

UV-Curable Methacrylic Epoxy Dispersions for Cationic Electrodeposition Coating

Y. B. Kim,¹ H. K. Kim,² J. W. Hong²

¹*Institute of Photonics & Surface Treatment, Q-Sys Co., Ltd., 971-14, Wolchul-Dong, Buk-Gu, Gwangju 500-460, South Korea*

²*Department of Polymer Science & Engineering, Chosun University, Gwangju 501-759, South Korea*

Received 2 November 2005; accepted 16 April 2006

DOI 10.1002/app.24766

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

ABSTRACT: UV-curable epoxy dispersions were prepared for cationic electrodeposition coating. Sequential reactions were used to introduce methacrylate groups to the epoxy-amine polymer as coupling agents to the multifunctional acrylates. The molecular weight values of the prepared epoxy-amine polymer were $M_n = 2800$ and $M_w = 4300$. The neutralized epoxy-amine polymer containing photoinitiator with or without multifunctional acrylate (pentaerythritol triacrylate, PETA) could be dispersed into a stable dispersion without any phase separation. The size of the particles in these epoxy dispersions was approximately 77.7 nm, and increased

with the incorporation of PETA. The electrodeposition process was introduced to the prepared epoxy dispersions, and the electrodeposited films were cured by UV irradiation after a 10-min flash off at 80°C. Studies of the kinetics using photo-DSC revealed that the crosslinked films containing PETA gave a higher conversion rate than those without PETA, resulting in better resistance to methyl ethyl ketone. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5566–5570, 2006

Key words: UV curable; epoxy dispersion; electrodeposition; photo-DSC; water-based resins

INTRODUCTION

The increasing demand to reduce the amount of volatile organic compounds used in coating industries presents challenges and opportunities to polymer chemists. In recent years, many important advances have taken place in polymeric binders, polymeric dispersants, polymeric thickeners, and polymeric colloidal stabilizers.¹ Water-based UV-curable resins have also increased in commercial significance over the past few years,^{2–5} resulting in a wide variety of technical approaches in industrial applications. These resins are classified into aqueous emulsions and aqueous dispersions, and both types should contain vinyl groups for UV curing and hydrophilic groups for stabilization in water.

The main drawback of water-based UV-curable resins is that the curing behavior is significantly dependent on the water content of the applied film. This problem is overcome by reducing the water content of the wet film before UV curing using, for example, the flash-off process. However this process requires energy, space, and time, as well as changes in production-line design.⁶ The water content can be reduced using electrodeposition, which involves electrophoresis, penetration, and deposition to form a uniform film even on recessed and shielded areas, which other coating meth-

ods cannot reach. Moreover, the electrodeposition technique exhibits a coating efficiency of more than 95%.⁷

Recently we reported that the combination of cationic electrodeposition and UV-curable dispersions such as acrylic and polyurethane polymers make curing in ambient temperatures possible after a relatively short flash-off process, comparable in duration to the conventional UV curing system.^{8–9} The performance of UV-curable electrodeposition coating depends greatly on the selection of materials. For example, acrylic polymer provides good glossiness and weather resistance, whereas epoxy polymer has superior anticorrosion and adhesion properties on various substrates.¹⁰ The objective of the present work was to introduce a UV-curable epoxy system as a primer to the electrodeposition process.¹¹

This study involved the preparation of UV-curable epoxy dispersions containing pendent methacryl groups as coupling agents to the multifunctional acrylates. These dispersions, with or without multifunctional acrylate, were then introduced into the electrodeposition process. We also studied the kinetics of the high-speed UV-curing reaction, and investigated the behavior of the electrodeposition process and the performance of UV-cured films.

EXPERIMENTAL

Materials

The epoxy resin used was Epon 1001 (Shell Chemical), which has an equivalent weight per epoxy group

Correspondence to: J. W. Hong (jhhong@mail.chosun.ac.kr).
Contract grant sponsor: Chosun University.

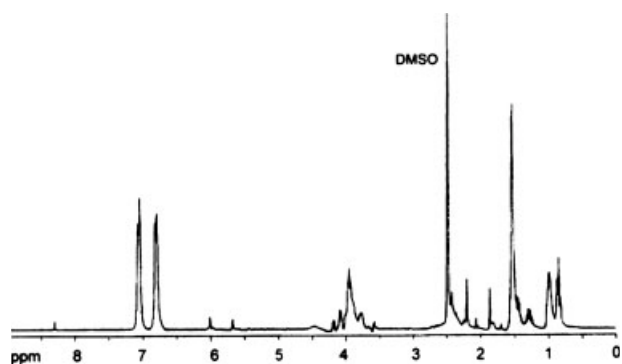


Figure 1 $^1\text{H-NMR}$ spectrum of the epoxy-amine polymer.

of 500. Poly(propyleneglycol)bis(2-aminopropylether), Jeffamine D-400, which has an average molecular weight of 400, was obtained from Huntsman Corp. Glycidyl methacrylate, 2-(methylamino)ethanol, pentaerythritol triacrylate (PETA), methyl ethyl ketone (MEK), and 2-butoxyethanol were purchased from Aldrich, and used without further purification. Acetic acid was used as the neutralizer. The photoinitiator, 2,2-dimethyl-2-hydroxyacetophenone, (Darocur 1173) was obtained from Ciba Specialty Chemicals.

Preparation of UV-curable epoxy dispersions

The epoxy-amine polymer containing the methacrylate groups was prepared in a 1-L, four-necked flask, equipped with a reflux condenser, stirrer, thermometer, and nitrogen-gas inlet. 50.0 g (0.125 mol) of poly(propyleneglycol)bis(2-aminopropylether) were charged into the reaction vessel, and 35.5 g (0.25 mol) of glycidyl methacrylate were slowly added over 30 min. The reaction mixture was then maintained at 80°C for 2 h, by which time the epoxy content had reduced to zero. 225 g of Epon 1001 and 250 g of 2-butoxyethanol were added into the above reaction product and heated at 100°C until the epoxy equivalent weight reached 2000. At that point, 16 g (0.21 mol) of 2-(methylamino)ethanol was added, and maintained for 2 h. This product was characterized by $^1\text{H-NMR}$ (in $\text{DMSO-}d_6$): δ 6.8 and 7.1 ppm aromatic CH , δ 5.7 and 6.0 ppm $\text{CH}_2=$, 4.09 ppm ($-\text{OCH}_2\text{CH}(\text{CH}_3)-$) $_n$, 3.96 ppm ($-\text{OCH}_2\text{CH}(\text{CH}_3)-$) $_m$, and 1.54 ppm ($-\text{OCH}_2\text{CH}(\text{CH}_3)-$) $_n$, as shown in Figure 1.

150.0 g of the prepared epoxy-amine polymer (56.6 wt % in 2-butoxyethanol) and 4 g of Darocur 1173 were charged to a reactor equipped with an electrical stirrer and neutralized with 2.44 g of acetic acid. Deionized water (412 g) was added into the mixture slowly and then agitated violently to disperse the polymer into a water phase to form a stable dispersion, having a resin concentration of 14.8 wt %. The mean particle size in the epoxy dispersion was 77.7 nm, as measured by a Coulter N4 Plus sub-

micron particle sizer (Beckman Coulter). Two additional dispersions containing PETA (15 wt % and 30 wt %) were prepared without changing the resin concentration and the degree of neutralization.

Electrodeposition of the UV-curable epoxy dispersion

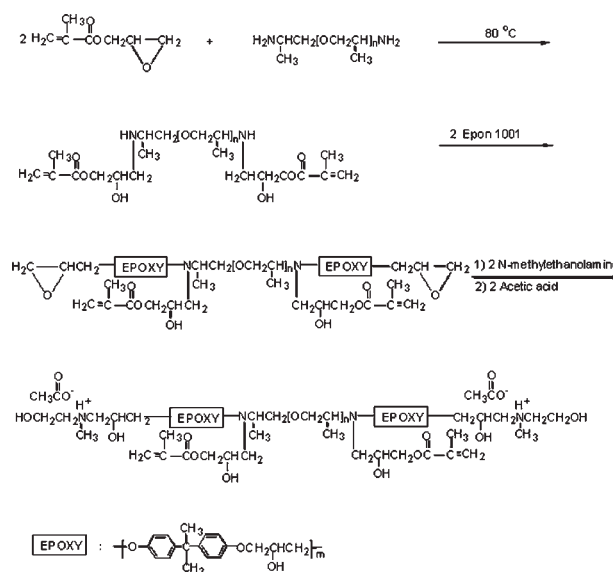
Cathode panels with an area of 130 cm^2 were cut from nickel-plated polyethylene terephthalate (PET) film, and the area of the stainless steel counter electrode (anode) was 100 cm^2 . The cathode-to-anode distance was 10 cm. The nickel-plated PET panels were coated at 100 V and 25°C for 90 s while the bath was stirred moderately using a paddle. After deposition, the coating was rinsed with distilled water and exposed to the radiation of a 200-W medium-pressure mercury lamp (the light intensity at the sample was 500 mW cm^{-2}) in the presence of air, at a passing speed of 60 m/min.

Surface properties

The pendulum hardness (ASTM D 4366) of the UV-cured films was measured using a pendulum hardness rocker (model 707KP, Sheen Instruments, Surrey, UK). MEK double rubs were measured according to ASTM D 4752.

Photo-DSC

The photo-DSC experiments were conducted using a differential scanning calorimeter equipped with a photocalorimetric accessory (DSC 2920/DPC System, TA Instruments). The light source was a 200 W high-pressure mercury lamp: the UV intensity at the sample



Scheme 1 The synthetic route of UV-curable epoxy-amine polymer containing pendent methacryl groups.

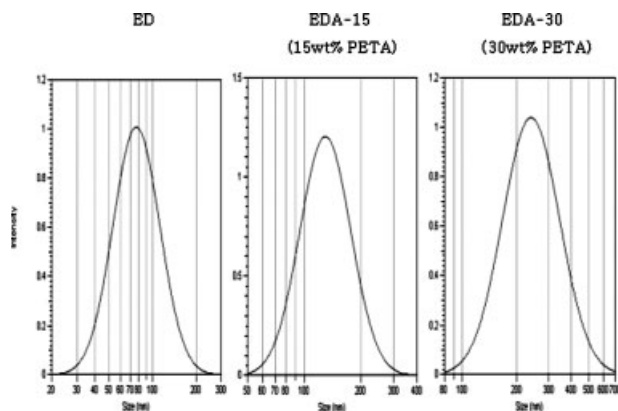


Figure 2 The particle-size distribution of UV-curable epoxy dispersions.

was 33 mW cm^{-2} over the wavelength range 285–440 nm. The samples were placed in uncovered aluminum pans. TA Instruments software was used to analyze the data from the photo-DSC experiments.

RESULTS AND DISCUSSION

Synthesis of epoxy polymer containing methacrylate groups

UV-curable epoxy dispersions were prepared by sequential reactions according to the protocol shown in Scheme 1. Methacrylate groups were introduced to the ends of the poly(propyleneglycol)bis(2-aminopropylether) by a reaction with glycidyl methacrylate. The reaction product was subsequently reacted with Bisphenol A epoxy resin (Epon 1001) and *N*-methyl ethanol amine to give an epoxy-amine polymer that included the pendent methacrylate groups. The molecular weight values of the epoxy-amine polymer containing the methacrylate groups were $M_n = 2800$ and $M_w = 4300$, as measured by gel-permeation chromatography with a polystyrene standard. In this study, epoxy-amine polymer was functionalized with methacrylate groups as the coupling agent to the multifunctional acrylates. The methacrylate group content of the prepared epoxy-amine polymer was calculated to be 0.714 meq g^{-1} , which was too low to provide MEK resistance. Therefore, two additional dispersions were prepared containing 15 wt % and 30 wt % of PETA as a multifunctional acrylate, and their particle size and crosslinking behavior were compared with those dispersions without PETA.

Particle-size control

Stable dispersions were obtained by the neutralization of the 2-(methylamino)ethanol group of the epoxy-amine polymer with acetic acid. Darocur 1173 was used as a liquid-type photoinitiator and PETA was

used as a multifunctional acrylates. The content of the photoinitiator was fixed at 4.0% of the total solid weight of the dispersion. In this study, the neutralized epoxy-amine polymer solution containing Darocur 1173 with or without PETA dispersed stably without any phase separation. The epoxy dispersions were prepared from the mixture of epoxy-amine polymer/PETA multifunctional acrylates with ratios of 100/0, 85/15, and 70/30 to obtain ED, EDA-15 and EDA-30 respectively. The size of the particles of methacrylic epoxy dispersion(ED) without PETA was 77.7 nm, and increased with the incorporation of PETA (Fig. 2). The particle sizes of epoxy dispersions (EDA-15 and EDA-30) containing 15 wt % and 30 wt % PETA were 127.8 and 240.5 nm, respectively.

Electrodeposition behavior and flash-off process

During the electrodeposition process, the methacrylic epoxy dispersions were deposited on the surface of a nickel-plated PET film to form a polymer film. Thus, the higher the concentration of the neutralized resin in the dispersion, the higher the yield of deposited material under the same applied voltage (100 V, direct current), as shown in Figure 3. The deposited yield of ED alone was smaller than that of ED containing PETA. This can be readily explained by the PETA—a low-molecular-weight monomer—acting as a coalescing agent that increases the conductivity of the deposited film.

During the electrodeposition of the epoxy dispersion containing 15 wt % PETA, 83 wt % of total amount of volatile compound including water was removed by electroosmosis. We have previously observed a similar

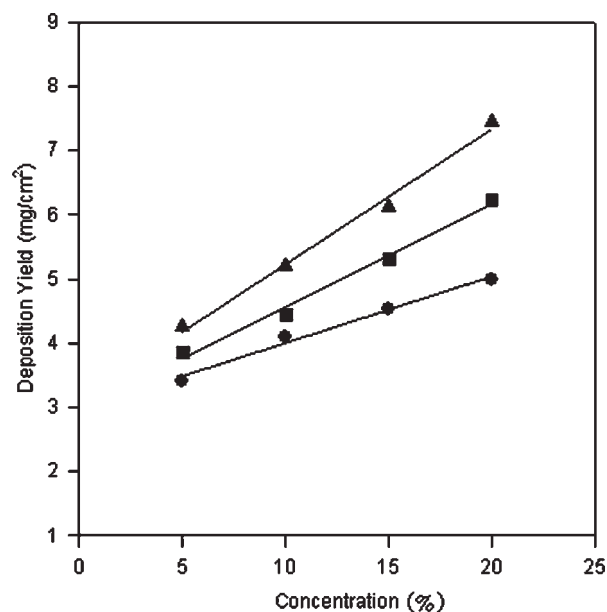


Figure 3 Effects of epoxy dispersion concentration on deposited yield. (●, ED; ■, EDA-15; ▲, EDA-30).

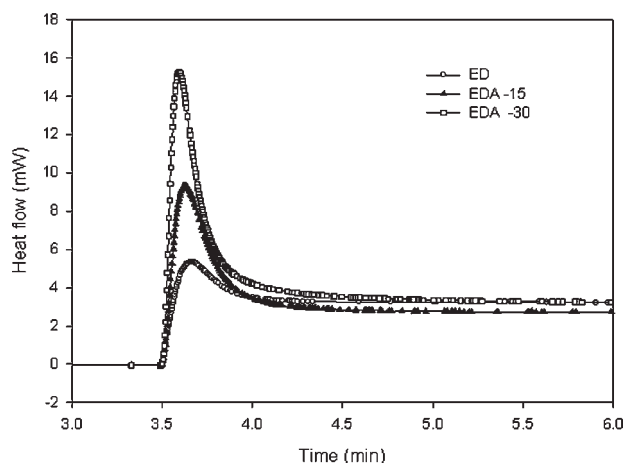


Figure 4 Photo-DSC exotherm curves for the photopolymerization of ED, EDA-15, and EDA-30.

result in UV-curable polyurethane dispersions using cationic electrodeposition.⁹ The remaining water could be completely evaporated by a 10-min flash-off process.

Curing and coating properties of UV-cured films

The reaction conversions and photopolymerization rates of the electrodeposited epoxy amine polymer were studied using photo-DSC. Figure 4 shows the photo-DSC exotherm curves for the photopolymerization of ED, EDA-15, and EDA-30, and related curing data are listed in Table I. Photo-DSC experiments are capable of providing kinetic data in which the measured heat flow can be converted directly to the ultimate percentage conversion and photopolymerization rate for a given formulation.¹²⁻¹³ The photo-DSC method assume that for a cure process the measured heat flow is proportional to the conversion rate. Therefore, the rate of change in the conversion can be defined as follows¹⁴⁻¹⁶:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{\text{total}}}$$

where $d\alpha/dt$ is the conversion rate or polymerization rate, dH/dt is the measured heat flow, and ΔH_{total} is the total exothermic heat of reaction. The degree of

TABLE I
Surface Properties and Curing Data for Various Coating Systems

Property	Sample		
	ED	EDA-15	EDA-30
MEK resistance (times)	79	156	235
Pendulum hardness (s)	83	129	186
ΔH (J/g)	14.8	37.2	83.6
Induction time (s)	1.9	1.2	0.9
Peak maximum (s)	6.0	5.4	4.8
Conversion (%)	12	31	75

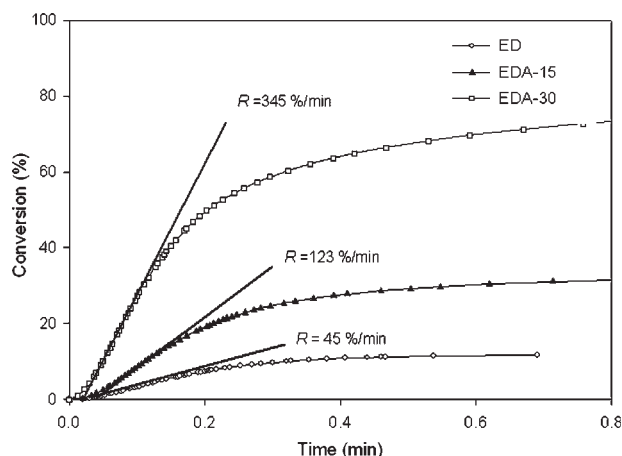


Figure 5 The conversion curves for the photopolymerization of ED, EDA-15, and EDA-30.

conversion is calculated from the integrated form of the above equation:

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{\text{total}}}$$

where α_t is the degree of conversion at time t and ΔH_t is the cumulative heat of reaction up curing time t . In this way, the ultimate percentage conversions and the polymerization reactivity, R , extracted from the exotherms in Figure 4 are shown in Figure 5. Here R is defined as the rate of polymerization derived from the slope of the portion of the percentage conversion versus time plot (Fig. 5) just after the early part of the curves, since this part is nonlinear and impossible to analyze because of it being influenced by factors such as oxygen and instrument response time. Figures 4 and 5 show that the exotherm values and the rate of polymerization, R , as well as the final conversion of ED are lower than the corresponding figures for EDA-15 and EDA-30. The low concentration of methacrylic groups in the ED formulation may result in reducing the exotherm values, the final conversion and the polymerization rate due to the difficult encountering of the propagating chains to the unreacted methacrylic groups. However, it is assumed that the increased multifunctional acrylates in EDA-15 and EDA-30 efficiently lead a reaction between the propagating species and acrylates, to give the high polymerization rate and conversion. In addition, the induction time (corresponding to 1% of the conversion) and the peak maximum time (related to the reactivity) decrease as the content of PETA is slightly increased as shown in Table I. These results also indicate that the addition of PETA in the dispersion decreased the viscosity of the total formulation and increased the diffusion mobility of propagating chains, thereby increasing the initial curing rate resulting in high exotherms and conversion rates.

Table I shows the effects of incorporating a multifunctional acrylate monomer (i.e., PETA) into the emulsion particles on the pendulum hardness and the MEK resistance of UV-cured emulsion films. This means that PETA increases the crosslinking density by copolymerizing with the methacrylate groups of the epoxy-amine polymer.

CONCLUSIONS

The combination of cationic electrodeposition and UV-curable epoxy dispersion was attempted in an effort to produce ambient UV curing after a relatively short flash-off process, which is advantageous to both UV coating and electrodeposition processes. UV-curable epoxy dispersions containing methacrylate groups for cationic electrodeposition coating were prepared by sequential reactions and neutralization with organic acid. The dispersions containing PETA had larger particles and exhibited a higher deposition yield than those without PETA. The UV crosslinking of cationic electrodeposition coatings is a powerful method for producing ambient curing with a shorter water flash-off time. The photo-DSC analyses showed that the coating formulation containing PETA had a higher conversion rate than

those without PETA, which resulted in a higher MEK resistance.

References

1. Glass, J. E., Ed. *Technology for Waterborne Coatings*; ACS Symposium Series 667; American Chemical Society: Washington, DC, 1997.
2. Reich, W.; Enenkel, P.; Lokai, M.; Menzel, K.; Schrof, W. *Proc RadTech Eur* 1997, 144.
3. Peeters, S.; Bleus, J. P.; Wang, Z. J.; Arceneaux, J. A.; Hall, J. *Proc RadTech Eur* 1997, 337.
4. Tirpak, R. E. *J Coat Technol* 1986, 58, 49.
5. Decker, C.; Masson, F.; Schwalm, R. *Macromol Mater Eng* 2003, 288, 17.
6. Stenson, P. H.; Coogan, R. G. *Proc RadTech Asia* 1993, 93, 243.
7. Pierce, P. E. *J Coat Technol* 1981, 53, 52.
8. Kim, Y. B.; Park, J. M.; Kim, H. K.; Hong, J. W. *Polym Bull* 2001, 47, 313.
9. Kim, Y. B.; Kim, H. K.; Yu, J. K.; Hong, J. W. *Surf Coat Technol* 2002, 157, 40.
10. Yang, C. P.; Ting, C. Y. *J Appl Polym Sci* 1997, 65, 233.
11. Krylova, I. *Prog Org Coat* 2001, 42, 119.
12. Clark, S. C.; Hoyle, C. E.; Jonsson, S.; Morel, F.; Decker, C. *Polymer* 1999, 40, 5063.
13. Pogue, R. T. *Thermochim Acta* 1999, 339, 21.
14. Keenan, M. R. *J Appl Polym Sci* 1987, 33, 1725.
15. Nam, J. D.; Seferis, J. C. *J Appl Polym Sci* 1993, 50, 1555.
16. Boey, F. Y. C.; Qiang, W. *Polymer* 2000, 41, 2081.