

Synthesis and Properties of Cationic Resins Derived from Aniline-Modified Epoxy Resins and Various Amines

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SYNOPSIS

Aniline-modified epoxy resin which contains tertiary amine in the middle of the polymer chain was synthesized by the reaction of aniline and epoxy resin. The resulting aniline-modified epoxy resin and two commercial epoxy resins with different epoxy equivalent weights were reacted with 2-ethylhexanol-blocked toluene diisocyanate (2-EH-blocked TDI) to obtain thermally crosslinkable epoxy resins. These epoxy resins were subsequently reacted with various secondary amines and partially neutralized with acetic acid to give thermally crosslinkable cationic resins. The resulting cationic resins were dissolved in suitable solvents and mixed with deionized water to form emulsions. The crosslinking properties, emulsion, and electrodeposition properties of these resins were studied in some detail. The electrodeposition yields of the emulsions prepared from aniline-modified epoxy resins were higher than those of other emulsions. The crosslinked films prepared from aniline-modified epoxy resins were also glossier than those prepared from commercial epoxy resins. High deposition yield and high glossiness were the characteristic properties of the aniline-modified epoxy resins. Thermal properties were not affected by aniline-modified epoxy resins.

INTRODUCTION

Electrodeposition of aqueous organic coatings has risen to industrial prominence in recent years. The process has many advantages, including uniformity and completeness of coating even for intricate shapes, labor savings, and pollution abatement. Virtually any electrically conductive substrate may be coated; however, the process has been primarily employed to prime or one-coat ferrous metal substrates. The deposition process includes anodic process and cathodic process. Particular interest has recently arisen in cationic electrodeposition coatings, that is, coatings which deposit on the cathode, since when the article is the cathode, there is greatly reduced metal ion dissolution, which phenomenon causes staining in certain anionic systems.

General routes to cationic resins use synthetic organic resins¹⁻⁸ containing amine groups derived from epoxy resin and secondary amines which are solubilized through the use of an acid counterion. These cationic resins dissolved in suitable solvents

and mixed with deionized water can form stable emulsions. But the deposition yields of these emulsions are low, that is, the deposition films are thin. In this study, aniline was used to modify the epoxy resin to give aniline-modified epoxy resin which contains tertiary amine groups in the middle of polymer chains. Aniline-modified epoxy resin and two commercial diglycidyl ethers of bisphenol A epoxy resin were reacted with 2-EH-blocked TDI to obtain thermally crosslinkable epoxy resin. These epoxy resins were subsequently reacted with various secondary amines, through the ring-opening reaction of epoxy groups, and partially neutralized with acid to obtain thermally crosslinkable cationic resins. Various emulsions were prepared by dissolving the cationic resins in suitable solvents and mixing with deionized water. The crosslinking properties, emulsion, and electrodeposition properties of these cationic resins were studied in some detail.

EXPERIMENTAL

Materials

Reagents used in synthesizing aniline-modified epoxy resin included the reagent-pure grade of an-

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iline (Hayashi Pure Chemicals, Ltd., Japan) and diglycidyl ether of bisphenol A epoxy resin (DGEBA).

Reagents used in synthesizing thermally cross-linkable cationic resins included the synthetic aniline-modified epoxy resin, 2-ethylhexanol (2-EH) (WAKO Extra Pure Grade), toluene diisocyanate (TDI), secondary amines, and acetic acid. Three secondary amines were used in this study. They are diethanolamine, methylethanolamine, and diethylamine. All of them are Hayashi Extra Pure Grade.

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

Apparatus

A thermal analyzer (DuPont 951 analysis unit), a conductivity meter, a pH meter, an electrodeposition apparatus, and a throwing power testing vessel were employed. The electrodeposition apparatus included a glass vessel with a cover. On the cover were suspended a clean plated iron pretreated with zinc phosphate (used as the cathode), and a copper electrode (as the anode), having a surface area of approximately 20 cm². The electrodes were connected to a dc power supply (PHI Hong Instrumental Co.; 0–500 V, 0–6 A). The throwing power testing vessel included a stainless steel vessel (used as the anode) with a height of 23 cm and an inner diameter of 6 cm and a stainless steel strip (as the cathode) with a length of 20.5 cm, a width of 0.8 cm, and a thickness of 0.08 cm. The stainless steel strip was suspended in a hollow glass vessel with a height of 20 cm and a diameter of 1 cm.

Synthesis

Aniline-Modified Epoxy Resin (1)

Epoxy resin (epoxy equivalent weight 650, 260 g, 0.2 mol) and toluene (300 mL) were added to a 500 mL flask equipped with an electric stirrer and a dropping funnel. The mixture was heated to 90°C to dissolve the epoxy resin in toluene. After cooling to 50°C, a calculated quantity of aniline (9.3 g, 0.1 mol) was added to the flask. The whole mixture was gradually heated to 90°C and kept at that temperature for 3 h for the completion of reaction. Finally, toluene was distilled off under reduced pressure. When cooled to room temperature, a golden brittle solid of aniline-modified epoxy resin was obtained.

2-Ethylhexanol-Blocked TDI (2)

A given quantity of TDI was added to a four-necked flask equipped with an electric stirrer, a reflux con-

denser, a dropping funnel, and an inert nitrogen blanket. A calculated quantity of 2-ethylhexanol was added dropwise into the flask under an ice bath. The mixture was kept at room temperature for 1 h, and was gradually heated to 40°C for an additional 30 min to give 2-ethylhexanol half-blocked toluene diisocyanate (2-EH-blocked TDI) (2).

Synthesis of Resins 4a–c and 4'a–b

Aniline-modified epoxy resin (135 g, 0.05 mol) or commercial epoxy resins (epoxy equivalent weight 950 and 650) and toluene (300 mL) 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 epoxy resin by azeotropic distillation. The azeotropic distillation was continued until no further evolution of water was observed. After cooling to 40–50°C, a calculated quantity of 2 was added into the flask. The whole mixture was gradually heated to 90°C and kept at that temperature for 3 h. After cooling the product to 60°C, 0.1 mol secondary amine (diethanolamine, methylethanolamine, or diethylamine) was added into the flask. The mixture was heated to 90°C and kept at that temperature for 3 h for the completion of reaction. Finally, toluene was distilled off under reduced pressure. When cooled to room temperature, a golden, brittle solid of resin 4a–c or 4'a–b was obtained.

Preparation of Emulsions

The general process for the preparation of the emulsion is as follows: In a reactor 17.5 g of resin 4 or 4' were dissolved in various amounts of BCS. Into the solution a desired amount of acetic acid was added and the mixture was heated at 60°C for 10 min. Then, 330 mL deionized water was added dropwise into the solution with vigorous stirring to produce an emulsion.

Characterization

Bath Conductivity

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

Electrodeposition

Approximately 350 mL of emulsion was placed in the glass of the electrodeposition apparatus as described in the previous publication.⁹ The electrodes were immersed in the emulsion and electrodeposi-

tion was carried out at various voltages for different deposition time. The cathode was removed from the emulsion, washed with water, and successively heated to 180°C to obtain the deposition yield.

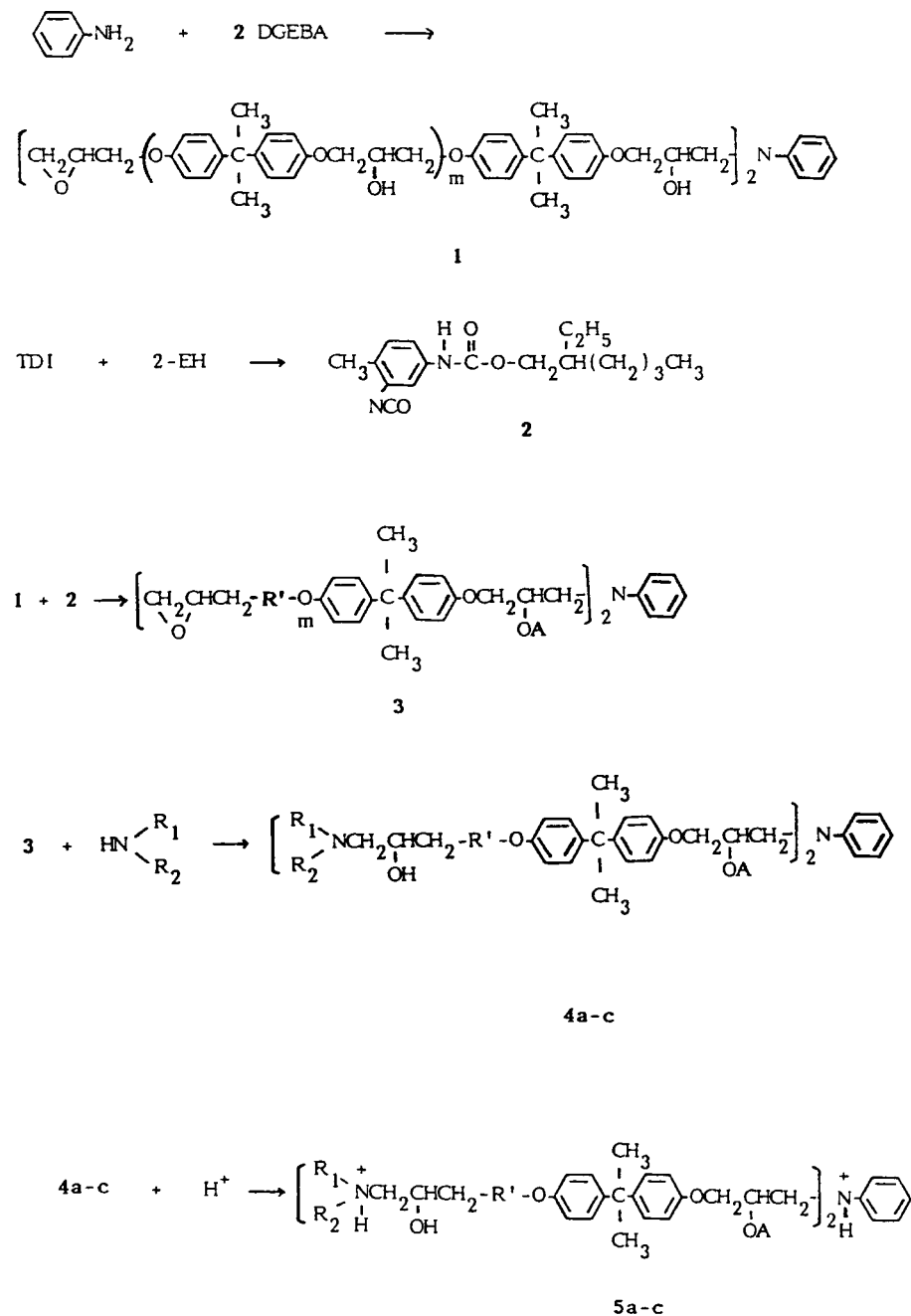
Throwing Power

The throwing power of the emulsion was measured by tube penetration test, which includes a stainless vessel connected to the cathode and a stainless strip

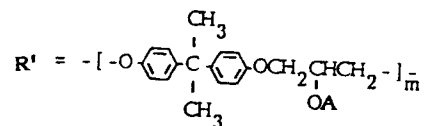
connected to the anode. The stainless strip and a hollow cylinder was immersed in the emulsion contained in the vessel. After the constant dc voltage was applied for 1 min, the strip was taken off and rinsed with water. The height (in cm) of polymer deposited is defined as throwing power.

Thermogravimetric Analysis

Resin 4 and 4' (Scheme 1) was baked at 180°C for 20 min to form the crosslinked films:



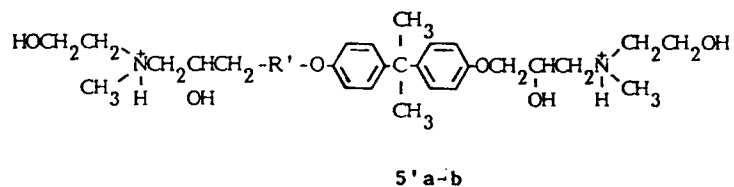
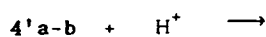
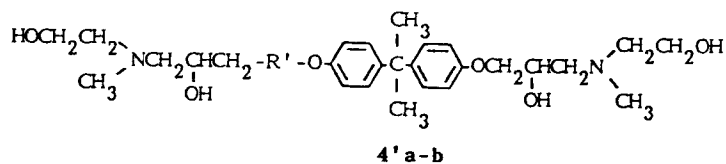
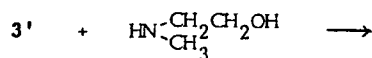
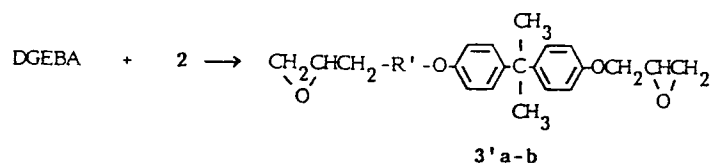
Scheme 1



A	number of A
-H	x
	y

$$x+y = 2m+2 \quad m = 3.38$$

	R ₁	R ₂	x/y
4a	-CH ₂ CH ₂ OH	-CH ₂ CH ₂ OH	0.84
4b	-CH ₂ CH ₂ OH	-CH ₃	0.73
4c	-CH ₂ CH ₃	-CH ₂ CH ₃	0.61



	m	x/(x+y+2)
4'a	5.7	0.5
4'b	3.38	0.5

x+y = m+2

Scheme 1 (Continued from previous page)

The thermogravimetric analysis for the crosslinked films was performed on a DuPont 951 thermogravimetric analyzer coupled to a DuPont 1090 thermal analyzer in flowing nitrogen ($50 \text{ cm}^3/\text{min}$) at a heating rate of $20^\circ\text{C}/\text{min}$.

Gel Content

A 40% resin solution, prepared by mixing the resin and toluene, was spread on aluminum foil and baked at various temperatures for 20 min to form crosslinked film. The crosslinked film of the resin obtained was immersed in acetone to reflux for 24 h. After drying, the gel content was calculated by dividing the residual weight by the initial weight of crosslinked film.

RESULTS AND DISCUSSION

Cationic resins (**5a–c** and **5'a–b**) were synthesized by reacting the three different secondary amine with 2-EH-blocked TDI modified epoxy resin (**4a–c** and **4'a–b**) and subsequent neutralization with acetic acid. As shown in Scheme 1, aniline contains two active hydrogens, so that it readily reacts with the epoxy groups in epoxy resin to form tertiary amine-containing epoxy resin. This aniline-modified epoxy

resin (**1**) and two commercial epoxy resins (epoxy equivalent weight 950 and 650) react with 2-EH-blocked TDI (**2**) to give thermal crosslinkable epoxy resins (**3** and **3'**). The synthesis of 2-EH-blocked TDI was controlled by reaction temperature. At low temperature, 2-ethylhexanol reacts with the isocyanate group of TDI in the para position and leaves the ortho isocyanate group, because the isocyanate group of TDI in the para position is about eight times as reactive as the isocyanate group of TDI in the ortho position at room temperature. The extent of reaction of epoxy resin and 2-EH-blocked TDI can be evaluated by the change in characteristic absorption of isocyanate groups in the infrared spectra. The end of reaction could be judged from the disappearance of the isocyanate absorption. It requires about 3 h for complete reaction at 90°C . Three secondary amines react with epoxy groups in resin **3** to form tertiary amine-terminated resin **4a–c** which also contains tertiary amine in the middle of polymer chain, while resin **3'** reacts with methylethanolamine (MEA) to produce tertiary amine-terminated resin **4'a–b**. Resin **4a–c** was treated with acetic acid to give cationic resin **5a–c**. Resin **4'a–b** was also converted to cationic resin **5'a–b** in the same way to compare with resin **5a–c**. The amount of cation (**5** or **5'**) formed and the solubility of these resins were determined by the quantity of acid added.

Table I Effects of BCS Content on the Solubility of Resins **5a–c** and **5'a–b** in Water (330 mL) at Room Temperature

Solution	Weight of Resin	Weight of BCS	Weight Ratio	pH	Remark of Solution
5a–I	17.5 g	1.75 g	10%	4.52	Precipitate
5a–II	17.5 g	3.50 g	20%	4.52	Emulsion
5a–III	17.5 g	4.25 g	30%	4.53	Emulsion
5a–IV	17.5 g	7.00 g	40%	4.64	Emulsion
5b–I	17.5 g	1.75 g	10%	4.28	Precipitate
5b–II	17.5 g	3.50 g	20%	4.27	Emulsion
5b–III	17.5 g	4.25 g	30%	4.29	Emulsion
5b–IV	17.5 g	7.00 g	40%	4.28	Emulsion
5c–I	17.5 g	1.75 g	10%	4.30	Precipitate ^a
5c–II	17.5 g	3.50 g	20%	4.29	Precipitate ^a
5c–III	17.5 g	4.25 g	30%	4.28	Precipitate ^a
5c–IV	17.5 g	7.00 g	40%	4.29	Precipitate ^a
5'a–I	17.5 g	1.75 g	10%	4.53	Precipitate
5'a–II	17.5 g	3.50 g	20%	4.54	Precipitate
5'a–III	17.5 g	4.25 g	30%	4.51	Emulsion
5'a–IV	17.5 g	7.00 g	40%	4.52	Emulsion
5'b–I	17.5 g	1.75 g	10%	4.30	Precipitate
5'b–II	17.5 g	3.50 g	20%	4.29	Precipitate
5'b–III	17.5 g	4.25 g	30%	4.29	Emulsion
58b–IV	17.5 g	7.00 g	40%	4.30	Emulsion

^a The resin adheres together after water added.

Properties of Cationic Resins

Effects of pH Value and Amount of Organic Solvents on the Formation of Emulsion

Resins 4 and 4' contain tertiary amine groups, and can be converted to cationic resin 5 and 5' when treated with acetic acid. The aqueous solution of cationic resin can form stable emulsions when mixed with proper amounts of organic solvent such as BCS. Resins 4 and 4' are readily dissolved in organic solvents, but difficult to dissolve in water. In the form of ammonium salts, resins 5 and 5' are readily soluble in hydrophilic solvents or polar solvents but are insoluble in hydrophobic solvents. The water solubility of resin 4 is significantly affected by the pH value of the emulsion. The conversion of resin 4 to 5 is reversible. For high pH solutions, resin 4 is predominant and the solubility of resin is reduced. Lower pH value, i.e., higher acidity, favors the formation of cationic resin 5. For example, at 5 wt % of solid content of the resin 5a, the solution with little BCS content (less than 10 wt % on the basis of resin) will precipitate quickly. When the BCS content is over 20 wt %, the resin solution forms a stable emulsion state at a pH value of 4.5. At 5 wt % of solid content of the resin 5b, a stable emulsion was formed at a pH value of 4.3 and the BCS content is over 30 wt %. Stable emulsions of resin 5c were not obtained no matter how much BCS or acetic acid was added, as shown in Table I. It indicates that the water solubility of resin 5a is good and that of resin 5c is poor. This phenomenon was caused

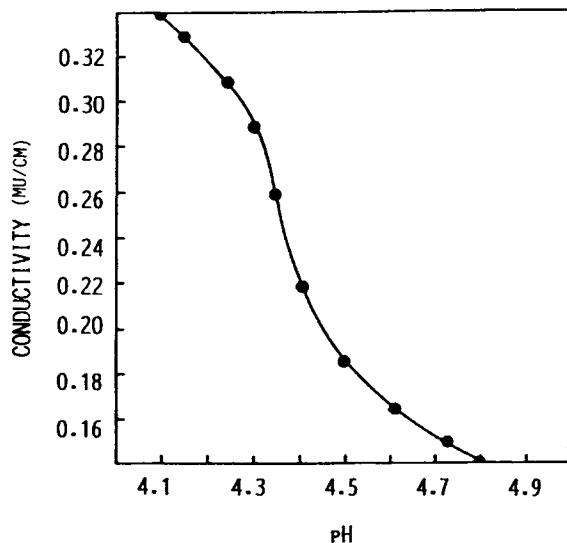


Figure 1 Effects of pH value on the conductivity of emulsion prepared from resin 5a: BCS content = 30 wt %; resin concentration = 5 wt %.

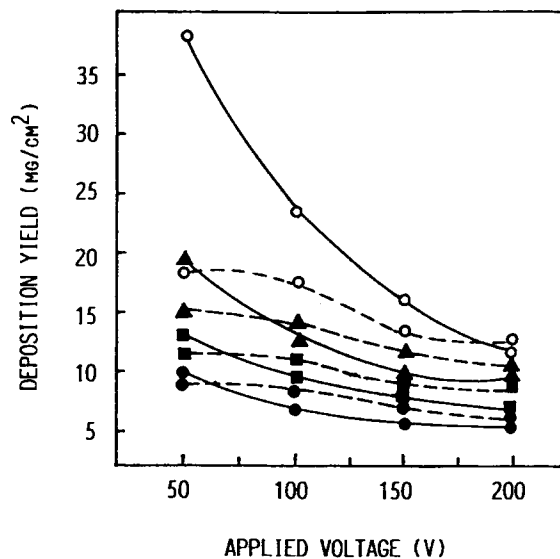


Figure 2 Effects of applied voltage on the deposition yield of the emulsion prepared from resin 5a-b with different BCS contents (wt %): (●) 40; (■) 30; (▲) 20; (○) 10. Deposition time = 3 min; (—) 5a, pH 4.53; (---) 5b, pH 4.28; resin concentration 5 wt %.

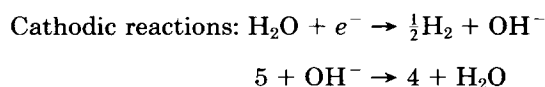
by the different terminal groups in the resin. For non-aniline-modified cationic resin (5'a-b), stable emulsions were obtained if the BCS content is over 20 wt % and the pH value is below 4.5.

Bath Conductivity

The bath conductivity of the emulsion is dependent on the pH values of the emulsion. Figure 1 shows the relationship between the bath conductivity and pH values of the emulsions of 5a. It can be seen that the conductivity of the emulsions decrease with increasing pH. Emulsion prepared from resin 5b gives a low conductivity and it is not significantly affected by the pH value of the emulsion. For example, changing the pH values of the emulsions from 4.29 to 4.58 only changes the conductivity from 0.13 to 0.10.

Electrodeposition Properties

The principle of electrodeposition is that of emulsion solution electrolysis when the voltage is applied. Hydroxyl anions are generated at the cathode and the cationic resin (5) is deposited on the cathode to form an insoluble resin 4. The cathodic reactions are shown as follow:



Electrodeposition Yield

The electrodeposition yields are dependent on the applied voltage, the amount of solvent added, pH value of the emulsion, and the kind and the molecular weight of the resins. Figure 2 shows the effects of applied voltage and the amount of solvent on the deposition yield of resin 5a and 5b. It can be observed that the deposition yield decreases as the applied voltage increases. This phenomenon is contrary to the deposition yield of general cationic resins which increase with the increase of applied voltage. An explanation is that the isolation film quickly formed on the cathode and prevented the cationic resin from continuing to deposit on the cathode when a higher applied voltage was applied. When a lower voltage was applied, the isolation film was formed slowly and the resin continues to deposit on the cathode. This phenomenon was also proved by the decrease of deposition current during the deposition. At higher voltage, the deposition current approaches to zero in a short time. But the current decreases slowly when a lower voltage is applied (Fig. 3). The effects of applied voltage and the amount of solvent on the deposition yield of non-aniline-modified cationic resin (5'a-b) are shown in Figure 4. It can be observed that the deposition yield increases as the applied voltage increases. Figures 2 and 4 show that the deposition yield of the emulsion prepared from aniline-modified epoxy resin is much higher than the deposition yield of the emulsion prepared from non-aniline-modified epoxy resin.

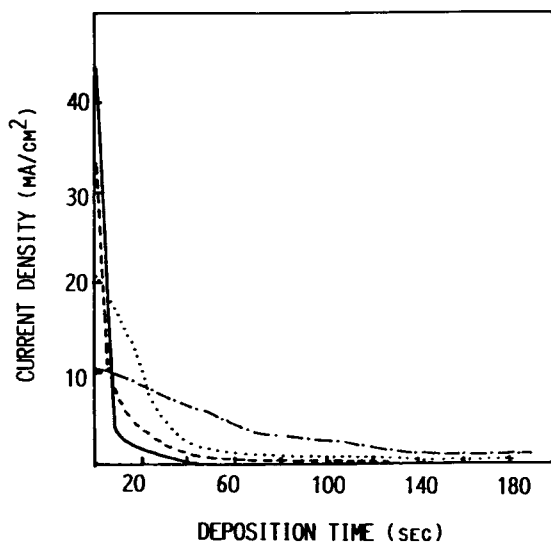


Figure 3 The relationship of deposition time and current density of the emulsion prepared from 5a: pH 4.29 resin concentration 5 wt %; BCS content 30 wt %.

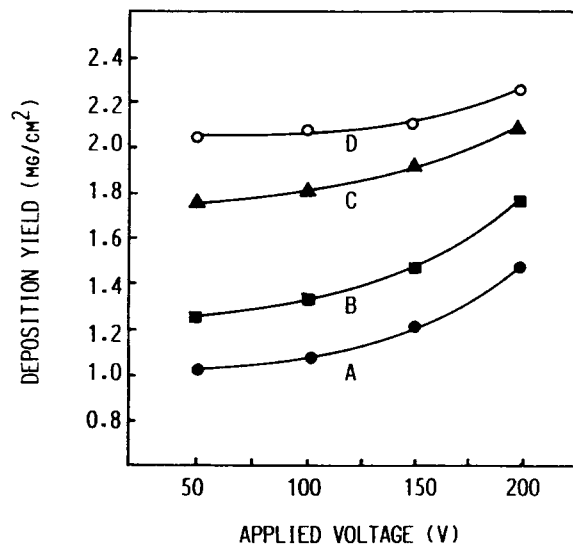


Figure 4 Effects of applied voltage on the deposition yield of the emulsion prepared from resin 5a-b with different BCS contents: (A) 5'b, 40 wt % BCS; (B) 5'b, 30 wt % BCS; (C) 5'a, 40 wt % BCS (D) 5'a, 30 wt % BCS. Deposition time = 3 min; pH 4.3; resin concentration 5 wt %.

High deposition yield is the characteristic property of the aniline-modified cationic resin. A higher BCS content of the emulsion leads to a lower deposition yield. This can be explained by the higher solvating power of BCS which can redissolve the deposited resin. Figure 5 shows the effects of pH value on the

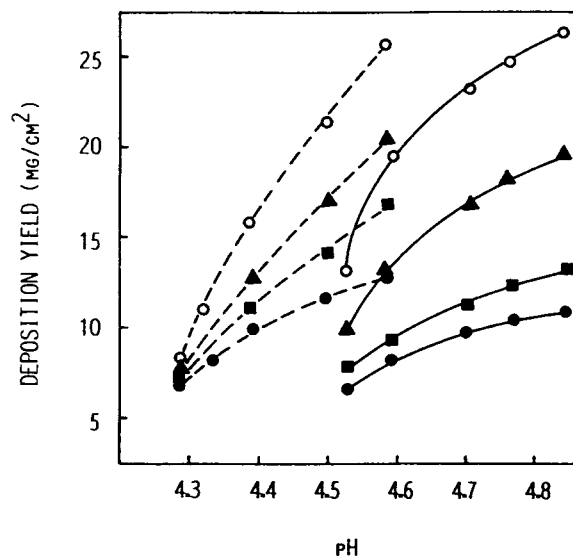


Figure 5 Effects of pH value on the deposition yield of the emulsion prepared from resin 5a-b under different applied voltages (V): (●) 200; (■) 150; (▲) 100; (○) 50. Deposition time = 3 min; BCS content 30 wt %; resin concentration 5 wt %; (—) 5a; (---) 5b.

deposition yield of resin **5a–b**. Emulsions having a higher pH value give a higher deposition yield. This can be attributed to the fact that the low pH value (i.e., high acidity) of the emulsion increases the solubility of deposited films.

Throwing Power

The throwing power of a paint is a term used to describe the ability of the paint to coat recessed and shielded areas. It depends on the electrical conductivity of the liquid paint and the resistance of the deposited films. The throwing power of the synthetic resins is dependent on the deposition time, the applied voltages, pH values of emulsions, and the content of solvent, as shown in Figures 6–8. The throwing power increases with increasing deposition time, as shown in Figure 6. Figure 7 shows that the throwing power increases with decreasing pH values. This is due to the fact that resin **5** predominates and the emulsion conductivity increases at lower emulsion pH. It can be observed that the throwing power also increases as the applied voltage increases, as shown in Figures 6–8. It is likely that the increase of applied voltage accelerates the migration rate of the resin. The amount of solvent added in the emulsion also affects the throwing power. Increasing the amount of solvent in the emulsion increases the solubility of the resin and reduces the resistance to motion of macrocations, leading to increasing throwing power

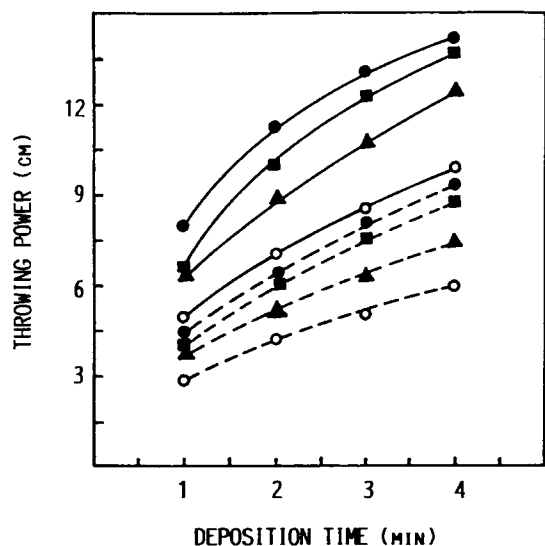


Figure 6 Effects of deposition time on the throwing power of the emulsion prepared from resin **5a–b**: BCS content 40 wt %; resin concentration 5 wt %; (—) **5a**, pH 4.53; (---) **5b**, pH 4.28. Applied voltage (V): (●) 200; (■) 150; (▲) 100; (○) 50.

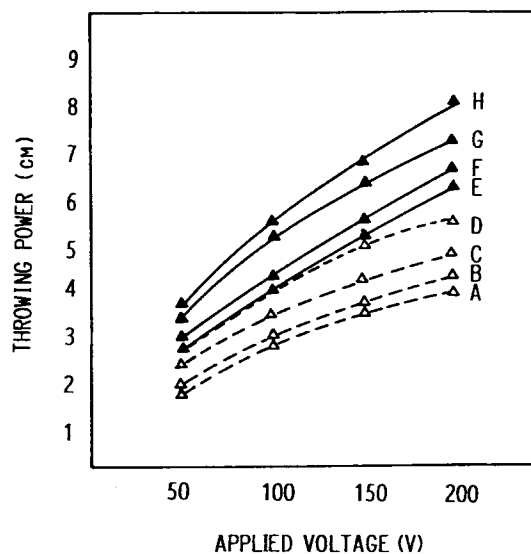


Figure 7 Effects of applied voltage on the throwing power of the emulsion with different pH's prepared from resin **5a–b**: (A) 4.59; (B) 4.45; (C) 4.32; (D) 4.29; (E) 4.85; (F) 4.70; (G) 4.58; (H) 4.53. BCS content 30 wt %; resin concentration 5 wt %; deposition time 1 min; (—) **5a**; (---) **5b**.

(Fig. 8). The throwing power of emulsion prepared from resin **5a** is higher than the throwing power of emulsion prepared from resin **5b**. But the throwing power of aniline-modified cationic resin is lower than that of non-aniline-modified cationic resin.

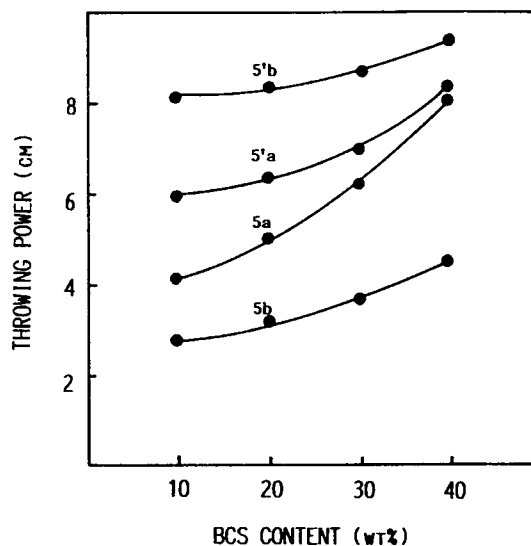


Figure 8 Effects of BCS content on the throwing power of the emulsion prepared from resin **5a–b** and **5'a–b**: deposition time 1 min; applied voltage 200 V; pH 4.3.

Crosslinking Properties of Resin 4a-c

When resins **4a-c** and **4'a-b** were heated at elevated temperature, the pendant blocked isocyanate will release the blocking agent, 2-EH, to generate free isocyanate. These free isocyanates react with the secondary hydroxyl groups of other molecules to form new urethane linkages and produce a cross-linked structure. The effects of curing temperature on the gel content of crosslinked films prepared from **4a-c** are shown in Figure 9. When the curing temperatures are lower than 150°C, all the gel contents are lower than 40%. The gel content of the crosslinked film increases with curing temperature when the curing temperature is above 150°C and then the gel content reaches a constant value at temperatures higher than 180°C. This shows that the crosslinking reaction takes place at temperatures above 150°C. Figure 9 also reveals that the gel content of the crosslinked film also increases with the amounts of hydroxyl group in the resins (i.e., **4a** > **4b** > **4c**).

The thermogravimetric analysis curves of the crosslinked films prepared from resin **4a-b** and **4'b** are shown in Figure 10. The initial pyrolysis temperature of the crosslinked films is above 250°C and the crosslinked films decompose quickly at temperatures higher than 400°C. The thermal behaviors of the crosslinked films prepared from different epoxy ring-opening agent-containing resins are analogous. When diethanolamine was used as the epoxy ring-opening agent, the crosslinked film gives a higher pyrolysis temperature. In the case of using diethylamine as the epoxy ring-opening agent, the cross-

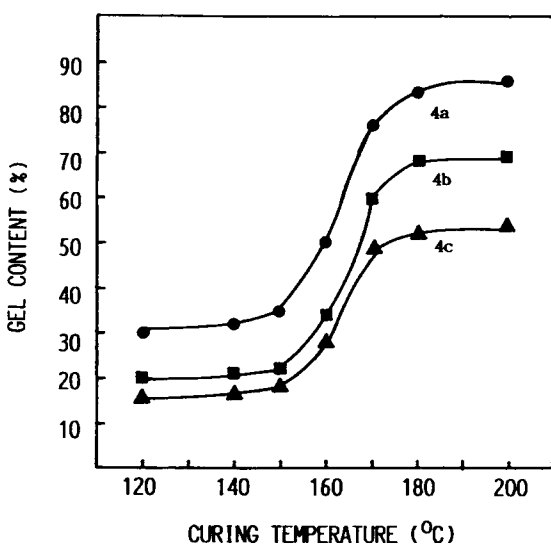


Figure 9 Effects of curing temperature on the gel content of the crosslinked films prepared from resin **4a-c**.

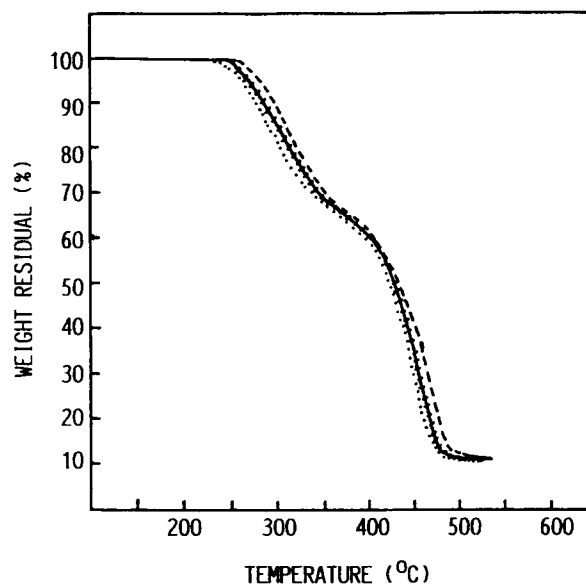


Figure 10 TGA curves of the resins **4a-c** and **4b** with a heating rate of 20°C/min in N₂: (---) **4a**; (—) **4b**; (···) **4c**; (#) **4'b**.

linked film gives a lower pyrolysis temperature. The thermogravimetric curves of crosslinked films prepared from resin **4b** and **4'b** are almost the same. This indicates that the aniline-modified epoxy cannot affect the thermal properties of the epoxy resins.

CONCLUSION

1. The deposition yield of emulsion prepared from aniline-modified cationic resin is larger than that prepared from non-aniline-modified cationic resin. The former gives a higher deposition yield at lower applied voltage, but the latter gives lower. The effects of BCS contents and pH values on the deposition yields of both series of cationic emulsions are the same.
2. The emulsion properties are strongly affected by the contents of tertiary amine terminated in aniline-modified cationic resins. The emulsion properties are also strongly dependent on the pH value of the emulsion and the amount of solvent added. The resin solution of **5a** forms a stable emulsion state when the BCS content is over 20 wt % and the pH value is 4.5. For resin **5b**, stable emulsion was obtained when the BCS content is over 30 wt % and the pH value is 4.3.
3. The bath conductivity of the emulsion de-

creases with increase in pH value of the emulsion.

4. The throwing power of the emulsion increases with decreasing pH values and also increases with increasing BCS content and applied voltage.

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