

A study of monomer's effect on adhesion strength of UV-curable resins

Tzu Hsuan Chiang^{a,*}, T.-E. Hsieh

^aDepartment of Materials Science and Engineering, National Chiao Tung University, 1001 Ta Hsueh Road, Hsinchu, 30050 Taiwan, ROC

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Abstract

This work studies the effects of the monomer types, the number of hydroxyl functional groups (–OH) on polyol monomers, and the equivalent weight ratio of dicycloaliphatic epoxide to polyol for cationic polymerization (the *R* value) on the adhesion strength of UV-curable epoxy resins applied to organic light-emitting device (OLED) packaging. It was found that the volume shrinkage of resins after UV curing is related to the crosslinking density of the resin. The smallest volume shrinkage implied the highest adhesion strength of resin on glass substrate since the internal stress was minimized. This study observed that the resin containing polyol monomer is able to achieve the smallest degree of shrinkage (1.72%) and the highest adhesion strength (153.35 kg/cm²) on glass substrate.

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Keyword: UV-curable epoxy resin; Monomer; Adhesion strength; Volume shrinkage

1. Introduction

UV-curable adhesive resin is an essential component for the packaging of present organic light-emitting devices (OLEDs) since the organic light-emitting materials have to be isolated from ambient moisture/oxygen. The UV-curable resins can be classified into free-radical curable and cationic curable. In OLED packaging applications, most of adhesive resins undergo cationic polymerization since they possess excellent adhesion strength, oxygen inhibition, and moisture resistance [1].

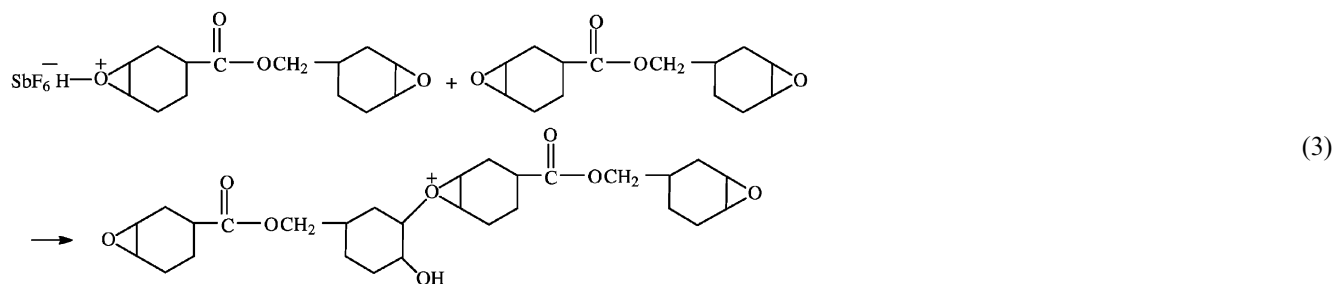
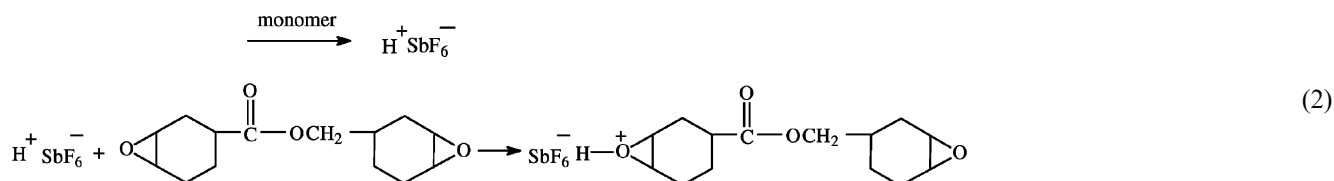
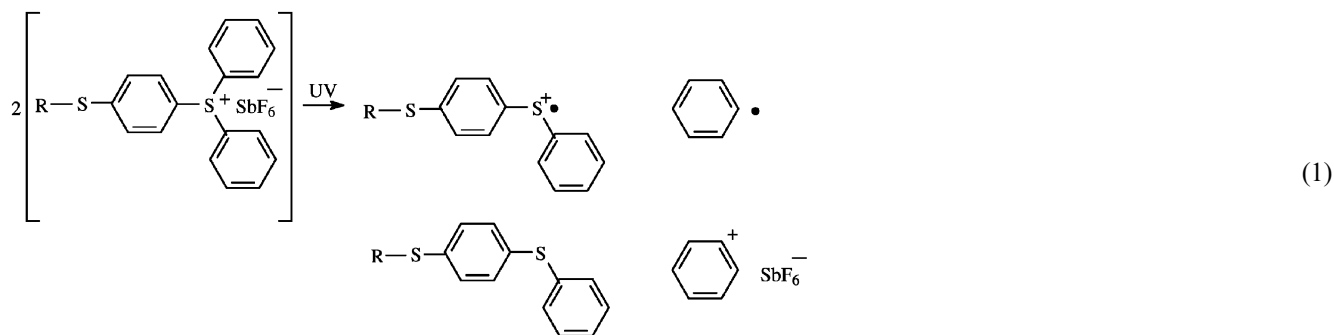
The effects of the monomers on the curing behavior of resins have been thoroughly investigated, mainly on the radical-induced photo-polymerization of acrylates [2–6], maleates [7], and maleimides [8,9], and also on the cationic polymerization of vinyl ethers [10,11] and polyol [12,13]. In addition, acrylate monomers, which may react via free-radical polymerization, are added in some epoxy resins to undergo cationic and free-radical polymerizations simultaneously [14]. The mechanisms of polymerization of polyol, vinyl ether, and acrylate monomers with cationic photoinitiator are briefly described as follows.

1.1. Reaction mechanisms of photoinitiator and epoxide resin

Both homolytic and heterolytic cleavage mechanisms are involved in the photolysis of the triarylsulfonium salts photoinitiator. As shown in Eq. (1), the photoinitiator results in the generation of a number of reactive species including aryl radicals, aryl cationic radicals, aryl cations, and the super acid HSbF₆ [15,16]. There are two processes for the initiation of photoinitiated cationic polymerization as depicted in Eqs. (1) and (2). The HSbF₆ is a strong Brønsted acid protonation which may induce the cationic polymerization of epoxide resin to produce oxiranium ion as present in Eq. (2). The cationic polymerization can take place by the attack of protonated epoxide on another epoxide resin, as shown in Eq. (3).

*Corresponding author.

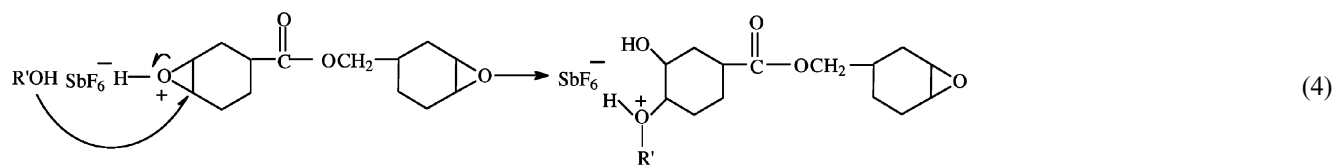
E-mail address: cjjiang@ms.chinmin.edu.tw (T.H. Chiang).



1.2. Mechanism of cationic polymerization for polyol monomer

Dicycloaliphatic epoxide and photoinitiator are added into the polyol adhesive resin system. The polymerization mechanisms are the same as depicted in Eqs. (1)–(3).

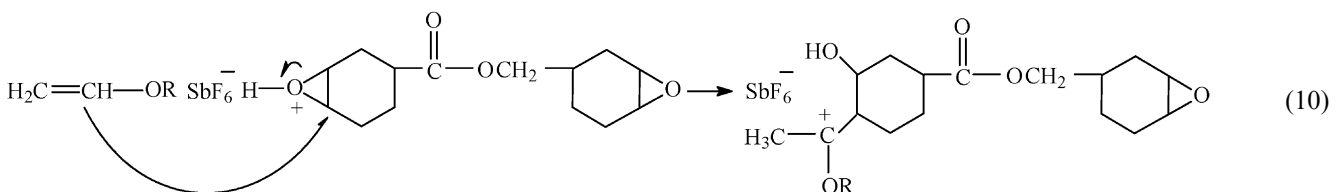
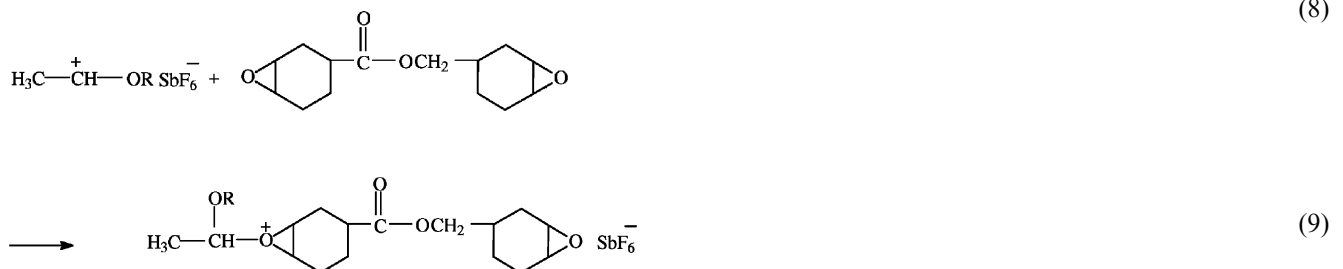
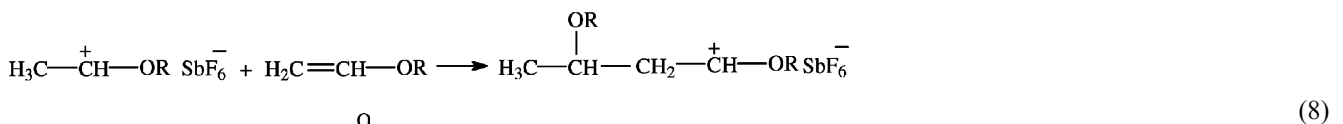
The growing oxiranium ion chain, the product of Eq. (2), undergoes nucleophilic attack by the polyol to generate protonated ether as shown in Eq. (4). Penczek et al. [17] has demonstrated that in the presence of polyols, the activated monomer mechanism, attack of the hydroxyl at the propagating oxonium ion chain end, takes place more rapidly than the usual ring opening mechanism. According to this mechanism, the hydroxyl group (–OH) of the polyol intercepts the oxonium ion terminus of the growing polyether chain. Deprotonation of hydroxyl groups of the polyol caused by the epoxide monomer, the products of Eq. (4) [18], results in the termination of the growing polymer chain and transfer to the monomer that thereafter can start new chains shown in Eq. (5). Repetition of this process generates a hydroxyl end group that continues the termination and transfer processes. This mechanism is expected to occur to some extent during cationic epoxide ring-opening polymerizations initiated by Brønsted acids because terminal hydroxyl groups are always formed as end groups shown in Eq. (6). Therefore, the presence of polyols has considerable effect on the cationic ring-opening polymerization of epoxides [19].





1.3. Mechanism of cationic polymerization for vinyl ether monomer

Vinyl ether monomers possess a much more pronounced tendency toward cationic polymerization and do not undergo free-radical polymerization because they contain electron-rich centers such as the highly nucleophilic nature of the double bond caused by onium ions, and alkoxy group [20,21]. Vinyl ether monomers, which are characterized by a combination of π -donor ($C=C$) and n -donor ($R-O(R)_2$, onium ions), contain two nucleophilic sites [22]. Dicycloaliphatic epoxide and photoinitiator were added into the vinyl ether adhesive resin system and the polymerization mechanisms are the same as shown in Eqs. (1)–(3). From Eq. (7), the formation of active species for the initiation of cationic polymerization takes place by the attack of nucleophilic on a vinyl ether group to generate the alkoxy-carbenium ion. In Eqs. (2) and (7), only the attack by protons is shown because they are the most prominent species involved in the initiation. The rates of both reactions are expected to be high. The carbocation, formed by the initial protonation of the vinyl ether groups, can induce polymerization of either other vinyl ether or an epoxide group as shown in Eqs. (8) and (9) [23,24]. Cationic polymerization of the protonated epoxide of Eq. (9) and oxiranium ion can take place by the nucleophilic attack of vinyl ether group as shown in Eq. (10). It results in the termination of the growing polymer chain and transfers to the monomer that thereafter can start new chains shown in Eq. (11). The two possible reactions, the propagating oxiranium ions are converted into alkoxy-carbenium ions and vice versa, are shown in Eqs. (9) and (10). Similar crossover reactions can be written for any reactive chain end generated during the course of the polymerization and the positions of these equilibration are dependent on the relative stabilities of the two types of reactive species and the corresponding reactivities of the two monomers. Repetition of this process regenerates an ether end group that continues the termination and transfer processes. This mechanism is expected to occur to some extent during the cationic epoxide ring-opening polymerizations initiated by Brønsted acids because terminal alkoxy groups always form as the end groups as shown in Eq. (12). Cationic polymerizations of vinyl ether adhesive resin system are shown in Eqs. (3) and (10) either does not occur or takes place very slowly due to the relatively high stability of the oxiranium ion compared to that of carbocation.





1.4. Mechanism of polymerization for acrylate monomer

Fast polymerization reactions are particularly easy to obtain with acrylates containing electron-deficient double bonds. Acrylate is often with the structure of $\text{H}_2\text{C}=\text{CHCOOR}$ in which R is an arbitrary group that does not significantly affect the mechanism of the polymerization. The phenyl free radicals produced by the photolysis of the cationic photoinitiator has sufficient energy to initiate the free-radical polymerization [25]. During cationic polymerization, photoinitiator and dicycloaliphatic epoxide may also react with acrylate monomer to undergo the free-radical polymerizations. The mechanisms are depicted in Eqs. (1)–(3) and Eqs. (13)–(15). The free-radical polymerization can be divided into three classes: the photochemical event which leads to the first monomer radical, the classical propagation, and the termination process of the reaction as shown in Eqs. (13)–(15) [26]. Phenyl radical (see Eq. (1)) can react with acrylate monomer to induce grafting, which is a homopolymerization reaction as shown in Eq. (13). The addition of acrylate monomer to a macroradical results in a larger macroradical, as shown in Eq. (14). Termination occurs when the macroradicals are recombined as shown in Eq. (15).

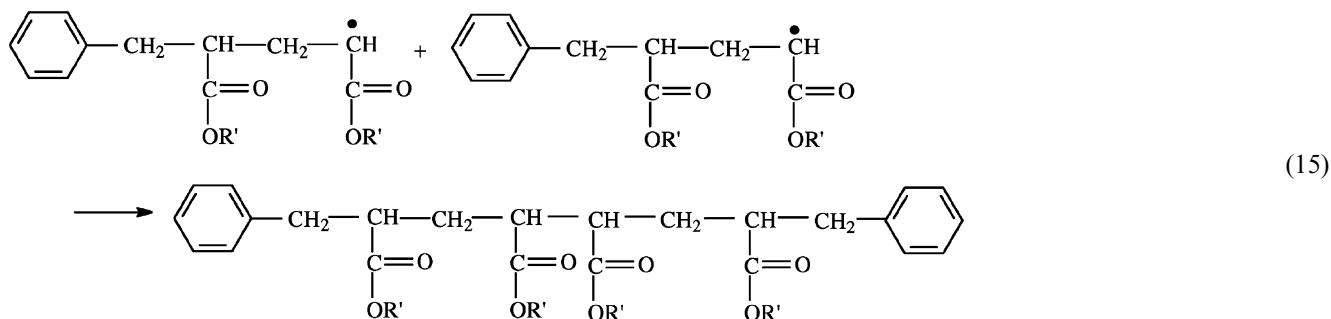
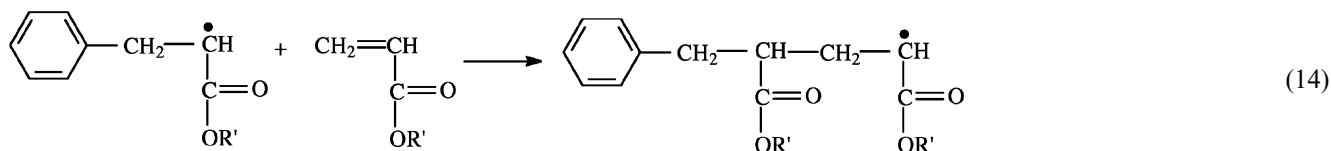
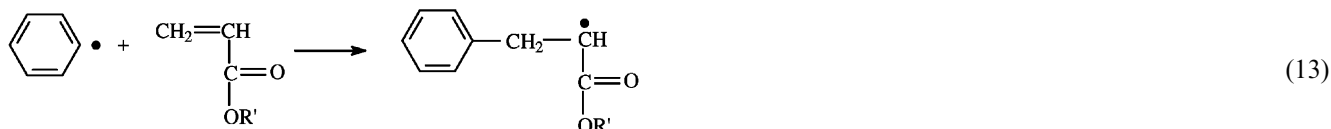


Photo-induced cationic polymerization has been applied to ring-opening polymerization of epoxy systems and other strained ring systems. This experiment focuses on the cycloaliphatic epoxides because they undergo photo-initiated cationic

polymerization at the highest rates among all known epoxy resins. The polymerization mechanisms described above affect the adhesion strength of photo-curable epoxy resins. This work studies the adhesion strength on glass substrate for the photo-induced epoxies containing various monomers, including polyol, vinyl ether, and acrylate monomers. In addition, the reactivity of the hydroxyl groups (–OH) along with the polymer chain and its effects on adhesion strength are also evaluated.

2. Experimental

2.1. Materials

The oligomer, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, the silane coupling agent, vinyltrimethoxysilane, the photoinitiator, triaryl sulfonium hexafluoroantimonate salts, and the monomers listed in Table 1, were all provided by Aldrich. thermal initiator, Benzol peroxide (BPO), was inquired from Fluka. glass substrates were purchased from Liehcher Co. Ltd (Taiwan). Mode of UV oven is CL-1000 M by UVP Co. Ltd. (USA).

The adhesive resin was prepared by mixing dicycloaliphatic epoxide and monomer at the ratio of 4:1 by weight and 3 wt.% of silane together then stirring for 1.5 h. 1.5 g of photoinitiator and 0.2 g of BPO were then added into the mix and stirred for 1.5 h. The glass substrates were cleaned and glued together by the various resin samples for adhesion test. The samples were cured in UV oven with wavelength ranging from 314 to 340 nm and the power of 40 W for various times, thereafter proceed a post cured at 80 °C for 1 h to complete the hardening process.

2.2. Adhesion test

For adhesion test, the glass blocks were first ground into a truncated form with the size illustrated in Fig. 1(a). The adhesive was applied onto the 7 mm × 7 mm surface area and glued onto another glass plate at the size of 10 mm × 10 mm × 3 mm. Two steel bars were then attached onto the two ends of the sample and sent to a pull tester (Model-HT-8116, Hung Ta Instrument Co. Ltd., Taiwan) for adhesion strength measurement at the pulling rate of 5 mm/min. Adhesion strengths of adhesive resins were measured by a test scheme corresponding to the ASTM D897 standard [27] shown in Fig. 1(b).

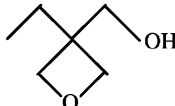
2.3. Measurement of shrinkage

The adhesives samples were glued onto glass substrates at the size of 10 mm × 10 mm × 3 mm for UV curing for 25 min. The volume shrinkage of sample was determined by measuring the density change of each resin sample before and after UV curing. The shrinkage of samples was calculated according to the following equation [13]:

$$\text{Shrinkage (\%)} = \frac{1/d_{\text{after}} - 1/d_{\text{before}}}{1/d_{\text{before}}} \times 100\%,$$

where d_{before} is the density of sample before curing, and d_{after} the density of a resin after curing. The densities of the cured samples were determined by the displacement method by using a Mettler AX105DR density determination kit. The weights of the adhesives samples were assumed to be constant at the temperature range of 25 °C. Surface morphologies of adhesives were observed by an optical microscope (model U-LH100-3, Olympus).

Table 1
The types and structures of monomers used in this work

Monomer	Type	Structures
3-ethyl-3-oxetanemethanol (EOM)	polyol	
Tri(propylene glycol) (TPPG)	polyol	H(OC ₃ H ₆) ₃ OH
Polycaprolactone triol (PCAT)	polyol	C ₂ H ₅ C[CH ₂ O[CO(CH ₂) ₅ O _n]H] ₃
Bis(4-vinylxy)butyl)isophthalate (BVBP)	vinyl ether	[CO ₂ (CH ₂) ₄ OCH = CH ₂] ₂
1,6-Hexanedol diacrylate (HDDA)	acrylate	CH ₂ = CHCOO(CH ₂) ₆ OOCH = CHCH ₂

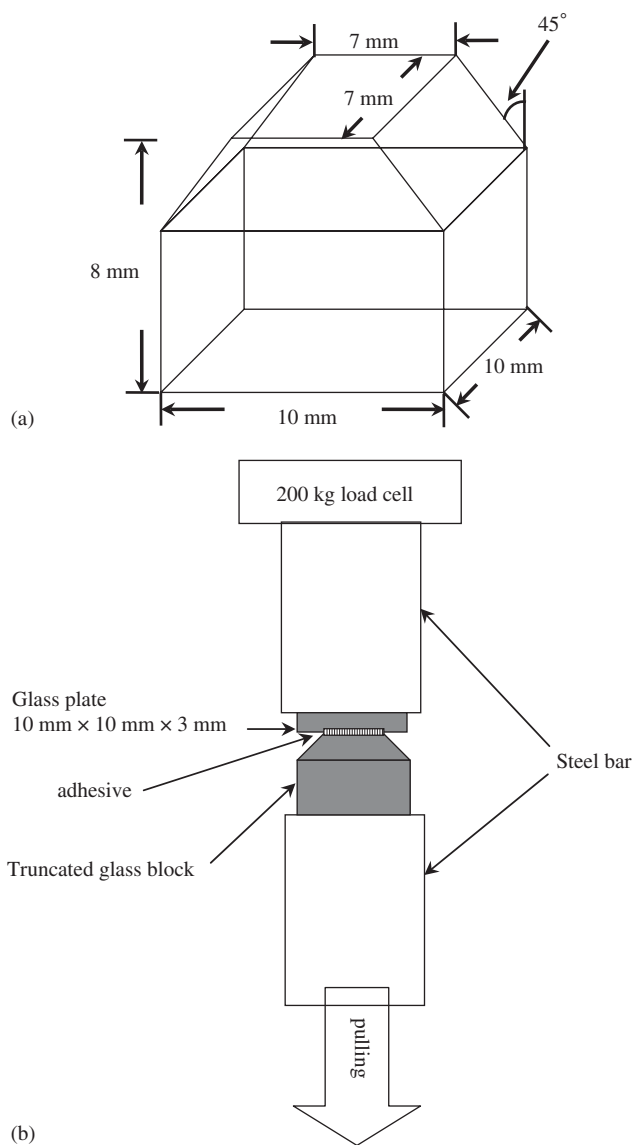


Fig. 1. (a) Form and size of the truncated glass substrate and (b) test scheme of adhesion strength.

2.4. FTIR characterizations

The FTIR samples were prepared by coating the adhesive resins on KBr discs and cured in the UV oven for various time spans. The samples were then transferred to a FTIR (Nicolet Protégé 460 Fourier-transform infrared spectrometer) for structure analysis. The conversion of the samples was determined from absorbance at 910 cm^{-1} from FTIR spectra. Since slight difference in thickness existed among all the samples and the thickness of samples might change during UV curing, an internal standard band method was hence chosen in order to compensate the change in sample thickness. The absorption band at 1728 cm^{-1} for C = O of dicycloaliphatic epoxide was adopted as an internal standard band for calculation. The conversion of samples was calculated according to the following equation:

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

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

3. Results and discussion

3.1. Kinetics of photo-polymerization of monomers

Kinetics of the photo-polymerizations was studied by FTIR spectroscopy to assess the polymer formation. Since the absorption intensity of epoxy group on dicycloaliphatic epoxide at the position of 910 cm^{-1} was decreased during cationic polymerization, the conversion of polymerization was hence calculated according to the intensity change of epoxy group and the result was presented in Fig. 2. Furthermore, the slopes of the linear portions of the plots shown in Fig. 2 are directly proportional to the rates of polymerization (slope = $R_p/[M_o]$) [24,28]. It was found that the rates of polymerization are 0.09 , 0.34 and 0.14 s^{-1} for HDDA, BVBP and TPPG adhesives, respectively. Therefore, the cationic polymerization reaction rates are in the order of: $\text{HDDA} < \text{TPPG} < \text{BVBP}$. The BVBP adhesive possesses the highest reaction rate since its mechanisms of cationic polymerization include the reactions depicted by Eqs. (1)–(3) and (7)–(12). Eqs. (1)–(3) and (4)–(6), describe the mechanisms for TPPG adhesive and hence it exhibits a slower reaction rate in comparison with that of BVBP adhesive. As to HDDA adhesive, it has the slowest reaction rate since only dicycloaliphatic epoxide executes the cationic polymerization and the polymerization of HDDA monomer with photoinitiator is via free-radical polymerization.

On the other hand, the absorption band at $802\text{--}817\text{ cm}^{-1}$ characterizes the $\text{CH}=\text{CH}$ - twisting motion of the acrylate group of HDDA which demonstrates the reaction rate of free-radical polymerization. The conversion rates of acrylate and epoxy groups of HDDA adhesive in Fig. 3 that reveal the rates of polymerization of these two functional groups are 0.39 and 0.09 s^{-1} , respectively. According to the result, the rate of free-radical polymerization is faster than the rate of cationic polymerization which is similar to the study of Decker et al. [29]. Due to UV irradiation, the acrylate monomer was polymerized via free-radical mechanism, while the dicycloaliphatic epoxide was polymerized via cationic mechanism. The acrylate mixed with cationic photoinitiator and epoxy resin thus generated an interpenetrating network [6]. It has been reported that the rate via free-radical polymerization of acrylate is faster than the cationic polymerization of the epoxy resins and other monomers [14], we hence observed the shortest curing time for the resin containing acrylate monomer. Both of the resins containing vinyl ether and polyol monomers were cured via cationic mechanism. However, unlike polyol monomer, vinyl ether monomer also reacts with photoinitiator and this makes the reaction rate of vinyl ether faster than that of polyol but slower than the rate of acrylate.

3.2. Effect of UV curing time on shrinkage of monomers

Polymerization leads to an increase in density of the material. If the polymerization were coupled with other chemical reactions, the increasing of density may be compensated or at least reduced [30]. Shrinkage, or volume reduction, of the resins, which occurs during the curing process may affect its adhesion strength because high shrinkage might induce a considerable amount of internal stress that pulls the adhesive resin away from substrate [31,32]. Fig. 4 shows the shrinkage

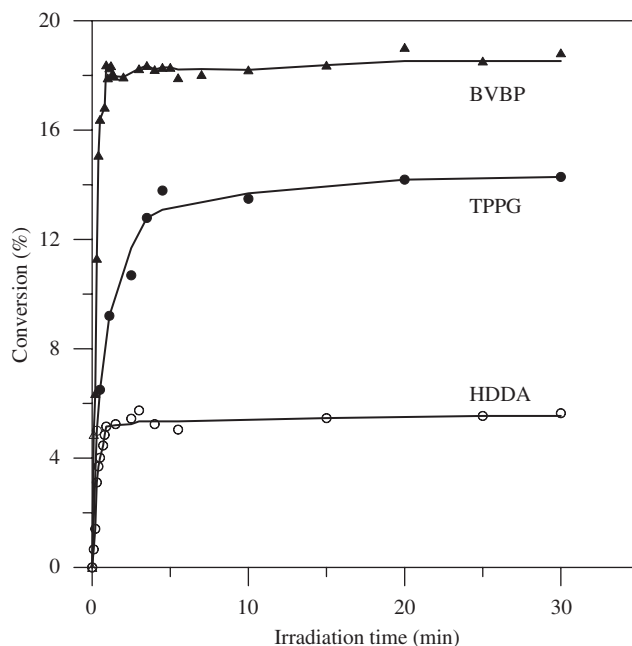


Fig. 2. Conversion versus the time of UV irradiation for various monomers.

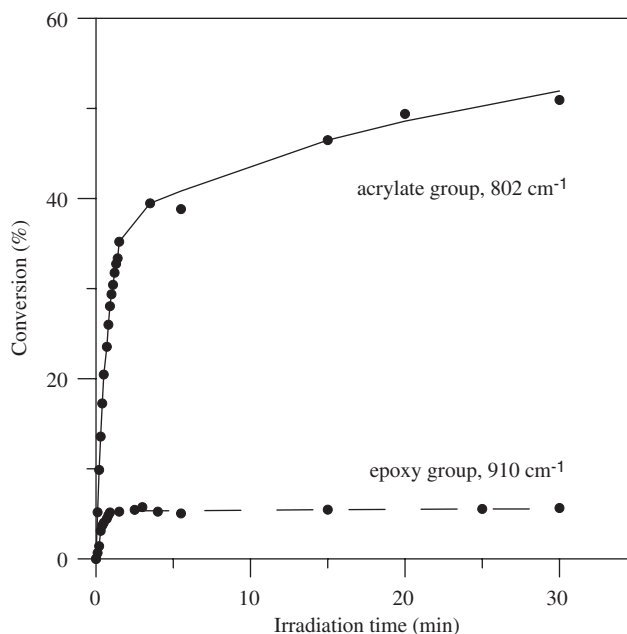


Fig. 3. Conversion rate versus UV irradiation time for acrylate and epoxy groups in HDDA.

of various resin systems cured at different UV irradiation time. The slope of each plot corresponds to the photopolymerization reaction rate of resin containing a particular type of monomer. A sharper slope means slower reaction rate and vice versa. The slope for resin containing HDDA turned to be flat after curing for 25 min, which means reaction has almost finished. For the resins containing BVBP and TPPG, the reactions terminated at 35 and 40 min, respectively. Fig. 4 shows that the curing times for the resins containing HDDA and BVBP are shorter than that containing TPPG. The experimental results above also demonstrate a feasible way to measure the degree of curing of resins affected by the type of monomer.

Figs. 5(a–c) show the morphology of epoxide resin containing various types of monomers after UV curing. The degree of shrinkage can be readily seen from the morphology change of sample surfaces. From Figs. 4 and 5, it was found that shorter curing time implies larger shrinkage and vice versa. As shown in Fig. 5(a), the resin containing TPPG exhibits the smoothest surface with the smallest degree of shrinkage and the longest curing time. The degree of shrinkage is in the order of: TPPG < BVBP < HDDA.

The type of monomer implies different reaction mechanism during UV curing. The epoxy resin hence exhibited different adhesion property when it was cured at different conditions. In the aspect of curing time, fast curing induces high internal stresses. This would result high shrinkage and poor adhesion strength. As shown in Fig. 6, adhesion strength of TPPG, BVBP and HDDA resin systems is 153.4, 28.1 and 20.1 kg/cm², respectively. Adhesion strength of the resins, if designated according to the monomer type, is thus TPPG > BVBP > HDDA. The resin containing the TPPG monomer, which exhibits the minimum shrinkage, also possesses the highest adhesion strength. Such a result was also reported by the study of Tilbrook et al. [13]. Furthermore, cationic polymerization of TPPG and BVBP generates the hydroxyl groups, but there is no hydroxyl group generated after the free-radical polymerization of HDDA. The hydroxyl groups are able to form hydrogen bonds on the glass substrate and hence the cationic polymerization provides better resin adhesion property in comparison with the free-radical polymerization.

During the experiment, we also observed the self-curing behavior of resin containing acrylate monomer. Such a phenomenon indicated that free radicals were formed by photolysis of cationic photoinitiator in the resin containing acrylate monomer.

3.3. Effect of *R* Value

This work also studied the effects of *R* value on the adhesion strength of epoxide resin containing polyol monomer since it possesses the highest adhesion strength. For the mixture of epoxy resin and polyol at equal proportion, the *R* value is defined as [33]

$$R = \frac{\text{epoxy/epoxy equivalent weight (g)}}{\text{polyol/hydroxyl equivalent weight (g)}}$$

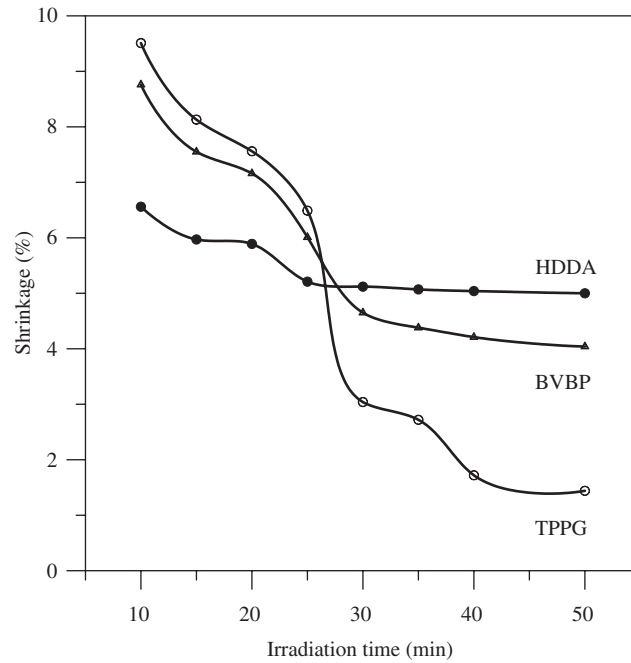


Fig. 4. Shrinkage change versus UV curing time of resin containing TPPG, BVBP and HDDA monomers.

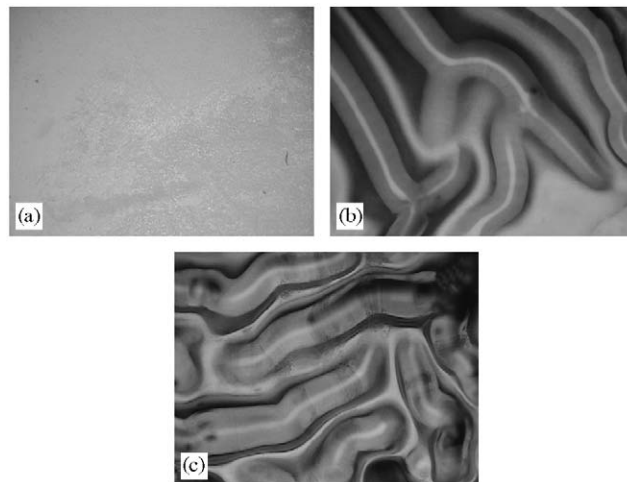


Fig. 5. Surface morphology of epoxide resins containing (a) TPPG (b) BVBP and (c) HDDA after UV curing (magnification = 20 ×).

The R value is an important parameter in modifying the properties of epoxy resin when formulating with polyols and has to be larger or equal to unity [13]. The mixtures with low- R values are in general flexible and soft. Increase of polyol equivalent weight would increase the flexibility, extensibility, and softness of resins, while decrease of polyol equivalent weight would increase the hardness and cure rate of resins [13].

As shown in Fig. 7, after UV curing for 25 min, the resin exhibits the highest adhesion strength of 153.4 kg/cm² at $R = 3$. When $R = 2.5$, excess polyol induced partial curing and hence decreased the adhesion strength due to insufficient curing time to achieve complete crosslinking. Similar result was also reported by Tilbrook et al. [13]. Furthermore, poor adhesion strength was observed in the samples containing less amount of polyol. It should be resulted from less crosslinking density due to the shortage of hydroxyl group. The resin samples with $R > 3$ means less polyol content in the resins. Under same radiation condition, it would result in over curing with exceeding energy to crosslink. The results above imply that appropriate polyol content is essential to obtain satisfactory adhesion strength for photo-curable epoxy resins.

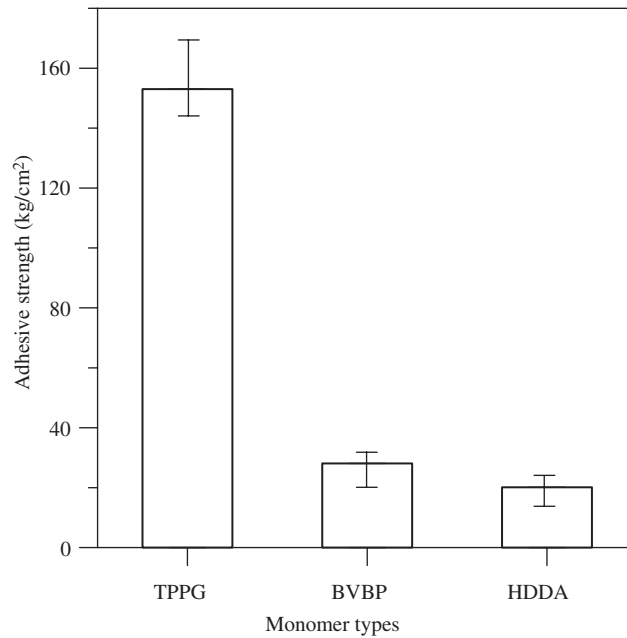


Fig. 6. Adhesion strength and scatter range for the various monomers.

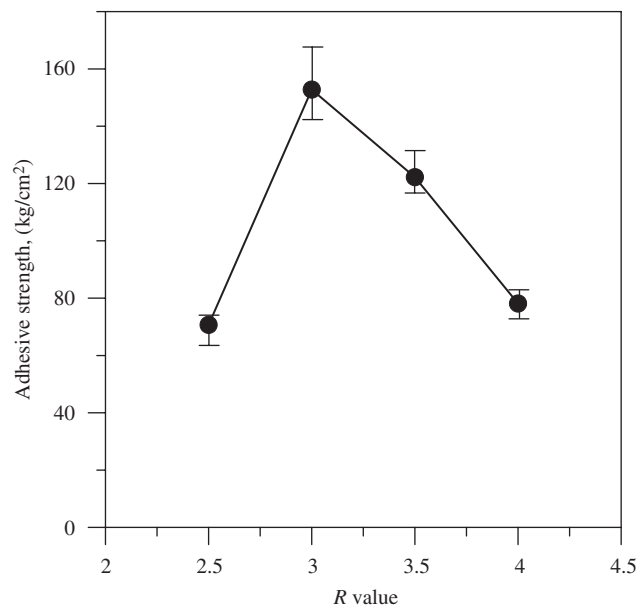


Fig. 7. R-value versus adhesion strength of resins containing polyol monomer.

3.4. Effects of the number of hydroxyl functional group on Adhesion Strength

The presence of hydroxyl groups has an important effect on the cationic ring-opening polymerization of epoxides. As shown in Table 2, the numbers of hydroxyl group on polyol monomers, EOM, TPPG and PCAT are 1, 2 and 3, respectively. Fig. 8 plots the adhesion strength of resins versus numbers of hydroxyl group on polyol monomers. Average adhesion strength of epoxide resins containing EOM, TPPG, and PCAT on glass substrate is 73.6, 153.4, and 126.9 kg/cm², respectively. For EOM monomer, it would result in over curing with excessive energy to crosslink at the same UV curing condition. The PCAT monomer contains three hydroxyl groups that may induce partial curing. It hence lowers the adhesion strength due to insufficient curing time to achieve complete crosslinking. This implies that appropriate amount of hydroxyl groups of monomer is also a critical factor to the adhesion strength of photo-curable epoxy resins. Table 2 shows

Table 2
OH number of various poly monomers

Polyol	OH number of poly monomers	Minimum shrinkage (%)
EOM	1	5.84
TPPG	2	1.72
PCAT	3	4.00

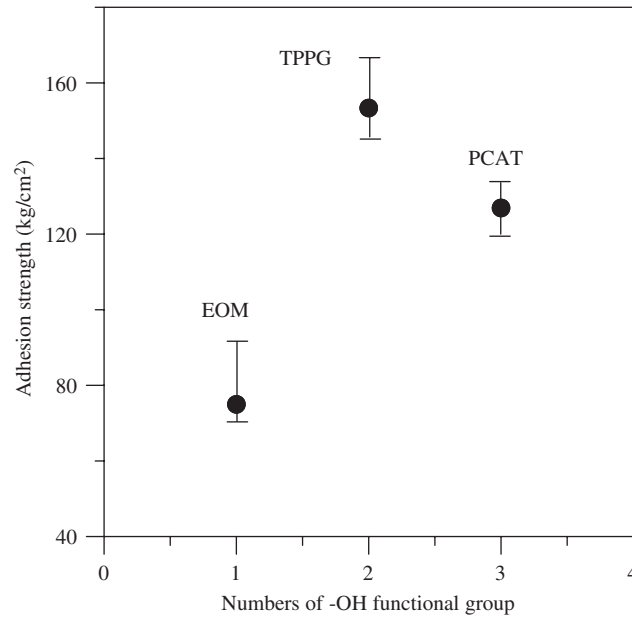


Fig. 8. Adhesion strength versus numbers of hydroxyl group of polyol monomers.

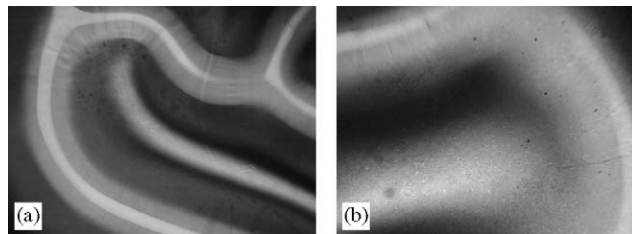


Fig. 9. Surface morphology of epoxide resin containing (a) EOM (b) PCAT after UV curing (magnification = 20 ×).

that the minimum shrinkage of EOM, TPPG, and PCAT is 6.40, 1.72 and 4.00%, respectively. Figs. 5(a), 9(a) and (b) showed the morphologies of epoxide resin containing various types of poly monomers after UV curing. As shown in Figs. 9(a) and (b), the pull-off surfaces of the resins containing EOM and PCAT indicate larger shrinkages in comparison with the resin containing TPPG. The degree of shrinkage was found to be in the order of: TPPG < PCAT < EOM. According to the results above, the resin containing TPPG possesses the highest adhesion strength due to the lowest degree of shrinkage.

4. Conclusions

This work demonstrated that the shrinkage of resins, the *R* value, and the numbers of hydroxyl groups of polyol monomer affect the adhesion strength of epoxy resins on glass substrate. Shrinkage induced by UV curing affects the adhesion strength because high shrinkage might induce a considerable amount of internal stress that pulls the adhesive resin away from substrate. Appropriate *R* value might improve the flexibility and softness of resin hence provides satisfactory adhesion strength. Furthermore, adequate numbers of hydroxyl group of monomers and UV curing times are important to achieve satisfactory adhesion strength for photo-curable epoxy resins.

The experimental results showed that the resin containing TPPG monomer with two hydroxyl groups, possesses the smallest shrinkage of 1.72% and the highest adhesion strength of 153.4 kg/cm² when R value = 3.

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References

- [1] Nelson EW, Carter TP, Scranton AB. *J Polym Sci A Polym Chem* 1995;33(2):247.
- [2] Tryson GR, Shultz AR. *J Polym Sci Polym Chem Ed* 1979;17(12):2059.
- [3] Sundell PE, Jonsson S, Hult A. *J Polym Sci A Polym Chem* 1991;29(11):1535.
- [4] Sangermano M, Malucelli G, Morel F, Decker C, Priola A. *Eur Polym J* 1999;35(4):639.
- [5] Decker C, Moussa K. *J Appl Polym Sci* 1995;55(2):359.
- [6] Decker C, Viet TNT, Decker D, Weberkoehl E. *Polymer* 2001;42(13):5531.
- [7] Decker C, Decker D. *Polymer* 1997;38(9):2229.
- [8] Jönsson S, Sundell PE, Hultgreen J, Sheng D, Hoyle CE. *Prog Org Coat* 1996;27(1–4):107.
- [9] Morel F, Decker C, Jönsson S, Clark SC, Hoyle CE. *Polymer* 1999;40(9):2447.
- [10] Crivello JV, Coulon DA. *J Polym Sci Polym Chem Ed* 1983;21(6):1785.
- [11] Toba Y. *J Polym Sci A Polym Chem* 2000;38(6):982.
- [12] Chen J, Soucek MD. *Eur Polym J* 2003;39(3):505.
- [13] Tilbrook DA, Clarke RL, Howle NE, Braden M. *Biomaterials* 2000;21(17):1743.
- [14] Vabrik R, Czajlik I, Turý G, Rusznak I, Ille A, Vig A. *J Appl Polym Sci* 1998;68(1):111.
- [15] Crivello JV, Lam JHW, Moore JE, Schroeter SH. *J Radiat Curing* 1978;5(1):2.
- [16] Price LN. *J Coatings Technol* 1995;67(849):27.
- [17] Penczek S, Kubisa P. In: *Proceedings of the IUPAC international symposium on macromolecules, Frontiers of macromolecular science*. 1988. p. 107.
- [18] Crivello JV, Ortiz RA. *J Polym Sci A Polym Chem* 2002;40(14):2298.
- [19] Crivello JV, Liu SS. *J Polym Sci A Polym Chem* 2000;38(3):389.
- [20] Matsumato A, Nakane T, Ouawa M. *Macromol Chem Rapid Commun* 1983;4:277.
- [21] Braun H, Yagci Y, Nuyken O. *Eur Polym J* 2002;38(1):151.
- [22] Gandini A, Cheradame H. In: Mark HF, Kroschwitz JI, editors. *Encyclopedia of polymer science and engineering vol 2/Anionic polymerization to cationic polymerization*. New York: Wiley; 1985. p. 729.
- [23] Crivello JV, Liu SS. *J Polym Sci A Polym Chem* 1999;37(8):1199.
- [24] Rajaraman SK, Mowers WA, Crivello JV. *J Polym Sci A Polym Chem* 1999;37(21):4007.
- [25] He JH, Mendoza VS. *J Polym Sci A Polym Chem* 1996;34(13):2809.
- [26] Dufour P. In: Fouassier JP, Rabek JF, editors. *Radiation curing in polymer science and technology, I. Fundamentals and methods*. London: Elsevier applied science; 1993. p. 1.
- [27] Pocius AV. *Adhesion and adhesives technology an introduction*. London: Habser; 1997 [chapter 3].
- [28] Hua YJ, Jiang FM, Crivello JV. *Chem Mater* 2002;14(5):2369.
- [29] Decker C, Moussa K. *J Polym Sci A Polym Chem* 1990;28(12):3429.
- [30] Yarovsky I, Evans E. *Polymer* 2002;43(3):963.
- [31] Braithwaite M, Davidson RS, Holman R, Lowe C, Oldring PKT, Salim MS, Wall C. In: Oldring PKT, editor. *Chemistry & technology of UV&EB formulation for coatings, inks & paints, IV. Formulation*; 1991. p. 37.
- [32] Bernhard P, Hofmann M, Hunziker M. In: Fouassier JP, Rabek JF, editors. *Radiation curing in polymer science and technology, IV, Practical aspects and applications*. London: Elsevier applied Science; 1993. p. 196.
- [33] Wu S, Sears WT, Soucek MD. *Prog Org Coat* 1999;36(1–2):89.