

# Waterborne Epoxy/Acrylic Resins Stabilized through the Neutralization of Basic Amine-Modified Epoxy and Acidic Acrylic Copolymers

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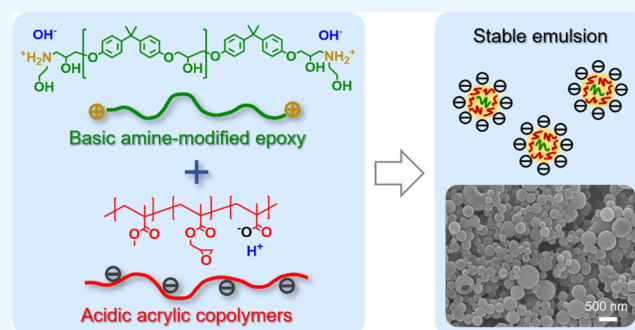
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**ABSTRACT:** In this work, a class of stable waterborne epoxy/acrylic resins with high performance is prepared through the simple blending of modified epoxy and acrylic copolymers. The bisphenol A-based epoxy resin is end-modified with ethanolamine (ETA) while the acrylic copolymers are synthesized with methyl methacrylate (MMA), glycidyl methacrylate (GMA) bearing epoxide, and methacrylic acid (MAA) bearing carboxylic acid. The mixtures of the modified epoxy and acrylic copolymers, both with molar masses above 10,000 g/mol and insoluble in water, can be successfully emulsified without additional dispersants. The key is that ETAs on the modified epoxy provide a basic condition to promote dissociation of the carboxylic acids on the acrylics in water, leading to the electrostatic stabilization. The particle size of the emulsions is less than 300 nm, and the emulsions are stable after storage for more than 9 months. The epoxy/acrylic resins are cross-linkable and show good thermal properties, with a high glass-transition temperature ( $T_g$ ) up to 104.6 °C and a thermal degradation temperature ( $T_d$ ) up to 330.4 °C. The application of the resins as the surface coating of steel was demonstrated, and the films exhibit a good corrosion resistance, less than 5% rusted area on the steel surface after 5-h salt spray test.

**KEYWORDS:** waterborne resin, epoxy, acrylic, neutralization, corrosion resistance

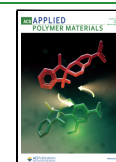


## 1. INTRODUCTION

Epoxy and acrylic resins are two types of resins most commonly used for a variety of applications. Epoxy resins are known for their superior adhesion to different substrates and high resistance to corrosion, chemicals, electrical damage, and thermal degradation such that they are widely used for surface coatings, fiber-reinforced plastics, and adhesives.<sup>1–5</sup> However, epoxy resins show poor weatherability as well as poor impact resistance due to their rigid and brittle nature.<sup>6,7</sup> In contrast, acrylic resins are durable and resistant to UV damage, making them ideal for outdoor usage.<sup>8</sup> Furthermore, the chemical structures and properties of acrylic resins are highly tunable because they can be copolymerized from a variety of acrylate monomers with desired functionalities.<sup>9–11</sup> The downsides of acrylic resins are their low water resistance, low hardness, poor staining resistance, and poor solvent resistance.<sup>12,13</sup> Thus, a combination of the two resins is a good strategy that takes advantage of both to make up for the individual shortcomings. The epoxy/acrylic resins have been applied in machinery, automobiles, anticorrosion primers for metals, and coatings for containers and architectures.<sup>14–17</sup>

To make resins easier for coating, along with good adhesion and self-leveling, solvents are frequently used as carrier agents. Organic solvent-based resins containing volatile organic compounds (VOCs) and other potential pollutants have been restricted by the progressively tighter government regulations in spite of their superior performance.<sup>18</sup> Waterborne resins in which organic solvents are replaced with water to minimize the solvent content and unfavorable odor are an economical and environmentally friendly alternative.<sup>19,20</sup> Although waterborne resins have been widely studied, the performance of most water-based coatings are not as good as that of the solvent-based counterparts, partly due to the limited types and restricted molar mass of resins that can be stably emulsified in water.<sup>21</sup> Waterborne resins that can fulfill all kinds of requirements and perform as well as, or even better

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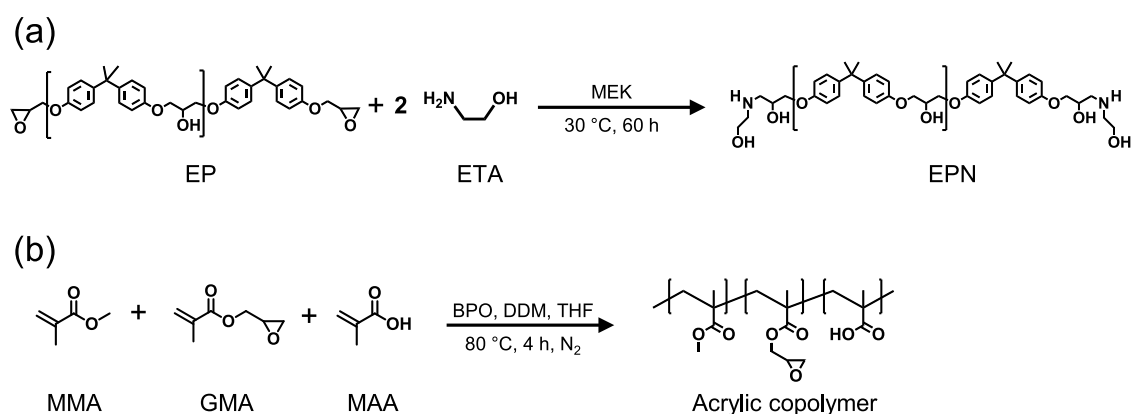


Figure 1. Synthesis routes of (a) modified epoxy and (b) acrylic copolymers.

than, the solvent-based resins remain a class of materials under development in academia and industry.<sup>15,22–34</sup>

Regarding the preparation of waterborne epoxy/acrylic resins, there have been two main strategies. One is the physical blending of epoxies and acrylics, and the blends are emulsified by additional dispersants. This method is simple and low-cost, but the colloidal stability and coating stability are generally poor due to the phase separation between epoxies and acrylics. The other strategy is chemical modification of epoxies by esterification or grafting reactions with water-soluble acrylics. Although the chemical modifications have been used to obtain emulsions with good stability,<sup>35–39</sup> these methods relatively lack the flexibility for tuning the chemical structure and properties of resins. In this study, we develop a strategy combining chemical and blending methods to prepare stable waterborne epoxy/acrylic resins. First, the bisphenol A-based epoxy is end-modified with ETA through the ring-opening reaction of the epoxide with the primary amine on ETA. This reaction can be carried out at low temperatures due to the high reactivity of the primary amines. The acrylic resins are separately copolymerized with MMA, GMA, and MAA monomers. Second, the modified epoxy and the synthesized acrylic copolymers are physically mixed in the common solvent and subsequently emulsified in water via the phase inversion method without additional dispersants. Note that the modified epoxy or the acrylic copolymers alone are unable to be dissolved or dispersed in water; their mixtures at specific fractions, surprisingly, can form stable emulsions with particle size less than 300 nm.

We systematically studied the interplay between the epoxy and acrylic copolymers and found that acrylic copolymers play multiple roles in this system. First, the emulsions are stabilized through the ionization of the carboxylic acids on MAA of the acrylic copolymers, and the ionization is facilitated by the neutralization of the acids in the basic environment provided by the amines on the modified epoxy. This mechanism can effectively stabilize the modified epoxy with a high molar mass over 10,000 g/mol in water in the absence of dispersing agents. Second, the acrylics can increase the  $T_g$ s of the resins. The conventional waterborne bisphenol A-based epoxy resins generally show a  $T_g$  below 80 °C.<sup>30</sup> With the incorporation of the rigid acrylic copolymers, the  $T_g$  of the epoxy/acrylic resins is over 100 °C. Third, the epoxide on GMA and the carboxylic acids on MAA of the acrylic copolymers can react with the secondary amines on the modified epoxy, thereby leading to a cross-linking that enhances the performance of the

resins. To the best of our knowledge, this simple, efficient method and the underlying mechanism have not yet been reported in regard to preparation of waterborne epoxy resins. The epoxy/acrylic resins were applied on the steel surface, and the coating shows a good anticorrosion property, demonstrating the feasibility of the resins as protective coatings.<sup>11,40</sup>

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Bisphenol A epoxy resin (EP) with an epoxy equivalent of 2300–3800 g/equiv was provided by Chang Chun Plastics Co., Ltd., Taiwan, in the trade name of BE509. The acrylic monomers, including MMA (Showa), GMA (Acros), and MAA (Acros), were distilled under reduced pressure to remove inhibitors and then stored in a refrigerator before use. The epoxy modifier ETA (Aldrich), the initiator benzoyl peroxide (BPO, Alfa Aesar), and the chain-transfer agent *n*-dodecyl mercaptan (DDM, Aldrich) were used as received. Solvents used in this study, including MEK, tetrahydrofuran (THF), methanol, and *n*-hexane were also used as received.

**2.2. Synthesis of Acrylic Copolymers and Modification of Epoxy.** The synthesis routes of the polymers are shown in Figure 1. The molar masses and  $T_g$ s of the modified epoxy and the acrylic copolymers are listed in Table 1. EP was end-modified with ETA

Table 1. Molar Masses and Thermal Properties of the Resins

sample	$M_{n,SEC}$ (g/mol)	$M_{w,SEC}$ (g/mol)	PDI ( $M_w/M_n$ )	$T_g$ (°C)	$T_d$ (°C)
Epoxy					
EP	9190	22,218	2.42	87.5	387.6
EPN	13,723	23,303	1.70	99.2	391.0
acrylic copolymers (MMA/GMA/MAA, wt %)					
AC10 (85:5:10)	16,443	27,275	1.66	150.7	290.0
AC5 (95:5:5)	21,303	32,145	1.51	147.7	264.7

through a ring-opening reaction between equimolar epoxides and primary amines. The feed mole ratio of EP/ETA was 1:2. In a general process, 75 g (12.3 mmol) of EP was first dissolved in 113 g of MEK at 60 °C. The well-dissolved solution was then cooled to 30 °C, followed by the slow addition of 1.502 g (24.6 mmol) of ETA. The reaction was carried out at 30 °C for 60 h. The low-temperature condition allowed the epoxides on EP to mainly react with the active hydrogens on the primary amines of ETA. The ETA-modified epoxy (EPN) was then dried for characterization or directly used for emulsification.

The copolymerization of the acrylics was carried out in a round-bottom flask with an oil bath and a flux condenser in a nitrogen atmosphere. Taking the synthesis of the acrylic copolymer, ACS

Table 2. Characteristics of the EPN/Acrylic Emulsions and Resins

sample	EPN/AC (wt %/wt %)	size <sup>a</sup> (nm)	ζ (mV)	pH	T <sub>g</sub> (°C)	T <sub>d</sub> (°C)
EPN/AC10						
AC10-10	90/10	766 ± 70	-43.2	9.7	100.6	371.5
AC10-20	80/20	453 ± 13	-40.0	8.7	101.2	367.3
AC10-30	70/30	298 ± 37	-22.2	7.7	101.3	352.6
AC10-40	60/40	475 ± 57	-33.5	7.3	103.9	325.4
AC10-50	50/50	1305 ± 402	-37.8	7.0	101.5, 131.4	319.1
AC10-60	40/60	2208 ± 397	-49.1	6.9	104.1, 135.6	313.7
EPN/ACS						
ACS-10	90/10	1152 ± 308	-14.3	9.6	100.4	367.9
ACS-20	80/20	405 ± 57	-20.5	9.7	102.8	347.2
ACS-30	70/30	214 ± 9	-22.6	9.5	104.6	330.4
ACS-40	60/40	221 ± 16	-46.2	8.9	106.6	326.0
ACS-50	50/50	286 ± 17	-23.7	8.4	107.7	293.6
ACS-60	40/60	439 ± 30	-23.0	8.2	106.1, 129.4	291.6
ACS-70	30/70	701 ± 282	-25.9	8.1	104.8, 131.5	295.5

<sup>a</sup>Particle size determined from DLS intensity distribution.

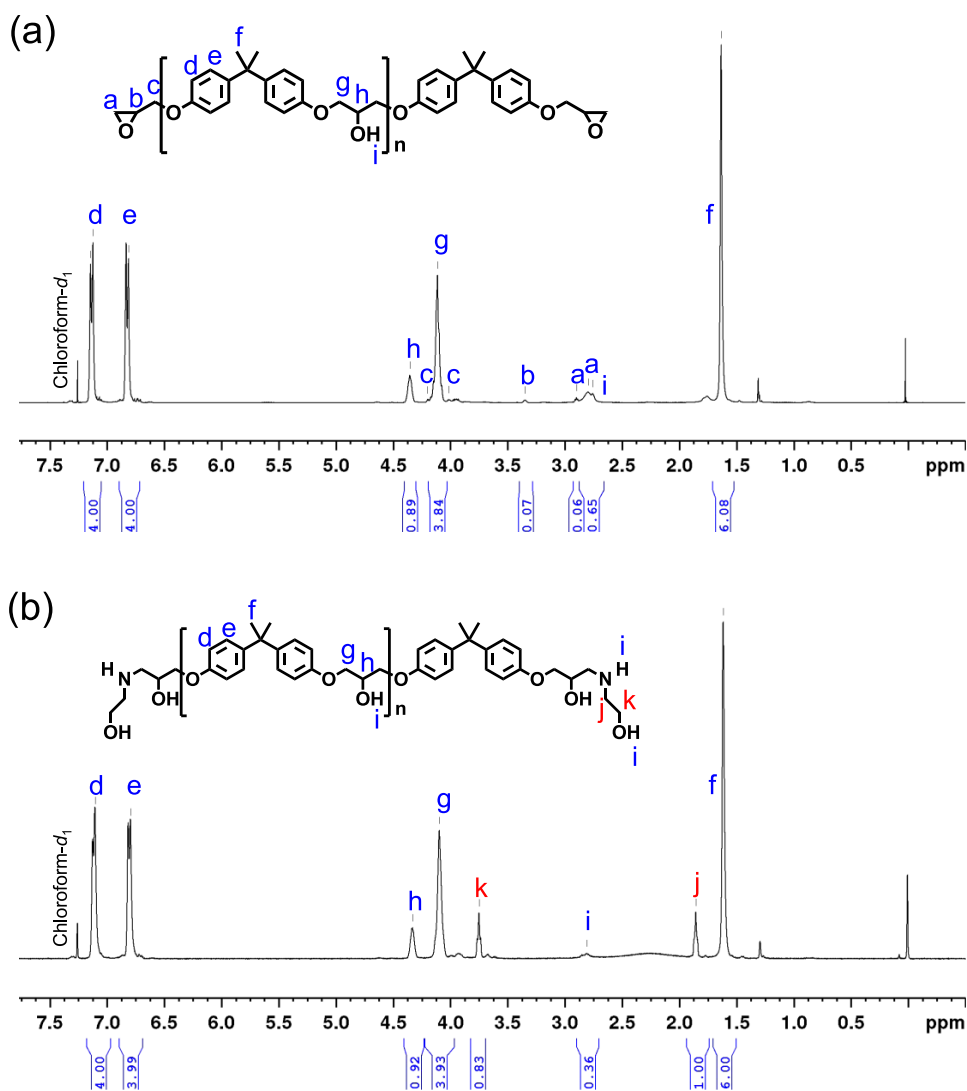


Figure 2. <sup>1</sup>H NMR spectra of (a) EP and (b) EPN.

(MMA/GMA/MAA = 95:5:5), as an example, 30 g of monomers (27 g of MMA, 1.5 g of GMA, and 1.5 g of MAA), 0.3 g of DDM, 1.5 g of BPO, and 45 g of THF were mixed and reacted at 80 °C for 4 h. After

the reaction, the solution was precipitated in methanol, and the solid product was collected by suction filtration. The product was further rinsed with methanol and then vacuumed at 60 °C for 1 day to obtain

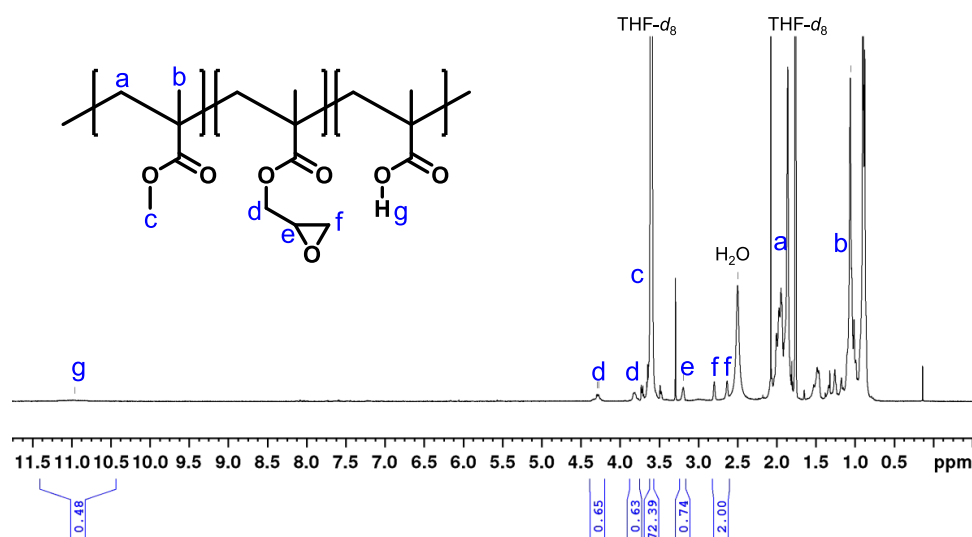


Figure 3.  $^1\text{H}$  NMR spectrum of ACS.

the acrylic powders. For the copolymer with more MAA, i.e., AC10 with MMA/GMA/MAA = 85:5:10, because it is soluble in methanol, the solvent used for precipitation was changed to *n*-hexane.

**2.3. Emulsification and Stability.** The phase inversion method was adopted to prepare the waterborne epoxy/acrylic resins. The schematic of the process is shown in Figure S1. 6 g of the resin with desired ratio of epoxy and acrylic was dissolved in 34 g of MEK. Subsequently, 10 g of deionized water was added using a syringe pump at a rate of 1 g/min to the solution that was vigorously stirred at a speed at 2000 rpm. After another 20 min of stirring, MEK was removed by reduced pressure distillation to obtain the emulsion with a solid content of more than 40%. The emulsification process was conducted at room temperature. The emulsions prepared in this work are listed in Table 2. To determine the critical coagulation concentration (CCC), the emulsions were first diluted to 0.5 wt %. 1 mL portion of the diluted emulsion was mixed with 1 mL of NaCl or  $\text{MgCl}_2$  aqueous solutions at various salt contents, which was then kept at room temperature for 24 h. The salt concentration that causes the upper layer of the emulsion to be visibly clear was designated as CCC.

**2.4. Characterization.**  $^1\text{H}$  NMR was conducted on a Bruker AVIII HD-600 spectrometer with deuterated THF or chloroform as solvents. The size exclusion chromatography (SEC) was performed on a Waters 717plus Autosampler equipped with a series of Sepax Mono GPC-100 and GPC-500 columns (both  $7.8 \times 300 \text{ mm}^2$ ) in the molar mass range of 100–100,000 g/mol. THF was used as the eluent, and polystyrene was used as the standard. The particle size distributions of the emulsions were measured by dynamic light scattering (DLS, Brookhaven NanoBrook 90Plus PALS) with a 15 mW solid-state laser of wavelength  $\lambda = 675 \text{ nm}$ , by which the  $\zeta$ -potentials were also determined. The samples were diluted to 0.01 wt % before DLS measurements. For the SEM imaging, the emulsions were diluted to 0.1 wt % and freeze-dried. The dried samples were sputtered with platinum, and the images were taken by a JEOL JSM-6700F microscope. To characterize the thermal properties of the resins, the emulsions were first dried at  $150 \text{ }^\circ\text{C}$  in a vacuum oven.  $T_g$ s were determined by differential scanning calorimeter (DSC, TA Discovery 25), and  $T_d$ s were determined at 5% weight loss by thermogravimetric analysis (TGA, TA Q50 thermogravimetric analyzer), both operated at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. The  $\text{N}_2$  flow rates were 60 and 50 mL/min for TGA and DSC, respectively.

**2.5. Salt Spray Test.** The salt spray tests were conducted following the method ASTM B117. A  $10 \text{ cm} \times 10 \text{ cm}$  nonoriented electrical steel containing 3.0 wt % silicon (China Steel Corporation, 35CS250) with a thickness of 0.35 mm was used. The emulsions were first applied on the steel surface by a #3 bar coater, followed by drying

in an oven at  $260 \text{ }^\circ\text{C}$  for 33 s. The coating thickness was  $3.5 \text{ }\mu\text{m}$ , measured by a magnetic coating thickness gauge (DIN EN ISO 2178). The coated steels were then placed in a chamber at  $35 \text{ }^\circ\text{C}$ , which was filled with the fog atomized from a 5% NaCl solution with a pH range between 6.5 and 7.2 at a spray rate of 1.5 mL/h. After the steel was sprayed for 5 h, the rusted area of the steel was calculated by visual inspection.

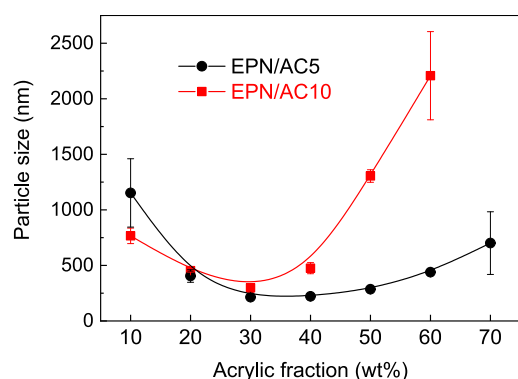
### 3. RESULTS AND DISCUSSION

**3.1. Characterization of Polymers.** Figure 2 shows the  $^1\text{H}$  NMR spectra of EP and EPN in deuterated chloroform. The signals of the protons on the epoxide methylene ( $\delta = 2.80$  and  $2.90 \text{ ppm}$ ) and methene ( $\delta = 3.35 \text{ ppm}$ ) can be seen on EP, and these signals disappear in the spectrum of EPN. Instead, the signals at  $\delta = 1.86$  and  $3.75 \text{ ppm}$  of the methylene protons on ETA appear, confirming that the epoxides at the two ends of the epoxy are successfully reacted with ETA. The molar masses of EP and EPN determined from SEC are 9190 and 13,723 g/mol, as shown in Figure S2, and the polydispersity indexes (PDI) are 2.42 and 1.70, respectively (Table 1). The molar mass of ETA is 61 g/mol. If only the primary amine of ETA reacts with the epoxides and modifies the two ends of the epoxy, the molar mass of EPN should be  $\sim 120 \text{ g/mol}$  higher than that of EPN. However, after the ring-opening reaction, EPN shows a much larger molar mass change in the SEC measurement. It is possible that the solubility of EPN in the mobile phase (THF) is higher than that of EP, which, in turn, causes a more swollen EPN chain in THF. As shown in Figure S3, the  $T_g$ s of EP and EPN are  $87.5$  and  $99.2 \text{ }^\circ\text{C}$ , and the  $T_d$ s of EP and EPN are  $387.6$  and  $391.0 \text{ }^\circ\text{C}$ , respectively. The significantly higher  $T_g$  of EPN is attributed to the stronger intermolecular interactions between ETAs on EPN.

The  $^1\text{H}$  NMR spectrum of the acrylic copolymer, ACS, in deuterated THF is shown in Figure 3. The appearance of the proton signals from the epoxide methylene ( $\delta = 2.63$  and  $2.80 \text{ ppm}$ , 2.00H) and methene ( $\delta = 3.21 \text{ ppm}$ , 0.74H) of GMA and from the carboxylic acid of MAA ( $\delta = 10.96 \text{ ppm}$ , 0.48H) evidence the successful incorporation of GMA and MAA into the acrylic copolymer. Note that the integrated area under the proton signal of the carboxylic acid ( $\delta = 10.96 \text{ ppm}$ ) is smaller than the theoretical stoichiometric value of MAA. This is possibly because of a strong interaction between the carboxylic

acid and the solvent that causes a much broader peak, thus affecting the accuracy of the measurement. The SEC data of the acrylics are shown in Figure S4. The  $M_{n,s}$  of AC10 and AC5 are 16,443 and 21,303 g/mol, respectively, and the PDIs are below 1.7. The DSC and TGA data of the acrylics are shown in Figure S5. The  $T_g$ s of AC10 and AC5 are 150.7 and 147.7 °C, respectively, both higher than that of the homopolymer PMMA (123.1 °C). Although the incorporation of GMA lowers the  $T_g$  of PMMA,<sup>41</sup> the interaction between the high-polar MAA can greatly hinder the molecular motion, thus leading to a net increase in  $T_g$ . The  $T_d$ s of AC10 and AC5 are 290.0 and 264.7 °C, respectively.

**3.2. Emulsification of Epoxy/Acrylic Resins.** The mixtures of the modified epoxy EPN and the acrylic copolymers (AC10 or AC5) at varying weight fractions were emulsified using the phase inversion method, as described in Section 2.3. Note that neither pure EPN nor pure AC10 or AC5 alone are able to dissolve or micellize in water. However, the mixtures of EPN and AC10 or AC5 can be successfully emulsified at a wide range of the weight fraction of the acrylics in the absence of dispersants. The sample codes and characteristics of the oil-in-water emulsions are summarized in Table 2. The dependences of the particle sizes determined from the DLS intensity distribution on the weight fraction of



**Figure 4.** Particle size vs acrylic weight fraction of the EPN/acrylic emulsions.

the acrylics in the emulsions are displayed in Figure 4. For the EPN/AC10 system, at AC10 fractions between 20 and 40%, the average particle size of the emulsion is less than 500 nm, among which AC10-30 shows the smallest size below 300 nm. For the EPN/AC5 system, the average particle size of the emulsion is less than 500 nm at the AC5 fraction between 20 and 60%. The size is less than 300 nm for AC5-30, AC5-40, and AC5-50, and no precipitation occurs after more than 9-month observation. The stable emulsions are milky white in appearance, as shown in Figure S6. The results manifest that the simple mixing of the modified epoxy and acrylic copolymers can effectively form stable oil-in-water emulsions.

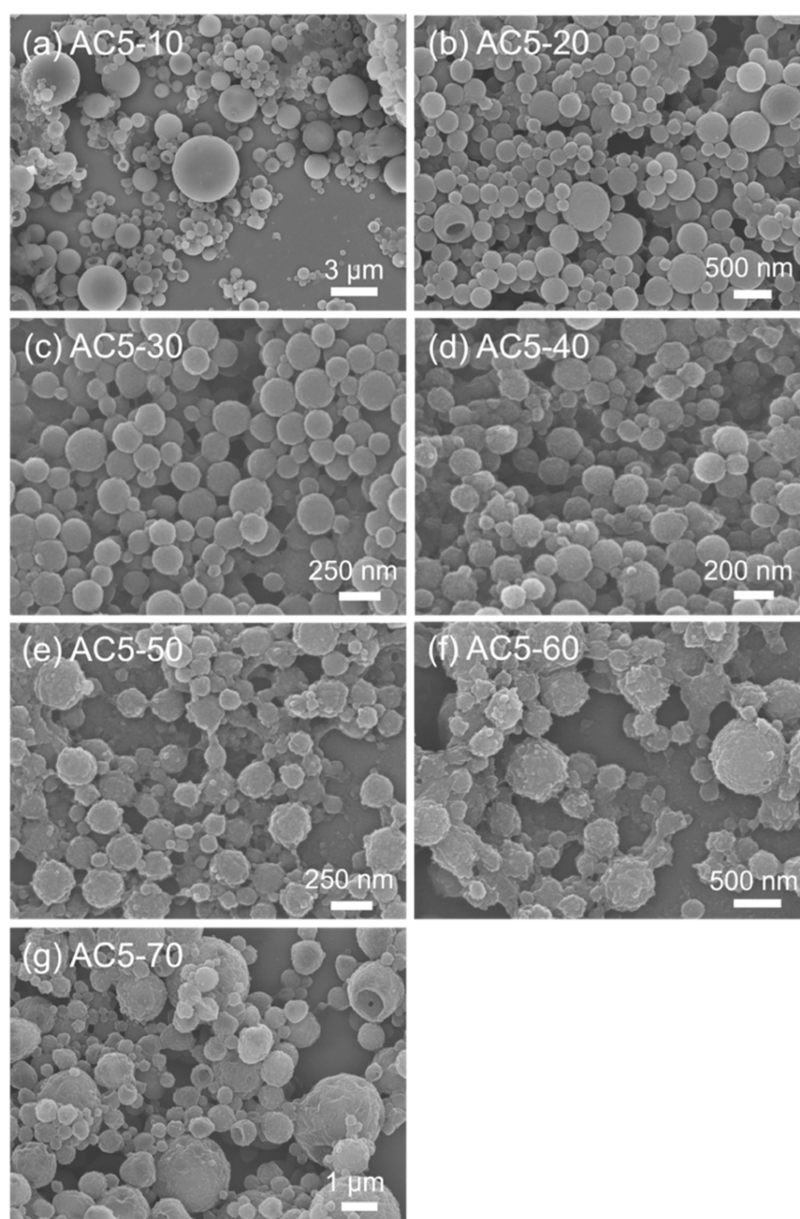
The SEM images of the dried EPN/AC5 particles at varying fractions are shown in Figure 5. The particles of AC5-30, AC5-40, and AC5-50 are rather uniform, and the particle sizes are mostly below 300 nm, in agreement with the DLS data. Some particularly large particles can be seen in other fractions. Moreover, as the AC5 fraction increases to above 50%, the particle surfaces turn out to be rougher. Because the particle surfaces composed of more hydrophilic carboxylic acids tend to be swollen more by water, the sublimation of water could leave rough surfaces upon freeze-drying. The SEM images of

the dried EPN/AC10 particles are shown in Figure S7. The size is consistent with the DLS data, and a similar rough surface can be seen for AC10-40. The rough surface occurs at a fraction lower than that of EPN/AC5 because AC10 contains more hydrophilic carboxylic acids.

**3.3. Mechanism.** EPN is a basic compound due to its end-capped ETAs that acquire protons in aqueous solutions. As shown in Table 2, the emulsions are gradually neutralized, and the pH values decrease with increasing fractions of the acrylics for both AC5 and AC10 systems. The pH values of the AC10 system (between 9.7 and 6.9) are lower than that of the AC5 system (between 9.6 and 8.1) because of a higher content of MAA on AC10. The  $\zeta$ -potentials of the particles in the emulsions shown in Table 2 are all negative, which is attributed to the dissociation of MAA into carboxylate anions on the surface of the particles. This implies that acrylics act as the anionic emulsifiers that stabilize the epoxy resin to form well-dispersed emulsions, known as electrostatic stabilization. To further verify this point, two salts, sodium chloride (NaCl) and magnesium dichloride ( $MgCl_2$ ) that provide monovalent and divalent cations, respectively, were used to determine the critical coagulation concentration (CCC) of the emulsions. The photographs of the EPN/AC5 emulsion containing 40% of AC5 in the presence of varying concentrations of the salts are shown in Figure S8, and the CCCs of NaCl and  $MgCl_2$  that cause the emulsion to precipitate are approximately 1.0 and 0.05 M, respectively. The much lower CCC for  $MgCl_2$  compared to that for NaCl indicates that  $Mg^{2+}$  is much more efficient than  $Na^+$  to screen the electrostatic repulsion between particles. Based on the well-known Schulze–Hardy rule,<sup>42</sup> this result evidence that the particle surface is negatively charged, caused by the dissociation of carboxylic acids.

Since acrylics alone are unable to be dissolved or dispersed in water, the basic ETAs on EPN must play an important role in facilitating the dissociation of the carboxylic acids on the acrylics to impart emulsification capability. As shown in Figure 4, the mixtures of EPN and acrylics form stable emulsions with uniform and small-size particles in specific fraction ranges. The acrylic fractions lower and higher than this range both lead to larger particle sizes. Taking the EPN/AC5 system as an example, when the AC5 fraction in the emulsion is below 30%, the particle size is above 400 nm, which is because the dissociated carboxylic acids that provide the electrostatic stability are limited, and thus, the particles coagulate into larger ones even though EPN provides sufficient basic conditions to dissociate the carboxylic acids on AC5. As the AC5 fraction is above 60%, EPN becomes the minor component, and the limited ETAs can only cause a low degree of dissociation of the carboxylic acids on AC5, thus giving rise to a poor stabilization and an increase in the particle size. The above results suggest that to create a stable emulsion, an appropriate ratio of EPN and acrylics is required. More specifically, the ratio of ETA on epoxy and MAA on acrylics should be optimized. In the present system, AC5 outperforms AC10 in emulsifying EPN, and 30% of acrylics shows the best stabilization efficacy.

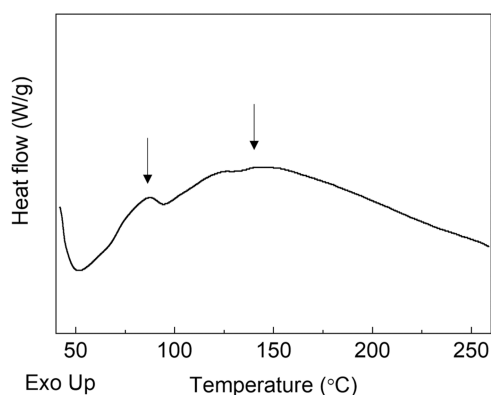
**3.4. Thermal Properties and Applications of Epoxy/Acrylic Resins.** The thermal properties of the EPN/AC10 and EPN/AC5 solid samples after drying from the emulsions were studied. The DSC thermograms are shown in Figure S9, and the  $T_g$ s of the samples are listed in Table 2. The  $T_g$ s of the EPN/AC10 and EPN/AC5 samples are all above 100 °C, increasing from that of pure EPN (99.2 °C), indicating that the acrylics can enhance the  $T_g$  of the resins. Single  $T_g$  is seen at



**Figure 5.** SEM images of the dried particles from the EN/ACS emulsions: (a) AC5-10, (b) AC5-20, (c) AC5-30, (d) AC5-40, (e) AC5-50, (f) AC5-60, and (g) AC5-70.

the acrylic fractions below 50% for both AC10 and AC5, which implies that the epoxy and acrylics form homogeneous mixtures in these compositions. As the fraction of acrylics increases,  $T_g$  increases slightly, and a second glass transition appears at fractions above 50%. The appearance of two  $T_g$ s between those of pure EPN and pure acrylics (150.7 and 147.7 °C for AC10 and AC5, respectively) is typical of glass transition behaviors of partially miscible polymer mixtures, where a phase separation occurs. At the acrylic fractions above 50%, the epoxy and acrylics segregate into epoxy-rich and acrylic-rich phases, which exhibit the lower and the higher  $T_g$ , respectively. The TGA data are shown in Figure S10, and the  $T_d$ s of the samples are listed in Table 2. As expected, the  $T_d$ s of the mixtures are between those of pure EPN and acrylics. Although the incorporation of acrylics lowers the degradation temperature of the resins, the  $T_d$ s of the samples drying from the stable emulsions with an acrylic fraction below 50% are above 300 °C, sufficiently high for most applications.

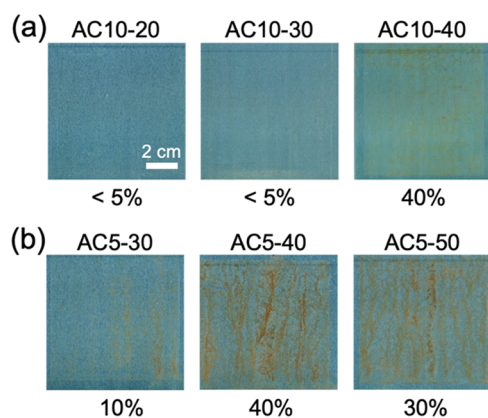
In addition to facilitating the emulsification, the secondary amines at the two ends of EPN provide another advantage, that is, they can react with the epoxides of GMA or even the carboxylic acids of MAA on the acrylics to cross-link the resins,<sup>30</sup> which can strengthen the thermal, chemical-resistant, and mechanical properties of the resins. To verify this curing reaction, the AC5-30 sample vacuum-dried at room temperature was heated from 40 to 260 °C at a rate of 10 °C/min in the DSC oven, and the thermogram was recorded. As shown in Figure 6, exothermic peaks around 80 and 140 °C were observed, which evidence the occurrence of the reaction. Figure S11 displays photographs of the unreacted and reacted AC5-30 samples that were mixed with dimethylformamide (DMF). The reacted sample treated at 150 °C for 2 min was only swollen in DMF while the unreacted one was fully dissolved in DMF, confirming that the sample was cured through the covalent bonding between EPN and the acrylic after thermal treatment. Note that the reaction rate of the



**Figure 6.** DSC heating data of AC5-30 resin. The arrows indicate the exothermic peaks of the curing reaction.

secondary amine with epoxides or carboxylic acids is much slower than that of the primary amine.<sup>43</sup> The cross-linking reaction in the emulsions is thus limited at room temperature, and the stability of the emulsions was found unaffected by the reaction after 9-month storage. Also note that different from the conventional epoxy formulas, EPN and the epoxide-containing acrylics in this work should be regarded as the amine-based hardeners and epoxy resins, respectively. The epoxy equivalent weight of the acrylics can be tuned to meet the demands of applications by varying the fraction of GMA monomers in the copolymerization.

The coatings of the EPN/AC10 and EPN/AC5 emulsions on a steel surface working as the protective layers were demonstrated. The stable emulsions were used, and the salt spray tests were conducted following the procedure described in Section 2.5. Note that the thin coating treated at 260 °C for 33 s during the drying process should be partially cross-linked. The images of the coated steels after the spray tests are shown in Figure 7, from which the rusted area related to the corrosion



**Figure 7.** Images of the steel surface coated by (a) EPN/AC10 and (b) EPC/AC5 resins after salt spray tests. The numbers are the percentages of the rusted areas after testing.

resistance was calculated. The AC10-20 and AC10-30 coatings show superior corrosion resistances with rusted areas below 5%, and the AC5-30 also shows a good corrosion resistance with rusted area ~10%. As the acrylic fraction increases, the rust area increases for both systems, indicating that the acrylics are unfavorable to corrosion resistance. In sum, the EPN/AC10 system and the EPN/AC5 system with 30% of acrylics show superior properties and performances, including stable

emulsions with the particle sizes below 300 nm, glass transitions above 100 °C, thermal degradation temperatures above 330 °C, and rusted areas after 5-h salt spray below 10%. These cross-linkable waterborne epoxy resins should meet the demands of various applications.

#### 4. CONCLUSIONS

We developed a class of stable waterborne epoxy/acrylic resins in which the epoxy was end-modified with ethanolamine of basic nature, and the acrylic copolymers were synthesized with the acrylic monomers bearing epoxides and carboxylic acids. Through the phase inversion method and the neutralization of the amine on epoxy and carboxylic acid on acrylic in water, the blends of the modified epoxy and acrylic copolymers were successfully emulsified in water to form surfactant-free waterborne resins with long-term stability. The acrylic copolymers are not merely part of the resin used to tune the properties of the resins but also the critical components that stabilize the resins. The resins are cross-linkable and show a high glass-transition temperature, high thermal degradation temperature, and excellent corrosion resistance. The preparation of these waterborne epoxy/acrylic resins is simple and economical, with potential for applications in coatings with high mechanical and resistance properties. Furthermore, the mechanism found in this work, i.e., the neutralization of basic and acidic polymers, can be applied to other systems for preparing waterborne resins.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.3c02424>.

Schematic of phase inversion method; SEC chromatograms of EP, EPN, and acrylics; DSC and TGA data of EP, EPN, acrylics, and EPN/acrylic blends; SEM images of EN/AC10 emulsions; photographs for CCC and cross-linking tests (PDF)

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## Notes

The authors declare no competing financial interest.

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