

# Modification of Aqueous Acrylic–Polyurethane via Epoxy Resin Postcrosslinking

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**ABSTRACT:** An epoxy resin (E-51)-modified acrylic–polyurethane emulsion with triethylenetetramine (TETA) serving as the postcrosslinking agent was synthesized. The curing reaction between E-51 and the curing agent TETA during the film-forming course was monitored and identified by an infrared spectrophotometer. The stabilities of the single-pack emulsion during the polymerization course as well as the storage stage were investigated. The effect of the epoxy resin was studied in terms of the dispersion size of the emulsion, the mechanical properties, as well as the swell in

water and toluene of the cast film. The emulsion was shown to be stable when the epoxy content was below 20% based on the mass of the polyacrylate in the system. The tensile strength and the modulus and the water and toluene resistance were enhanced with increase of the epoxy resin. In contrast, the elongation at break was decreased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 470–475, 2003

**Key words:** polyurethanes; modification; crosslinking; films

## INTRODUCTION

Solvent-based polyurethanes (PUs) are restricted in many applications due to environmental regulations, economical concerns, and safety considerations. As a replacement, waterborne PUs are environmentally friendly materials that contain significantly reduced volatile organic compounds (VOCs) and, therefore, play an increasingly more important role in many application areas previously serviced only by solvent-based analogs, especially as coatings, adhesives, primers, pigment pastes, textile dyes, and paint additives.<sup>1–9</sup> Typically, waterborne PUs are prepared in the form of ionomers which contain pendant acid or tertiary nitrogen groups. The potential ionic groups are neutralized or quarternized to form salts<sup>10,11</sup> as the hydrophilic nature of the ionic groups inevitably provides the waterborne PUs with poor solvent and water resistance.

Many works have been carried out to resolve these problems;<sup>12–17</sup> the most widely used method is the posttreatment of waterborne PUs with the grafting of various acrylate monomers.<sup>14–16</sup> In the process, the hydrophobic unsaturated monomers (such as hydroxyethyl acrylate) are first grafted onto the PU backbone. Grafting copolymerization was then accomplished with further added acrylate monomers in an

aqueous media. Obviously, the better water resistance and solvent resistance could be obtained due to the introduction of polyacrylate. However, due to the dispersion stability and the chemical structure of the acrylate monomer, the crosslinking structure in the acrylic–PU emulsion is limited and the crosslinking density could not be enhanced further. Thus, the water resistance and some other mechanical properties are still lower than those of conventional solvent-based PUs.

A modified method for acrylic–PU emulsion using epoxy resin was explored in this article. The epoxy resin was introduced into the interior of the latex during the preparation of the acrylic–PU emulsion. After the polymerization, triethylenetetramine was dispersed into the aqueous medium as a latent epoxy curing agent. During the film-forming course, with the volatilization of the water and the cracking of the latex, the epoxy resin will encounter and react with the triethylenetetramine; thus, the crosslinking density is enhanced subsequently. The curing reaction during the film-forming course was monitored and verified by an infrared spectrometer. The emulsion stability, dispersion size, mechanical properties, as well as water and toluene resistance of the cast films were also investigated.

## EXPERIMENTAL

### Materials

A polyether diol with a molecular weight of 1000 (N210) was distilled at reduced pressure. Dimethylol propionic acid (DMPA) was dried at 110°C for 2 h

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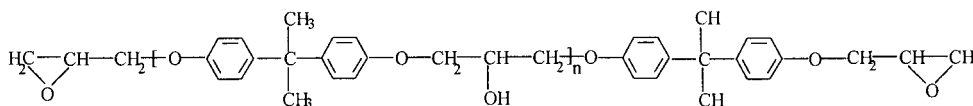


Figure 1 Molecule structure of E-51 resin (molecule weight of E-51 is 380).

under a high vacuum. Dimethylformamide (DMF) and triethylamine (TEA) (extrapure grades) were dried over 4Å molecular sieves. 2-Hydroxyethyl acrylate (HEA), methyl methacrylate (MMA), and butyl acrylate (BA) were purified by fractional distillation and dried *in vacuo*. Triethylenetetramine (TETA) was distilled before use. E-51 (diglycidyl ether of bisphenol-A type epoxy resin, 0.513 epoxide equivalent/100 g resin, molecule structure as shown in Fig. 1), extrapure-grade isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), and potassium persulfate (KPS) were used as received.

### Synthesis

A 500-mL four-necked round-bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, and a condenser with a CaCl<sub>2</sub> drying tube was used as a reactor. The reaction was carried out in a constant temperature oil bath. N210, DMPA, IPDI, and DBTDL (0.04 wt % based on base PU) were put into the flask. At the same time, some NMP and DMF were added as the solvent. The mixture was stirred and reacted at 85°C for 3 h to obtain the NCO-terminated prepolymer. The prepolymer was then cooled to 70°C. TEA and HEA were then added and reacted further until the NCO content reached zero as evidenced by the disappearance of the IR peak of NCO (2270 cm<sup>-1</sup>). After the hydrophilic PU was obtained, E-51 was added and stirred homogeneously. With vigorous agitation, water was added and a PU dispersion with pendent anions (—COO<sup>-</sup>) was then obtained after the removal of DMF under a vacuum.

At 40°C, the starting materials, including the monomers (1/4 mixed monomers of MMA and BA) and deionized water were added to the prepared PU dispersion and stirred for 0.5 h. The dispersion was heated to 75°C; meanwhile, the first portion of KPS (0.2 wt % based on total unsaturated monomers) was added and the polymerization was carried out for 1 h; then, the other portion of KPS (0.3 wt % based on total unsaturated monomers) and the residue of 3/4 mixed monomers were fed from two funnels simultaneously dropwise for 2 h. After the total addition, the reaction mixture was heated for an additional 1 h for complete conversion. While stirring, the temperature was lowered to 30°C and TETA was added. In this study, the solid content of PU and polyacrylate in the whole emulsion was equally controlled at 13%. The use epoxy resin (E-51) was changed, but the dosage of TETA

was fixed at a rate of 1.2 (the equivalent ratio of the active hydrogen of TETA and the epoxy group of E-51 resin) throughout the experiment. These prepared emulsions were stored in a closed container for testing. See Table I for the monomer compositions of the Acrylate-PU Emulsion.

### Fourier transform infrared spectra

The IR spectra of the film were recorded with an FTIR Nicolet 5DX spectrometer at a resolution of 2 cm<sup>-1</sup>. Two different samples of the dry films for infrared analysis were prepared from the emulsion. One sample was air-dried from the emulsion without adding TETA under a temperature of 35°C; the other one was air-dried at 35°C from the emulsion with TETA added and then dried at 95°C for 3 h.

### Measurement of mechanical properties

Films were cast and air-dried from these prepared emulsions under a temperature of 35°C and then dried at 95°C for 3 h. The resulting films were then heated overnight in an oven at 60°C under 2–3 mmHg.

The mechanical properties of the film [100 × 10 × (0.05–0.1) mm<sup>3</sup>] were measured on an universal testing machine (CMT6503, Shenzhen SANS Test Machine Co., Ltd.) according to ISO6239-1986(E) to obtain the tensile strength, modulus, and ultimate elongation. Five tests of each PU sample were taken and the mean values were selected.

### Stability studies

The coagulum content of the polymerization course preparation was evaluated. After the emulsion polymerization, the coagulation was filtrated immediately and dried to a constant weight:

$$\% \text{ Coagulation} = 100 W_c / W_s$$

TABLE I  
Monomer Compositions of the Acrylate-PU  
Emulsion (× 10<sup>3</sup> mol/1 g Emulsion)

N210	IPDI	DMPA	HEA	MMA	BA
5.56	21.26	13.56	4.41	73.62	46.03

All the dates were the mol numbers (× 10<sup>3</sup>) in 1 g emulsion (exception the use of epoxy resin).

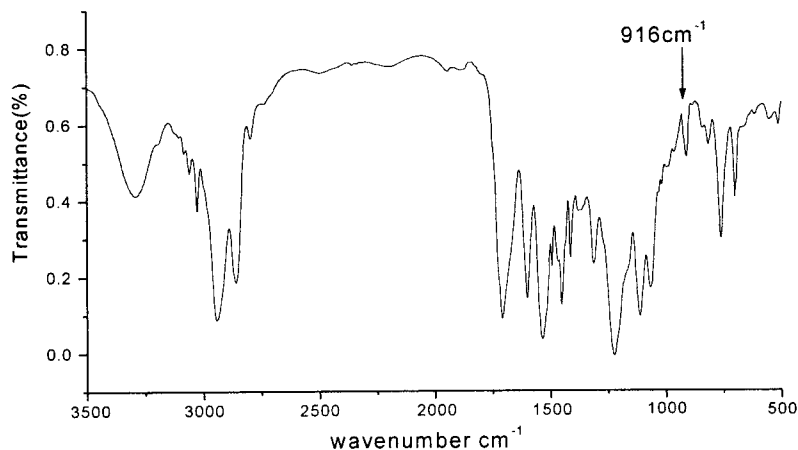


Figure 2 IR spectra of the film dried from the emulsion without adding TETA.

where  $W_c$  is the weight of the coagulation and the  $W_s$  is the total solid of the emulsion.

The storage stability of the prepared emulsion was evaluated as follows: The emulsion was placed in a sealed weighing bottle and stored at  $40 \pm 1^\circ\text{C}$ . The changes of the sample's state (including the precipitation or the dramatic increasing of viscosity) were observed and the corresponding time interval was recorded.

#### Swelling studies

The swell of the film in water was measured as follows: The weighed films were immersed in deionized water for 48 h at room temperature, and the percentage swelling was calculated by drying the surface water of the film and measuring the weight increase.

The toluene resistance of the film was measured according to the following procedure: A  $10 \times 10\text{-cm}^2$  film was dipped into toluene for 24 h, and the swelling ratio of the film was measured after weighing:

$$\% \text{ Swelling} = 100(W - W_0)/W_0$$

$W_0$  is the weight of the dried film and  $W$  is the weight of the film at swelling.

#### Particle-size measurements

The particle size of the emulsion was measured by light scattering using a Malvern Autosizer. The samples were diluted to the required concentration with distilled water before measurement.

## RESULTS AND DISCUSSION

#### Synthesis

Generally, the epoxy resin is not being applied as a single pack due to the high reactive activity between the epoxy group and the active hydrogen atom in the curing agent (e.g., the compound contains amino groups). Therefore, in the case using epoxy resin as

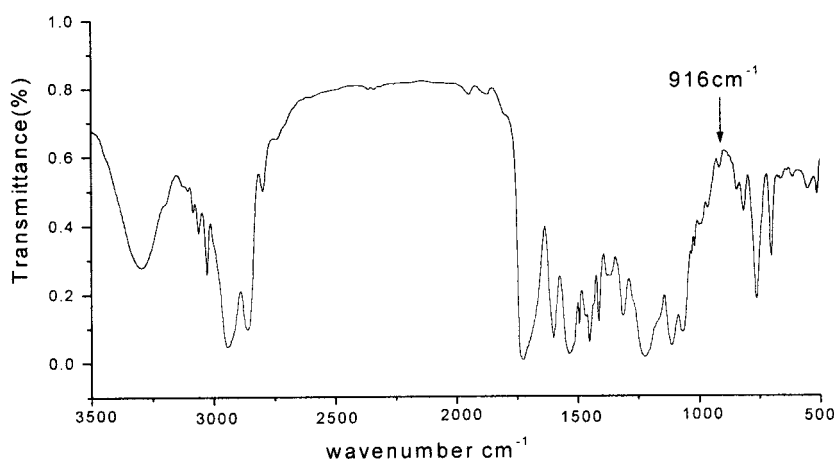
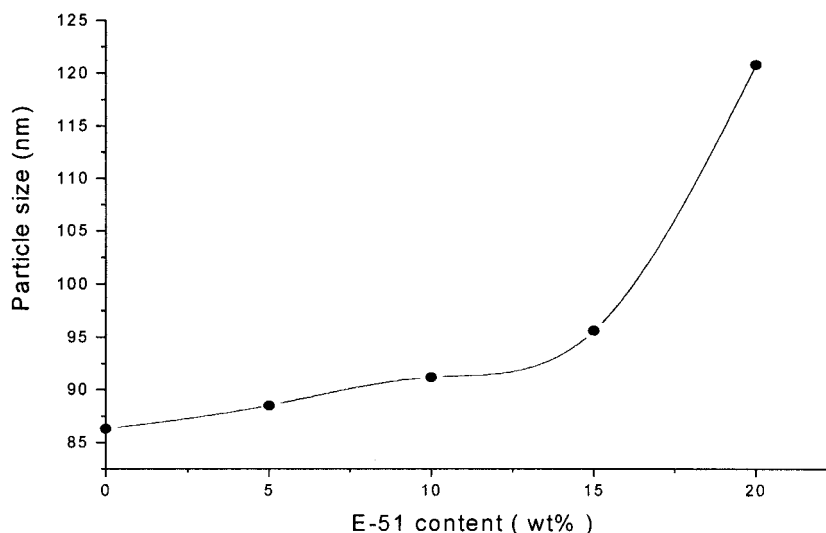


Figure 3 IR spectra of the film dried from the emulsion with TETA added.



**Figure 4** Particle size as function of weight percent of epoxy resin content (based on the total solid of the polyacrylate and E-51).

well the curing agent in a single pack to modify the acrylic-PU emulsion, the latex's conformation should be designed. The synthetic route is the decisive factor for the successful achievement of a stable and homogeneous emulsion.

Typically, the aqueous PU dispersion was prepared by a PU prepolymer process, in which the isocyanate component was in excess and the residual NCO group was attached at the end of the prepolymer molecular chain. After the neutralization, the NCO groups would be further reacted through a chain-extension process in the aqueous phase, and many amino group would inevitably come into being during the chain-extension course.<sup>17</sup> Thus, the epoxy resin would be cured by the amino groups that led to a more reticular structure occurring in the PU dispersion. These would affect the following emulsion polymerization and make the polymerization course unstable. To synthesize the epoxy-modified acrylic-PU emulsion, in this article, excess HEA was introduced to consume the entire residue NCO group of the PU prepolymer<sup>15,16,18</sup> by monitoring with IR. As a result, neither gel formation nor enhanced viscosity was encountered during the preparation of the PU dispersion. During the course of the emulsion copolymerization of the unsat-

urated acrylate monomer, another novel design was used to enhance the emulsion stability. Part of the monomer was first added into the aqueous PU dispersion and a preemulsion course proceeded. With stirring, the hydrophobic monomer moved into the PU particles and the radical initiator was added to start the reaction. After a certain reaction period, the remaining monomer was added into the reactor by feed addition. Through the above synthetic process, the epoxy resin was inserted into the core of latex droplets and capsulated tightly by the polyacrylate as well as by the hydrophobic chain of PU. Thus, the epoxy resin was protected against the attack of the TETA, which was water-soluble and stayed in the aqueous phase.

#### Identification of reactions

The curing reactions between the epoxy groups and the latent curing agent, TETA, during the film-forming course were identified by IR spectroscopy (see Figs. 2 and 3). As a comparison, the examined films were prepared from the emulsions with or without the added curing agent TETA. To certify the curing reaction, the characterized absorption bands of the epoxy group at  $916\text{ cm}^{-1}$  were generally used. The absorp-

**TABLE II**  
Properties of the Epoxy-modified Acrylic-PU Emulsion

Sample	E-51 <sup>a</sup> (wt %)	Coagulation (wt %)	Storage (day)	Water swell (wt %)	Toluene swell (wt %)
S <sub>0</sub>	0	0.21	30	12.4	18.4
S <sub>1</sub>	5	0.27	30	9.7	15.1
S <sub>2</sub>	10	0.46	30	6.8	12.9
S <sub>3</sub>	15	0.81	5	5.3	10.2
S <sub>4</sub>	20	2.92	2	5.9	9.3

<sup>a</sup> Epoxy resin content was based on the total solid of the polyacrylate and E-51.

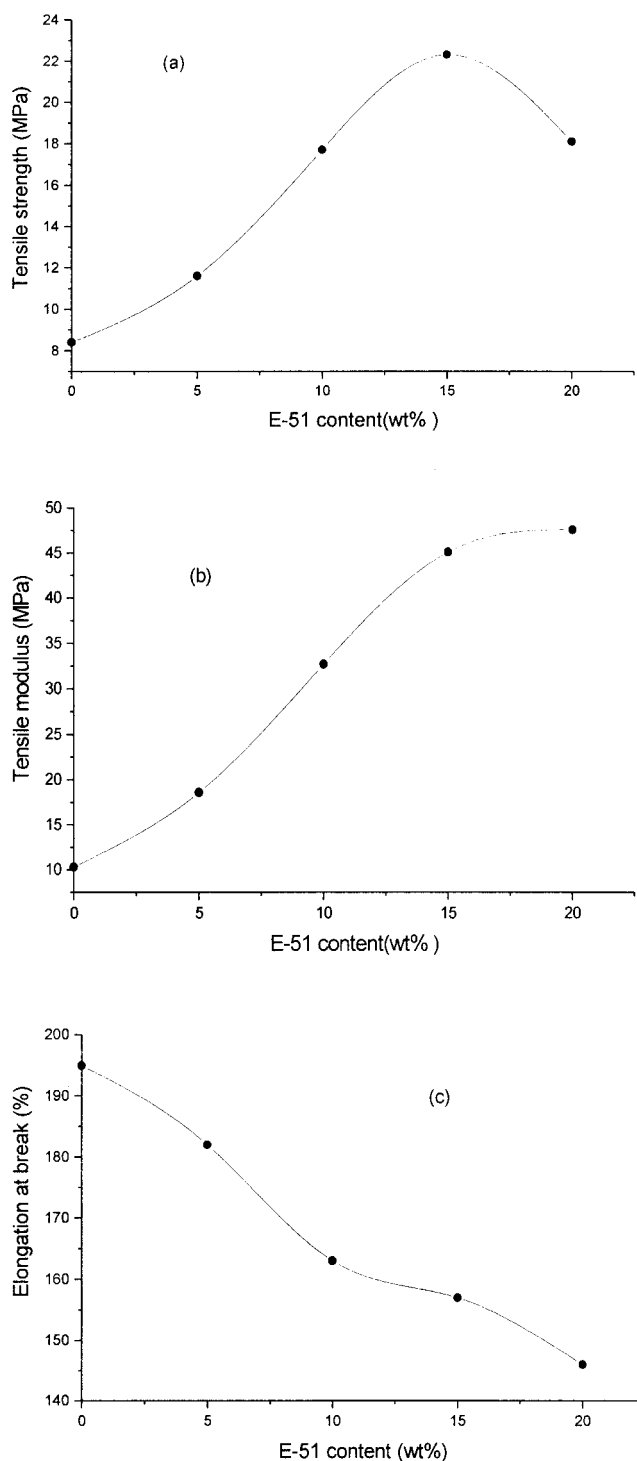
tion peak of the epoxy group was reduced dramatically in intensity with the use of TETA. We also observed that the absorption peak of the epoxy group was almost depleted with an equivalent ratio of the active hydrogen of TETA and an epoxy group of the E-51 resin of 1.2. These observations supported our previous assumptions that TETA could serve as a post-crosslinking agent. During the film-forming course, the latex is deformed and ruptured. TETA and E-51 would then come into contact and react with each other.

### Properties of the modified emulsion

Figure 4 shows the average particle size of the emulsion as a function of the epoxy resin E-51 content in the core (i.e., based on the total solid of the polyacrylate and E-51 within the emulsion). As can be seen, the particle size was insensitive to the addition of epoxy resin when the dosage of the epoxy resin introduced was comparatively low and the average particle size increased from about 86.3 to about 94.6 nm as the E-51 content increased from 0 to 15%. Since E-51 is hydrophobic, it would be embedded into the PU particles during the dispersion course and, therefore, would not increase the average particle size dramatically. However, when the epoxy content exceeded 20%, the latex became coarse. This indicated the instability of the emulsion.

The stability properties of the emulsion during the polymerization course and the storage stage were studied (see Table II). Due to that the collision between the latex particles was drastic during the polymerization course, the epoxy resin might be separated from the emulsion system and precipitate out. Meanwhile, with the addition of the epoxy, the solid content of the emulsion increased and the latex became unstable. As regards the stability during the storage stage, the instability was attributed to the diffusion of the TETA as well to the incomplete wrapping of the epoxy resin by polyacrylate in the core and PU in the shell; the TETA might encounter and react with the epoxy resin in the core of the latex. As a result, the viscosity of the system might be enhanced and precipitation would be observed. In this experiment, the polymerization reaction proceeded smoothly and the coagulum content was low when the epoxy content was below 15%, and, thereby, the yielding emulsion could be stored for more than 30 days without any apparent performance change.

In this work, the hydrophilic TETA is water-soluble and stayed in the aqueous phase after its addition as a part of the system. Furthermore, during the seeding polymerization, E-51 was encapsulated tightly by the polyacrylate as well by the PU. So, the TETA in the aqueous phase could not contact the epoxy resin in the core of the latex during the storage course. Of course, the stability of the emulsion would decrease when incorporated with an increased dosage of the epoxy



**Figure 5** Effects of the epoxy resin content on mechanical properties: (a) tensile strength; (b) tensile strength; (c) elongation at break.

resin, which led the incomplete enwrapping and an unstable core-shell structure.

### Mechanical properties

Figure 5 shows the effects of the epoxy content ( $W_{E-51}$ ) on the tensile strength, tensile modulus, and elonga-

tion at break. It indicates that, with an increase of the epoxy content, both the tensile strength and the tensile modulus of the films were enhanced and the elongation at break decreased. It is seen that the effect is more pronounced with the epoxy resin. Since the crosslinking density of the films increased with increase of the epoxy content, the number of interpenetrating polymer networks (IPNs), which were composed of epoxy, polyacrylate, and PU, was subsequently enhanced. As a result, the film performance was improved. When the epoxy content exceeded 15%, the mechanical performance appeared to slightly decrease. This would be due to the particle instability at a high epoxy loading. With a high epoxy loading, the particles were unstable and part of the epoxy might come out of the particle and exist in the aqueous phase. During evaporation, this portion of the epoxy resin reacted with TETA, but did not form semi-IPNs with the PU acrylates, which resulted in the lower tensile strength at 20 wt % E-51.

### Swell properties

The swell of the prepared films in water and toluene is shown in Table II. As we expected, the water and toluene swell ratio diminished with increase of the epoxy content, that is, the water and solvent resistance appeared to increase. The decrease was slight at the lower epoxy content, and the water resistance of the films were enhanced rapidly with further addition of the epoxy. As can be seen, the presence of epoxy has played a significant role in the increase in water and toluene resistance of the emulsion, and from another point of view, the results indicate that the postlinking reaction does take place in the system, which improved the performance of the latex.

### CONCLUSIONS

A practical synthetic route was designed and executed to prepare the epoxy resin-modified acrylic-PU emulsion. The postlinking reaction between the epoxy resin and the curing agent during the film-forming course was verified. The prepared emulsion exhibited satisfactory stability. The cast film showed enhanced water and toluene resistance as well as improved mechanical properties, which include stress and modulus. However, the elongation at break decreased.

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