

Electrodeposition Properties of Self-Crosslinking Epoxy–Amine Cationic Resin Modified by Polycaprolactone Diol

CHIN-PING YANG and CHIH-YANG TING

Department of Chemical Engineering, Tatung Institute of Technology, Taipei, Taiwan, Republic of China

SYNOPSIS

A self-crosslinking polycaprolactone diol (PCD)-modified epoxy–amine adduct was prepared by first synthesizing the PCD-modified epoxy resin from diglycidyl ether of bisphenol A (DGEBA), PCD and bisphenol A (BPA), then reacting the partially pendant hydroxyl groups of this modified resin with 2-ethylhexanol half-blocked with toluene diisocyanate (2-EH half-blocked TDI), and finally reacting the terminal epoxy groups with secondary amines such as *N*-methyl ethanol amine (MEA) and di(2-methylisobutylketiminoethyl)amine (DKI). This epoxy–amine adduct was neutralized by acetic acid and could be dispersed in deionized water to form a stable emulsion, which could be used for the electrodeposition coating. The effects of solid content, pH value, solvent content of the emulsion, bath temperature, and applied voltage on the deposition yield and the throwing power of the resin were investigated. Meanwhile, the optimum crosslinking condition of the deposition film was also studied. It was found that the electrodeposition properties of the emulsion derived from the modified epoxy resin are superior to those of emulsion derived from the unmodified DGEBA epoxy resin.

INTRODUCTION

Cationic electrodeposition coating (CED) is widely used for primer coating automobiles. When the metallic substrate is connected with the cathode and immersed in the CED emulsion bath, the ionized resin can be electrically deposited on the substrate to form a deposited polymer film during the electrodeposition process. After rinsing and thermal curing, the deposited film would crosslink and form a smooth protective film.

The resins generally used as the backbone of the CED are acrylic resins,^{1–7} epoxy resins, their copolymers,^{8–13} and polyurethanes.^{14–19} With such advantages as resistance to chemical agents, high decomposition temperature, and good adhesion and toughness, the epoxy resin is still the best backbone for the CED. But the commercial DGEBA epoxy resin has too many rigid-type benzene rings which affect the electrodeposition properties of the CED, and some modifiers^{20,21} need to be introduced to improve the DGEBA epoxy resin.

In this study, PCD was used as the modifier and reacted with DGEBA epoxy resin (Epon 828) and BPA to synthesize the PCD-modified epoxy resin. Then, the partial pendant hydroxyl groups of this resin were ring-opened with 2-EH half-blocked TDI and the terminal epoxy groups were reacted with MEA and DKI to prepare a self-crosslinking PCD-modified epoxy–amine adduct. Lastly, by neutralizing with acetic acid and adding ethylene glycol mono-butyl ether as the coalescing solvent, the adduct could be dispersed in deionized water to form a stable emulsion.

Factors affecting the deposited yield and the throwing power were investigated. Meanwhile, the optimum crosslinking conditions were also estimated. In addition, the properties of emulsion prepared from the commercial DGEBA epoxy resin (Epon 1004) were also studied for comparison.

EXPERIMENTAL

Materials

The PCD-modified epoxy resin was prepared from Epon 828 (Shell Chemical Co.) having equivalent

weight per epoxy group (EEW) of 184–194, polycaprolactone diol (commercial name PCP0200, Union Carbide Co., MW = 530), and bisphenol A (Hon-sho, Japan). *N,N*-dimethyl benzylamine (DMBA) (Merck EP grade) was used as the catalyst.

DKI was prepared from methyl isobutyl ketone (MIBK) and diethylene triamine (DETA) (Hayashi extra pure grade), and Dowex 50W-X8 ion exchanger was the catalyst.

The commercial DGEBA epoxy resin (Epon 1004, EEW = 950) or the PCD-modified epoxy resin, toluene diisocyanate (TDI), 2-ethylhexanol (2-EH) (Hayashi extra pure grade), MEA (T.C.I. EP grade), DKI, and acetic acid (Wako EP grade) were used in the preparation of cationic resin. BCS and ethylene glycol mono-hexyl ether (HCS) (Wako EP grade) were used as coalescing solvents.

Synthesis

PCD-Modified Epoxy Resin

First, 39.48 g (0.105 mol) Epon 828 and 27.27 g (0.051 mol) PCD were added to a three-necked 300 mL reactor equipped with an electric stirrer and an inert nitrogen blanket, and preheated to 100°C for thorough mixing. After 2 g (0.16 wt %) of DMBA catalyst was added, the mixture was reacted at 100–120°C to obtain the Epon 828-PCD adduct. Then, supplemental 34.35 g (0.09 mol) Epon 828 and 20.65 g (0.09 mol) BPA were added to the adduct; the mixture was continuously heated at 100–120°C until the average EEW of the adduct reached 900.

Di(2-Methylisobutylketiminoethyl)amine

A mixture of 47.4 g (0.463 mol) DETA, 112 g (1.12 mol) MIBK, 0.25 g Dowex 50W-X8 ion exchanger, and 300 mL benzene was added to a 500 mL three-necked flask equipped with an electric stirrer and a Dean-Stark reflux trap. When reflux began, the generated water was distilled off azeotropically. This process was continued until evolution of water was no longer observed. Di(2-methylisobutylketiminoethyl)amine (DKI), a colorless liquid (sp. gr. 1.17) at ambient, was obtained and purified by distillation at 116–118°C under 0.8 torr.

2-Ethylhexanol Half-Blocked TDI

Into a 300 mL three-necked flask equipped with a magnetic stirrer and an inert nitrogen blanket, 36.7 g (0.21 mol) TDI were added. The flask was placed in an ice bath, and 28.8 g (0.22 mol) 2-EH were

added dropwise into the flask by a dropping funnel. After complete addition of 2-EH, the mixture was reacted at ambient for another 1 h to ensure complete reaction.

TDI-Blocked Amine-Terminated Adduct

One hundred grams of PCD-modified epoxy resin or Epon 1004 and 300 mL toluene were added to a five-necked reactor equipped with an electric stirrer and a Dean-Stark reflux trap. The mixture was heated to reflux to remove any water in it by azeotropic distillation for 3 h. After cooling to 40–50°C in an inert nitrogen blanket, the 2-EH-blocked TDI was added to the reactor, while the temperature was rising slowly to 80°C for 3 h. Finally, 4.9 g (0.064 mol) MEA and 4.4 g (0.016 mol) DKI were subsequently added to the adduct to induce the ring-opening reaction at 80°C for 3 h. When toluene was distilled off under reduced pressure, the TDI-blocked amine-terminated adduct was obtained.

Preparation of Emulsion

Twenty-eight grams of the TDI-blocked amine-terminated adduct and 7 g of BCS were added to a five-necked reactor equipped with an electric stirrer and a dropping funnel. The mixture was heated to 80°C for better mixing. Then, 0.51 g of acetic acid was added at 80°C for 40 min to convert 50% of tertiary amine into ionizable amine salt theoretically, and 105 g of deionized water was added dropwise with vigorous stirring to obtain a stable emulsion.

Characterization

Bath pH Value and Conductivity

The pH value and conductivity of the emulsion were established by the amount of acetic acid which was added to the emulsion bath. These two values were measured by a pH meter and a conductivity meter individually.

Electrodeposition

A steel plate, which was pretreated with zinc phosphate, was used as the cathode, and two stainless strips (the anode) were both immersed in the emulsion bath. The surface area ratio of the anode to the cathode is $\frac{1}{4}$. After 225 dc voltage was applied for 3

min, resin was deposited on the surface of the steel plate during the electrodeposition process. Then, the steel plate was removed from the emulsion bath, rinsed, and baked at 185°C for 18 min to obtain the cured film. The deposition yield is defined by the net weight (mg) of the cured film dividing the area (cm²) of the cured film.

Throwing Power

Throwing power of the emulsion was measured by a tube penetration test using an aluminum vessel connected to the anode and a stainless steel strip surrounded by a hollow glass cylinder connected to the cathode. The strip and glass cylinder were immersed in the emulsion bath contained in the vessel. After 100 dc voltage was applied for 1 min, the strip was rinsed and dried. The height (in cm) of the deposited resin is defined as the throwing power.

Gel Content

After deposition on the aluminum substrate, the deposited film was baked at various temperatures for 18 min (or various curing times at 185°C) to form cured film. These cured film/aluminum substrates were immersed in acetone and heated to reflux for 24 h. After drying, the gel content was calculated by dividing the residual weight of cured film by the initial weight of cured film.

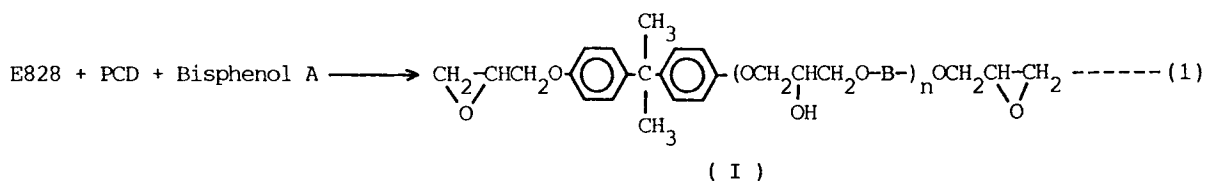
RESULTS AND DISCUSSION

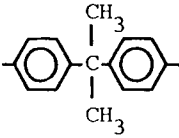
Synthesis

The PCD-modified epoxy resin was prepared from Epon 828, PCD and BPA. Since the epoxy group is more easily reacted with a phenolic group than with an alcoholic group, epoxy resin could react with BPA either at higher temperature without catalyst (DMBA) or at lower temperature with a small amount of catalyst. The reaction of an epoxy group with PCD would proceed only at higher temperature in the presence of DMBA. So the process for the preparation of PCD-modified epoxy resin was first to react Epon 828 with PCD at higher temperature in the presence of DMBA; then BPA was added and reacted at a lower temperature.

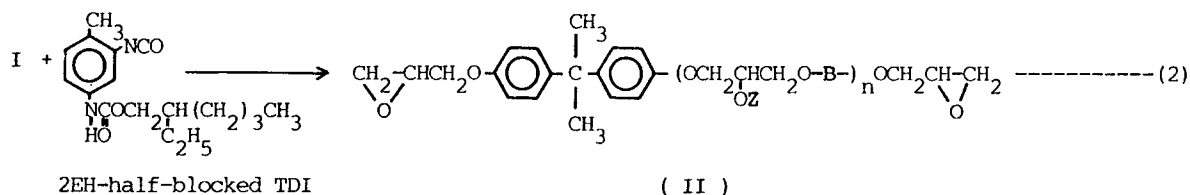
Varying the molar ratio of PCD to BPA in the backbone of the resin can adjust the ratio of soft segment to hard segment and the average molecular weight. In this study, the modified resin with the desired 6/1 ratio of soft to hard segment in the polymer backbone and average EEW of 900 was used.

The attached 2-EH half-blocked TDI on the epoxy resin backbone can serve as latent thermal-crosslinking sites. When MEA and DKI are added and reacted with epoxy group, the ring-opening addition reaction proceeds. The final product is the TDI-blocked amine-terminated adduct. Neutralizing the terminated amine with acetic acid and dispersing in deionized water converts the adduct to an electrodepositable cationic emulsion:

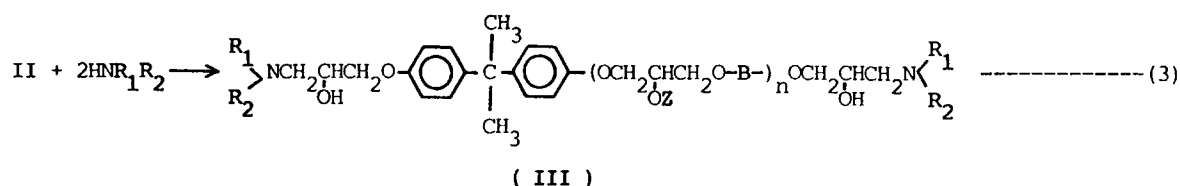


B	number of B		
$\left[(\text{CH}_2)_4 - \overset{\text{O}}{\parallel}{\text{C}} - \text{O} \right]_m (\text{CH}_2)_4$	X_1		
	X_2		
modified resin	$X_1/X_2=1/4$	$n=3.82$	E.E.W. 900
reference resin	$X_1/X_2=0/1$	$n=5.5$	E.E.W. 950 (E1004)

Scheme 1

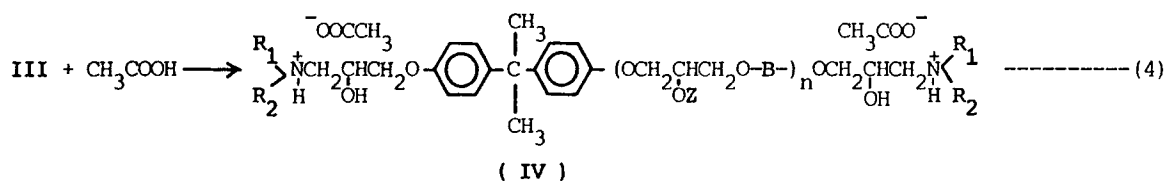


Z	number of Z
-H	Y_1
$\begin{array}{c} \text{OH} \\ \\ \text{---CN} \\ \\ \text{CH}_3 \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} \begin{array}{c} \text{OH} \\ \\ \text{NCOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$	Y_2
$Y_1 = n/2$	$Y_2 = (n/2) + 1$



R_1	R_2
MEA: $-\text{CH}_3$	$-(\text{CH}_2)_2\text{OH}$
DKI: $-\text{CH}_2\text{N}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$	$\text{R}_2 = \text{R}_1$

MEA/DKI=4/1 (mole)



Scheme 1 (continued from previous page)

The purpose of acetic acid is to ionize the amine end group of the resin, so that an increase in the amount of acetic acid makes more of the terminated amine of the emulsion turn into the ionizable amine

salt. This lowers the pH value of the emulsion and raises the conductivity, as shown in Figure 1. From this figure we also know that the emulsion conductivity of the modified resin is higher than that of

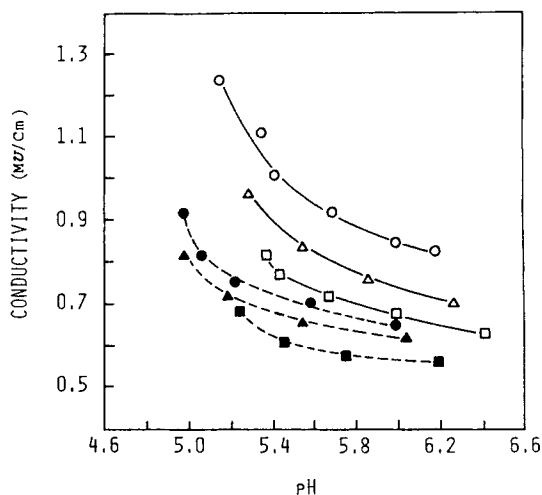


Figure 1 Effects of the pH value of emulsions on the conductivity of emulsions at 25°C: BCS content = 5 wt %; (—) modified resin; (---) Epon 1004; (○, ●) solid content = 20 wt %; (△, ▲) solid content = 15 wt %; (□, ■) solid content = 10 wt %.

the DGEBA resin at the same pH value, and the higher the solid content of the emulsion, the higher the conductivity for the same resin.

Properties of Electrodeposition

Figure 2 shows that the lower the pH value, the smaller the deposition yield. This diminution is due to the "redissolution" of the deposited resin on the

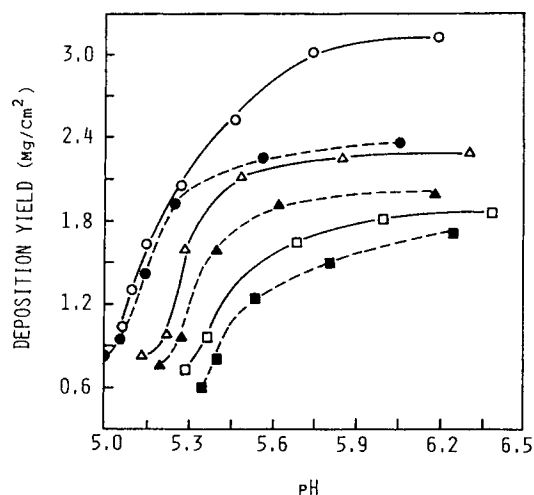


Figure 2 Effects of the pH value of emulsions on the deposition yield of resins: BCS content = 5 wt %; applied voltage = 225 V; deposited time = 3 min; (—) modified resin; (---) Epon 1004; (○, ●) solid content = 20 wt %; (△, ▲) solid content = 15 wt %; (□, ■) solid content = 10 wt %.

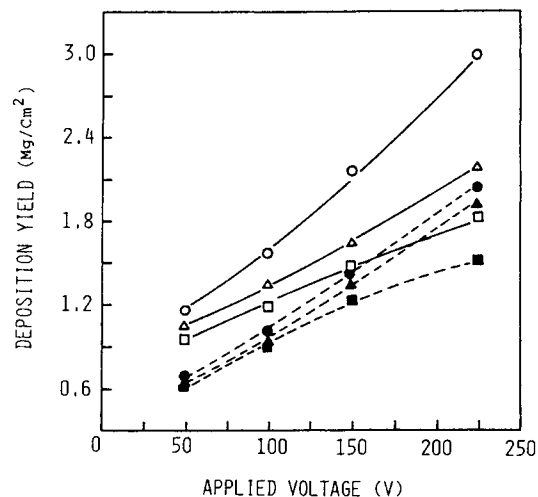


Figure 3 Effects of applied voltages on the deposition yield of resins: pH = 5.8–6.0; BCS content = 5 wt %; deposited time = 3 min; (—) modified resin; (---) Epon 1004; (○, ●) solid content = 20 wt %; (△, ▲) solid content = 15 wt %; (□, ■) solid content = 10 wt %.

cathodic substrate, because acid promotes the redissolution rapidly at the lower pH value. We also find that the deposition yield of the modified resin is higher than that of the DGEBA resin, and the higher the solid content of the emulsion, the higher the deposition yield for the same emulsion at the same pH value.

Because the higher voltage applied induces a large driving force, it causes an increase of the deposition yield (Fig. 3). Figure 4 shows that the deposition

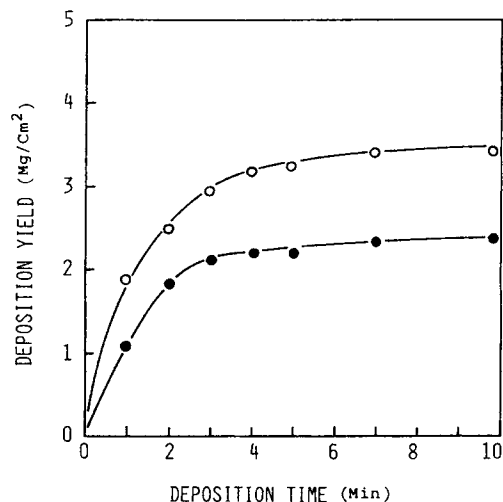


Figure 4 Effects of deposited time on the deposition yield of resins: solid content = 20 wt %; pH = 5.8–6.0; BCS content = 5 wt %; applied voltage = 225 V; (○) modified resin; (●) Epon 1004.

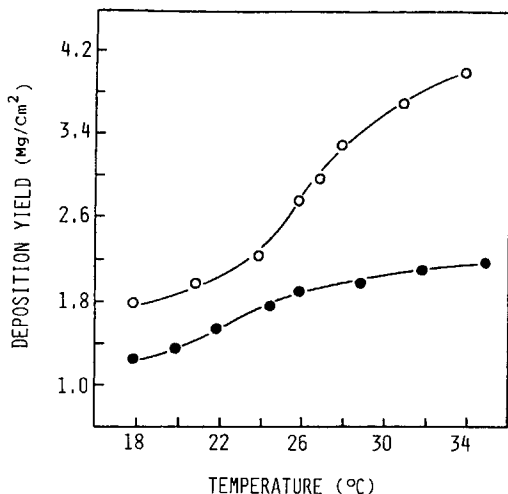


Figure 5 Effects of bath temperatures on the deposition yield of resins at 225 V for 3 min: solid content = 20 wt %; (○) modified resin; (●) Epon 1004.

yield increases initially with the deposition time but tends to reach a limit after 3 min. The explanation of this phenomenon lies in the insulation characteristics of the deposited polymer film. During the electrodeposition, the deposited film, a polymeric insulator, becomes thicker until it can prevent an electric current. At this time there is no electrodeposition process, so that the thickness of the deposited film will not increase any longer.

In Figure 5 we find that the bath temperature affects the deposition yield. When the temperature

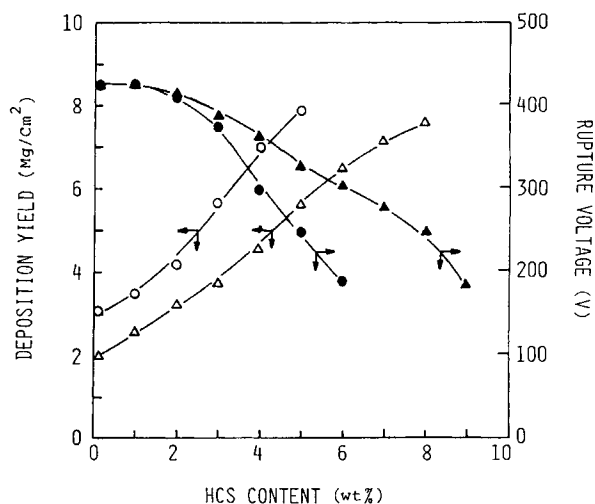


Figure 6 Effects of HCS content on the deposition yield of resins and rupture voltages: applied voltage = 225 V; deposited time = 3 min; solid content = 20 wt %; BCS content = 20 wt %; (○, ●) modified resin; (△, ▲) Epon 1004.

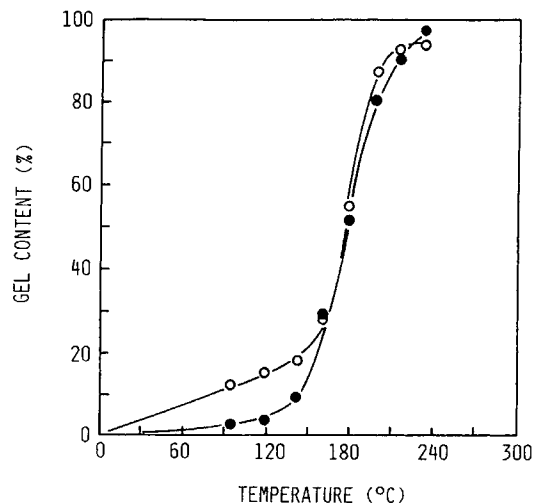


Figure 7 Effects of curing temperatures on the gel content: curing time = 18 min; (○) modified resin; (●) Epon 1004.

is rising, the deposition yield will increase simultaneously, possibly an effect on the velocity of electrophoresis and the conductivity of the deposited film. For this reason we always control the bath temperature at 25–27°C.

The organic solvent content affects the stability of the emulsion and the properties of the electrodeposition.^{23,24} Adding high-boiling-point HCS (<10 wt %) can raise the deposition yield but diminishes the rupture voltage (Fig. 6). In view of needs such as increasing the deposition yield, keeping a high rupture voltage, and preventing environmental pol-

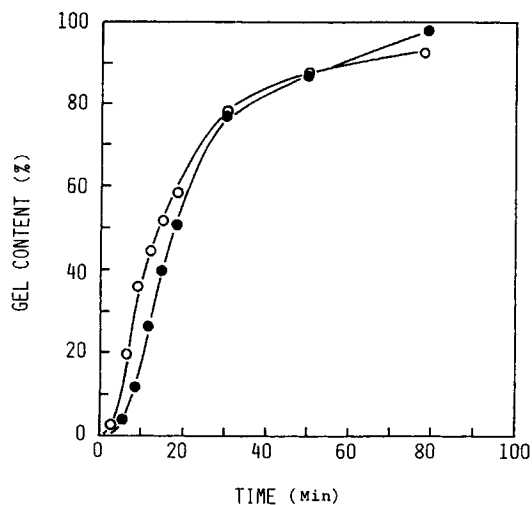


Figure 8 Effects of curing time on the gel content: curing temperature = 185°C; (○) modified resin; (●) Epon 1004.

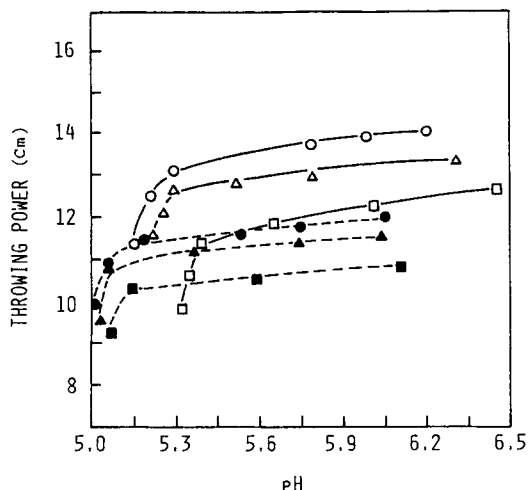


Figure 9 Effects of the pH value of emulsions on throwing power: applied voltage = 100 V; deposited time = 1 min; (—) modified resin; (---) Epon 1004; (○, ●) solid content = 20 wt %; (△, ▲) solid content = 15 wt %; (□, ■) solid content = 10 wt %.

lution, the content of HCS is better maintained below 2 wt % in the emulsion.

Crosslinking Reaction

Figure 7 shows the relationship between the gel content at different curing temperatures at constant time. We find that both curves show a rapid increase in gel content over 150°C. This means the film will crosslink at this temperature. Because 2-EH (b.p. 183°C) volatilizes fast in this temperature range, the blocked isocyanate groups are turned into the active ones, and then react with the rest free hydroxyl groups of the epoxy resin to form a network structure.

The gel content reaches over 90% when the curing temperature exceeds 200°C. At higher temperature (>200°C) the gel content of the DGEBA resin is higher than that of the modified resin, because the

DGEBA resin has the larger hydroxyl equivalent weight. Looking at the appearance of the cured film, we find that the higher the cured temperature, the more the yellowing of the film.

Figure 8, which plots the relationship between the gel content and the cured time at 185°C, shows that when the cured time exceeds 50 min, the gel content can be over 90%.

Throwing Power²⁵

The most obvious advantage of CED is that it can deposit a uniform film on the overall surface of a complicated object. This ability can be estimated by throwing power.

The factors in throwing power were studied by Furuno and Ohyabu²⁶ and Pierce.²⁷ Furuno pointed out that throwing power is proportional to the square root of the conductivity. We already know from Figure 1 that the conductivity rises when the pH value comes down. So according to Furuno's formula, throwing power should also rise when the pH value comes down. But from Figure 9 we find that the lower the pH value, the lower the throwing power; meanwhile, throwing power diminishes rapidly at the lower pH value. This result is in opposition to the Furuno's result. The reason is that the increase in conductivity comes from the proton rather than the ionizable resin. Especially, at the lower pH value the emulsion has a high level of protons. Since the proton will compete with the ionizable resin during the electrodeposition process, it quickly diminishes the throwing power. Figure 9 also points out that throwing power of the modified resin is superior to that of the DGEBA resin. This result may be caused by the flexible modifier (PCD).

Physical and Chemical Properties of the Cured Deposited Film

All the cured films were characterized for 6 hardness, adhesive strength, acid resistivity, and alkali resis-

Table I The Physical and Chemical Properties of the Cured Deposited Film

Backbone Resin	Test Item			
	Hardness	Adhesive Strength	Alkali Reagent Resistance ^a	Acidic Reagent Resistance ^b
Epon 1004	3H	100/100	OK	OK
Modified resin	1H	100/100	OK	OK

^a 0.1N NaOH_(aq) × 48 h.

^b 0.2N H₂SO_{4(aq)} × 48 h.

tivity. The results are shown in Table I. The hardness of the DGEBA's cured film is 3H pencil hardness, but that of the modified resin's cured film is only 1H. The difference is brought about by the partial replacement of the rigid benzene rings with the flexible modifier (PCD). In addition, all cured films show excellent adhesive strength, acid resistivity, and alkali resistivity.

CONCLUSION

The emulsions of the PCD-modified epoxy resin have better electrodeposition properties when compared with those from DGEBA resin. On the other hand, when the acidity is near neutrality (pH 7), the emulsion has better electrodeposition properties. In addition, the physical and chemical properties of all cured films are excellent.

REFERENCES

1. E. J. Murphy, U.S. Pat. 4,187,203 (1980).
2. K. Sekmakas and R. Shah, U.S. Pat. 4,195,147 (1980).
3. K. Sekmakas and R. Shah, U.S. Pat. 4,198,495 (1980).
4. G. Minami, Y. Manabe, and Y. Suematsu, U.S. Pat. 3,988,281 (1976).
5. J. E. Jones, U.S. Pat. 4,009,133 (1977).
6. I. Hazan, U.S. Pat. 4,177,124 (1979).
7. S. L. Bachwalter, J. F. Bosso, and R. M. Christenson, U.S. Pat. 4,102,863 (1976).
8. J. F. Bosso and M. Wismer, U.S. Pat. 3,975,346 (1976).
9. J. F. Bosso and N. T. Castellucci, U.S. Pat. 4,144,159 (1979).
10. R. M. Christerson, J. F. Bosso, M. E. Hartman, and W. H. Chang, U.S. Pat. 4,081,341 (1978).
11. J. F. Bosso and M. Wismer, U.S. Pat. 3,962,165 (1976).
12. J. F. Bosso and M. Wismer, U.S. Pat. 4,001,101 (1977).
13. J. F. Bosso and M. Wismer, U.S. Pat. 4,001,156 (1977).
14. Y. Matsunaga and Y. Kobagyashi, U.S. Pat. 3,823,118 (1974).
15. G. Pampouchidis and H. Hong, U.S. Pat. 4,179,425 (1979).
16. G. Pampouchidis and H. Hong, U.S. Pat. 4,176,009 (1979).
17. H. Hong and G. Pampouchidis, U.S. Pat. 4,174,332 (1979).
18. J. R. Marchetti and R. D. Jerabek, U.S. Pat. 3,975,250 (1976).
19. R. D. Jerabek, U.S. Pat. 3,925,180 (1975).
20. J. R. Marchetti, R. R. Zwack, and R. D. Jerabek, U.S. Pat. 4,148,772 (1979).
21. J. R. Marchetti, R. R. Zwack, and R. D. Jerabek, U.S. Pat. 4,104,147 (1978).
22. Henry Lee and Kris Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1982, pp. 4-17.
23. M. Wismer, P. E. Pierce, J. F. Bosso, R. M. Cristerson, R. D. Jerabek, and R. R. Zwack, *J. Coatings Technol.*, **54**(688), (1982).
24. Peter M. Grant, *J. Coatings Technol.*, **53**(677), (1981).
25. S. B. A. Qaderi, D. R. Bauer, J. W. Holubha, and R. A. Dickie, *J. Coatings Technol.*, **56**(719), (1984).
26. N. Furuno and Y. Ohyabu, *Progr. Org. Coatings*, **5**, 201-217 (1977).
27. L. C. Sturai and J. F. Bosso, U.S. Pat. 3,894,922 (1976).

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