

# Poly(oxyethylene)diamine-Derived Hydrophilic Copolymers for Emulsifying Diglycidylether of Bisphenol-A

Jiang-Jen Lin, Shi-Min Chen, Shang-Siou Hu

Department of Chemical Engineering, National Chung-Hsing University, Taichung 402, Taiwan

Received 22 December 2003; accepted 22 June 2004

DOI 10.1002/app.21124

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of reactive surfactants were synthesized by the reaction of hydrophilic poly(oxyethylene)diamines of 2000–6000 g/mol molecular weight and diglycidylether of bisphenol-A resin. The synthesized surfactants consisted of multiple functionalities including tertiary amines, hydrophobic alkylphenoxys, and reactive oxirane groups. After treatment with hydrochloric acid, the surfactants consisted of two different hydrophilic groups: cationic quaternary ammonium salts and nonionic oxyethylene segments. By prudent selection of the proper hydrophile–lipo-

phile balance, the surfactant can be highly effective for solubilizing the epoxy resin in water to form a stable emulsion at a fine particle size of 350 nm. Another advantage is that the surfactant may participate in a curing process through the built-in oxirane reaction and become a nonextractable component in polymer matrix. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1797–1802, 2004

**Key words:** water-soluble polymers; resins; surfactants; emulsion; poly(oxyethylene)

## INTRODUCTION

Because of the environmental concerns and strict emission regulations, it is required that the coating industries minimize the use of volatile organic compounds (VOC). A great deal of effort has been expended to develop new coating systems that have low or zero VOC in the formulations while still maintaining satisfactory film formation and physical properties.<sup>1–4</sup>

Epoxy coatings are well developed for use in electronic components and in protection of metal, concrete, glass, and wood substrates. The two-component epoxy curing could provide highly crosslinked polymers with beneficial properties of adhesion, toughness, transparency, and chemical/moisture resistances.<sup>5</sup> However, because of its high viscosity and hydrophobic characteristics, the epoxy resin component is practically diluted in organic solvents. The use of organic solvents has several disadvantages, including possible harmfulness of vapor to one's health, air pollution toward the environment, and the characterization of being a fire hazard. Furthermore, the solvent-based epoxy coating materials are actually less compatible with the moisture surfaces in certain applications,<sup>6</sup> whereas the waterborne epoxy may gain the advantage of fast drying during the application.

Generally, there are two technological approaches for preparing waterborne epoxy resin emulsions.<sup>7</sup> The first is to modify the hydrophobic epoxy resin. It is structurally anchored with hydrophilic chemical moieties, rendering the resin self-dispersible in water as fine suspension particles. In the second and more common approach, an external surfactant is used to emulsify the hydrophobic epoxy resin.

The resin, diglycidylether of bisphenol-A (DGEBA), is composed of hydrophobic alkylphenoxyl groups and epoxy moieties, which may be reactive with water at elevated temperatures. Therefore, for developing a waterborne epoxy, the scope of selecting the process conditions, such as temperature and surfactant type, is limited. The selection for a suitable surfactant is particularly challenging. The common surfactants generally are classified into four types of structures according to their hydrophilic functionalities<sup>8,9</sup>: (1) anionic, (2) cationic, (3) amphoteric, and (4) nonionic types. A review of the literature shows that, besides the low molecular weight surfactants, polymeric and nonionic emulsifiers are commonly used for waterborne epoxy applications.<sup>10–16</sup>

In our approach of synthesizing a potential surfactant, we adopted the hydrophobic functionalities from the epoxy resin itself. This approach allows the preparation of novel surfactants that are compatible with the epoxy resins. Furthermore, we used the hydrophilic poly(oxyethylene)-*block*-diamines (POE-amines) to react with diglycidylether of bisphenol-A at a controlled molar ratio. The emergence of the hydrophobic bisphenol-A and the hydrophilic POE-amine imparted the surfactant structure of analogous oli-

Correspondence to: J.-J. Lin (JJLin@dragon.nchu.edu.tw).

Contract grant sponsor: National Science Council (NSC) of Taiwan.

gomers. With the addition of hydrochloric acid, the tertiary amines were further converted into the corresponding quaternary ammonium salts. Thus the surfactant consists of dual hydrophilic groups, including the nonionic POE segments and the quaternary ammonium cationic functionalities.<sup>17,18</sup>

## EXPERIMENTAL

### Materials

A family of commercially available polyoxyalkylene amines (trade name: Jeffamine<sup>®</sup> amines) were obtained from Huntsman Chemical Co. (Port Arthur, TX) or Aldrich Chemical Co. (Milwaukee, WI). These hydrophilic and water-soluble amines have a major block of poly(oxyethylene) backbone as the hydrophilic moiety. They include poly(oxypropylene)-*b*-poly(oxyethylene)-*b*-poly(oxypropylene)-bis(2-propylamine), having molecular weights of about 2000 and 6000 (POE-2000, white waxy solid, m.p. 35°C, amine content 0.95 mequiv/g; POE-6000, white waxy, m.p. 58°C), and methoxy-poly(oxyethylene-oxypropylene)-2-propylamine of 2000 MW (POE-M2000). According to patent disclosures,<sup>19,20</sup> these POE/POP amines were prepared from the ammonia amination of polyol precursors. The NMR and amine titration analyses confirmed the chemical structures to have an average of 39.5/5 oxyethylene/oxypropylene unit ratio for POE-2000, 138/4 ratio for POE-6000, and 32/10 ratio for POE-M2000.

The liquid epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) with an epoxide equivalent weight of 188 (trade name: BE-188) was purchased from Chang Chun Co. (Taiwan).

### Preparation of surfactants from POE-amine and DGEBA

Several POE-amine/DGEBA adducts were prepared according to the molar ratios of POE-2000/DGEBA = 1/10, POE-6000/DGEBA = 1/10, POE-6000/DGEBA = 1/4, POE-M2000/DGEBA = 1/2, POE-M2000/DGEBA = 2/3, and POE-M2000/DGEBA = 3/2. The typical experimental procedures for preparing the POE-6000/DGEBA = 1/10 surfactant mixture are described below. POE-6000 amine (33.8 g, 0.056 mol) and toluene (60 mL) were charged to a 250-mL three-neck round-bottom glass reactor, equipped with a thermometer, a dropping funnel, a Dean-Stark trap, and a heating mantle. The mixture was heated to 70°C with agitation using a magnetic stirrer until complete dissolution. Then it was heated to 110–120°C, the temperature at which the water moisture is azeotropically removed through a Dean-Stark trap and nitrogen flow. The reactor was cooled to 70°C and DGEBA (21.1 g, 0.056 mol) added through

a dripping funnel over a period of 1 h. After completing the DGEBA addition, the mixture was heated to 150°C for 3 h. At this ambient temperature, the product mixture was recovered as a yellowish solid.

### Waterborne emulsification of DGEBA in water

The following describes the typical emulsifying procedures. First, POE-6000/DGEBA (1/10) surfactant precursor (5 g) and deionized water (50 g) were charged to a round-bottom flask, equipped with a mechanical stirrer, thermometer, dripping funnel, reflux condenser, and a heating mantle. This precursor amine solution was heated to 70°C and then one equivalent amount of hydrochloric acid (37 wt %, 0.1 g) was added. While the surfactant was vigorously stirred at 200 rpm, the viscous DGEBA resin (50 g) was slowly added in a dropwise manner for over a period of 5 h. The immediate emulsion was continuously stirred for over 12 h at 70°C. The resultant product recovered was a white emulsion with a solid content of 50 wt %.

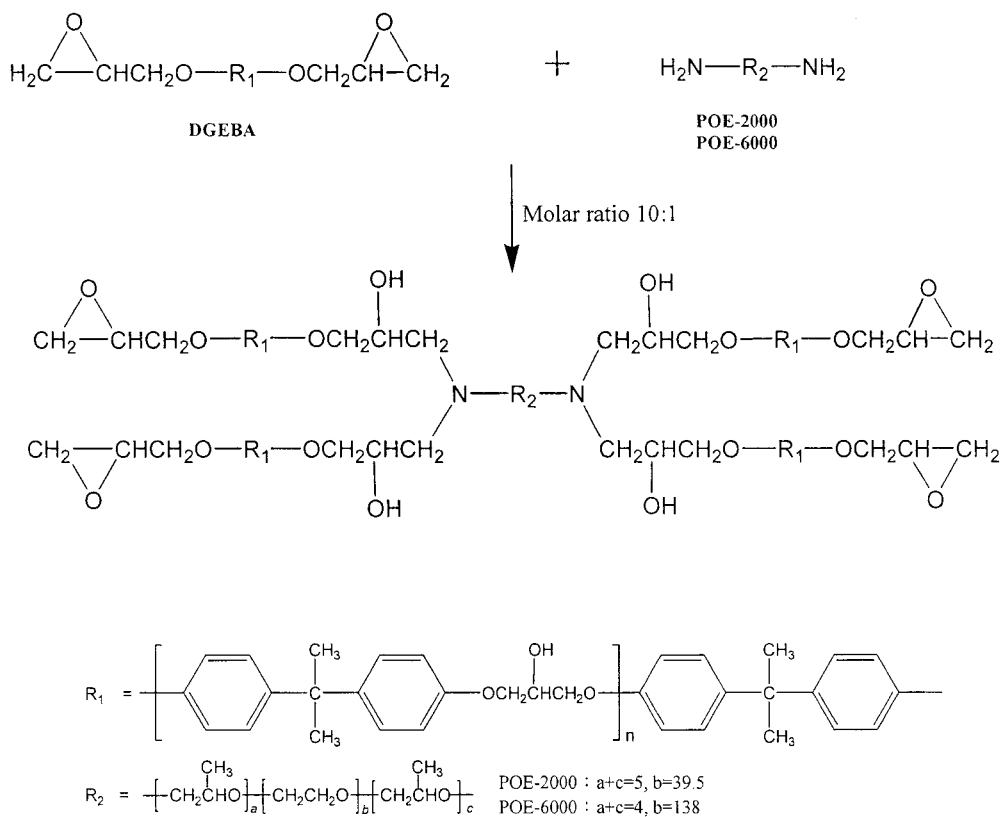
### Measurements

<sup>1</sup>H-NMR analyses were performed on a Bruker MSL-300 NMR spectrometer (Bruker, Darmstadt, Germany) using CDCl<sub>3</sub> as solvent. The FTIR absorption was recorded on a Paragon 500 FT-IR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). Gel permeation chromatography (GPC) analyses were performed in a Waters apparatus (515 HPLC pump, 717 autosampler 2410 refractive index detector; Waters Associates, Milford, MA), with a calibration using the polystyrene standard. Surface tension and interfacial tension were measured by using a K9 Krüss tensiometer (Krüss GmbH, Hamburg, Germany). The particle size of the emulsion was analyzed using a 90 Plus Particle Sizer (Brookhaven Instrument Corp., Holtsville, NY). The amine contents were estimated according to the ASTM D2073-92 titration method.

## RESULTS AND DISCUSSION

### Preparation and characterization of surfactants with dual hydrophilic groups

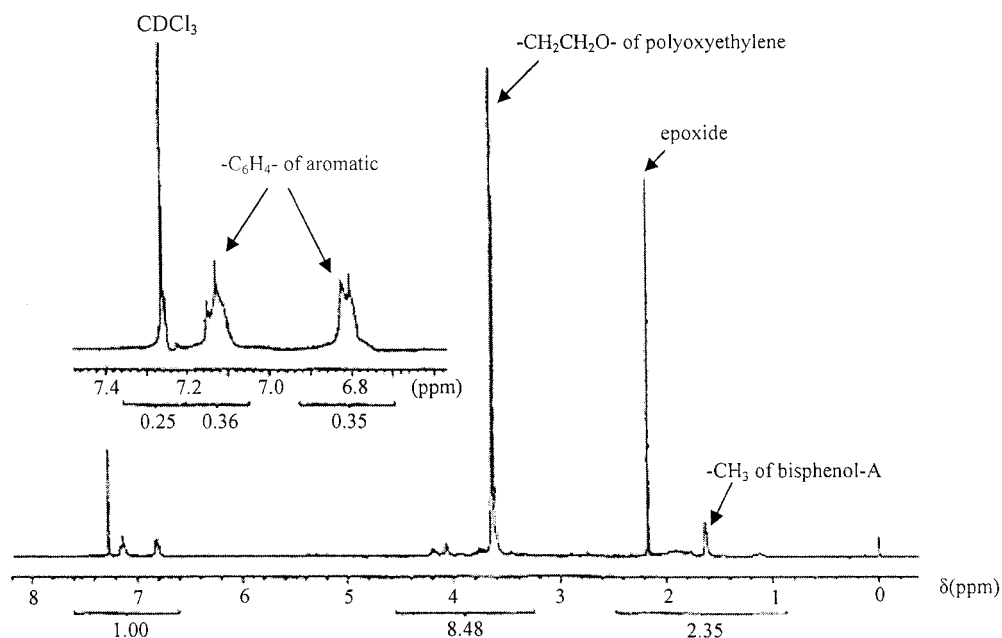
Both POE-6000 and POE-2000 diamines, consisting of poly(oxyethylene) segments and primary amines, were allowed to react with DGEBA resin to generate oligomeric amines. The reaction of primary amine and epoxides proceeded with the sequential conversion into secondary amines and then tertiary amines. The POE diamines containing four equivalents of –NH reactive sites were coupled with four moles of epoxy molecules. With the excess amount of diepoxide, each POE diamine could be chemically bonded with four



**Figure 1** Oligomerization of Jeffamine® amines (POE-2000 and POE-6000) and diglycidylether of bisphenol-A (DGEBA).

DGEBA. However, because of the presence of difunctional epoxide groups in DGEBA, the product is a mixture of oligomers with a statistical molecular weight distribution. In using an excess amount of

DGEBA over four equivalents, the oligomeric adducts higher than the 1 : 4 amine/epoxide coupling are minimized. For example, the adduct of POE-6000/DGEBA, at a 1 : 10 ratio, has the major oligomer at 1 : 4



**Figure 2** <sup>1</sup>H-NMR spectrum of synthesized surfactant (DGEBA : POE-6000 = 10 : 1).

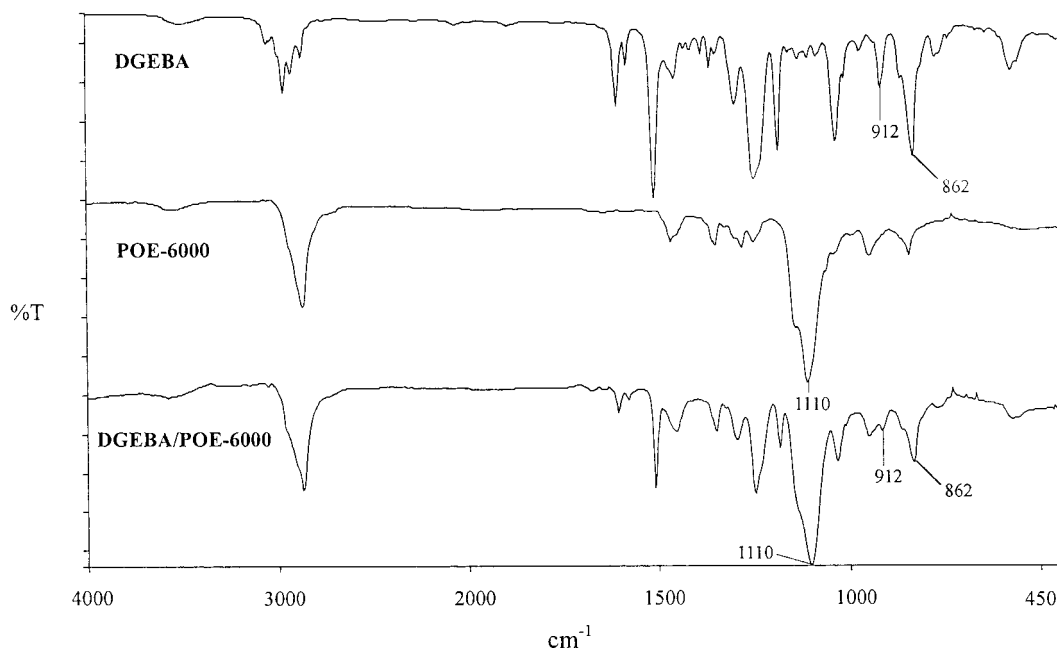
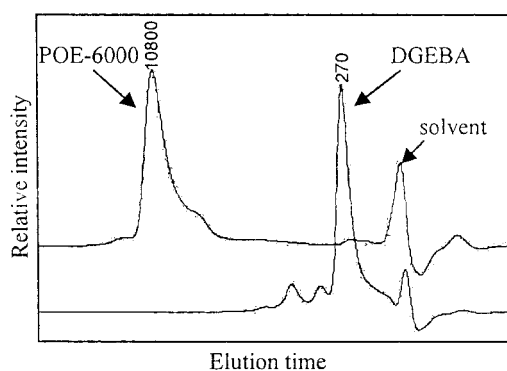


Figure 3 FTIR spectrum of materials and emulsifier of DGEBA/POE-6000 (10 : 1).

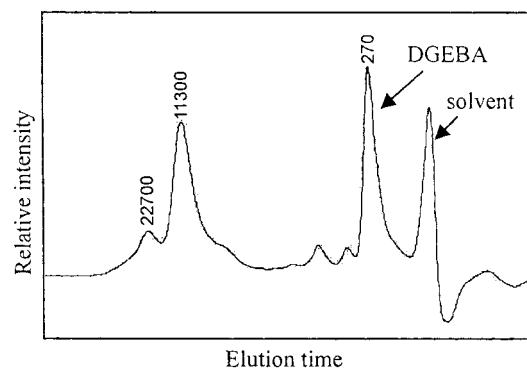
and the unreacted DGEBA in approximately 6 equivalents. The ideal structure of the 1 : 4 adduct is conceptually depicted in Figure 1. In this structure, there are four DGEBA moieties linked to a middle POE block. This also represents four hydrophobic groups at the terminals and the hydrophilic POE segment in the center of the molecule. The hydrophilic/hydrophobic balance depends on the molecular weight of the POE block (6000 g/mol in POE-6000) and the DGEBA moieties (396 g/mol  $\times$  4). According to the calculation of hydrophile-lipophile balance (HLB),<sup>21,22</sup> the value is estimated to be 16.0 in the scale of 20 for the hydrophilicity, implying the surfactant is highly hydrophilic.

The oligomeric analogs were analyzed using a <sup>1</sup>H-NMR instrument, with the spectrum shown in Figure 2. The characteristic chemical shifts are assigned for the presence of chemical functionalities: 7.07–6.78 ppm (aromatic,  $-\text{C}_6\text{H}_4-$ ), 3.6 ppm [poly(oxyethylene) segments,  $-\text{CH}_2\text{CH}_2\text{O}-$ ], 2.5 ppm (epoxide), 1.6 ppm (the methyl group of bisphenol-A). The representative FTIR spectrum is shown in Figure 3, in which the absorption at 1110  $\text{cm}^{-1}$  ( $-\text{COC}-$ , ether) indicates the presence of POE segments ( $-\text{CH}_2\text{CH}_2\text{O}-$ ), and the absorption at 912 and 862  $\text{cm}^{-1}$  is attributed to epoxide functionalities.

Results of gel permeation chromatography, as illustrated in Figure 4, exhibit the product peak at 11,300 (Mp). This is different from the starting material POE-6000 (at 10,800 retention time), based on the polystyrene standard. In the reaction of POE-6000/DGEBA at 1/10M ratio, the product mixtures show the total conversion of POE-6000 starting material, and three major

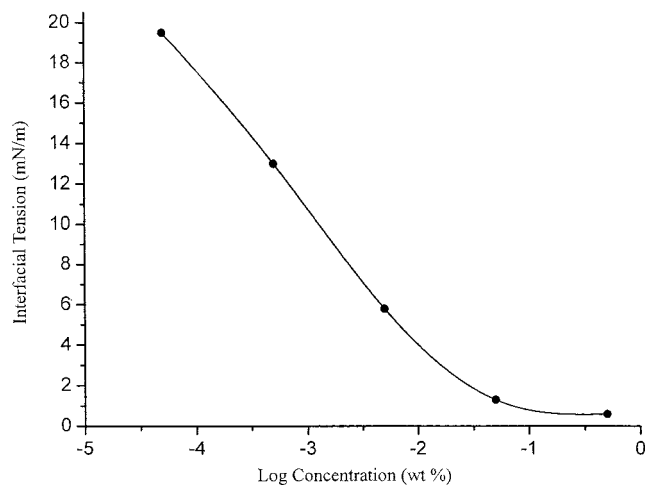


(a) starting materials: DGEBA and POE-6000



(b) surfactant mixtures: DGEBA/POE-6000 (10 : 1)

Figure 4 GPC analysis for the average molecular weight: (a) starting materials: DGEBA and POE-6000; (b) surfactant mixtures: DGEBA/POE-6000 (10 : 1).



**Figure 5** Interfacial tension of DGEBA/POE-6000 (10 : 1) in toluene/water.

peaks: DGEBA (average MW 270), POE/DGEBA (average MW 11,300), and a higher molecular weight oligomer (average MW 22,700). Presumably, the higher oligomer is an analog that is derived from 2 equivalents of POE-6000 in coupling with DGEBA. The amine titration (according to the ASTM method) demonstrated the conversion of primary amine to tertiary amine in the absence of secondary amine, 0.33 mequiv/g for the total amine, 0 mequiv/g for the primary, 0 mequiv/g for the secondary, and 0.33 mequiv/g for the tertiary amine.

The reaction of POE-2000 and DGEBA at various molar ratios afforded similar products to POE-6000, except for a difference in molecular weight of the middle POE block (2000 versus 6000 g/mol). With the POE-M2000 monoamine, the reaction generated a quadruple adduct of DBEBA, based on the GPC analysis. The amine titration also confirmed the conversion of primary amine to tertiary amine.

### Emulsification of DGEBA epoxy in water

In general, the preparation of waterborne epoxy is affected by process parameters such as surfactant con-

**TABLE II**  
Comparative Emulsification of Using POE-2000 and POE-M2000 Derived Surfactants

Surfactant	Hydrophilic type	Result
DGEBA : POE-2000 = 10 : 1	Nonionic	Homogenous
DGEBA : POE-2000 = 10 : 1	Cationic	Two phase
DGEBA : POE-M2000 = 2 : 1	Nonionic	Two phase
DGEBA : POE-M2000 = 2 : 1	Cationic	Two phase
DGEBA : POE-M2000 = 2 : 3	Nonionic	Two phase
DGEBA : POE-M2000 = 2 : 3	Cationic	Two phase

<sup>a</sup> Reaction conditions: surfactant 5.0 g, DGEBA resin 50 g, deionized water 50 g; 24 h, 70°C. Addition order: resin to surfactant in water.

centration, viscosity, temperature, time, mixing order, and mass transfer condition. To obtain a fine emulsion, all of these factors must be optimized. Among these parameters for preparing the emulsion, the surfactant is particularly important.

For comparison, three surfactant mixtures were used for emulsifying the DGEBA (50 wt % in water) under identical conditions, including surfactant concentration, mixing temperature, and agitation speed. In the emulsification, the concentration is maintained at 5 wt % of the epoxy resin used. The POE-6000/DGEBA (1/10) surfactant itself was shown to be effective for lowering the toluene/water interfacial tension to 1.3 dyn/cm at a critical micelle concentration (cmc) of 0.05 wt % (Fig. 5). The comparative effectiveness for using the surfactants for emulsification is summarized in Tables I and Table II. Table I demonstrates the emulsification of DGEBA in water by using POE-6000/DGEBA at 1/10 or 1/4, allowing the formation of fine particle sizes. In particular, the 1/10 adduct with the HCl addition was capable of emulsifying 50 wt % epoxy resin in water at 300 nm particle size, which further remained in the range of 300–370 nm for over 11 days of long-term standing. For comparison, the same surfactant mixture without the quaternary ammonium salt conversion by HCl addition resulted in an emulsion of 890 nm particle size in average, whereas the 1/4 ratio surfactant achieved 850 nm

**TABLE I**  
Emulsification of POE-6000/DGEBA Surfactant for Diglycidyl Ether of Bisphenol-A Resin in Water<sup>a</sup>

Surfactant (prepared from DGEBA:amine)	Hydrophilic type	Process condition (addition sequence)	Particle size (nm)
10 : 1	Nonionic/cationic	Resin to surfactant	300
10 : 1	Nonionic/cationic	Surfactant to resin	490
10 : 1	Nonionic	Resin to water	890
4 : 1	Nonionic	Resin to water	670
4 : 1	Nonionic/cationic	Resin to water	850

<sup>a</sup> All reactions were carried out at the stirring rate of 200 rpm, adding resin and surfactant in a specified sequence; reaction conditions (24 h, 70°C); surfactant 2.5 g, resin 50 g, and deionized water 50 g.

particle size in emulsion. These results imply the importance of the surfactant structural variations, in which fine emulsion was obtained only by the cationic POE-6000 derivative. By comparison, the amine surfactants without the acid treatment are less effective for the formation of fine emulsion.

Using the HLB = 16.0 for the POE-6000-derived surfactant as a comparison, the POE-2000/4 DGEBA surfactant is less hydrophilic, with a calculated HLB = 11.4 and the POE-M2000/2 DGEBA with a HLB = 14.4. As summarized in Table II, both 2000 g/mol POE-derived surfactants failed to emulsify the epoxy resin in water and instead formed a phase separation; thus, the surfactant with high molecular weight and HLB is required for the emulsion. Although the cationic groups further contribute to the hydrophilic POE corona, causing stabilization of fine particle formation, the hydrophobic core of high molecular weight surfactant is effective for solubilizing epoxy resins. In the acidified POE-6000/DGEBA surfactant, the presence of cationic quaternary amine salts in the structure further provides additional hydrophilic functionalities and contributes to high HLB value and emulsion stability.

### CONCLUSION

A series of poly(oxyethylene)-amine-derived diglycidyl ethers were prepared from the reactions of POE-amine and epoxy resin at the controlled stoichiometric ratios. The multifunctional tertiary amines, after converting into the corresponding quaternary ammonium salts, were found to be effective surfactants for emulsifying the epoxy resin in water. Fine emulsion (300–400 nm particle diameter) and high stability for the epoxy resin (50 wt %) emulsion in water were

achieved. High molecular weight POE segment (6000 g/mol) and cationic quaternary ammonium salts, used as the dual hydrophilic groups in the surfactant structure, are essential for the performance. The presence of oxirane functionalities, derived from the diglycidylether of bisphenol-A synthesis, conferred the unique features of components to the surfactant in the subsequent curing process.

We acknowledge the financial support from National Science Council (NSC) of Taiwan.

### References

1. Destreri, M. D. G. *Prog Org Coat* 1999, 37, 57.
2. Destreri, M. D. G. *Prog Org Coat* 1999, 37, 69.
3. Matthews, J. F.; Sommerfeld, E. G. U.S. Pat. 4,247,439, 1981.
4. Williams, P. R., Jr.; Burt, R. V.; Golden, R. U.S. Pat. 4,608,406, 1986.
5. Lin, J. J.; Lin, S. F. *J Appl Polym Sci* 2000, 78, 615.
6. Chebbi, R. *J Colloid Interface Sci* 2000, 229, 155.
7. Zhang, Z.; Huang, Y. *Eur Polym J* 2000, 37, 1207.
8. Shaw, D. J. *Introduction to Colloid and Surface Chemistry*, 4th ed.; Butterworth-Heinemann: London, 1996.
9. Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989.
10. Piechocki, C. U.S. Pat. 5,118,729, 1992.
11. Shimp, D. A.; Hicks, D. D.; Graver, R. B. U.S. Pat. 4,246,148, 1981.
12. Becker, W.; Karasmann, H. U.S. Pat. 4,197,389, 1980.
13. Waddill, H. G.; Sellstrom, K. B. U.S. Pat. 4,421,906, 1983.
14. Wegmann, A. *J Coat Technol* 1993, 65, 27.
15. Verkholantsev, V. V. *J Coat Technol* 1996, 68, 49.
16. Johnson, R. *J Coat Technol* 1997, 69, 117.
17. Lin, J. J.; Cheng, I. J. *J Appl Polym Sci* 2002, 85, 612.
18. Nagarajan, R.; Ganesh, K. *J Colloid Interface Sci* 1996, 184, 489.
19. Moss, P. H. U.S. Pat. 3,152,998, 1964.
20. Yeakey, E. L. U.S. Pat. 3,654,370, 1972.
21. Griffin, W. C. *J Soc Cosmet Chem* 1945, 5, 249.
22. Lin, J. J.; Hsu, Y. C.; Chou, C. C. *Langmuir* 2003, 19, 5184.