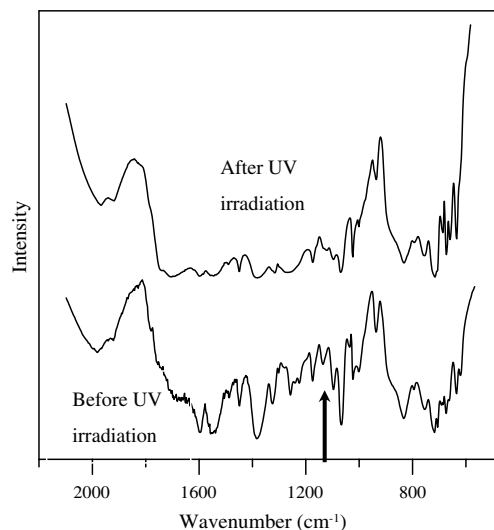


Fig. 5. 1-Amine mixed with BPO before and after UV irradiation.

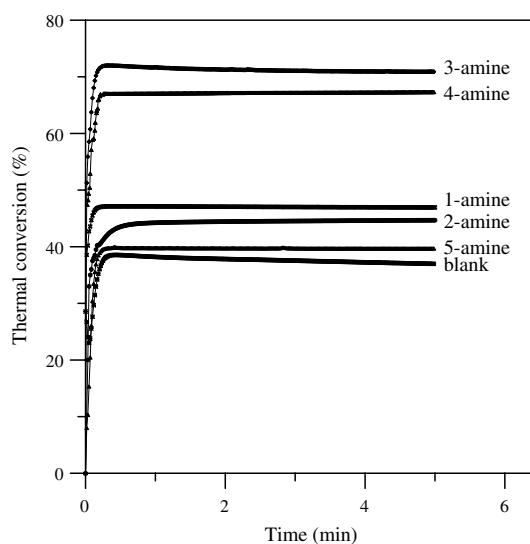
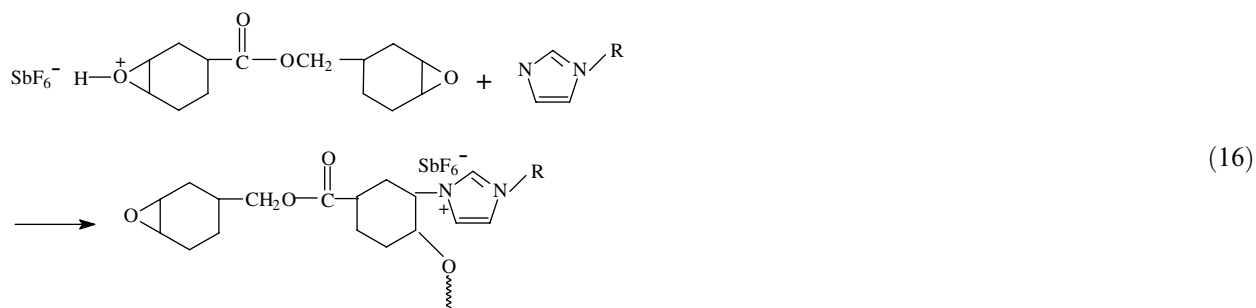
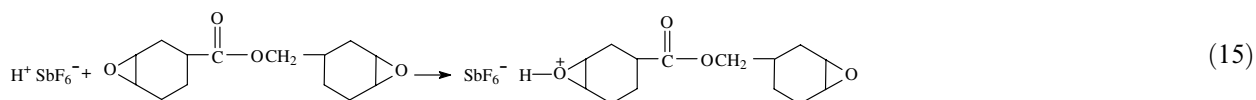


Fig. 6. Thermal conversion of resin samples containing various types of amines subjected to post-curing at  $80\text{ }^\circ\text{C}$ .

room-temperature. During the photo-polymerization process, the attack of  $\text{HSbF}_6$  produces oxiranium ions in accordance with the reaction depicted by Eq. (15). The oxiranium ions then react with the amines to induce cationic thermal polymerization according to the reaction shown in Eq. (16). It has been reported that triarylsulfonium salts is developed as the photoinitiator and cationic catalyst during cationic thermal polymerization [19,27]. Therefore, the thermal conversion of resin contained with amine is larger than that of blank resin.



The highest conversion resulted from the addition of 3-amine, which implicated such a tertiary amine is able to provide the fastest thermal polymerization in UV-curable epoxide resins, is attributed to the following: (1) the presence of phenol hydroxyl groups that may offer further reactive sites containing active-hydrogen of  $-\text{OH}$  to react with oxirane of resin [12,27] and (2) the nitrogen in 3-amine may react with oxirane. For instance, it is known that phenol-compounds such as poly(*p*-vinylphenol) and 2,3,6-tris(dimethylamino-methyl) may serve as the curing accelerators of epoxy resins due to its faster thermal polymerization and better crosslinking capability in comparison with imidazole amine [28]. The ring-opening rate of epoxides containing amine-type curing agents could thus be enhanced by the presence of phenol-compounds [29] so that high thermal conversion was observed in the resin sample containing 3-amine [30].

Imidazole exhibits distinct curing behaviors when the substituents at 1- and 2-positions are different [15]. The thermal reactivity of methyl substituent ( $\text{CH}_3-$ ) at the 1-position of 2- and 4-amines are faster than that of pyrrole-type nitrogen substituent

( $\text{NH}-$ ) at 1-position of 1- and 5-amines since the methyl substituent tends to push electrons towards the active nitrogen [15]. It is easier for methyl substituent to release electrons in comparison with hydrogen substituent ( $\text{H}-$ ). This implies a richer electrons and better reactivity of 3-position nitrogen on 4-amine in comparison with 3-position nitrogen on 1-amine. Therefore, thermal conversion of resin containing 4-amine is faster than that of resin containing 1-amine. There is no effective steric hindrance for 1- and 4-amines due to the existence of

hydrogen substituent at the 2-position; on the contrary, methyl substituent at the 2-position provides effective steric hindrance for 2- and 5-amines and hence promotes the thermal polymerization. Thermal polymerization of 1-amine is faster than that of 2-amine since there is pyrrole-type nitrogen on 1-position and no steric hindrance at 2-position. The 5-amine exhibits the slowest thermal polymerization owing to the pyrrole-type nitrogen substituent at 1-position and methyl substituent at 2-position. The thermal polymerization of resin samples rated according to the amine type is hence in the order of: 3-amine > 4-amine > 1-amine > 2-amine > 5-amine.

The values of  $T_g$  and CTE of the resin samples containing 1.0 wt.% of various types of amines obtained by TMA are presented in Table 1. The sample containing 3-amine possesses the highest  $T_g$  (72.3 °C) and lowest CTE (70.8 ppm/°C). This is attributed to the highest crosslinking density resulted from the fastest thermal polymerization among the amines under study. The blank resin possesses the lowest  $T_g$  (67.3 °C) and largest CTE (157.9 ppm/°C). Therefore, the UV-curable resin



Table 1  
CTE and  $T_g$  of resin samples containing various types of amines

Amine type	$T_g$ (°C)	CTE (ppm/°C)
Blank	67.3	157.9
1-Amine	70.6	109.8
2-Amine	68.8	124.9
3-Amine	72.3	70.8
4-Amine	71.3	85.8
5-Amine	68.1	139.7

contained with tertiary amine which will improve the thermal property of UV-curable resin.

### 3.4. Effect of tertiary amines on adhesion strengths

The individual of resin samples contained one of various amines with 1.0 wt.% and all of the samples were subjected to 10-min UV curing and followed with post-curing at 80 °C for 1 h, respectively, which were studied for adhesion strength of resin to different substance. First, Fig. 7a compares the adhesion strengths of resin-on-glass by individual sample containing 3-amine and 5-amine which were UV-cured in air ambient or airtight environment. The airtight environment was accomplished by wrapping the samples tightly with Scotch tape. It can be seen that, regardless of resin types, the adhesion strengths of samples cured in air ambient are much higher than those cured in airtight environment. Hence sufficient oxygen supply is required in order to complete the UV curing of epoxide resins containing tertiary amines.

Fig. 7b and c present the adhesion strengths of resin-on-glass and resin-on-ITO samples, respectively. The adhesion strength of resin-on-glass, rated by amine type, is in the order of: 3-amine (199 kg/cm<sup>2</sup>) > 4-amine (181 kg/cm<sup>2</sup>) > 1-amine (136 kg/cm<sup>2</sup>) > 2-amine (124 kg/cm<sup>2</sup>) > 5-amine (170 kg/cm<sup>2</sup>) > blank resin (151 kg/cm<sup>2</sup>) and the adhesion strength of resin-on-ITO is in the order of similarly: 3-amine (182 kg/cm<sup>2</sup>) > 4-amine (162 kg/cm<sup>2</sup>) > 1-amine (130 kg/cm<sup>2</sup>) > 2-amine (106 kg/cm<sup>2</sup>) > 5-amine (147 kg/cm<sup>2</sup>) > blank resin (136 kg/cm<sup>2</sup>). We however note that the adhesion strength data presented in Figs. 7b and c do not represent the true adhesion strengths on these substrates for the samples containing 1-, 2-, 3-, and 4-amines since subsequent examination of fracture morphologies revealed that the failures of these four types of specimens occurred in the resins matrix rather than at the resin/substrate interfaces [31]. Hence the adhesion strengths of resin samples containing 1-, 2-, 3-,

and 4-amines on glass and ITO substrates must be higher than those presented in Figs. 7b and c. For these four types of specimens, the adhesion strengths presented in Figs. 7b and c in fact correlated with the mechanical strengths of resin bulks. In this work, the hardness of resin samples was measured in order to reveal such a correlation.

Fig. 7d shows that the Shore D hardness of the samples containing 1-, 2-, 3-, and 4-amines. It reveals that the values of hardness are arranged in the same order of adhesion strengths presented in Figs. 7b and c as well as the thermal conversion (*i.e.*, 3-amine > 4-amine > 1-amine > 2-amine) presented in previous section. Such results not only evidence the correlation between adhesion strengths and mechanical strengths of the resins containing 1-, 2-, 3-, and 4-amines, it also demonstrates that crosslinking density of resin affects its bulk fracture strength. Apparently, fast thermal conversion not only implies high crosslinking density, it also provides high adhesion strength so that the resin containing 3-amine exhibits the highest adhesion strengths in comparison with other types of resin samples prepared in this study.

The fractures of resin free of amine and resin containing 5-amine occurred at the resin/substrate interfaces. The resin contained 5-amine reacted with fewer oxygen in air ambient due to its relatively slow thermal conversion rate in comparison with the resins containing other four types of amines (see Fig. 6). The resin sample free of amine exhibited the lowest adhesion strength since neither oxygen reaction nor thermal cationic polymerization occurred in it.

The adhesion strengths of resin samples on PET and stainless steel are presented in Figs. 7e and f, respectively. The purpose of adhesion test related to PET was to evaluate the applicability of our resin samples on advanced flat panel displays (FDPs) such as flexible organic light-emitting devices (FOL-EDs). As to stainless steel, recently poly-Si TFT on stainless steel foil has been demonstrated [32,33] owing to the advantages of steel such as high mechanical strength, durability, flexibility, and thermal stability [34]. Fabrication of OLEDs on stainless steel substrate containing TFT is hence plausible and thus we evaluate the adhesion strengths of encapsulation resins on stainless steel. In these two types of samples, all the fractures propagated along the resin/substrate interfaces and the adhesion strengths for resin-on-PET and resin-on-stainless steel samples, if rated according to the

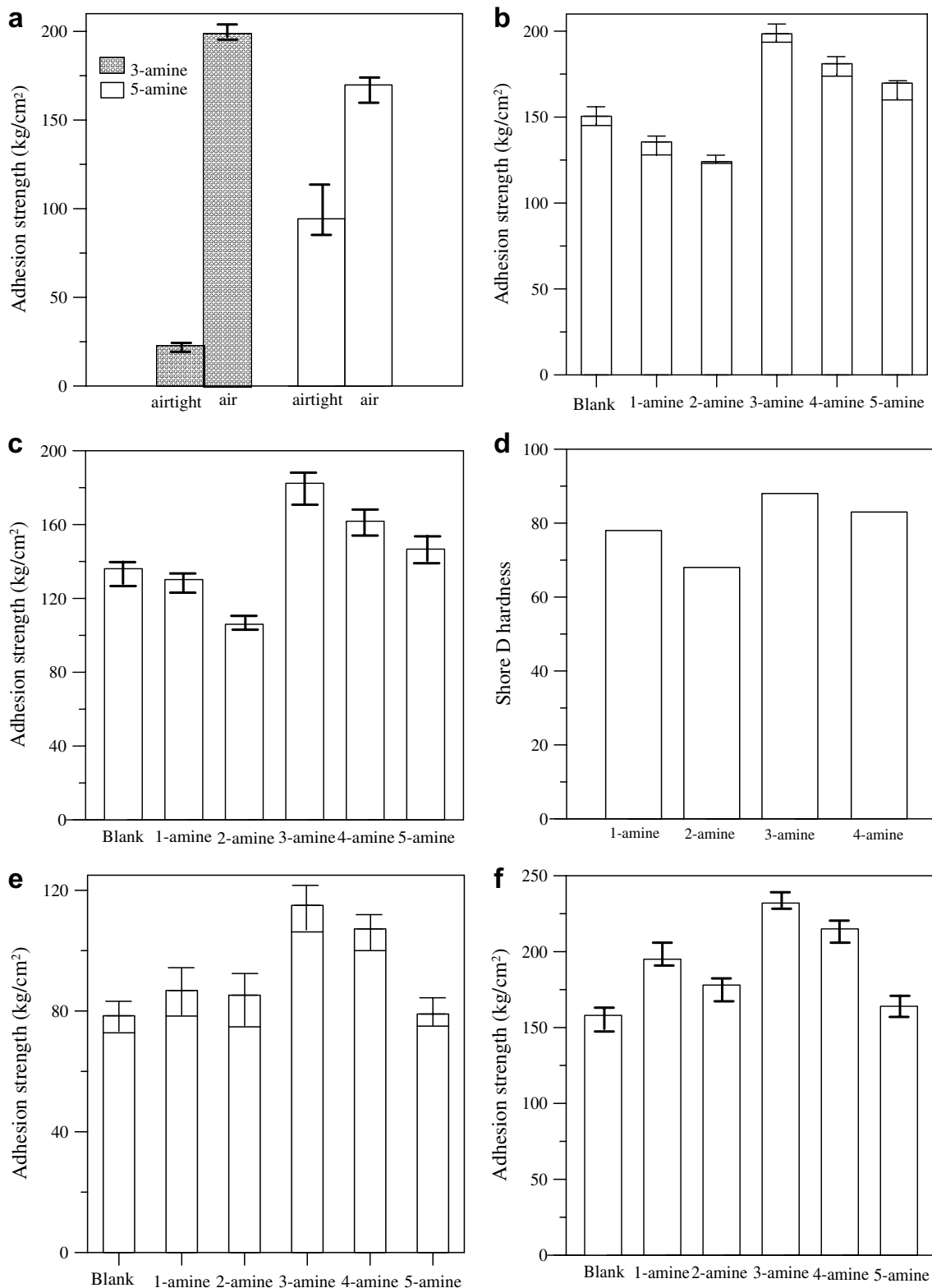


Fig. 7. (a) Adhesion strengths of resins containing 3-amine and 5-amines cured in air ambient and airtight environment. Adhesion strengths of resins contained various types of amines on (b) glass and (c) ITO substrates; (d) shore D hardness of resins contained 1- to 4-amines. Adhesion strengths of resins contained various types of amines on (e) PET and (f) stainless steel substrates.

amine type, were in the order of: 3-amine (115/232 kg/cm<sup>2</sup>) > 4-amine (107/215 kg/cm<sup>2</sup>) > 1-amine (87/195 kg/cm<sup>2</sup>) > 2-amine (85/178 kg/cm<sup>2</sup>) > 5-amine (79/164 kg/cm<sup>2</sup>) > blank resin (78/158 kg/cm<sup>2</sup>). Previous analyses revealed the addition of 3-amine provides satisfactory curing behaviors and thermal properties for the UV-curable epoxide resins. In conjunction with the good adhesion properties reported in this section, it is speculated that the resin containing 3-amine would possess great potentials for the packaging applications of opto-electronic products.

#### 4. Conclusions

This work demonstrates that the addition of imidazole and tertiary amines may accelerate the UV and thermal conversions of dicycloaliphatic epoxide resins. Addition of amines may also effectively improve the thermal and adhesion properties of the UV-curable resins. Among the five amine types under studying, the 3-amine, 2,4,6-tris(dimethylamino-methyl)phenol, was found to be the best that the highest  $T_g$  (72.3 °C) and lowest CTE (70.8 ppm/°C) were achieved in the resin samples. Improvement on thermal properties was attributed to the highest crosslinking density resulted from the fastest thermal polymerization in comparison with other types of amines.

The fastest thermal conversion and highest crosslinking density occurring in the resin containing 3-amine also implied satisfactory adhesion properties on various types of substrates. It was found that the average adhesion strengths of such a resin sample on glass, ITO, PET and stainless steel substrates are: 199 (greater than), 182 (greater than), 115, and 232 kg/cm<sup>2</sup>, respectively. However, the data for glass and ITO could not represent the true adhesion strengths of resin on these substrates samples since subsequent examination of fracture morphologies revealed that the failures are in fact propagate in the resin matrix rather than at the resin/substrate interfaces. Higher adhesion strengths on glass and ITO substrates are hence expected for the resin containing 3-amine prepared in this work.

Adhesion sample preparation found that sufficient supply of oxygen is required for the complete UV curing of epoxide resins containing tertiary amines. Further, the amount of amine addition was limited to 1.0 wt.% since excessive content resulted incomplete curing of resin samples. This was due to the fact that the lone pair of electrons

owned by nitrogen atom on tertiary amines might react with HSBF<sub>6</sub>, a derivative of photoinitiator, to produce ammonium salts that, in turn, inhibit the UV curing of resins.

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