

Synthesis and Properties of Cationic Resins Derived from Polyether/Polyester-Modified Epoxy Resins

LUNG-TA LEE and CHIN-PING YANG*

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

SYNOPSIS

Four polyether and one polyester-modified cationic resins were synthesized by reacting polyether/polyester-modified epoxy resins with 2-ethylhexanol-blocked-toluene diisocyanate (2-EH-blocked TDI) and diethanolamine and subsequently neutralizing the resins with acetic acid. Four different polyethers and one polycaprolactone diol (PCP) were used to react with epoxy resin to form polyether-modified epoxy resins (1a-d) and polyester-modified epoxy resin (1e). The extent of reaction of epoxy resin and polyether or polyester was evaluated by the change of epoxy equivalent weight and the gel permeation chromatography curve of the resulting product. Cationic resins were dissolved in suitable solvents and were mixed with deionized water to form emulsions. Some factors, such as pH value of emulsion, solvent content, and applied voltage affecting the emulsion and electrodeposition properties, were investigated. Cationic resins, prepared from PPG (#1000)-modified epoxy resins, yielded a wider pH range of stable emulsion and also yielded deposited films with a pleasing appearance. PEG (#1000)-modified cationic resins produced a higher deposition yield, but higher throwing power was obtained by deposition of the PCP (#530)-modified cationic resins.

INTRODUCTION

Since the Ford Motor Co. first commercially applied anionic electrodeposition, the process has been used almost universally in highly valued coating operations, such as priming motor cars, electrical appliances, and many other commercial articles. Recently, major emphasis has been placed on converting all automotive paint facilities to cathodic electrocoat systems, due to the superior corrosion protection provided as compared with earlier anodic and spray primer systems. The electrodeposition process has many advantages, including uniformity and completeness of coating, even for intricate shapes, labor savings, and pollution abatement.

Cathodic electrodepositing resin systems generally consist of epoxy¹⁻⁷ or acrylic⁸⁻⁹ polymer backbones with cationic groups being provided by pro-

tonated salt groups. The preferred resin for electrodeposition is the DGEBA-type epoxy resin, obtained by reacting epichlorohydrin with bisphenol A in the presence of sodium hydroxide. The deposition yields of the cationic resins, directly prepared by DGEBA epoxy resins with secondary amine, were low and their crosslinked deposited films were brittle. In this study, four different polyethers and one polyester were used to react with DGEBA epoxy resin to yield polyether/polyester-modified epoxy resins (1a-e). These modified epoxy resins were reacted with 2-ethylhexanol-blocked TDI to obtain thermally crosslinkable epoxy resins. The resulting epoxy resins were reacted with diethanolamine and subsequently neutralized with acetic acid to yield polyether/polyester-modified cationic resins. The extent of reaction of polyether/polyester and epoxy resin can be evaluated by the change of epoxy equivalent and gel permeation chromatography curve of the resulting product. Subsequently, suitable solvents and acetic acid were used to investigate the emulsion and electrodeposition properties.

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials

Reagents used in the preparation of polyether/polyester-modified epoxy resins included diglycidyl ether of bisphenol A epoxy resin (epoxy equivalent 650), polyethers, and polyester. Four polyethers and one polyester were used in this study. They were polyethylene glycols [PEG (#400), PEG (#600), and PEG (#1000)], polypropylene glycol [PPG (#10000)], and polycaprolactone diol [PCP (#530)]. All of them were extra pure grade. N,N-dimethylbenzylamine (DMBA) (Merck) was used to catalyze the reaction.

Reagents, used in the preparation of thermally crosslinkable cationic resins, included polyether/polyester-modified epoxy resins, ethylhexanol (2-EH) (Hayashi Extra Pure Grade), toluene diisocyanate (TDI), diethanolamine (DEA) (Fluka agent grade), and acetic acid.

Organic solvents used in this study were toluene and ethylene glycol mono-*n*-butyl ether (BCS) and ethylene glycol mono-*n*-hexyl ether (HCS).

Apparatus

A liquid chromatograph (Shimadzu LC-6A), a conductivity meter, a pH meter, an electrodeposition apparatus, and a throwing power testing vessel were employed. The electrodeposition apparatus and throwing power testing vessel were described in a previous publication.¹⁰

Synthesis

Polyether-Modified Epoxy Resins (1a-e)

Epoxy resin (epoxy equivalent weight 650) (260 g, 0.2 mol) was charged to an 1000-mL, five-necked flask, equipped with an electric stirrer, a reflux condenser, a dropping funnel, and an inert nitrogen blanket. After the epoxy resin was heated to 100°C to melt the epoxy, 0.1 mol polyether [PEG (#400), PEG (#600), PEG (#1000), PPG (#1000), or PCP (#530)], and 0.52 g N,N-dimethylbenzylamine were added into the flask. The mixture was heated to 120°C and kept at that temperature for 24 h for the completion of reaction. Finally, the resultant products were polyether-modified epoxy resins (1a-d).

Polyester-Modified Epoxy Resin (1e)

The synthetic procedures for the preparation of polyester-modified epoxy resin were as described above.

2-Ethylhexanol-Blocked TDI (2)

The synthetic procedures for preparation of 2-ethylhexanol-blocked TDI were described in a previous publication.¹⁰

Synthesis of Resin 4a-e

A desired amount of polyether/polyester-modified epoxy resin and toluene were added to a five-necked flask equipped with an electric stirrer, a Dean-Starck trap, a dropping funnel and an inert nitrogen blanket. The mixture was heated to 110–120°C to remove any water in the polyether/polyester-modified epoxy resin by azeotropic distillation. After cooling to 40–50°C, a calculated quantity of (2) was added to the flask. The whole mixture was gradually heated to 90°C and was kept at that temperature for 4 h. After cooling the product to 60°C, a calculated quantity of diethanolamine was added to the flask. The mixture was heated to 90°C and was kept at that temperature for 3 h for the completion of reaction. Finally, toluene was distilled off under reduced pressure.

Preparation of Emulsion

The general process for the preparation of the emulsion was also described in a previous publication.¹⁰

Measurement of Epoxy Equivalent Weight

Epoxy compound (about 1 g) and 25 mL of pyridium chloride pyridine solution (16 mL conc. HCl per L of pyridine) were added to a 200 mL, round-bottom flask, equipped with a reflux condenser and with a magnetic stirrer. The solution was stirred and heated gently until all the sample had been dissolved; later, the solution was heated to reflux temperature for 25 min. After cooling the solution to room temperature, 15 drops of phenolphthalein indicator (0.1 g phenolphthalein per 100 mL ethanol) was added to the solution; the solution was then titrated with 0.2–0.25 N methanolic NaOH to a pink end point.

Epoxy equivalent weight

$$= \frac{16 \times (\text{sample weight in g})}{(\text{g of oxirane oxygen in sample})}$$

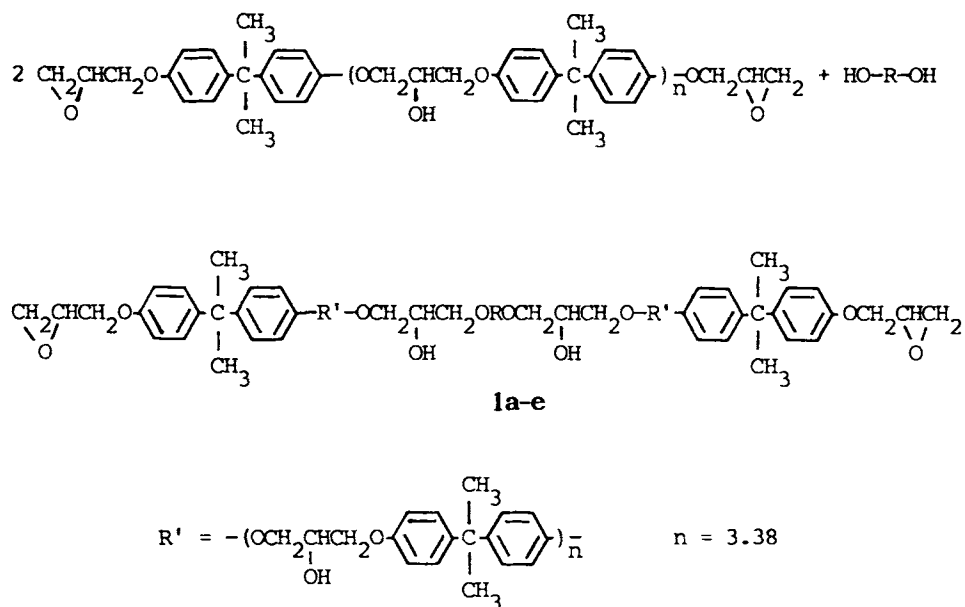
Grams of oxirane oxygen in sample

$$= (A-B)(N)(0.016)$$

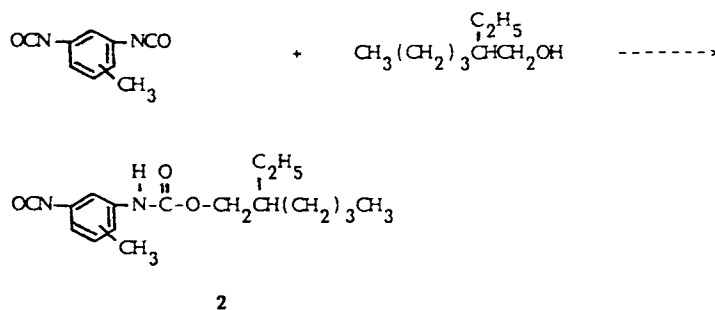
A = milliliter of NaOH for blank

B = milliliter of NaOH for sample

N = normality of NaOH



1	R	Mn
1a	$\text{---}(\text{CH}_2\text{CH}_2\text{O})_m\text{---CH}_2\text{CH}_2\text{---}$	400
1b	$\text{---}(\text{CH}_2\text{CH}_2\text{O})_m\text{---CH}_2\text{CH}_2\text{---}$	600
1c	$\text{---}(\text{CH}_2\text{CH}_2\text{O})_m\text{---CH}_2\text{CH}_2\text{---}$	1000
1e	$\text{---}(\text{CH}_2\text{CHO})_m\text{---CH}_2\text{CH---}$ $\quad \quad \quad \quad \quad \quad $ $\quad \quad \quad \text{CH}_3 \quad \quad \quad \text{CH}_3$	1000
1d	$\text{---}(\text{CH}_2)_4\text{---C(=O)}_m\text{---}(\text{CH}_2)_4\text{---}$ $\quad \quad \quad $ $\quad \quad \quad \text{O}$	530



Scheme 1

Characterization

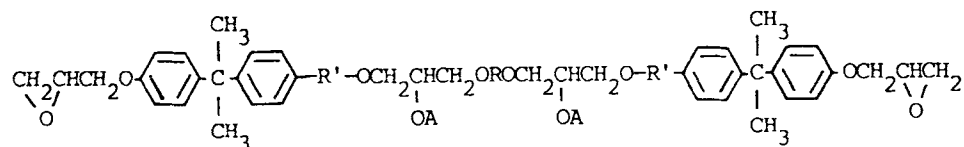
Bath Conductivity

The bath conductivity and pH value of the emulsion were measured by adding acetic acid dropwise into the emulsion at room temperature.

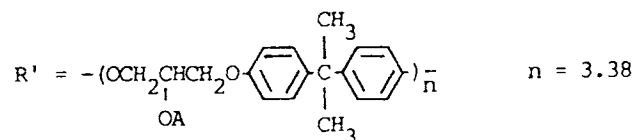
Electrodeposition

The electrodeposition process was described in a previous publication.¹⁰ After deposition, the iron plate was rinsed to remove any nonadhering material and the coating was cured at 200°C for 20 min to obtain the deposition yield.

1a-e + 2

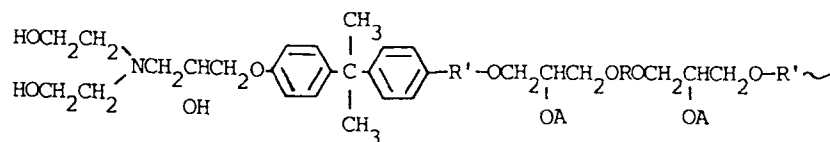
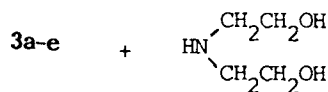


3a-e

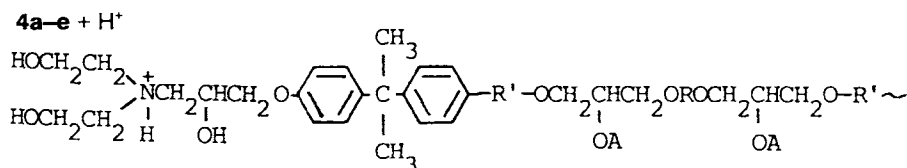


A	Number of A
-H	x
	y

$$x + y = 2n + 2, \quad n = 3.38, \quad y/(x+y+2) = 0.5$$



4a-e



5a-e

Scheme 1 (continued from the previous page)

Throwing Power

The throwing power of the emulsion was measured by tube penetration test, as described in a previous publication.¹⁰

RESULTS AND DISCUSSION

Synthesis

Cationic resins (5a–e) were synthesized by reacting polyether/polyester-modified epoxy resins (1a–e) with 2-ethylhexanol blocked toluene diisocyanate (2-EH-blocked TDI) (2) and diethanolamine and subsequent neutralization with acetic acid. As shown in Scheme 1, polyether/polyester-modified epoxy resins (1a–e) were synthesized by reacting the epoxy resin possessing epoxy equivalent weight of 650 with various polyether or polyesters. The reaction extent of epoxy resin with polyethers or polyester can be evaluated by the change of epoxy equivalent weight and the gel permeation chromatography curve of the resulting product. Hydroxyl groups contained in the epoxy polymer backbones will react with the epoxy groups at high temperatures, but at low temperatures the reaction only takes place in the presence of catalyst (such as tertiary amine). As shown in Figure 1, without catalyst, epoxy equivalent weight did not change with the reaction time at temperatures below 140°C, but temperatures above 160°C will cause the epoxy equivalent to increase with the reaction time. The higher the reaction temperature, the faster the rate of the increase of epoxy equivalent weight. At 120°C, if 0.2 wt % N,N-dimethylbenzylamine (DMBA) was used as catalyst, the epoxy equivalent weight will quickly increase with the reaction time. Figure 2 shows the effects of reaction time on the epoxy equivalent weight for the reaction products of various polyethers or polyester with epoxy resin in the presence of 0.2 wt % DMBA. Hydroxyl groups contained in polyethers or polyester are primary hydroxyl groups. The reactions of these primary hydroxyl groups with epoxy groups in epoxy resins are faster than those of secondary hydroxyl groups contained in epoxy polymer backbones with epoxy groups, so the polyether/polyester-modified epoxy resins can be obtained. Figure 3 illustrates the GPC curves of epoxy resin, PEG (#400), initial mixture of epoxy resin, and PEG (#400) and PEG (#400)-modified epoxy resin. From Figure 3, it can be seen that PEG (#400) will be consumed after 24 h of the reaction at 120°C with the presence of 0.2 wt % DMBA, which causes the disappearance of the absorption peak at 24.2 min of elution time. After the

completion of reaction, if PEG (#400) was added again into the reaction product, the absorption peak at 24.2 min of elution time will appear again. This phenomenon indicates that PEG (#400) was indeed incorporated in the reaction. Meanwhile, the molecular weight of PEG (#400)-modified epoxy resin was higher than that of initial mixture of PEG (#400) and epoxy resin, so the absorption peak of PEG (#400)-modified epoxy resin shifts to a lower elution time. Epoxy equivalent weight of the synthetic polyether/polyester-modified epoxy resins and their hydroxyl contents are shown in Table I. 2-EH-blocked TDI (2) was obtained by reacting a sufficient quantity of 2-ethylhexanol (as the blocking agent) with toluene diisocyanate (TDI) to provide a product having one free isocyanate group remaining. The reaction between TDI and the blocking agent is generally exothermic and is preferably carried out at low temperature to promote isocyanate group selectivity. Usually, a temperature of 18°C or even lower can be employed. Hydroxyl group and pendant urethane linkage-containing thermal crosslinkable epoxy resins (3a–e) were prepared by reacting polyether/polyester-modified epoxy resins (1a–e) and 2-EH-blocked TDI. Preferably, sufficient 2-EH-blocked TDI was employed to provide an adequate number of crosslinking sites to provide a cured film. Usually, less than 120°C was required to preserve the capped isocyanate groups to avoid gelation and to retain latent crosslinking sites. The completion of reaction can be confirmed by disap-

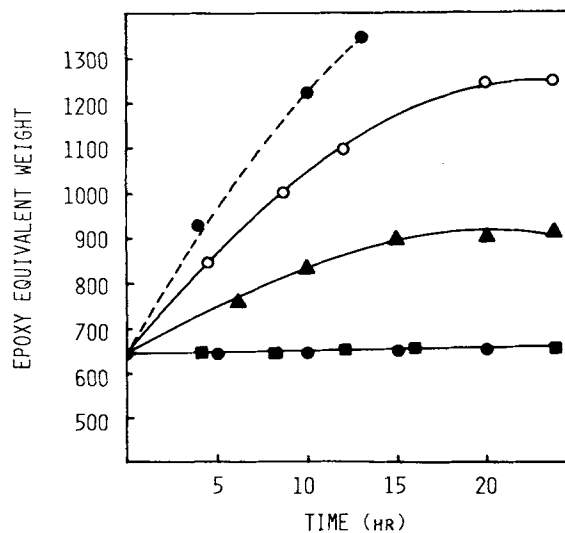


Figure 1 Effect of reaction time on the epoxy equivalent weight of DGEBA resins: (●) 120°C, (■) 140°C, (▲) 160°C, (○) 200°C; (—) without catalyst, (---) 0.2 wt % DMBA as catalyst.

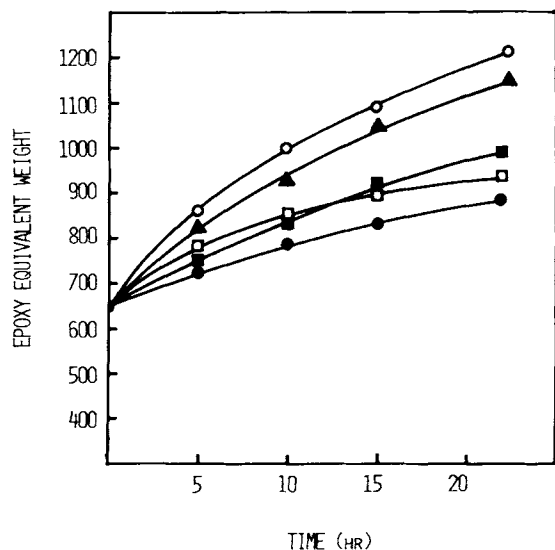


Figure 2 Effect of reaction time on the epoxy equivalent weight of polyether/polyester-modified epoxy resin: Reaction temperature = 120°C; catalyst content = 0.2 wt % DMBA; (●) PEG (#400), (■) PEG (#600), (▲) PEG (1000), (○) PPG (#1000), (□) PCP (#530).

pearance of the IR absorption peak at 2250 cm^{-1} of isocyanate groups.

After the completion of the above reaction, the resulting product was reacted with diethanolamine to form thermal crosslinkable tertiary amine-terminated resins 4a–e. Finally, the obtained epoxy-amine adducts were neutralized with acetic acid and dispersed in deionized water, yielding an electrodepositable emulsion.

PROPERTIES OF CATIONIC RESINS

Factors Affecting the Formation of Stable Emulsion

The epoxy-amine adducts (4a–e) were readily soluble in various organic solvents, such as acetone, toluene, DMF, and BCS, whereas they were insoluble in water. It was necessary to add a neutralizing agent to obtain a suitable aqueous composition for electrodeposition. Neutralization of these adducts was accomplished by all or part of the amino groups with a water-soluble acid, such as acetic acid. The amount of acetic acid used can control the ratios of ammonium salt and amine contained in the resin to adjust the dispersion to give the best emulsion state. The optimum extent of neutralization depends upon the structure and the molecular weight of the resins. Moreover, the state of the aqueous dispersion was

also affected by organic solvent content. Higher organic solvent content makes the resins easier to be solubilized or dispersed in water. When the organic solvent content was too low, precipitation occurred. The critical solvent content and pH value range for the preparation of stable emulsions for resins 5a–e are shown in Table II. Stable emulsions can be obtained when the solvent content is higher than 0.5 wt %, except for resin 5d. The pH value range for stable emulsion, prepared from resin 5d, was wider than that of other emulsions, that is, from 3.95 to 5.73. When the pH values of solutions were higher than the pH value range of stable emulsions, the resins precipitated quickly. Clear solutions were obtained if the pH value of solutions was lower than the pH value range of stable emulsions. For resins 5a–c, it also can be seen that the higher molecular weight of polyether or polyester contained in cationic resins yielded poor solubility. The lower pH value range was required to form stable emulsions. Introducing polyether or polyester in cationic resins generally lowers the water solubility of these polyether/polyester-modified cationic resins, so the pH value of stable emulsions of the polyether/polyester-modified cationic resins was lower than that of

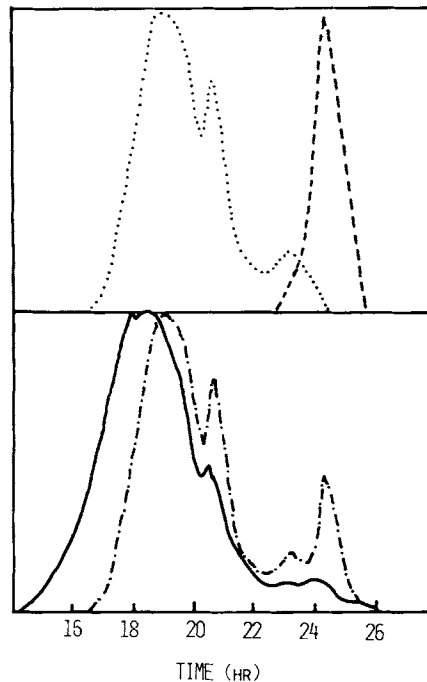


Figure 3 GPC curves of PEG (#400), epoxy resin, the initial mixture of PEG (#400), and epoxy resin, and PEG (#400)-modified epoxy resin: (---) PEG (#400), (.....) Epoxy resin, (-.-.-) initial mixture, (—) PEG (#400)-modified epoxy resin.

Table I Epoxy Equivalent Weight and Hydroxyl Content of the Synthetic Polyglycol-Modified Epoxy Resins

1	E. E. W. of Epoxy Resin	Polyglycol (PG)	E. E. W. of PG-modified Epoxy Resin	Hydroxyl Content ^a (mol/100 g)
1a	650	PEG (#400)	890	0.33
1b	650	PEG (#600)	990	0.31
1c	650	PEG (#1000)	1150	0.25
1d	650	PPG (#1000)	1220	0.25
1e	650	PCP (#530)	940	0.31

^a Theoretical value.

emulsions prepared from nonpolyether/polyester-modified cationic resins. However, the introduction of polyether or polyester in cationic resins improved the stability of emulsions.

Conductivity of Emulsion

The properties of electrodeposition were strongly affected by the conductivity of emulsions. High conductivity accelerated the mobility of charged resin and increased their throwing power, but yielded low deposition yield and low rupture voltage. The conductivity of emulsion was greatly influenced by the pH value of the emulsion and the concentration of cationic resin. From Table II, it can be seen that the conductivity of the emulsions decreased with increasing pH value of the emulsions. The conductivity of emulsions was also affected by the molecular weights of cationic resins. Cationic resins with lower molecular weight showed a higher conductivity. This is due to the fact that the emulsion prepared from the resin with lower molecular weight contained more conductive ions. The conductivity of the emulsions prepared from polyether/polyester-modified epoxy resin was generally lower than that of emulsions directly prepared from DGEBA epoxy resins.

Factors Affecting Electrodeposition Yield

Some factors, such as pH value, the organic solvent content, the resin content of electrodeposition bath, the kind and the molecular weight of cationic resin, will affect the yield of the deposited film. The pH value of emulsion determines the dispersibility of cationic resin and hence it will affect the deposition yield of the emulsion. As shown in Figure 4, the deposition yield increased with the pH value of emulsion. This was reasonable because higher acidity enhanced the solubility of the deposited resin, lowering the yield. The mol wt of resin 5c is almost equal to the mol wt of resin 5d, but the former gives a higher deposition yield. This can be attributed to the different molecular structures of resin 5c and resin 5d. For the emulsions prepared from the same molecular structure, resins having a higher mol wt produce a higher deposition yield (i.e., 5c > 5b > 5a). The mol wt of PCP-modified cationic resin is lower than that of cationic resins 5b and 5d, but the different molecular structure of PCP yields the PCP-modified cationic resin with a higher deposition yield.

Figure 5 shows the effect of BCS content on the deposition yield of emulsions. Lower organic solvent contents might cause precipitation of the resin so-

Table II Critical Solvent Content and pH Value Range for the Stable Emulsions of 5a-e

Resin	Weight of Resin (g)	Weight of Water (g)	Critical BCS Weight (g)	BCS Weight Ratio (%)	pH Value Range	Conductivity ^a (mv/cm)
5a	17.5	330	1.75	0.5	4.15-4.98	0.48-0.31
5b	17.5	330	1.75	0.5	4.15-4.75	0.47-0.29
5c	17.5	330	1.75	0.5	3.92-4.44	0.42-0.26
5d	17.5	330	2.63	0.75	3.95-5.73	0.43-0.25
5e	17.5	300	1.75	0.5	4.25-5.35	0.49-0.27

^a The conductivity was measured at the emulsions having 5 wt % resin concentration and 1.5 wt % BCS content at room temperature.

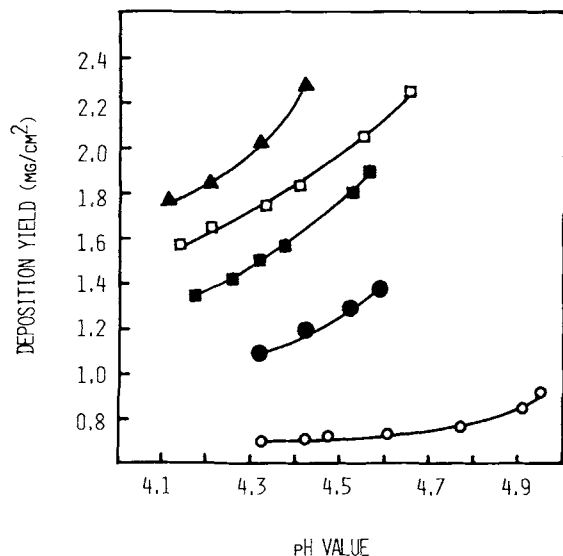


Figure 4 Effects of pH value of emulsions on the deposition yield: Applied voltage = 200 V; resin concentration = 5 wt %; deposition time = 3 min; BCS content = 1.5 wt %; (●) 5a, (■) 5b, (▲) 5c, (○) 5d, (□) 5e.

lutions, and the suspended precipitated particles might migrate with the dispersed macro-cations onto the cathode, leading to deposited films with rough surfaces. Higher BCS contents yield deposited films with a pleasing appearance with a lower deposition yield. The lower yields may account for the redissolution of the deposited resin particles on the cathode during electrodeposition at higher BCS contents.

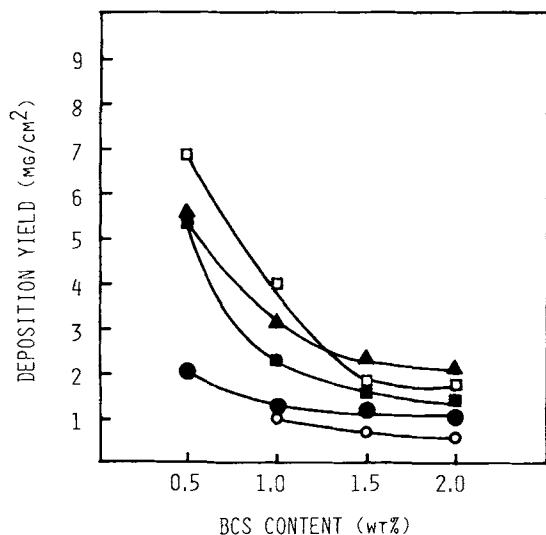


Figure 5 Effects of BCS content on the deposition yield: applied voltage = 200 V; resin concentration = 5 wt %; deposition time = 3 min; pH = 4.34; (●) 5a, (■) 5b, (▲) 5c, (○) 5d, (□) 5e.

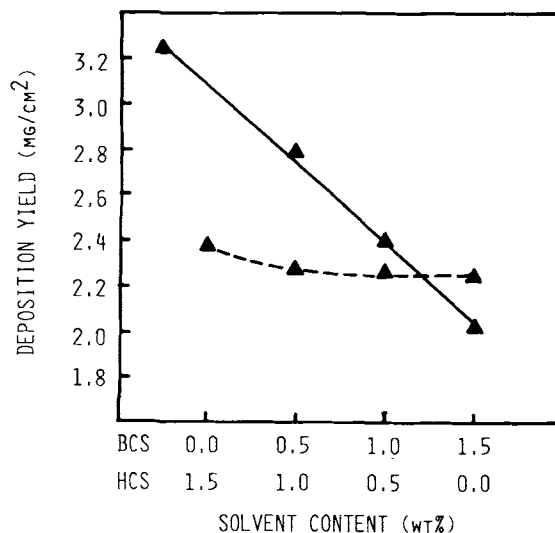


Figure 6 Effects of the ratios of BCS and HCS on the deposition yield of 5c: Resin concentration = 5 wt %; deposition time = 3 min; pH = 3.34; applied voltage = (—) 200 V, (---) 50 V.

When the organic solvent content was lower than 0.5 wt %, PCP-modified cationic resins produce the highest deposition yields. Figure 6 shows the effect of molar ratios of BCS and HCS on the deposition yield of emulsions when the solvent content is 1.5 wt %. From Figure 6, it can be seen that emulsions having higher HCS contents produce higher deposition yields when a higher applied voltage (200 V) was applied. Because HCS is more hydrophobic than

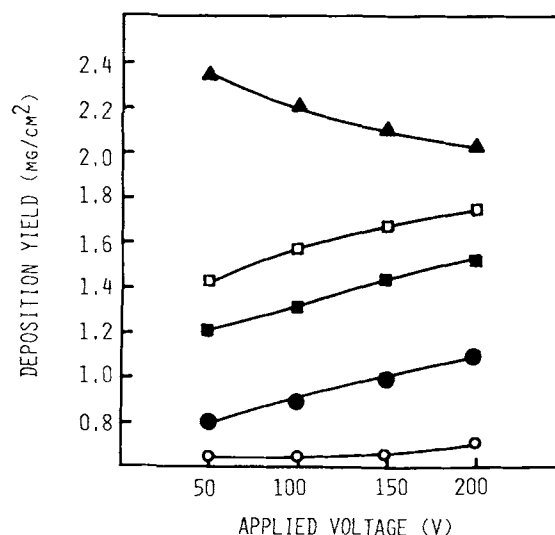


Figure 7 Effects of applied voltage on the deposition yield of resin 5a-e: Deposition time = 3 min; resin concentration = 5 wt %; BCS content = 1.5 wt %; (●) 5a, (■) 5b, (▲) 5c, (○) 5d, (△) 5e.

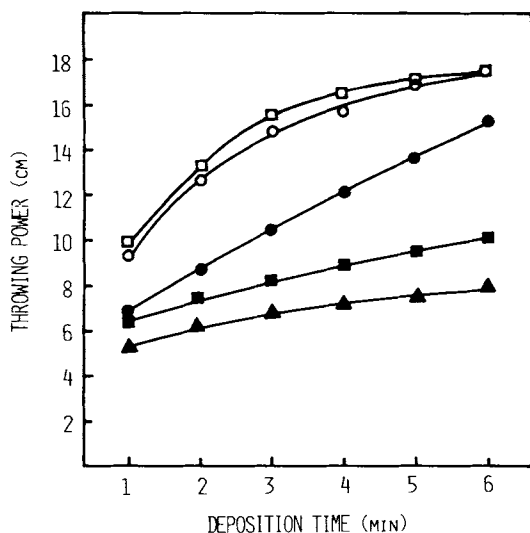


Figure 8 Effects of deposition time on the throwing power of resin 5a-e yield: Applied voltage = 200 V; resin concentration = 5 wt %; BCS content = 1.5 wt %; (●) 5a, (■) 5b, (▲) 5c, (○) 5d, (△) 5e.

BCS, the deposited film on the cathode was not easily redissolved during electrodeposition. When deposition occurs at a lower applied voltage (50 V), the different molar ratios of BCS and HCS no longer significantly affect the deposition yield.

The relationships between applied voltage and deposition yield when the BCS content, resin concentration, deposition time, and pH value of emulsion were kept at a constant value, were shown in Figure 7. The deposition yield increased with the increase of applied voltage, except for resin 5c. This was due to the fact that the high applied voltage accelerated the migration of the resin, producing higher deposition yields. But this increase was contrary to the resin 5c. An explanation for this phenomenon is that the isolation films quickly formed on the cathode and prevented the cationic resin from continuing to deposit on the cathode when a higher voltage was applied. When a lower voltage was applied, the isolation film was formed slowly and the resin continued to deposit on the cathode.

Factors Affecting Throwing Power

Throwing power, one of the most favorable characteristics of electrocoatings, is defined as the way in which uniformly electrodeposited film is built and how deeply it penetrates and deposits inside hollow and complicated structures. Deposition time, pH value of emulsion, solvent content, applied voltage, and the kind and mol wt of cationic resin can affect

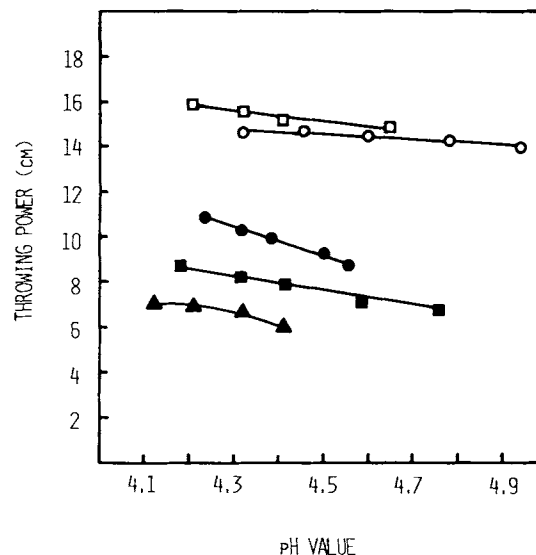


Figure 9 Effects of pH value of emulsions on the throwing power of resin 5a-e: Applied voltage = 200 V; resin concentration = 5 wt %; deposition time = 3 min; BCS content = 1.5 wt %; (●) 5a, (■) 5b, (▲) 5c, (○) 5d, (△) 5e.

the throwing power. The increase of deposition time can enhance the throwing power, as shown in Figure 8. Lower pH emulsion, having a higher conductivity, yields better throwing power, as shown in Figure 9. Increasing the amount of BCS in the emulsion increases the solubility of the resin and reduces the

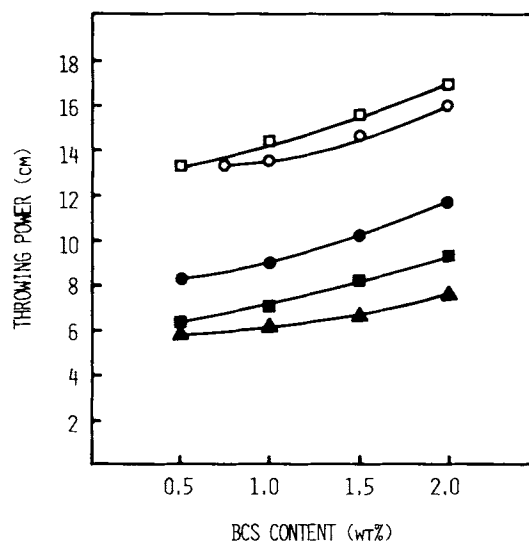


Figure 10 Effects of BCS content on the throwing power of resin 5a-e: Applied voltage = 200 V; resin concentration = 5 wt %; deposition time = 3 min; pH = 4.32; (●) 5a, (■) 5b, (▲) 5c, (○) 5d, (△) 5e.

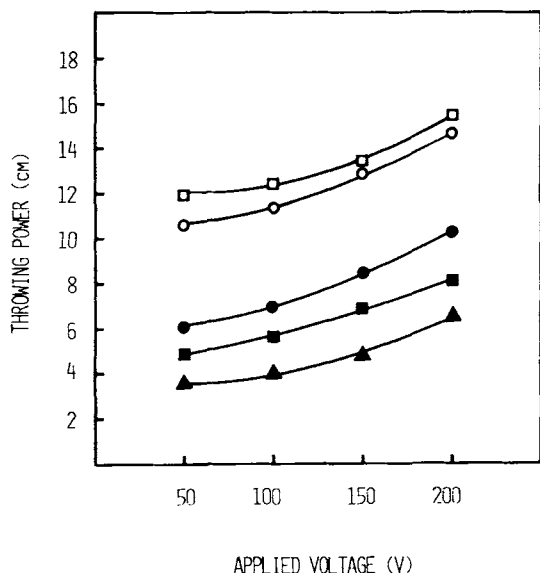


Figure 11 Effects of applied voltage on the throwing power of resin 5a–e: Resin concentration = 5 wt %; deposition time = 3 min; BCS content = 1.5 wt %; pH = 4.32; (●) 5a, (■) 5b, (▲) 5c, (○) 5d, (□) 5e.

resistance to motion of macrocations, leading to increased throwing power, as shown in Figure 10. Figure 11 shows the effect of applied voltage on the throwing power. The throwing power had a tendency to increase with increasing voltage. This can be rationalized readily by taking into account the higher potential drop, leading to a deeper penetration of the cationic resin into the shielded portions. From Figures 8–11, it also can be seen that the PCP-modified cationic resin had the best throwing power. For different mol wt, containing PEG-modified cationic resins, the resin with a higher molecular weight yielded lower throwing power at the same conditions of electrodeposition. The molecular weight of resin 5c was almost equal to that of resin 5d, but the throwing power of resin 5d was higher than that of resin 5c. This indicates that the throwing power of PCP-modified cationic resin was higher than that of PEG-modified cationic resins.

CONCLUSION

1. The extent of the reaction of epoxy resin and polyether or polyester can be evaluated by the change of the epoxy equivalent weight and the gel permeation chromatography curve of the resulting product.
2. The introduction of polyether or polyester in cationic resins can improve the stability of emulsions.
3. Cationic resins, prepared from PPG (#1000)-modified epoxy resins, yield a wider pH range of stable emulsion and also give the deposited films a pleasing appearance.
4. PEG (#1000)-modified cationic resins yield a higher deposition yield, but higher throwing power is obtained by deposition of the PCP (#530)-modified cationic resins.

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