Study on Synthesis of Polyurethane-Epoxy Composite Emulsion

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ABSTRACT: The stable polyurethane-epoxy composite emulsion with the epoxy-amine oligomer (DEA-EP) and the epoxy resin oligomer has been prepared by step-growth polymerization and controlled crosslinking technique. The emulsion forming transparent films can be cured at room temperature with trimethylolpropane tris (1-ethyleneimine) propionate (TMPTA-AZ). The DEA-EP structure and its reaction with urethane prepolymers were proved by Fourier transform infrared spectra (FTIR). The studies on particle size, the particle size distribution, viscosity, and the films' transmittance (Tr) indicated that both trimethylol propane (TMP) and DEA-EP contributed to improving the resin blends' compatibility and reducing the viscosity. The epoxy resin content can increase up to 20.0 wt % (based on the total content of the polyurethane and epoxy resin) and the emulsion was still stable. The data from the tensile test experiments showed that with the epoxy content increasing, the tensile strength (σ_b) and Young's modulus were propor-tionately raised, but the elongation at break (ε_b) decreased. Tensile tests also revealed that introducing TMPTA-AZ as an outside-crosslinker can increase the tensile strength. By adding 0.3 wt % of TMPTA-AZ, the ε_b reduced from 429% to 371% and the σ_b increased from 4.4 to 13.73 MPa; by adding 1.8 wt % of TMPTA-AZ, ε_b of the film was 67% of ε_b of the film with 0.3 wt % of TMPTA-AZ, but its σ_b was 24.77 MPa and 180% of σ_b of the film with 0.3 wt % of TMPTA-AZ. The cured films possessed excellent water and toluene resistance: water uptake (48 h, 3.1%; degree of curing: 70%), toluene uptake (210 h, 8%. degree of curing: 70%). Better properties of the composite emulsion will confer it as a potential application in low volatile industrial coatings. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 451–459, 2010

Key words: composite emulsion; polyurethane; epoxy resin; mechanical properties

INTRODUCTION

Polyurethane dispersions (PUDs) are environmentally friendly materials with wide applications in coating, adhesive, ink, etc.[1] However, single PUDs still cannot meet the needs of the people because of poor solvent and water resistance. Some work has been carried out to resolve the problems, including grafting various acrylate monomers,[2] blending, and crosslinking.[3–5] The crosslinking structure of PUDs can be obtained by collecting raw materials with multifunctionalities, such as polyols, polyamine chain extending agents, and multi-isocyanate crosslinkers.[6] There are some crosslinking modification technology at ambient temperature of PUDs, such as crosslinking between carbonyl and hydrazide group,[7] crosslinking of Michael addition reaction,[8] crosslinking of isocyanate groups, and crosslinking between aziridinyl groups or their derivatives and carbonyl groups,[9] etc. Moreover, epoxy resin (EP) was also used as multifunctional polyols in the synthesis of PUDs.[10,11] Obviously, better water and solvent resistance could be obtained by introducing epoxy resin. However, because of the dispersion stability and the chemical structure of the epoxy resin, the crosslinking structure in the polyurethane-epoxy emulsion was often limited and the crosslinking density could not be enhanced further.

In this article, a novel method has been reported to prepare a stable polyurethane-epoxy composite emulsion with good properties. The combination of crosslinking and blending modification technology has been used to modify PUDs. First, a linear urethane prepolymer was prepared by using isophorone diisocyanate (IPDI), diol oligomers and dimethylol propionic acid (DMPA). Then the linear urethane prepolymer modified via introducing inner-crosslinkers trimethylolpropane (TMP) and the epoxy-amine oligomer (DEA-EP). DEA-EP was synthesized by the reaction of diethanolamine (DEA) and EP, and also used as a hydrophilic macromolecular chain extender. DEA-EP can introduce hydrophilic groups into the prepolymers; at the same

time, it can also increase the length of the polymer chain and can generate the soluble microgel. Microgels are defined as intramolecularly crosslinked macromolecules.[12] By crosslinking, the DEA-EP containing hydrophilic groups was grafted to polyurethane chain which was rich in carboxyl and tertiary amine groups. Thus, polyurethane and EP can be partly crosslinked and the hydrophility of latex particles would not vary; by blending, EP can be introduced into crosslinking-modified prepolymers and then embedded into the interior of the latex particles by the process of preparing polyurethane-epoxy composite emulsions (EPUs). Thus, some problems can be solved, such as high viscosity of the epoxy-modified polyurethane prepolymer solutions, difficult emulsified phase conversion, and emulsion instability.[11] Furthermore, the curing behavior at room temperature and film properties of the EPUs were studied by using trimethylolpropane tris (1-ethyleneimine) propionate (TMPTA-AZ) as an outside-crosslinker. The results showed that the composite emulsion will have a special significance for the application in low volatile industrial coatings.

EXPERIMENTAL

Materials

Dimethylol propionic acid (DMPA, Aldrich Chemical Co.) and trimethylol propane (TMP, Aldrich Chemical Co.) were dried at 100°C for 2 h in a drying oven; isophorone diisocyanate (IPDI), polyester diol (Mn = 2000, hydroxyl value 55 mg KOH/g) and polycarbonate diol (Mn = 2000, hydroxyl value 57 mg KOH/g) purchased from Japan Polyurethane Industry Co., were dried and degassed in a vacuum oven (80°C, 1.33 MPa) for 5 h before use; ethylenediamine (DEA), triethylamine (TEA), diethanolamine and butanone were purchased from Sinopharm chemical reagents Co., China; Bisphenol A epoxy resin (EP, Epoxy Value EV = 0.58–0.35; Mn = 370–500) from Yueyang Petrochemical Co., China; Trimethylolpropane tris (1-ethyleneimine) propionate (TMPTA-AZ) from Wuhan Qianglong New Chemical Material Company, China were used. Butanone and the solvents used in titration were dried over 4-Å molecular sieves before use.

Preparation of polyurethane-epoxy composite emulsion

Synthesis of DEA-EP

In a 250 mL three-necked flask equipped with a reflux condenser, stirrer and thermometer, EP, DEA and butanone were added first. After that, the mixture was heated to 60°C and stirred until the absorption peak of the epoxy groups (910 cm^{-1}) in the Fourier transform infrared spectra (FTIR) spec-

tra disappeared. The product was a colorless viscous liquid (See Fig. 1, Step I). The molecular structure was confirmed by FTIR spectrum (See Fig. 3, Nicolet FTIR 170SX spectrometer). The determination of the epoxy value was carried out by a potentiometric titration as described in the literature.[13] Epoxy Value (EV) can be calculated by the following equation:

$$EV(\text{mol/100g}) = C(V - V_0)/10W_1$$

where C was the concentration of HClO$_4$-HAc standard solution (mol/L), V_0 and V were the blank and sample consumption of HClO$_4$-HAc standard solution (mL) respectively, and W_1 was the weight of sample used (g).

Preparation of urethane prepolymer

In a 250 mL four-necked flask, equipped with a reflux condenser, stirrer, thermometer, and inlet of nitrogen gas, the diol oligomers and butanone were added and stirred for 1.0 h at 90°C. The reaction mixture was cooled down to 75°C and IPDI was added, the temperature of the reaction mixture was raised gradually up to 90°C within 1.0 h, and then DMPA was added, the polyaddtion reaction was continued for 2.0 h at 90°C. So the —COOH groups containing urethane prepolymer was obtained (See Fig. 1, Step II). The change in the —NCO value during the reaction was determined by a standard dibutylamine (n-DBA) back-titration method.[14] The —NCO value was calculated by the equation:

$$[-\text{NCO}](\%) = 4.2M(V_1 - V_2)/W_2$$

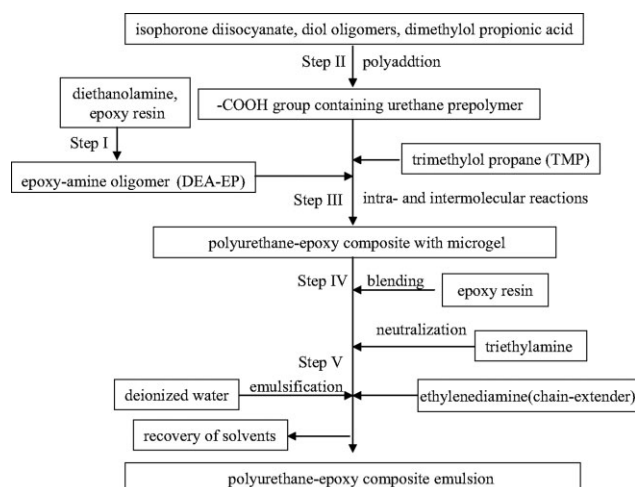where M was the concentration of HCl standard solution (mol/L), V_1 and V_2 were the blank and sample

Figure 1 Flow diagram of preparation of polyurethane-epoxy composite emulsion.

TABLE I
Formula of Polyurethane-Epoxy Composite Emulsions

Code number	$n_{\text{-NCO}}/n_{\text{OH}}$	TMP (wt %)	DEA-EP (wt %)	EP (wt %)	Epoxy content (%)
EPU-1	1.6	0.0	0.0	12.0	12.0
EPU-2	1.6	0.4	0.0	12.0	12.0
EPU-3	1.6	0.4	4.0	8.0	12.0
EPU-4	1.6	0.0	0.0	4.0	4.0
EPU-5	1.6	0.0	1.0	4.0	5.0
EPU-6	1.6	0.2	2.0	6.0	8.0
EPU-7	1.6	0.6	6.0	10.0	16.0
EPU-8	1.6	0.8	8.0	12.0	20.0
EPU-9	1.6	1.0	10.0	14.0	24.0

consumption of HCl standard solution (mL), respectively, and W_2 was the weight of sample used (g).

Preparation of polyurethane-epoxy composite with microgel

A certain amount of inner-crosslinker TMP was added and mixed with the product prepared in the preparation of urethane polymer section. The mixture was stirred for 40 min at 90°C. Then, a certain amount of DEA-EP prepared, as mentioned in synthesis of DEA-EP section, was added and reacted for 60 min at 90°C. The reaction can be proved by FTIR spectra (See Fig. 4, curve a-e). In this step, by intramolecular and intermolecular reactions, soluble microgel (See Fig. 6) can be formed, leading to preparing polyurethane-epoxy composite with microgel (See Fig. 1, Step III). The amount of TMP amd DEA-EP was shown in Table I.

Preparation of polyurethane-epoxy blends

According to Table I, EP was added into the polyurethane-epoxy composite with microgel. The mixture was stirred for 15 min at 60°C and a polymer blend was prepared (See Fig. 1, Step IV). The product was a colorless viscous liquid. The amount of polyurethane-epoxy blends were shown in Table I.

Emulsification and chain extension of polyurethane-epoxy composites

1. Neutralization: The reaction mixture was cooled down to 50°C and TEA was added to neutralize the free carboxyl groups. Butanone was used to adjust the viscosity.
2. Emulsification: At high speed shear condition, deionized water was added gradually to the reaction mixture to induce the phase inversion.
3. Chain extension: The neutralized prepolymer was chain-extended by the dropping of EDA at 40°C for 1 h, and the reaction continued until

the -NCO peak (2270 cm^{-1}) in the FTIR spectra had completely disappeared (See Fig. 6). Finally, ammonia was used to adjust the pH. The polyurethane-epoxy composite emulsion was filtrated by 200 mesh sieve filter.

Emulsion characterization

Viscosity

The viscosity of emulsion was measured by Brookfield viscometer (0.56 mm) at room temperature.

Particle size distribution

Particle sizes and particle size distributions of the composite emulsions were measured by a Zeta PALS particle size analyzer (Brookhaven, USA). The samples of emulsions were diluted with ion-exchanged water to adjust the solid content to 1 wt % and directly placed in the cell. The temperature of the cell was kept at around 25°C.

Solid contents of the composite emulsion

The method calculating the solid contents was described in the literature.[15]

Emulsion stability studies

1. Study on the freeze-thaw stability: the sealed samples were placed in the refrigerator to freeze for 18 h at −20°C, and then they were thawed for 6 h at the room temperature, later they were placed into the refrigerator, which was a cycle. The state changes of the samples (including the precipitation, stratification, crust, flocculation or the dramatic increase of viscosity) should be observed and the corresponding time interval should also be recorded.
2. Study on the shelf-life[16]: The shelf-life of the emulsions was investigated by the observation

of the coagulation or viscosity of the latexes for months at 50°C.

3. Study on pH stability[17]: The modified and unmodified emulsions prepared above were free-flowing liquids, translucent or visually opaque, similar to the conventional waterborne dispersions. The emulsions were diluted with water to the solid content of 10%, placed in beaker equipped with electromagnetic stirring, and given different pH by the standard HCl solution until the emulsion was completely precipitated.

Film formation and characterization

Film formation

The curing process and film properties of polyurethane-epoxy composite emulsion have been studied by using TMPTA-AZ as an outside-crosslinker (Fig. 2) with different contents. The content of TMPTA-AZ was indicated in Figure 11. Films were cast onto a tetra-fluoro-ethylene test panels and air-dried at room temperature for 7 days.

Measurement of degree of curing

The weighed films (30 mm × 30 mm) were immersed in tetrahydrofuran solvent and taken Soxhlet extraction for 15 h. The degree of curing can be determined by the formula.

$$\text{Degree of curing}(\%) = 100(W_3/W_4)$$

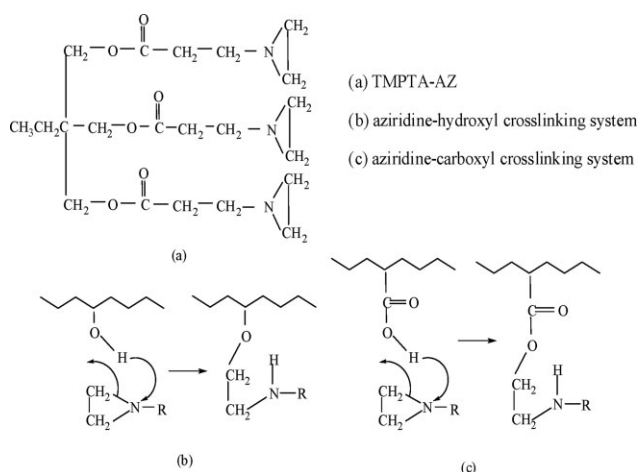W_3 is the weight of the dried film before extraction, and W_4 is the weight of the dried film after extraction.

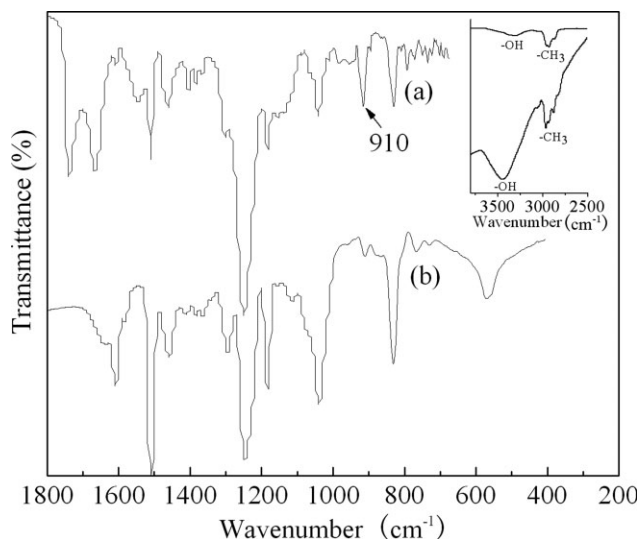**Figure 2** The outside-crosslinker TMPTA-AZ and its crosslinking reaction.

Figure 3 FTIR spectra of (a) epoxy resin; (b) DEA-EP.

Measurement of films' transmittance

Transmittance of film[18] was measured to judge compatibility of blends. The films' transmittance (Tr) was measured by UV spectrometer (Shimadzu UV-160, Japan) at $\lambda = 800$ nm. The thickness of film was around 120 μm. The light transmittance (Tr) values of the films at 800 nm were shown in Figure 9.

Measurement of mechanical properties

The mechanical properties of the film [100 × 10 × (0.05∼0.1) mm^3] were measured on an electronic tensile testing machine (CMT6503, Shenzhen SANS Test Machine Co.) according to ISO 6239-1986(E). Five tests of each EPU sample were taken and the mean value was calculated.

Swelling studies

The swell of the film in water was measured as follows: the weighed films (30 mm × 30 mm) were immersed in deionized water for 48 h at room temperature (25°C), and the percentage swelling was calculated by drying the surface water of the film and measuring the weight increase immediately. The toluene resistance of the film was measured according to the following procedure: A 10 cm × 10 cm film was dipped into toluene for 210 h, and the swelling ratio of the film was measured after weighing.

RESULTS AND DISCUSSION

FTIR of DEA-EP

From Figure 3, the absorption peak at 1250 cm^{-1} is because of the symmetric stretching vibration peaks
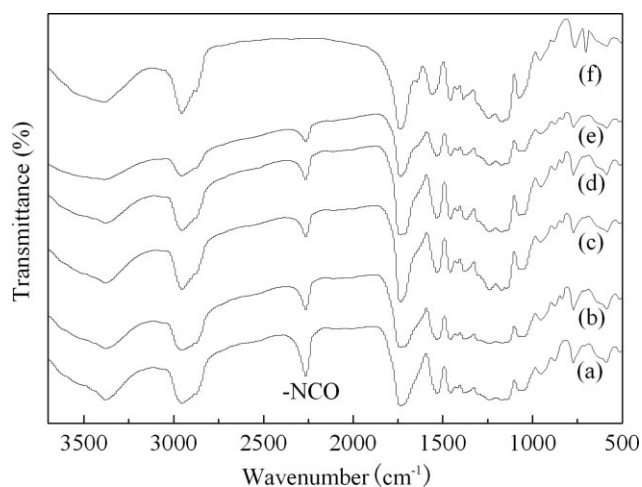
Figure 4 FTIR spectra taken for synthesis process of polyurethane-epoxy composite emulsion. DEA-EP introduced into urethane prepolymer after (a) 10 min; (b) 20 min (c) 40 min (d) 60 min (e) 90 min (f) after EDA expanded the chain in water phase. The samples of the dry films for FTIR analysis were prepared from the emulsion after the chain extension in aqueous phase. The sample was air-dried under a temperature of 35°C, then, the film was washed by acetone reflux.

Figure 5 Comparison of particle size and particle size distribution of EPU-1, EPU-2, and EPU-3. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the epoxy groups. The hydroxyl absorption peak is at 3413 cm^{-1}. The absorption peak at 910 cm^{-1} is attributed to the chain-end epoxy groups.[19] After epoxy groups reacted with DEA, hydroxyl absorption peak is clearly widened and stronger. The disappearance of the peak at 910 cm^{-1} proves the completion of the reaction between DEA and epoxy groups.

FTIR of polyurethane-epoxy composite emulsion at different reacting stages

From Figure 4, the absorption peak at 2280–2260 cm^{-1} is characteristic high-intensity peak for ─NCO group, and its position is not affected by conjugation effects,[20] so the changes in the peak shape can indicate reactive degree. The absorption peaks at 3300–3470 cm^{-1}, 1700–1735 cm^{-1}, and 1520–1550 cm^{-1} are corresponding to the amino carbamate groups, carbonyl, and ester groups.[21] With the reaction proceeding, the absorption peak at 2280–2260 cm^{-1} is decreasing gradually. After the chain extension in aqueous phase, the absorption peak at 2280–2260 cm^{-1} disappears, which indicated that ─NCO groups had reacted.

Characterization of particle size and distribution

From Figure 5 and Table II, the results showed that EPU-3 had the smallest average size and the best size distribution. It was indicated that the inner crosslinkers, TMP and DEA-EP, were conducive to improving compatibility of waterborne polyurethane
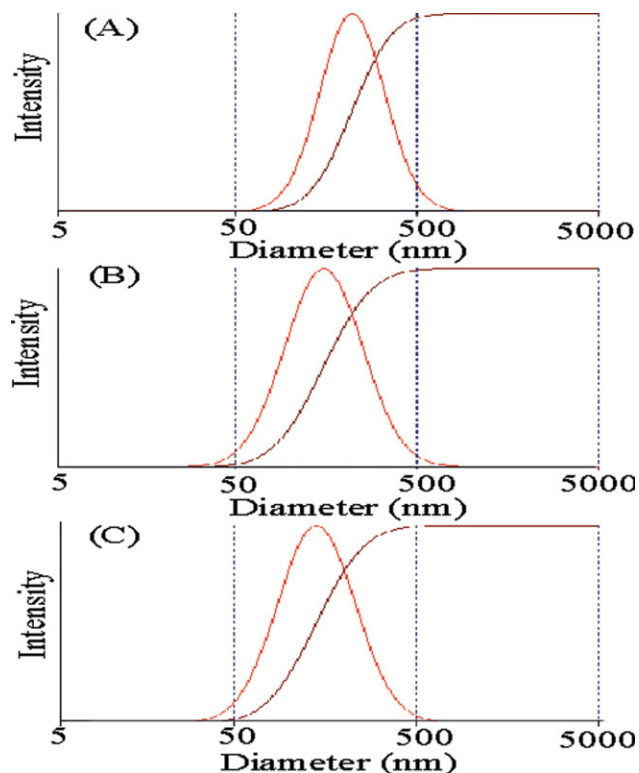
and epoxy resin. The main reactions in the synthesis process were shown in Figure 6. Theoretically, two possibilities (1: crosslinking, 2: chain extension) would happen. However, in this study, a controllable reaction was designed to ensure crosslinking reaction more competitive than chain extension reaction. Prepolymers with ─NCO and ─OH groups on the chains were prepared at the early stage of the polymerization. The functional degree of DEA-EP and the amount of prepolymers have different influences on the inner and inter coil environment, therefore, changes in these factors will inevitably change the ratio of intracoil to intercoil reactions. These factors are essential to controlling the crosslinking polymerization process and for synthesizing soluble crosslinking macromolecules with a limited molecular weight. The prepolymers in butanone solution

TABLE II
Particle Size and Polydispersity of EPU-1, EPU-2, and EPU-3

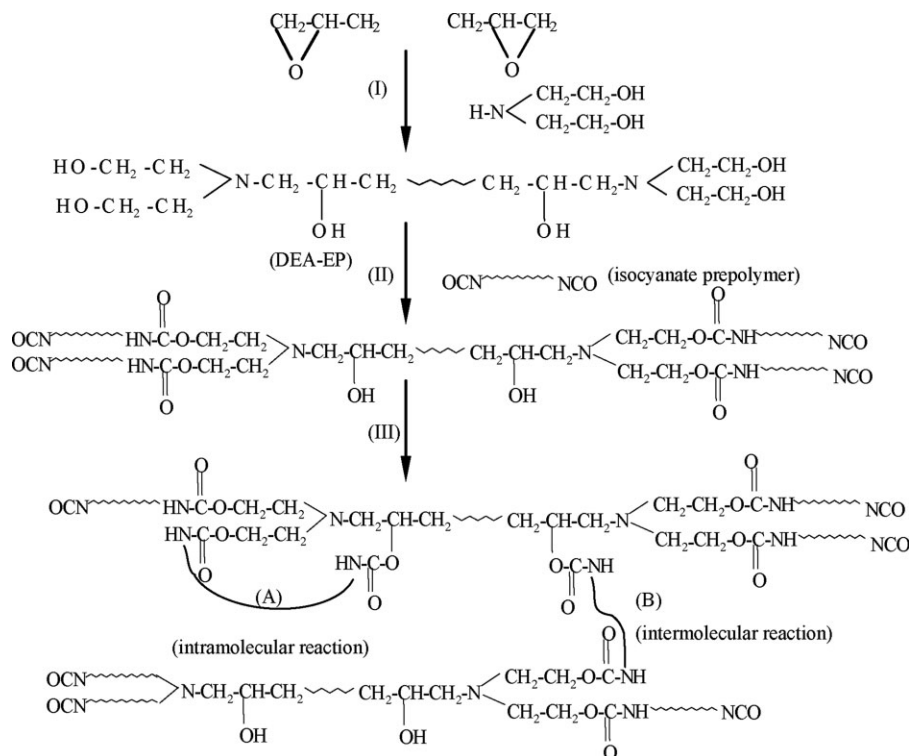| Sample	Particle size (nm)	Average particle size (nm)	Polydispersity
EPU-1	111.0–430.4	218.6	0.185
EPU-2	67.5–343.5	152.3	0.277
EPU-3	62.5–314.2	140.1	0.272

Figure 6 The schematic representation for the synthesis of microgel: intramolecular and intermolecular reactions.

were coiled with each other. —NCO groups were prone to react with —NHCOO— groups in the coils. Thus, intramolecular reactions dominated forming microgel. Hydrophobic domains in microgel, which comprising epoxy resin matrix (derived from DEA-EP) and hydrophobic segments of polyurethane chain, contributed to compatibility of the resin blends at the phase conversion stage as the infiltration of epoxy resin in the hydrophobic domains.

The effect of epoxy content on viscosity of the composite emulsions

The results from Figure 7 showed that without the inner-crosslinkers TMP and DEA-EP, the emulsion viscosity significantly increased with the increase of the epoxy resin content. The viscosity exceeded 300 mPa·s when the epoxy resin content was 4.0 wt %. However, by introducing 1.0 wt % of DEA-EP, the viscosity decreased from 330 mPa·s to 118 mPa·s, and by introducing 0.2 wt % of TMP, the viscosity can be as low as 92 mPa·s, which indicated that TMP and DEA-EP both contributed to improving the resin blends compatibility and reduced the viscosity. DEA-EP made the branched prepolymers formation of microgel in the emulsion particles. TMP was used to make the linear urethane prepolymers into ramose ones. The ramose prepolymers in solvent had lower viscosity and frizzier coil than lin-

ear ones, which was more convenient for formation of microgel that was benefit to compatible blends and stable emulsion with low viscosity. When the epoxy content was 24.0 wt %, the viscosity was 310 mPa·s, nearly half of the hybrid emulsion without TMP and DEA-EP (680 mPa·s). Therefore, without TMP, microgel would be difficult to synthesize and emulsion would be unstable as the epoxy content was progressively increased.
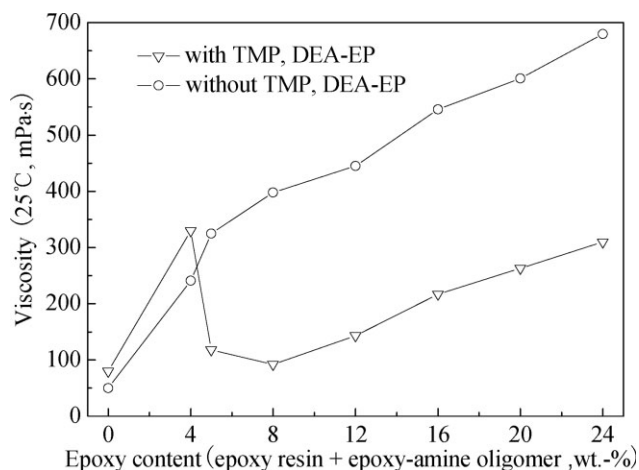

Figure 7 Effect of epoxy resin content on viscosity of the composite emulsions.

TABLE III
Effect of TMP, DEA-EP, and EP on Properties of Polyurethane-Epoxy
Composite Emulsion

Code number	Appearance of the emulsion	Solid content (%)	Freeze–thaw stability	Appropriate pH value span	Shelf-life (month)
EPU-1	Milky	33 ± 2	1 cycles	7.5–8.5	1
EPU-2	Milky	33 ± 2	3 cycles	7.5–9.5	2
EPU-3	Bluish and translucent	33 ± 2	6 cycles	7.5–10.5	>6
EPU-4	Milky and translucent	33 ± 2	5 cycles	7.5–8.5	3
EPU-5	Bluish and translucent	33 ± 2	6 cycles	7.5–10.5	6
EPU-6	Bluish and translucent	33 ± 2	6 cycles	7.5–10.5	>6
EPU-7	Bluish and translucent	33 ± 2	6 cycles	7.5–10.5	>6
EPU-8	Bluish and translucent	33 ± 2	6 cycles	7.5–10.5	>6
EPU-9	Milky and translucent	33 ± 2	5 cycles	7.5–10.5	5

The effect of TMP, DEA-EP, and EP on stability of polyurethane-epoxy composite emulsion

As shown in Table III, the sample EPU-1 without TMP and DEA-EP was milky and had only one month shelf-life, but the sample EPU-2 with 0.4 wt % of TMP was more stable than EPU-1, which showed that TMP contributed to the emulsion stability. There were 12.0 wt % of epoxy resin in the samples EPU-1, EPU-2, and EPU-3, respectively, but the sample EPU-3 containing 4.0 wt % of DEA-EP has been stable more than six months. Moreover, the range of pH for stabilizing EPU-3 was 7.5–10.5 and wider than that of EPU-1 and EPU-2, which displayed that both TMP and DEA-EP played an important role in contribution to the emulsion stability.

The shelf-life of waterborne dispersions is a very important characteristic, which determines their safe storage period. The result reported in Table III revealed that the composite emulsion EPU-3, EPU-5, EPU-6, EPU-7, and EPU-8 with appropriate content of inner-crosslinker and epoxy resin showed very good performance in terms of shelf-life. However, the shelf-life of EPU-9 was 5 months, which showed that 24.0 wt % of epoxy content was excessive, but 20.0 wt % of epoxy content was pretty good.

Epoxy resin is hydrophobic and poorly compatible with linear polyurethane. If epoxy resin is added into polyurethane emulsion, the emulsion will destabilize. In this study, TMP and DEA-EP were designed to confer emulsion stability as introduction of epoxy resin into the emulsion. TMP was a useful curing agent with multifunctional —OH groups, reacting with —NCO groups of urethane prepolymers, and therefore to make linear urethane prepolymers into ramose ones. The ramose urethane prepolymers in butanone solution were coiled with each other, facilitating the controllable crosslinking reaction to produce microgel with epoxy resin matrix. Thus, the added epoxy resin into prepolymers solution would be compatible with microgel. But exces-

sive amount of epoxy resin cannot be accommodated in microgel. The result showed that 24.0 wt % of epoxy resin was excessive.

Compatibility of waterborne polyurethane and epoxy resin

From Figure 8, Tr value of the blend films with 4.0 wt % of EP and without TMP and DEA-EP reached the minimum value. This indicated the poor compatibility of the linear polyurethane and the epoxy resin. Tr value of the film with 5.0 wt % of the epoxy, 0 wt % of TMP and 1.0 wt % of DEA-EP increased significantly, which indicated that the introduction of DEA-EP bettered the compatibility of the resin blends. The Tr value hit the highest value 88.3% when the film contained 6.0 wt % of epoxy resin, 0.2 wt % of TMP and 2.0 wt % of DEA-EP, which showed best compatibility of the blends. With epoxy content increasing, the Tr value decreased slowly. However, the Tr values of the blend films were lower than that of pure waterborne polyurethane film, which indicated that a certain degree of phase separation existed between the polyurethane and the epoxy resin.
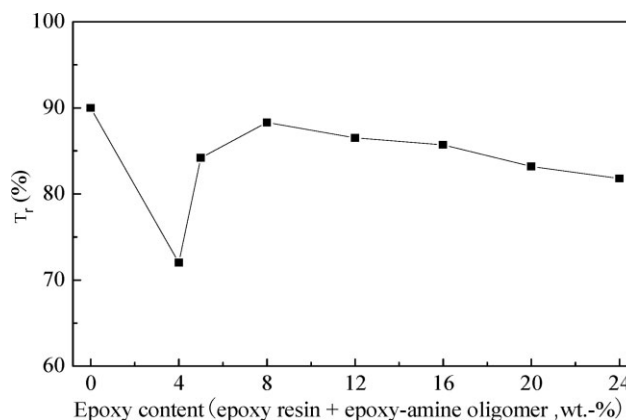

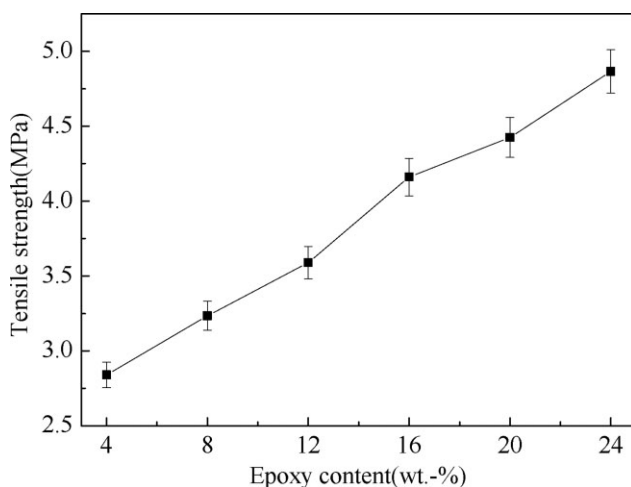**Figure 8** The light transmittance (Tr) values of the films with different epoxy contents.

Figure 9 The tensile stress-strain curves of composite emulsions films with different epoxy contents at room temperature) (25°C) without outside-crosslinker. The epoxy contents were indicated in Figure 9.

Evaluation of film characteristics: tensile tests

The results shown in Figure 9 revealed the effects of epoxy contents on tensile strength (σ_b), and elongation at break (ε_b) of the films without outside-crosslinker. The film with 4 wt % of epoxy content had the best ε_b (715%) and the lowest tensile strength ($\sigma_b = 2.84$ MPa). The elongation at break of the film with 24 wt % of epoxy content was 333%, and its σ_b was 4.83 MPa, which indicated that with the epoxy content increasing, the tensile strength and Young's modulus were proportionately increased, but the elongations at break decreased. However, the mechanical properties of the films without outside-crosslinker were expected to be improved further.

The results shown in Figure 10 revealed that introducing TMPTA-AZ improved the tensile strength. With 0.3 wt % of TMPTA-AZ added, the elongation at break decreased from 429% to 371%, the σ_b increased from 4.4 MPa to 13.73 MPa, and the Young's modulus also significantly increased. With 1.8 wt % of TMPTA-AZ, ε_b of the film was 249% and 67% of ε_b of the film with 0.3 wt % of TMPTA-AZ. However, its σ_b was 24.77 MPa and 180% of σ_b of the film with 0.3 wt % of TMPTA-AZ.

Evaluation of film characteristics: water uptake and chemical resistance

From Figure 11, with the TMPTA-AZ content increasing, the degree of curing increased and the water absorption decreased. The films without TMPTA-AZ had the lowest degree of curing (6%) and the highest water uptake (13.2%). However, by adding 0.3 wt % of TMPTA-AZ, the degree of curing was 11% and nearly two times higher than that of
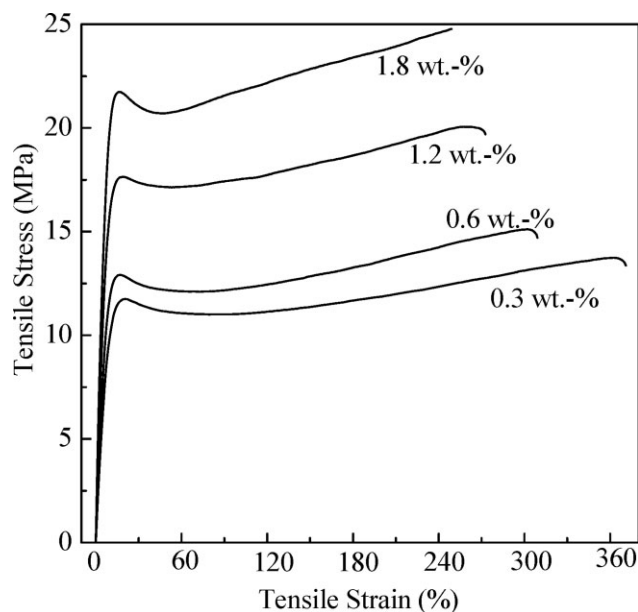
Figure 10 Typical stress vs strain curves of films cured by TMPTA-AZ at room temperature (25°C). The films were obtained from emulsions with 20.0 wt % of epoxy content. The TMPTA-AZ contents were indicated in Figure 10.

the film without TMPTA-AZ, and the water uptake decreased 29%. By adding 1.8 wt % of TMPTA-AZ, the degree of curing was 70% and the water uptake was 3.1%.

The results in Figure 12 indicated that the toluene uptake decreased as the degree of curing increased. When the degree of curing was around 70%, the toluene uptake (210 h) was below 8%. After 8 h the films were immersed in toluene, the absorption rate slowed down. During the process of curing and film formation, the pendent acid groups present in polyurethane backbones can react with ethylene imine groups and epoxy groups, which can consume
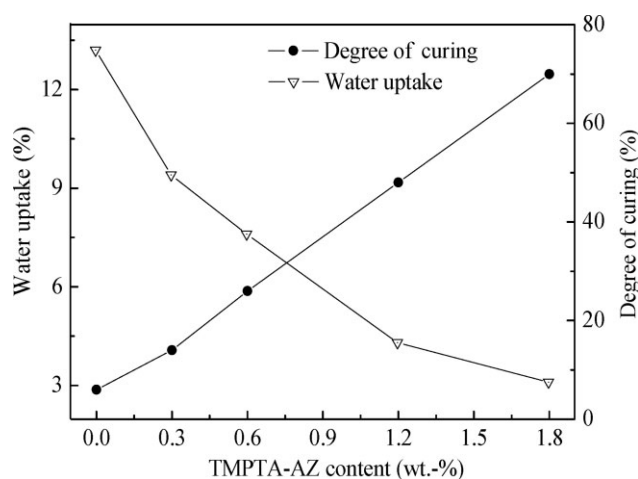

Figure 11 Effect of TMPTA-AZ content on degree of curing (%) and water absorption (%) of films.
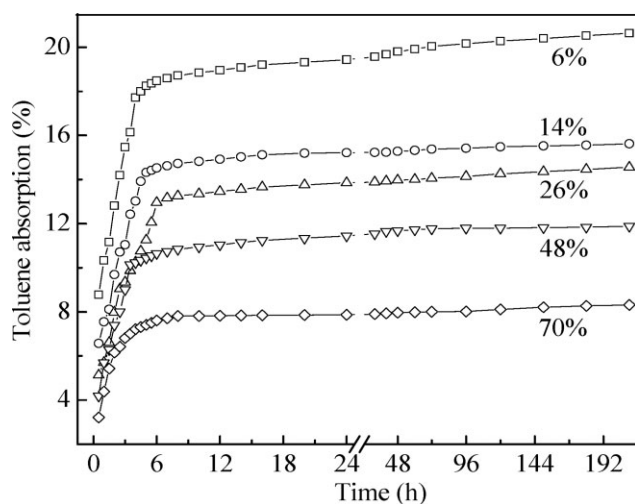
Figure 12 Variation of toluene uptake of film samples on time at room temperature (25°C). The degrees of crosslinking are indicated. Solid lines served to guide the eye.

hydrophilic groups. Moreover, TMPTA-AZ made the films form denser crosslinked network, which contributed to decreasing the toluene absorption. Thus, the solvent-resistance of the films has been greatly improved.

CONCLUSIONS

1. The stable polyurethane-epoxy composite emulsions with microgel have been prepared by step-growth polymerization and crosslinking techniques. The combination of crosslinking and blending modification technology has been used to modify waterborne polyurethane dispersions. The studies on particle size, the particle size distribution, viscosity, and the films' transmittance (Tr) indicated that TMP and DEA-EP both contributed to improving the resin blends compatibility and reducing the viscosity. The epoxy resin content can reach 20.0 wt % (based on the total content of the polyurethane and epoxy resin) and the emulsion was still stable.
2. The emulsion forming transparent films can be cured at room temperature with trimethylolpropane tris (3-propylene imine) propionate (TMPTA-AZ). The results from the tensile test experiments gave clear evidence that with the epoxy content increasing, the tensile strength

(σ_b) and Young's modulus was proportionately increased, but the elongation at break (ε_b) was reduced. Tensile tests revealed that introducing TMPTA-AZ as an outside-crosslinker also improved the tensile strength. With 0.3 wt % of TMPTA-AZ added, the elongation at break reduced from 429% to 371%, the tensile strength increased from 4.4 MPa to 13.73 MPa; With 1.8 wt % of TMPTA-AZ added, ε_b of the film was 67% of ε_b of the film with 0.3 wt % of TMPTA-AZ, but its σ_b was 24.77 MPa and 180% of σ_b of the film with 0.3 wt % of TMPTA-AZ. The cured films possessed excellent water and toluene resistance: water uptake (48 h, 3.1%; 70% degree of curing), toluene uptake (210 h, 8%; 70% degree of curing). The results expect that the composite emulsion will have wide applications in low volatile coatings.

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