

Tetrafunctional Aliphatic Epoxy I. Synthesis and Characterization

WEN-CHANG SHIH, CHEN-CHI M. MA

Institute of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan, Republic of China 30043

Received 30 September 1996; accepted 6 January 1997

ABSTRACT: A low viscosity tetrafunctional epoxy resin was synthesized by reacting amino-terminated polydimethylsiloxane with epichlorohydrin followed by dehydrohalogenation. The synthesized tetrafunctional aliphatic epoxy resin had an epoxy equivalent weight of 382, M_n of 1492, M_w of 2296, and a viscosity of 4.2 poise at 25°C. The chemical structure of the tetrafunctional aliphatic epoxy resin was studied by gel permeation chromatography (GPC), Fourier transform infrared spectra (FTIR), and $^1\text{H-NMR}$ spectra. Results showed the tetrafunctional aliphatic epoxy-blended aromatic epoxy resin possessed high impact strength and flexural strength. SEM photographs were investigated to study the compatibility of the blended epoxy system. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 51–58, 1998

Key words: tetrafunctional epoxy resin; synthesis; chemical structure

INTRODUCTION

Epoxy resins based on diglycidyl ether of bisphenol-A (DGEBA) are used extensively in various industrial applications, for example, casting, coating, adhesive, and composite, etc.¹ The versatility of this matrix is largely due to its high environmental resistance, good electrical properties, good mechanical and thermal properties, outstanding adhesion to various substrates, and its ability to be processed under various conditions. However, its poor weathering resistance, low toughness, particularly in the presence of sharp cracks, and poor thermal resistance, are its primary restrictions.

Siloxane-containing polymer materials possess excellent properties, for example, good weathering resistance, flexibility, heat resistance, outstanding surface property, and gas permeability. The conventional practice of introducing siloxane

compounds into polymers is achieved by blending those polymers with polydimethylsiloxanes.² However, phase separation limits the incorporation of a large amount of silicone component. Such limitation leads to a more serious problem of bleeding of silicone components. Therefore, to reduce this limitation, silicones with reactive groups are utilized to prepare polymers that possess siloxane bonds in the backbones or on side chains. Siloxane possesses many unique properties, such as high flow, low surface energy, high toughness, and imparting nonflammability to the resins. Previous investigators have prepared epoxy resins containing siloxane linkages from 1,4-bis(hydroxydimethylsilyl)benzene with epichlorohydrin³ and 1,1,3,3-tetramethyldisiloxane with 3-vinyl-7-oxabicyclo(4.1.0)heptane.⁴ The siloxane linkages are also used as impact modifiers for epoxy resin.⁵

For the past decades, the toughening of epoxy resin has received much attention. Elastomer has been widely utilized to enhance the toughness of epoxy resin. However, their applications are limited at lower temperatures because the enhanced fracture toughness is accompanied by lower ther-

Correspondence to: C.-C. M. Ma.
Contract grant sponsor: National Science Council.

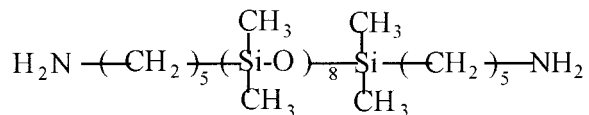


Figure 1 α,ω -amino-organofunctional polydimethylsiloxane.

mal and mechanical properties.⁶ Recently, epoxy resins blended with thermoplastic polymers were successfully utilized for toughening the epoxy resin. However, this leads to a rise in the viscosity of resin, thereby increasing the difficulty in the processing of resin and causing phase separation.^{7,8} In this study, α,ω -amino polydimethylsiloxane oligomer was used to react with epichlorohydrin to prepare the tetrafunctional epoxy resin containing siloxane linkages.

EXPERIMENTAL

Materials

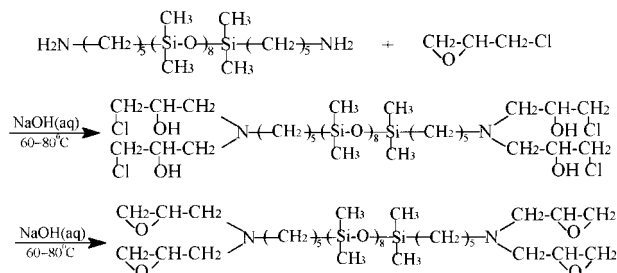
The α,ω -amino-organofunctional polydimethylsiloxane oligomer (Tegomer-2120) was supplied by Goldschmidt AG Co., Germany. The oligomer has a M_w of 822, and its chemical structure is shown in Figure 1. The epichlorohydrin (1-chloro-2,3-epoxypropane) was purchased from Tedia Co., USA, and was used as received. The sodium hydroxide from Fluka Co., USA, and benzyltrimethylammonium chloride from Merck Co., USA, were used as catalysts. Epon 828, a DGEBA type epoxy resin, was obtained from Shell Corporation, USA. The polyamine (JEFAMINE T-403) with an amine equivalent weight of 80 was used as a curing agent (Texaco Chemical Co., USA).

Synthesis of Tetrafunctional Aliphatic Epoxy Resin

Both the α,ω -amino-organofunctional polydimethylsiloxane oligomer (49.32 g, 1 mol) and epichlorohydrin (223.2 g, 40 mol) were heated under nitrogen atmosphere at 60°C in a three-necked round-bottomed flask equipped with a stirring device and thermometer. Sodium hydroxide (4.8 g, 2 mol) was then added dropwise as a catalyst by dissolving in 7.2 g of distilled water for 15 min while maintaining the reaction temperature at 65°C. The reaction was continued by heating at 65°C for various periods, 4 h, 8 h, and 12 h.

After the reaction was complete, the mixture was cooled to room temperature and washed with

an aqueous solution of sodium hydroxide (20% 600 mL) and then washed twice with deionized water (600 mL) to remove the residual sodium chloride. After separation, the organic layer was washed out and placed in a rotary evaporator under a high vacuum for 30 min at 120°C to remove the excess epichlorohydrin monomer completely. Consequently, an amber liquid of the tetrafunctional epoxy product with an epoxy equivalent weight of 382 and a viscosity of 4.2 poise at 25°C was obtained. The reaction scheme for tetrafunctional epoxy resin made from Tegomer-2120 and epichlorohydrin is illustrated as follows:



Characterization and Properties Measurement

The viscosity of the tetrafunctional epoxy resin was determined by a Brookfield Digital Rheometer at 25°C. The density was measured by the ASTM D792-72a hydrostatic method. The refractive index was measured by a yellow sodium light at 20°C. The color of resin was determined by Gardner color. Epoxy equivalent weight (EEW) of the resin was determined by the HClO_4 /potentiometric titration method. IR spectra were investigated by the Bio-Rad SPC-3200. An infrared spectrometer was used with a resolution of 2.4 cm^{-1} in the transmission mode. The $^1\text{H-NMR}$ spectra were measured with a Bruker 400FK-NMR spectrometer. Samples were diluted by deuterated chloroform (CDCl_3) and tetramethylsilane was used as an internal standard. The gel permeation chromatography was performed with a Water 510 using a refractive index (RI) detector, Ultrastayragel 10A, 500 Å, and 100 Å columns, and the mobile phase used was tetrahydrofuran (THF). The flow rate was maintained at 1 mL/min. The differential scanning calorimetric (DSC) test was carried out with a DuPont 2100 DSC at a heating rate of 10°C/min in nitrogen. Tensile property was measured using an Instron Testing Machine, model 4468. The test procedure is described in ASTM D-638. At least five specimens

were used for the test. Finally, the Izod impact strength was measured according to ASTM D-256. At least five specimens were used for the test.

RESULTS AND DISCUSSION

Preparation of the Tetrafunctional Aliphatic Epoxy

The tetrafunctional aliphatic epoxy resins were synthesized by reacting the α,ω -amino-terminated polydimethylsiloxane with epichlorohydrin. The mixture was added slowly at 60–80°C to an aqueous solution (20 wt %) of sodium hydroxide in a quantity sufficient to bind the hydrochloric acid during the reaction between the aforementioned components. After reaching the desired consistency, the resin was washed to ensure it was free from alkali solution. Excess epichlorohydrin and water were removed in vacuum.

Because the siloxane bonds can be easily hydrolyzed under strong basic or strong acid condition; hence, these reactions were used at the lower concentration of catalyst. Higher molecular weight and the branched chain of the tetrafunctional aliphatic epoxy resin can be obtained by the reaction of the amino-terminated polydimethylsiloxane. Preparation of tetrafunctional epoxy resin requires using an excess of epichlorohydrin. Theoretically, a 1 : 4 molar ratio of the amino-terminated polydimethylsiloxane to epichlorohydrin was used, which may lead to form higher molecular weight components and branched chain. Because a molar ratio of 1 : 40 (amino-terminated polydimethylsiloxane : epichlorohydrin) of the aforementioned monomer was used in this study, only different reaction temperatures and times were changed to prepare epoxide-terminated polysiloxane. The reaction was carried out for 4 h, 8 h, and 12 h at 65, 95, 125°C, respectively. Consequently, a highly viscous epoxy resin with a high epoxy equivalent will be obtained at a higher reaction temperature, for example, at 95 or 125°C. High temperature may cause the amino-terminated polydimethylsiloxane to attack the epoxy rings of the tetrafunctional epoxy resins. Hence, a higher molecular weight and the nonlinear molecular of the branched chain can be obtained. Experimental results indicated that temperatures within the range of 60 to 80°C will be the most appropriate, because at those temperatures, a higher yield and a better quality of tetrafunctional epoxy could be obtained.

Table I Physical Properties of Tetrafunctional Aliphatic Epoxy Resin

Physical Properties	This Study	Epon 828
Density (at 20°C)	1.0260	1.165
Viscosity, poise (25°C)	4.2	120
Color, Gardner	5	1
Epoxy equivalent (EEW)	382	188

Physical Properties

When the reaction was carried out for 12 h at 65°C, a low viscosity (4.2 poise at 25°C), light amber liquid epoxy resin with an epoxy equivalent weight of 382 was obtained. The viscosity of Epon 828, a conventional bisphenol-A-type epoxy resin, is 120 poise at 25°C. The existence of siloxane bonds shows the tetrafunctional epoxy resin has much lower viscosity than that of Epon 828. Table I lists the physical properties of the tetrafunctional aliphatic epoxy resin.

Structure Identification

The synthesized resins were identified by IR spectral measurements; the glycidyl group was confirmed as occurring in the reaction. Furthermore, IR spectrum indicates that a band appeared at 915 cm^{-1} , owing to the deformation of the oxirane ring.

Figure 2 shows the IR spectra of α,ω -amino-terminated polydimethylsiloxane and tetrafunctional epoxy. The line A denotes the α,ω -amino-terminated polydimethylsiloxane. The line B represents the tetrafunctional epoxy resin. The IR spectrum (A) indicates that the stretching vibration peak of the amino-terminated group appears at 3300 cm^{-1} and the bending vibration peak appears at 1560 cm^{-1} . The characteristic absorptions of siloxane (1260, 1100–1000, 800 cm^{-1}) were found.

Following the completion of the reaction, the absorption band of the amino-terminated group disappeared entirely while the hydroxyl band and epoxy band were formed. From the IR spectrum (B), the absorption bands of the amino-terminated group at 3300 cm^{-1} and 1560 cm^{-1} disappeared completely. The absorption bands of deformation of the oxirane ring always appeared at 915 cm^{-1} . The CH_2 stretching vibration of terminal epoxide peak appeared at 3056 cm^{-1} . The characteristic absorption peak of siloxane did not change

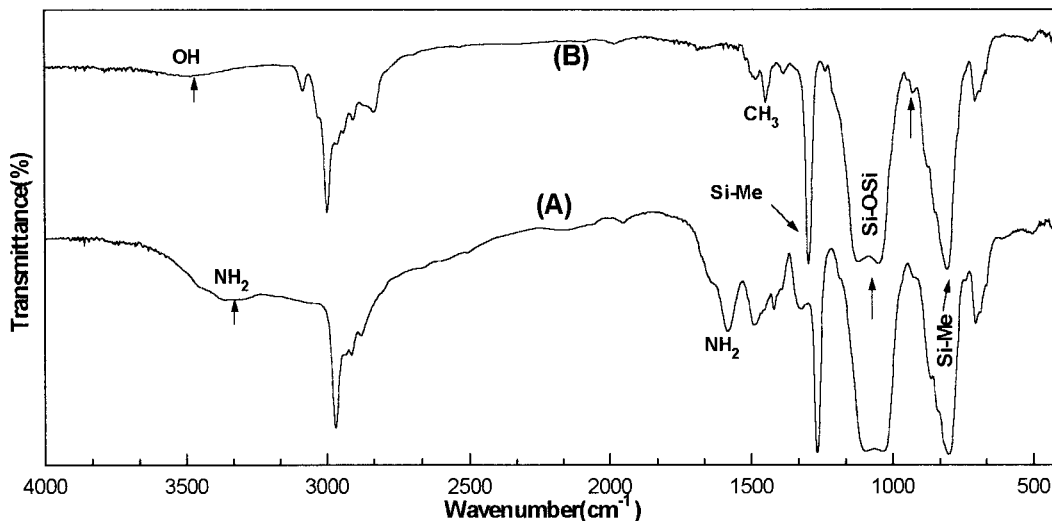


Figure 2 IR spectra of amino-terminated-silicone (A) and tetrafunctional epoxy resin (B).

during the reaction. In addition, the absorptions of the hydroxyl at 3400 cm^{-1} (OH stretching) and 1190 cm^{-1} (OH deformation) were observed. The occurrence of the hydroxyl peak may be due to the possibility of forming higher molecular weight oligomer of the tetrafunctional epoxy resin.⁹

Nuclear magnetic resonance (NMR) was utilized to identify the structure of the tetrafunctional epoxy resin. The $^1\text{H-NMR}$ spectra in Figures 3 and 4 show sharp signals. Figure 3 represents the $^1\text{H-NMR}$ spectrum of α,ω -amino-terminated polydimethylsiloxane. The chemical shift at 1.25 ppm in $^1\text{H-NMR}$ spectrum is assigned to the proton 3 of the unreacted amino group. The chemical shift at 7.15 ppm is attributed to the residual proton in the deuterated chloroform. The chemical shift of siloxane group absorption

spectra was in the higher magnetic field side at approximately 0.08–0.26 ppm (protons 1) for $-\text{OSi}(\text{CH}_3)_2-$. The methylene group absorption spectra of diastereotopic proton was in the lower magnetic field side at approximately 0.6 ppm, 0.98 ppm, 1.5 ppm, and 2.65 ppm (protons 2). Figure 4 shows the $^1\text{H-NMR}$ spectrum of tetrafunctional epoxy resin in deuterated chloroform. The resulting products obtained from the complete reaction did not show the absorption of the amino group. Therefore, the chemical shift of the amino at 1.25 ppm (proton 3 in Fig. 3) entirely disappeared and the chemical shift of siloxane group absorption did not change.

In addition, on the siloxane chain, the hydrogen on amino group was substituted by dehydrohalogenation reaction to form a glycidyl group. Pro-

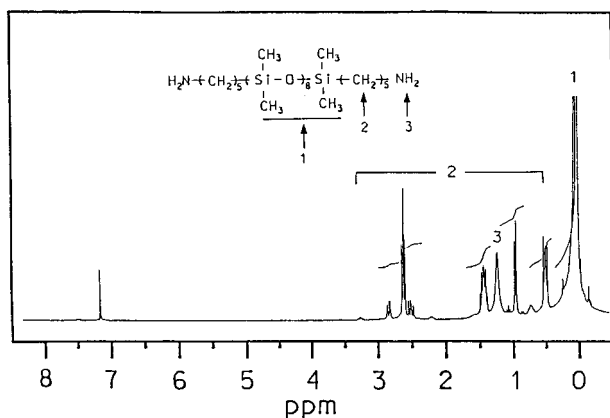


Figure 3 $^1\text{H-NMR}$ spectrum of amino-terminated silicone.

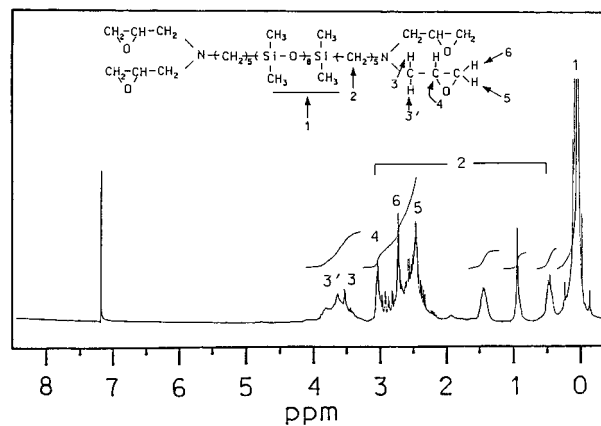


Figure 4 $^1\text{H-NMR}$ spectrum of tetrafunctional epoxy resin.

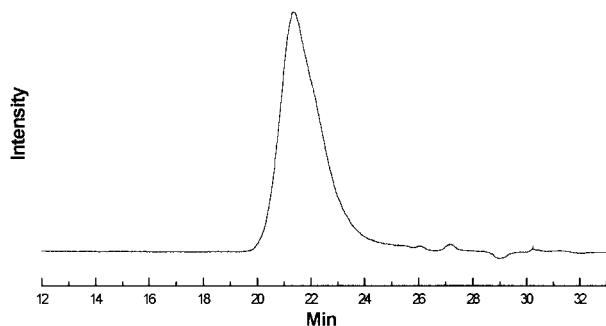


Figure 5 Gel permeation chromatography (GPC) curve of tetrafunctional epoxy resin.

tons 3, 3', 4, 5, and 6 show different chemical shifts and are magnetically nonequivalent. Hydrogen 5 is on the same side of the methylene while hydrogen 6 is on the opposite side of the methylene. Those hydrogens have slightly different chemical shifts, i.e., $H_5 = 2.5$ ppm and $H_6 = 2.7$ ppm. Moreover, they exhibit spin-spin splitting with respect to one another. The chemical shift of proton 4 is 3.0 ppm, and it will be coupled and is different from H_5 and H_6 . Protons 3 and 3' have other chemical shifts ($H_3 = 3.5$ ppm, $H_{3'} = 3.6$ ppm). Moreover, by taking into account coupling with every other hydrogen, each coupling is independent of the other hydrogen.¹⁰

Molecular Weight Determination

The GPC curves were used directly to determine the epoxy equivalent weight (EEW) and the hydroxyl value (a conventional bisphenol-A type epoxy resin). Those values were obtained from the relative amounts of oligomers presented. Figure 5 displays a GPC curve of tetrafunctional epoxy resin and indicates that the reaction occurred

after 12 h at 65°C. From the GPC results, the number-average molecular weight (M_n) of 1492, the weight-average molecular weight (M_w) of 2296 and the polydispersity of 1.54 were obtained from the GPC curve directly. Under those reaction conditions, a lower viscosity and light amber liquid epoxy resin was obtained. An epoxy equivalent weight of 382 was determined by the $HClO_4$ /potentiometric method. If we assume that two epoxy groups terminate each end of the resin, epoxy equivalent weight is one-fourth of the number average molecular weight. Thereby, the GPC measurement result shows the epoxy equivalent weight is 373 by calculating the average molecular weight.

Thermal and Mechanical Properties

The tetrafunctional aliphatic epoxy-blended Epon 828 with a stoichiometric amount of hardener causes a crosslinking reaction and the formed product possesses high toughness and good mechanical properties. The sample descriptions and T_g s of the blends are listed in Table II.

Thermal properties of tetrafunctional aliphatic epoxy-blended Epon 828 were studied by DSC analysis in which polypropyleneamine (T-403) was used as a curing agent. The DSC samples were prepared and are illustrated in Table II. The glass transition temperature (T_g) curves are shown in Figure 6. The changes in T_g of the cured resins were slightly depressed with tetrafunctional aliphatic epoxy. This result indicates that the tetrafunctional aliphatic epoxy has relatively flexible alkyl groups exhibit as the soft segment, while the epoxy matrix (Epon-828) has relatively rigid groups exhibit as the hard segment; hence, tough products were obtained.

Table II summarizes the T_g of the tetrafunc-

Table II The Tetrafunctional Aliphatic Epoxy Blended Epon 828

Sample ^a	Epon 828	Tetrafunctional Aliphatic Epoxy	Hardener T-403 (phr)	T_g (°C)
1	0 g		0 g	-108
2	0 g	100 g	23 g	16
3	100 g	0 g	50 g	72
4	100 g	5 g	49 g	70
5	100 g	10 g	48 g	69
6	100 g	15 g	47 g	68
7	100 g	20 g	46 g	67
8	100 g	25 g	45 g	65

^a Sample was cured for at 80°C, 2 h and then for at 125°C, 3 h.

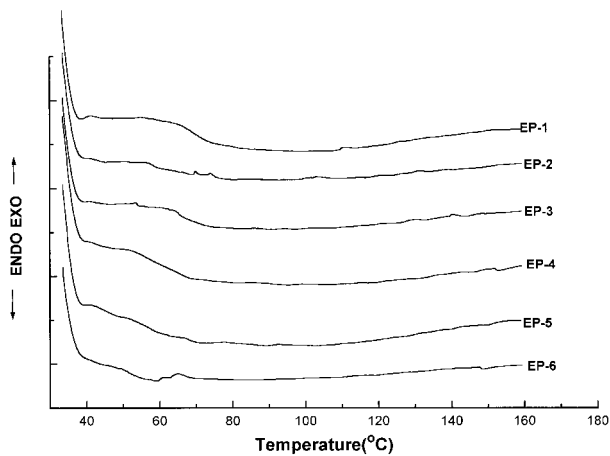


Figure 6 Effect of tetrafunctional aliphatic epoxy content on the glass transition temperature of tetrafunctional aliphatic epoxy-toughen Epon-828.

tional aliphatic epoxy/T-403 is 16°C and Epon-828/T-403 is 72°C. According to the Fox equation, the T_g of blend may be determined with various components and structures; hence, the glass transition temperature was reduced when the tetrafunctional aliphatic epoxy content of the soft segment increased.

Figure 7 shows the Izod impact strength vs. tetrafunctional aliphatic epoxy content of tetrafunctional aliphatic epoxy-blended Epon 828. Aromatic epoxy can be toughened by blending with tetrafunctional aliphatic epoxy. It shows a maximum value of Izod impact strength at the composition of 10 phr. The tetrafunctional aliphatic epoxy containing siloxanes linkage and aliphatic

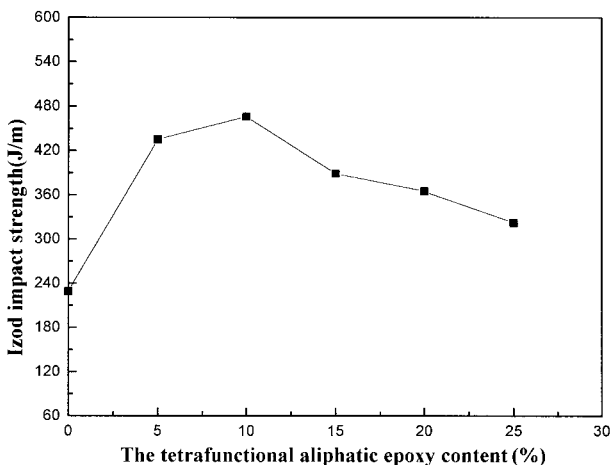


Figure 7 Effect of tetrafunctional aliphatic epoxy content on the Izod impact strength of tetrafunctional aliphatic epoxy-toughen Epon-828.

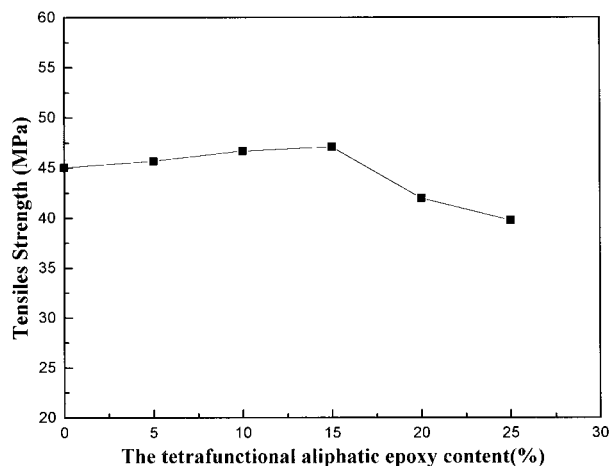


Figure 8 Effect of tetrafunctional aliphatic epoxy content on the tensile strength of tetrafunctional aliphatic epoxy-toughen Epon-828.

group may act as a modifier, which enhances the Izod impact strength of blend.

Figure 8 shows the tensile strength vs. tetrafunctional aliphatic epoxy content of tetrafunctional aliphatic epoxy-blended Epon 828. It was found that the tensile strength changes very slightly. In general, as the amount of modifier increased, the tensile strength of the cured epoxy resin will be decreased. However, the Epon-828 blend with 15 phr tetrafunctional aliphatic epoxy shows a higher tensile strength than that of neat epoxy resin. For the blend containing more than 20 or 25 phr tetrafunctional aliphatic epoxy, the tensile strength will be reduced slightly. This could probably be due to a higher crosslinking density and a higher degree of compatibility of tetrafunctional aliphatic epoxy with Epon-828.

Morphological Properties

Figure 9A and B are the SEM photographs of Izod impact test specimen of pure epoxy resin. River patterns can be observed clearly, and occurs when a crack propagates to different planes, and joins together by a secondary cleavage matrix or by a shear matrix to minimize the surface energy by exposing a minimum of extra free surface. It shows that the specimen broke under cleavage fracture.^{11,12}

Figure 10A and B are the SEM photographs of Izod impact fracture surfaces of 10 phr tetrafunctional aliphatic epoxy-toughened epoxy resin. The micrographs of the blend showed shorter crack paths existed after interference by particles,

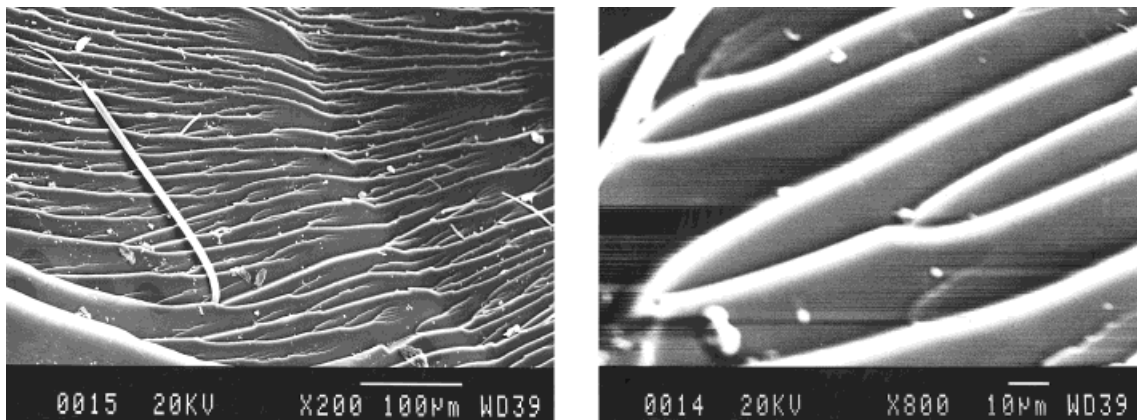


Figure 9 (A) SEM photograph of pure Epon 828 (160 \times). (B) SEM photograph of pure Epon 828 (640 \times).

which indicated that the tetrafunctional aliphatic epoxy is compatible with epoxy matrix and accompany with excellent impact property. First, it shows stress whitening clearly, but no visible flexible deformation occurs. Secondary, it shows a significant difference in local irregularity crazes with transverse contraction of impact fractured surface. It means that the tetrafunctional aliphatic epoxy content affects not only the amount of energy absorbed, but also on the interference craze propagation in the impact test.

CONCLUSIONS

In this study, a tetrafunctional aliphatic epoxy from α,ω -amino-terminated polydimethylsiloxane and epichlorohydrin was synthesized. Sodium hy-

droxide was used as a catalyst and the reaction was conducted at 65 $^{\circ}$ C for 12 h. A low viscosity and light amber aliphatic tetrafunctional epoxy resin having an epoxy equivalent weight of 382, M_n of 1492 and M_w of 2296 was obtained. The viscosity of the synthesized resin is 4.2 poise at 25 $^{\circ}$ C, which is much lower than the conventional epoxy resin. The chemical structure of tetrafunctional aliphatic epoxy has been identified by the FTIR, 1 H-NMR, and GPC.

The tetrafunctional aliphatic epoxy blended Epon 828 (epoxy) with a stoichiometric amount of hardener will cause a crosslinking reaction. The blended system exhibits a higher toughness, good mechanical properties, and slightly depressed glass transition temperature. The blended system also exhibits good compatibility; consequently, the impact strength was improved significantly.

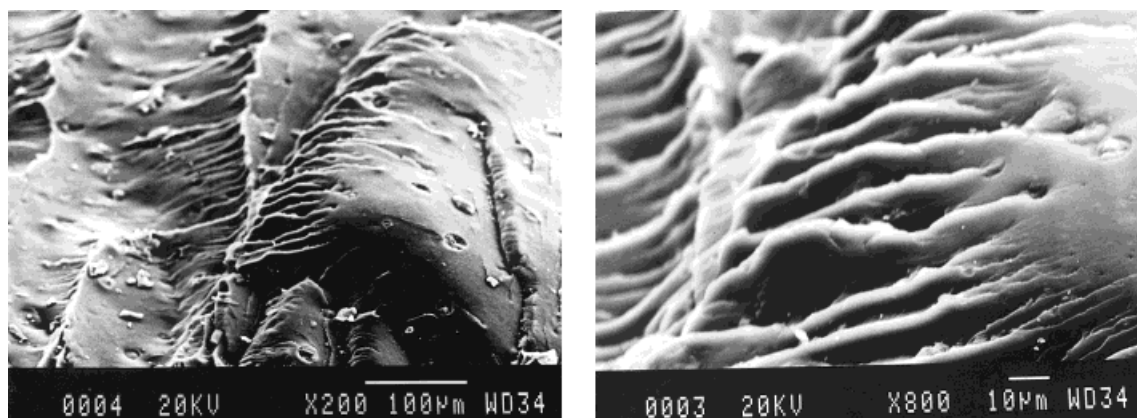


Figure 10 (A) SEM photograph of 10 phr tetrafunctional aliphatic epoxy-toughened Epon-828 (160 \times). (B) SEM photograph of 10 phr tetrafunctional aliphatic epoxy-toughened Epon-828 (640 \times).

This research was financially supported by the National Science Council, Taiwan, Republic of China, under Contract No. NSC-86-2216-E007-010.

REFERENCES

1. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
2. K. Matsukawa, K. Hasegawa, H. Inoue, A. Fukuda, and Y. Arita, *J. Polym. Sci., Part A*, **30**, 2045 (1992).
3. D. Rogers and W. Township, U.S. Pat. 2,883,395, Apr. 21, 1959.
4. J. V. Crivello and J. L. Lee, *J. Polym. Sci., Part A*, **28**, 479 (1990).
5. T. Kasemura, S. Takahashi, K. Nishisara, C. Komatsu, *Polymer*, **34**, 3416 (1993).
6. D. L. Hunston, *J. Mater. Sci. Lett.*, **5**, 1207 (1986).
7. C. B. Bucknall and I. K. Partridge, *Polymer*, **24**, 639 (1983).
8. J. L. Hedrick, I. Yilgor, M. Jurek, J. C. Hedrick, G. L. Wilkes, E. McGrath, *Polymer*, **32**, 2020 (1991).
9. D. L. Pavia, G. M. Lampman, and G. S. Kriz, *Introduction to Spectroscopy*, Saunders College Publishing, Philadelphia, 1979.
10. B. Boutevin, J. P. Parisi, J. J. Robin, and C. Roume, *J. Appl. Polym. Sci.*, **50**, 2065 (1993).
11. H. Inoue, *Int. Polym. Sci. Technol.*, **21**, 4 (1994).
12. D. Broek, *Elementary Engineering Fracture Mechanics*, 4th ed., Martinus Nijhoff Publishers, The Hague, 1986.