

Synthesis and Characterization of Emulsion-Type Curing Agent of Water-Borne Epoxy Resin

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ABSTRACT: Self-emulsified water-borne epoxy curing agent of nonionic type was prepared using triethylene tetramine (TETA) and derivative of epoxy resin as a capping agent, which was synthesized by liquid epoxy resin (E51) and polyethylene glycol (PEG), and the curing agent possessed emulsification and curing properties at the same time. The curing agent with good property of emulsifying liquid epoxy resin could be obtained under the condition of the molar ratio of PEG : E51 : TETA as 0.8 : 1 : 3.5 at 80°C for 5 h. The mean particle size of the emulsion liquid was about 220 nm with the prepared curing agent and epoxy resin at the mass ratio of 1 : 3. The structure of the emulsion-type curing agent was confirmed by FTIR and ¹H NMR spectra, and the mechanism of cured film formation was also analyzed by SEM photographs. The cured film prepared by the emulsion-type curing agent and epoxy resin under ambient cure conditions showed good properties even at high staving temperature. This study provides useful suggestions for the application of the water-borne epoxy resins in coating industry. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2652–2659, 2013

KEYWORDS: water-borne epoxy curing agent; synthesis; self-emulsified; size distribution

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INTRODUCTION

Epoxy resins are considered to be one of the most important classes of thermosetting polymers with outstanding properties, including good heat resistance, high modulus, and high electrical resistance.¹ Coatings based on a combination of epoxy resins and amine hardeners (curing agents), which react to form a cross-linked film, have enjoyed widespread use for decades. Because of the combination of properties achievable, they have developed strong market positions in those applications where a high degree of resistance to water, chemical reagents, or corrosive environments is required.^{2–5} With the development of coating technology, as well as new ideas and awareness of laws and regulations on environmental protection, points to the high-solids coatings, and water-based paint coating development have become a community consensus. The use of water-borne epoxy resins has made it possible to control environmental pollution with lower volatile organic content (VOC), reducing risks of fire, and improving aspect of occupational health and safety.^{6–9}

Most commercially available water-borne epoxy coating systems are composed of water-borne dispersions of epoxy resins

and amine-functional curing agent. The methods to prepare water-borne dispersions of epoxy resins are roughly classified into chemical polymerization¹⁰ and physical emulsification,¹¹ which has been proved to be highly effective in improving the hydrophilicity of epoxy resin. Besides the water-borne dispersions of epoxy resins, the curing agent and the mode of curing also play an important role in the performances of cured epoxy resin film, so the preparation of a water-borne curing agent has received considerable attention in industrial field.^{12–16} Waler¹² prepared a water-borne curing agent using liquid epoxy resin and polyamine, but the performance of cured film was limited due to the poor intermiscibility of the curing agent with epoxy resin. Zhou¹³ synthesized a self-emulsified waterborne epoxy curing agent of nonionic type by using diglycidyl ether of polyglycol (DGEPEG), triethylene tetramine (TETA), and liquid epoxy resin (EPON828) as raw materials, which showed good property of emulsifying liquid epoxy resin. Lu¹⁴ synthesized a novel water-borne epoxy curing agent using 3-glycidoxypropyl trimethoxysilane (GPTMS), triethylene tetramine (TETA), and liquid epoxy resin. The hardness, water resistance, and adhesion of the cured film were improved significantly, but the emulsifying property of the water-borne curing agent was not evaluated.

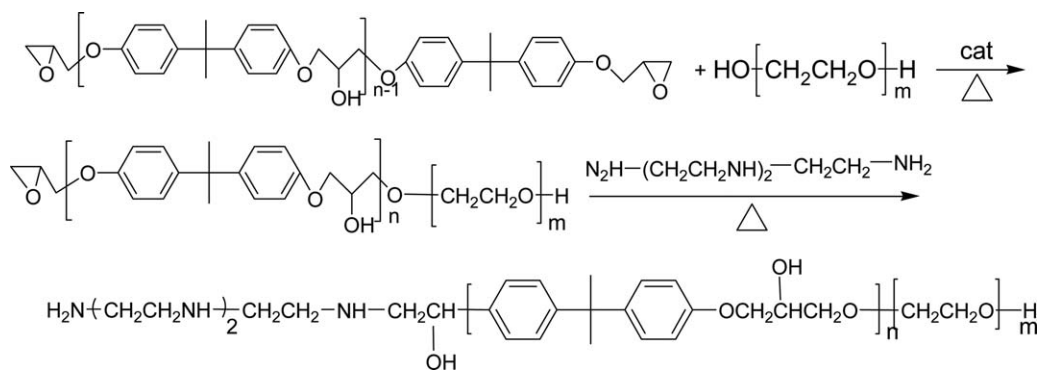


Figure 1. The chemical reaction of the emulsion-type curing agent.

The emulsification of curing agents on epoxy resin is rarely involved in the process of cross-linking. The main advantage of this new type of curing agent consists of improving the chemical resistance of the resulting cross-linked films, especially against acids, and a very good emulsifying behavior. In this article, a water-borne epoxy curing agent was prepared with TETA and modified liquid epoxy resin (E-51) by polyethylene glycol (PEG). The linked epoxy group and hydroxyl group in TETA curing agent improved the compatibility and hydrophilicity between curing agent and epoxy resin. The emulsion-type water-borne curing agent possessed emulsification and curing properties at the same time. The reaction conditions, such as the content of PEG, E-51 and TETA, the reaction time and temperature, on the final synthesized emulsion particle size and the properties of cured film had been studied systematically. The emulsifying performances of the curing agent and the formation mechanism of the cured film were also investigated.

EXPERIMENTAL

Materials

Bisphenol-A type epoxy resin (E-51, epoxy equivalent mass 0.44 mol/100 g) was supplied by Wuxi Resin Factory (China). TETA, PEG 400, propylene glycol methyl ether and boron trifluoride etherate were purchased from Sinopharm Chemical Reagent Co. (China). Solvents of analytical grade such as acetic acid and glycerol were supplied by Hangzhou Chemical Regent Company (China). All solvents were used as received without further purification.

Synthesis of Emulsion-Type Curing Agent

A 500 mL four-necked round-bottom flask equipped with a stirrer, thermometer, reflux condenser, and heating mantle was charged with 50 wt % epoxy resin E-51 using propylene glycol methyl ether as the solvent, then PEG400 was added dropwise evenly (Boron trifluoride etherate as a catalyst with the content of 0.3 wt %) with the molar ratio to epoxy resin as 0.4 : 1, 0.6 : 1, 0.8 : 1, 1 : 1, and 1.5 : 1, respectively. The reaction was maintained at 80°C for 2 h. Then a certain amount of TETA in the molar ratio of active amine hydrogen to epoxy group of 1 : 1, 1.5 : 1, 2 : 1, 3 : 1, 3.5 : 1, and 4 : 1, respectively, was dropped to the reaction flask keeping at the temperature of 60, 70, 80, 85, and 90°C, respectively. At the interval

of 1 h from the beginning of the reaction, the epoxy value and epoxy conversion were measured. After reaction, small molecule amine was steamed out by vacuum distillation. The reaction mixture was added dropwise for neutralization using acetic acid (HAc) with the molar ratio of HAc to N-H as 5, 10, 15, and 20%, respectively. Then water dispersion of epoxy curing agent with solid content of 60 wt % was obtained by adding deionized water dropwise with stirring. Figure 1 displays the chemical reaction of the emulsion-type curing agent.

Curing of Water-Borne Epoxy Resin

The curing agent synthesized as mentioned above was mixed with the water-borne epoxy resin E-51 emulsion (made in our lab) by the mass ratio of 1 : 3, and the mixture solution was stirred at a speed of 800–1000 r/min for 5 min. The mean particle size of the emulsion liquid was measured by Zetasizer 3000 HAS Zeta laser nanometer particle size analyzer (Malvern Instruments, Worcestershire, UK) at 25°C. Prior to analysis, the samples were 1000-fold-diluted with ethanol. Then the solution was coated on the tinplate with the film thickness of about 25–30 μm , and the film was solidified slowly at room temperature.

Measurement and Characterization

The epoxy value and the epoxy group conversion were measured by non-aqueous titration with HBr/glacial acetic acid.¹⁷ The hydrophile-lipophile balance (HLB) value of mixed surfactants was calculated on a weight prorated basis.¹⁸ The surface tension of the curing agent was measured as a function of concentration by JWY-200A automatic interfacial tension analyzer (Chengde Jiande Detection Instrument Co., China). Both the cuvette and the syringe were temperature controlled at 25°C.

The FTIR spectra of the products were recorded with Avatar 370 RCT spectrophotometer (Thermo Nicolet) using KBr pellet technique. The ¹H NMR spectra were measured on a Bruker AC-600 instrument at room temperature with CDCl₃ as the solvent. The surface morphology of the cured film was characterized by S-4800 scanning electron microscope (SEM; Hitachi, Japan) after being coated with a conductive layer of sputtered gold. The performances of cured film, such as water resistance, adhesion, surface drying time, and pencil hardness were

Table I. The Influence of the Molar Ratio of PEG/E51 on Emulsifying and Curing Properties of the Curing Agent

PEG/E51	Emulsion particle size (nm)	Solubility in water	Pencil hardness (H)	Surface drying time (h)
0.4 : 1	1000	Water insoluble	3	0.2
0.6 : 1	580	Poor water soluble	2	2
0.8 : 1	220	Miscible with water	4	4
1 : 1	240	Miscible with water	2	5
1.5 : 1	324	Miscible with water	1	6

characterized according to methods of Chinese National Standards GB/T6739-2006/ISO.

RESULTS AND DISCUSSION

The Optimization of Synthesis Conditions

It is well known that the smaller the emulsion particle size, the better emulsion property of the curing agent. Therefore, the synthesis conditions of curing agent, such as the molar ratio of PEG and E51, the molar ratio of TETA and E51, the reaction temperature and time, were optimized, and evaluated by its emulsifying effect.

Effects of the Molar Ratio of PEG400 and Epoxy Resin E-51 on Emulsifying and Curing Properties of the Curing Agent.

In order to improve the hydrophilicity of the self-emulsified water-borne curing agent, PEG 400 is used to react with the epoxy resin E-51 as a capping agent, which is favorable for the aqueous polyamine (TETA) to link with the epoxy resin molecular. The influences of the molar ratio of PEG400 to epoxy resin E-51 on emulsifying and curing properties of the curing agent are illustrated in Table I, with the molar ratio of TETA to epoxy resin of 3.5 : 1 at 80°C for 5 h.

From Table I, it can be seen that the composition of PEG400 and epoxy resin evidently influences the emulsifying and curing properties of the curing agent. With the increase of the PEG content, the particle size of the emulsion decreases and the water solubility of the emulsion is improved. However, when the molar ratio of PEG to epoxy resin is above 0.8 : 1, the particle size of the emulsion increases and the pencil hardness of the cured film decreases. Curing agent shows good emulsifying and curing properties when emulsion particle size is about 220 nm. The structure of PEG influences the HLB value of the curing agent, and the suitable HLB could emulsify the epoxy resin well and balance the performance of the cured film, such as curing time, hardness, flexibility, and so on.

Effects of the Molar Ratio of TETA and Epoxy Resin on Emulsifying and Curing Properties of the Curing Agent. The purpose of preparing emulsion-type water-borne curing agent

Table II. The Influence of the Molar Ratio of TETA/E51 on Emulsifying and Curing Properties of the Curing Agent

TETA/E51	Emulsion particle size (nm)	Solubility in water	Pencil hardness (H)	Surface drying time (h)
1 : 1	2500	Water insoluble	1	6
1.5 : 1	1500	Poor water soluble	1	6
2 : 1	800	Miscible with water	3	4.5
3 : 1	330	Miscible with water	4	4
3.5 : 1	220	Miscible with water	4	4
4 : 1	280	Miscible with water	2	3

is to get the linear polymer with amine groups as the terminal groups, which participates in curing reaction of the film-formation. The content of the active hydrogen in the amine groups decides the curing reaction period and the performance of the coated film. Therefore, the molar ratio of TETA and epoxy resin also has important impact on the emulsion mean particle size and physical properties of the curing agent (Table II).

As can be seen from Table II, with the increase of the amount of TETA, the mean particle size of the emulsion decreases and the solubility of the prepared emulsion-type curing agent in water increases until the molar ratio of TETA and epoxy resin reaches 3.5 : 1 under the condition of the molar ratio of PEG to epoxy resin as 0.8 : 1, with the reaction temperature of 80°C for 5 h. The epoxy groups reacts with the active hydrogen of the amine groups, which are favorable to reduce the lipophilicity of epoxy resin, so that the synthesized adduct of an amine with an epoxy resin increases the HLB value of the curing agent gradually, showing good water solubility and emulsifying properties. With further increasing the amount of the amine, the water solubility of the curing agent remains excellent; however, the particle size of the emulsion tends to increase. A reasonable explanation is that the active hydrogen content accelerates the curing rate, and the less proportion of epoxy resin in the composites reduces the emulsifying properties of the synthesized curing agent.

Tables I and II show that the emulsion particle sizes are 240 and 324 nm with the molar ratio of PEG to E51 as 1 : 1 and 1.5 : 1, respectively, which are lower than that of the same molar ratio of TETA and E51 systems (2500 and 1500 nm). PEG has the emulsifying property itself, and the emulsifying activity increases when it is grafted to the epoxy resin. The amine TETA grafted onto the epoxy resin mainly reduces the velocity of the curing agent which is favorable for the improving of the performance of the cured film. In our opinion, the emulsifying property of the curing agent is highly dependent on the molar ratio of the PEG and E51, and the amount of the amine is

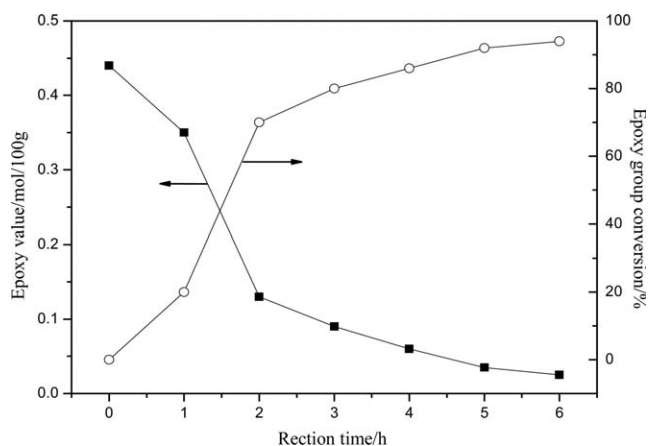


Figure 2. The effects of reaction time on epoxy conversion and epoxy value (temperature: 80°C).

mainly related to the curing reaction velocity of the film. However, with the increase of the content of TETA, the abundant hydrophilic group of TETA increases the compatibility of the curing agent with the epoxy resin, and the emulsion particle size decreases.

Compared to Tables I and II, it can also be seen that when the molar ratio of PEG to E51 is above 1 : 1, there is less epoxy group in curing agent, which decreases the crosslinking density and it is coincident with the decrease in the pencil hardness of the cured film. However, in Table II, with the increase of the amount of the amine TETA, the cross-linking density increases with coincidental increase in the pencil hardness of the cured film. From Tables I and II, it can be concluded that the pencil hardness of the cured film is determined by its cross-linking density.

Effects of Reaction Time on Epoxy Value of E51 and the Conversion of Epoxy Group. The emulsifying property of curing agent strongly depends on the conversion of epoxy group. Figure 2 shows the effects of reaction time on epoxy value of E51 and the conversion of epoxy group.

It can be seen from Figure 2 that the epoxy value of E-51 decreases and the conversion of epoxy group increases with prolongation of the reaction time. The epoxy value is approached to 0.03 mol/100 g and epoxy conversion reaches about 92% after 5 h reaction, which is considered as the proper reaction time.

Effects of Reaction Temperature on the Water Solubility of Curing Agent. The reaction temperature has important influences not only on the reaction velocity and conversion rate, but also on the physics properties of the curing agent. The effects of

Table III. The Influence of the Temperature on the Water Solubility of the Curing Agent

Temperature (°C)	60	70	80	85	90
Solubility in water	Water insoluble	Poor water soluble	Miscible with water	Miscible with water	Gel

Table IV. Performances of Films Cured by the Synthesized Curing Agent with Different Amount of HAC

HAc/N-H (%)	Pencil hardness (H)	Appearance	Surface drying time (h)	Water resistance
5	5	Transparent	4	>10 d
10	4	Transparent	5	7
15	3	Slight yellow	5	5
20	Soft	Creamy	Not curing	2

the temperature on the water solubility of curing agent are listed at Table III.

From Table III, it can be seen that the epoxy groups does not react with the amine groups of TETA sufficiently at temperature lower than 70°C, which results in the poor water solubility of the synthesized curing agent. However, when the temperature is up to 90°C, the curing agent tends to form gel. In this experiment, 80°C is an optimal reaction temperature considering the physics properties of the curing agent.

Effects of the Amount of HAC on the Performances of Cured Film. The influences of the amount of HAC, using as neutralization agent, on the performances of cured film are showed in Table IV under the reaction condition of the molar ratio of PEG : epoxy resin : TETA as 0.8 : 1 : 3.5 at 80°C for 5 h. It can be seen that the pencil hardness of the cured film drops from 5H to soft and water resistance turns into 2d from 10d with the increase of the amount of HAC, and the intermiscibility of the curing agent with the epoxy emulsion also decreases. As a result, the system of epoxy emulsion and water-borne curing agent could not be cross-linked completely because the diffusion of curing agent into epoxy emulsion particle becomes more difficult, and the color of the cured film becomes darker due to the oxidation of the un-reacting N-H during the curing process.¹⁹ So the amount of HAC using as neutralization agent should be below 5% with the molar ratio to the N-H.

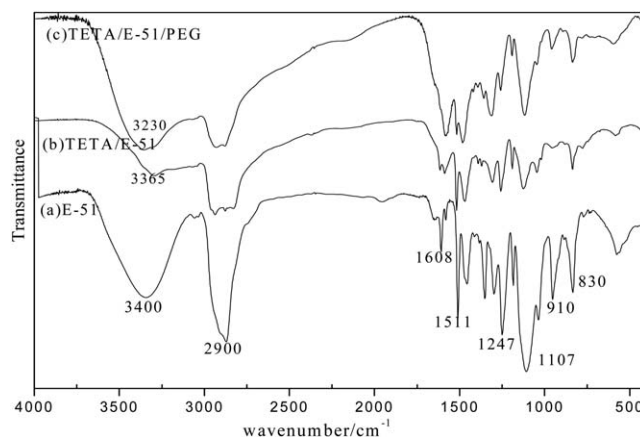


Figure 3. FTIR spectra of (a) E-51, (b) E-51/TETA adduct, and (c) product terminated by PEG.

Characterization

FTIR. The FTIR spectra of E-51, adduct of TETA/E-51, and products terminated by PEG400 are showed in Figure 3. The peaks in Figure 3(a) at wavenumber 1511 and 1608 cm^{-1} are attributed to the presence of stretching vibration of benzene ring, the peaks at wavenumber 2900, 1247, and 830 cm^{-1} are corresponding to the diglycidyl ether of bisphenol A,²⁰ and the intensity of these peaks in spectrum (b) are smaller than those in spectrum (a). The peak at around 910 cm^{-1} in spectrum (a) shows the vibration of the epoxy group²¹ of bisphenol A. There is slight characteristic peak of epoxy group in the spectra (b)

and (c) because of the additional reaction between epoxy group and $-\text{NH}_2$, which indicates that there is small amount of epoxy group remained.

As the hydroxyl associating, wavenumber of IR exhibits a red shift. The peak at around wavenumber 3230 cm^{-1} in spectrum (c) is assigned to $-\text{OH}$ and $-\text{NH}_2$ bands. So, it can be reasoned out that the reaction between PEG and polyamine happens.

¹H NMR Spectra. ¹H NMR spectra of E-51 is shown in Figure 4(a). Aromatic protons are shown at δ : 6.8–7.2 (1), protons on CH_3 of diglycidyl ether of bisphenol A at δ : 1.67 (2), protons of epoxy

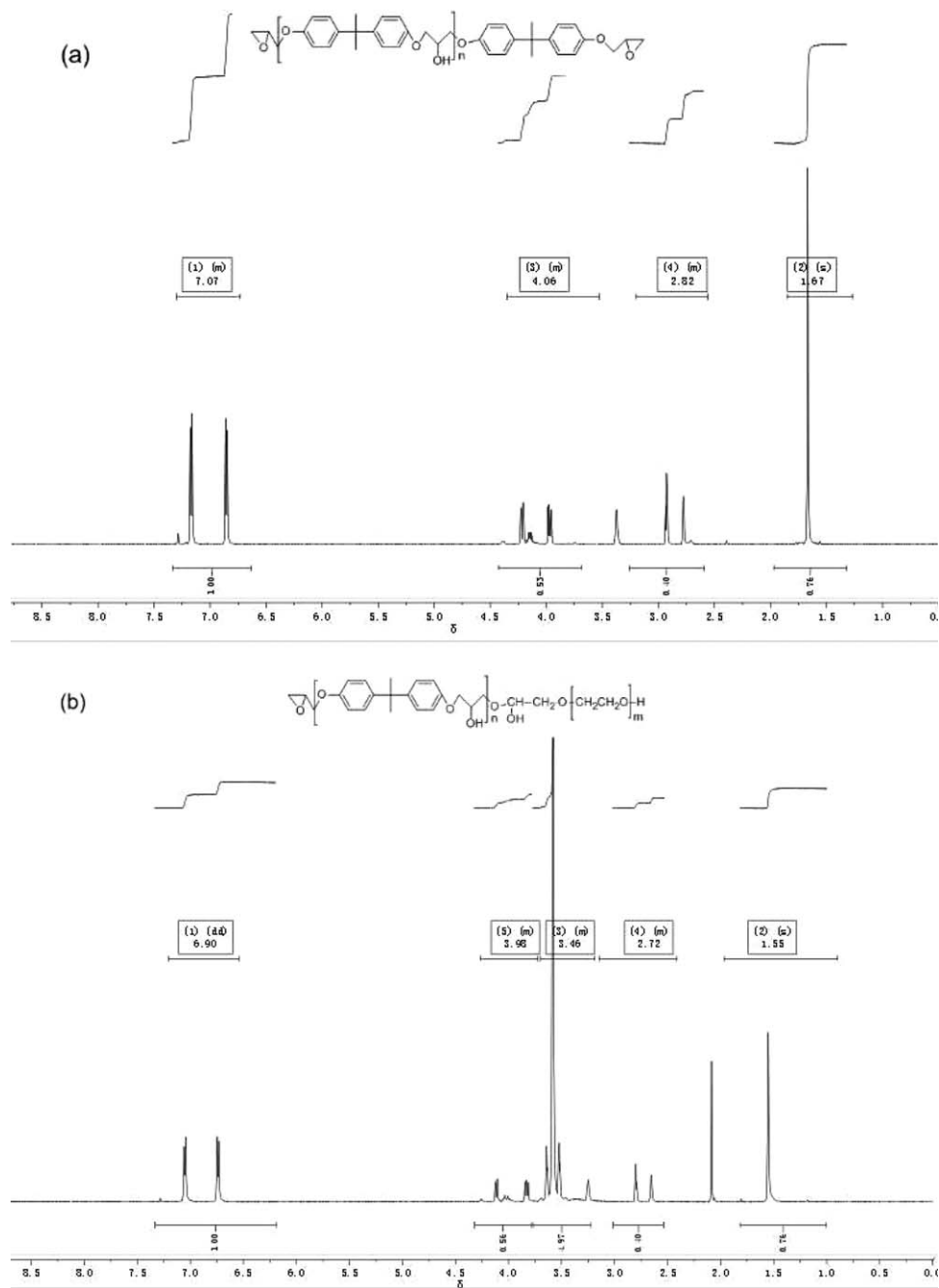


Figure 4. ¹H NMR spectrograms of (a) E-51, (b) E-51/PEG adduct, and (c) product terminated by TETA.

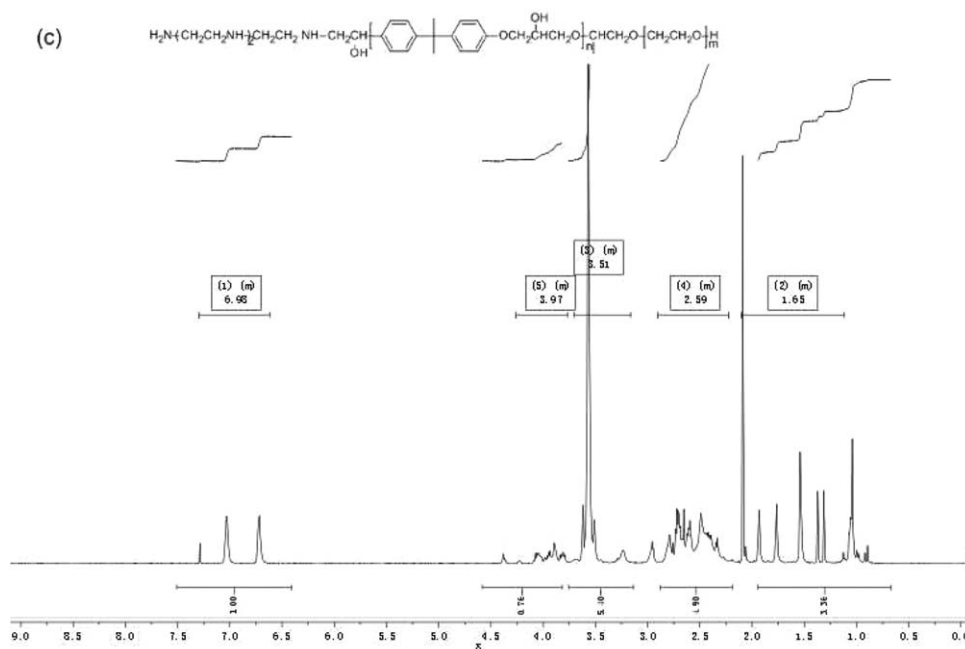


Figure 4. (Continued)

group at δ : 2.7–3.0 (3), protons of carbon which is combined with oxygen in diglycidyl ether of bisphenol A at δ : 3.9–4.3 (4).²² All the integral areas are normalized by integral area of aromatic protons, and the same normalization is conduct in Figure 4(b) and (c).

¹H NMR spectrogram of E-51/PEG adduct is shown in Figure 4(b). Aromatic protons can be seen at δ : 6.7–7.1 (1), protons of CH₃ of diglycidyl ether of bisphenol A at δ : 1.5 (2), protons of epoxy group at δ : 2.7–3.0 (3), and protons of carbon which is combined with oxygen in diglycidyl ether of bisphenol A at δ : 3.9–4.1 (4). Signals corresponding to the protons of carbon combined with oxygen in PEG present at δ : 3.2–3.8 (5). Since there still remains epoxy group and protons of carbon which is combined with oxygen in PEG in molecule, it can be deduced that only one epoxy group reaction happened for each E-51 molecular. According to Figure 1, it has also been proved that additional reaction happens between PEG and E-51.

¹H NMR spectra of the product terminated by TETA is shown in Figure 4(c). Aromatic protons can be seen at δ : 6.7–7.3 (1), protons of carbon which is combined with nitrogen at δ : 2.3–3 (2), protons of carbon which is combined with oxygen in PEG at δ : 3.2–3.8 (4), protons of carbon which is combined with oxygen in diglycidyl ether of bisphenol A at δ : 3.9–4.1 (5). The new signals at δ : 1–2 (3) can be assigned to the saturated aliphatic protons in TETA, which means that there are protons of carbon combined with nitrogen. Therefore, the structure of the product terminated by TETA in Figure 1 could be confirmed.

Surface Tension. Surface active groups, such as hydroxyl groups and amine groups, are favorable to improve the emulsifying properties of the water-borne curing agent, and the surface tension could affect the water solubility and emulsification performance of curing agent. Generally, surface tension of sample solutions decreases as the increasing of emulsifying property.²³

Figure 5 illustrates the influence of the concentration of synthesized emulsion-type curing agent on the surface tension. The emulsion-type curing agent shows a rapid decrease in surface tension compared with PEG 400 and the adduct of PEG400/E51. The critical micelle concentration (CMC) of the curing agent is less than 0.01 g/mL and the surface tension is 40–45 mN/m. The reduction degree of surface tension indicates the ability of curing agent to localize or accumulate at air-water interface. There are both hydrophilic and oleophilic segments in the molecular structure of synthesized curing agent. The hydrophilic segments induce the polymer to dissolve in water, and the oleophilic segments cover on the interface of the air/water or oil/water, which reduce the surface tension of the curing agent. When the mass concentration of the curing agent is

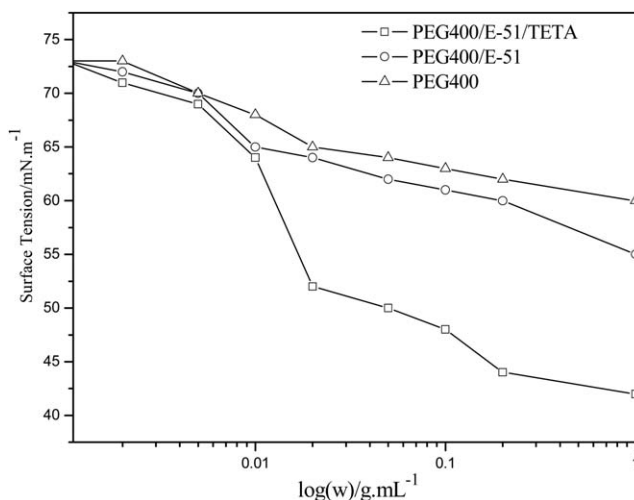


Figure 5. Plots of surface tension versus logarithm of concentration on synthesized emulsion-type curing agent.

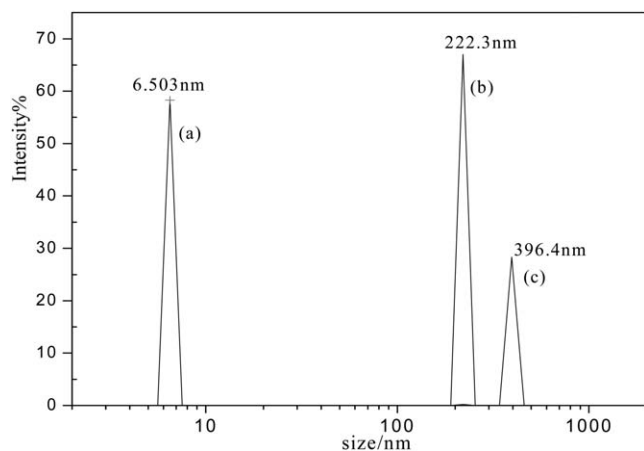


Figure 6. The particle size of the synthesized emulsifying-type curing agent (a), the emulsion liquid made by the epoxy resin with synthesized curing agent (b) and the emulsion liquid made by the epoxy resin with the commercial waterborne curing agent (c).

above the CMC, the surface tension of the aqueous solution shows a slight decline. The emulsion-type water-borne curing agent with an HLB value over than 10 is obtained.

Emulsifying and Curing Properties of Curing Agent

Emulsifying properties of the curing agent has a significant effect on the coating film during mixing process of the curing agent and the epoxy resin. The excellent emulsifying character of the curing agent leads to small particle size of the emulsion formed by the curing agent and epoxy resin, which improves the performance of the cured coating film.

Figure 6 shows the mean particle size distribution of the emulsified epoxy resin with different kinds of curing agent, determined by Zeta laser nanometer particle size analyzer. It can be seen that the emulsion particle diameter mixed by the epoxy resin with the commercial water-borne curing agent is 396.4 nm, and the emulsion particle diameter of the epoxy resin with the synthesized emulsifying-type curing agent under the optimal reaction condition is 222.3 nm. The segments in synthesized curing agent contain both hydrophilic amine and oleophilic epoxy group, thus the synthesized curing agent exhibits an emulsifying function. Therefore, the prepared emulsifiable water-borne

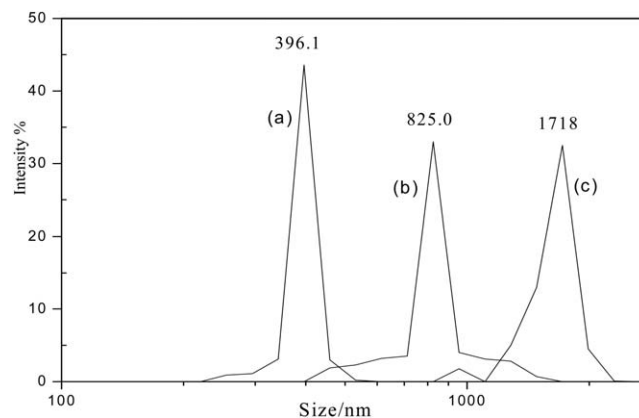


Figure 7. The change of the particle size of emulsion liquid with the curing time of (a) 1 h, (b) 2 h, and (c) 3 h.

curing agent in this study can emulsify epoxy resin well to give smaller particle size without any external emulsifiers.

The mean particle size of emulsion as a function of the curing time is illustrated in Figure 7. With the increasing of curing reaction time, the distribution of mean particle size tends to increase, and the particle size exhibits an irregular trend. It has been showed that curing agent has the active sites, where the cross-linking reaction occurs with increasing reaction time and it leads to a furthermore extension to the network structure.⁷ The water in network structure is gradually volatilized, and membrane structure and coating hardness are gradually reinforced.

The Mechanism of Cured Film Formation

Figure 8 (a,b) shows the surface morphology of cured films. It can be seen that there shows a uniformly dense layered structure on membrane surface, which indicates that the cross-linking reaction of curing agent and epoxy resin is completed. And the crystal particles are regularly arranged in the nanometer level [Figure 8(b)].

The volatile velocity of water from the emulsion system is the key factor of waterborne epoxy coating. From SEM photographs of the cured film, it can be deduced that the active centers of curing agent are orderly arranged and the cured film is formed spreading around the active centers of curing agent, which

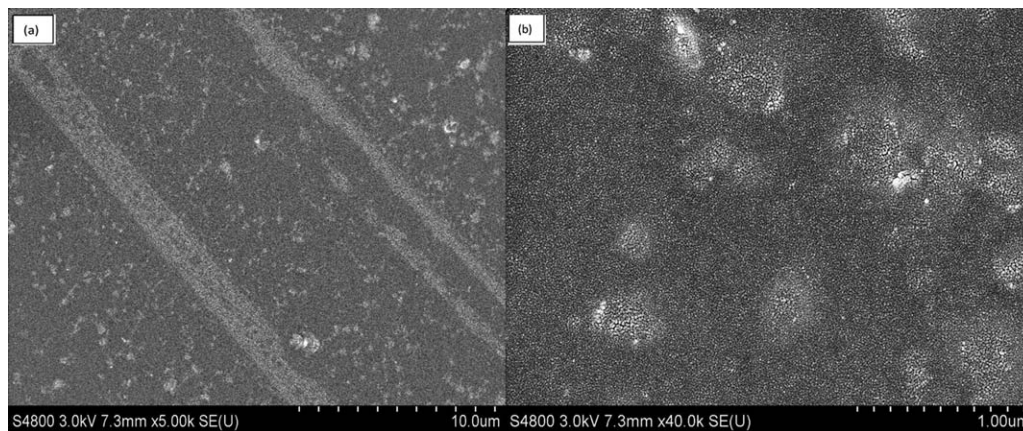


Figure 8. SEM images of the surface morphology of the cured film with magnification (a) 5000 \times and (b) 40,000 \times .

Table V. Performances of Self-Emulsified Water-borne Curing Agent

	Results
Appearance	Transparent yellow liquid
Viscosity (25°C/MPa-s)	3000-5000
Amine value (mg KOH/g)	280-320
Solidity (wt %)	60
Density (g/cm ³)	1.09
Diluents	Water

suggests that the cross-linking reaction of network structure takes place. However, a certain gap is also observed in the formed membrane structure during water evaporation process.

A reasonable molecular model of the cured film formed by the emulsion-type water-borne curing agent and epoxy resin is described as follows: the epoxy resin molecular locates in the center of the curing agent molecular. With the evaporation of water, the molecular of curing agent contacts with epoxy resin, which causes the reaction of chemical cross-linking. Curing agent molecules act as active centers and spread into the interior of epoxy resin particles for cross-linking. Finally, a dense film is formed.

CONCLUSIONS

An emulsion-type water-borne epoxy curing agent of nonionic type was synthesized by using TETA, liquid epoxy resin, and PEG400. The curing agent with good property of emulsifying liquid epoxy resin could be accomplished at 80°C for 5 h with the molar ratio of TETA, PEG400, and E-51 as 3.5 : 0.8 : 1, and the appropriate molar ratio of HAc to N-H was 5%. FTIR and ¹H NMR spectra analysis demonstrated the structure of the emulsion-type curing agent, and the surface tension showed a rapid decrease compared with PEG 400 and the adduct of PEG400/E51. The amine value of emulsifiable curing agent was about 300 mg KOH/g (Table V) and the emulsion mean particle size was around 220 nm with the curing agent prepared and epoxy resin at the mass ratio of 1 : 3. SEM photographs analysis suggested that a network film structure was formed after cross-linking reaction, and the film spread around the active center of the curing agent.

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