

The Effect of Molecular Weight of Epoxy Resin on the Deposition Behaviour of Water-borne Epoxy-amine Adducts

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ABSTRACT

Water-borne epoxy resins were prepared by reacting epoxy resins with different molecular weights (360, 900, 1700, 3200) with diethanolamine. The resins were then neutralized with 10% by wt acetic acid and emulsified in water. The resins were applied onto steel panels by a cathodic electrodeposition procedure. The deposition behaviour of the resins were studied using the effect of voltage-time (at constant current) and current density-time (at constant voltage) variations on the determined coulombic efficiency and the throwing power.

Key Words:

electrodeposition;
waterborne;
epoxy resin;
cathodic electrocoating;
coulombic efficiency;
throwing power.

INTRODUCTION

Organic coatings can be applied from aqueous media onto the surface of a conductive substrate by a process known as electrodeposition. The water-borne coatings utilized in the electrocoating processes are commonly based on film forming resin

dispersions in water [1]. Upon the application of a direct current, charged polymers will migrate electrophoretically to the electrode of opposite charge, become insoluble and form an insulating film, which limits further deposition. When nega-

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tively charged polymers are deposited on the anode, the process is termed anionic or anodic electrodeposition. Similarly if positively charged polymers deposit on the cathode, it is referred to as cathodic electrodeposition [1-4]. The main reasons for the universal and rapid acceptance of these processes are [4]:

- Very uniform coverage is obtainable, including the edges and corners.
- Greater operating flexibility.
- Superior mechanical and corrosion performance properties.
- Greatly reduced solvent emissions and fire hazards.
- Highly automated and mechanized process.
- Low maintenance and manpower costs.
- Highly efficient with up to 95% of the coating material being utilized.
- New technology with great potential for future technological innovations and applications.

Additional advantages of the cathodic electrodeposition process are:

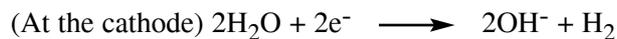
- Significant improvement (3-4 folds) in corrosion performance.
- Superior throwing power (penetration) performance.
- Improved resistance to saponification.
- Reduced conversion coating (zinc/iron phosphate) disruption.
- Inherent stability and chemical resistance [5-6].

Epoxy resins play a leading role in the cathodic electrodeposition processes. For such processes the related epoxy resins should be waterbased. There are different methods for obtaining aqueous polymer dispersions. The most convenient way to prepare resin dispersions for electrocoatings is the dispersion of concentrated hydrophilic polymer solutions.

The underlying principles for polymer design developed for solutions of resins still remain valid. The solvent levels required for such dispersions are low and the films obtained are water resistant containing no surfactants [6]. Therefore, in order to obtain a water-based resin it is sufficient to simply prepare the esterified epoxy-amine adduct and neutralize it with an acid.

The important mechanisms that occur during the electrodeposition process have been studied by Beck [7,8] and Pierce [9] and comprise the followings:

- Electrolysis of water resulting in hydrogen gas evolution and the production of hydroxyl ions at the cathode surface, which increases the local pH.



- The time needed for increasing the pH and making the following step to take place, and it is being termed as [induction time].
- Electrophoretic migration of the resin micelles towards the cathode.
- Electrocoagulation of the resin micelles at the cathode surface by neutralization of positively charged groups in the resin with electrochemically generated hydroxyl ions:



- Electroosmosis of water in the submicron pores of the deposited films, caused by the potential difference across the film and the surface charges on the pore walls.
- Heteroagulation, which is the process of film deposition on the metal substrate.
- Addagulation, which is the process of further film deposition upon the already deposited layers [10].

EXPERIMENTAL

Materials

The epoxy resins used in this study were the derivatives of diglycidylether bisphenol A (DGEBA) of four different molecular weights namely: 350-400(A), 900-1100(B), 1600-1800(C) and 3200-3600(D) (from Shell Chemical Co.). The other chemicals used were: diethanolamine (ANALR), acetic acid (ANALR), glycidyl ester of versatic 10 acid (Cardura E10, from Shell Chemical Co.) and hexamethoxymethyl melamine (HMMM, Mapranal MF900 from Hoechst Co.). All the materials were used as received without any further purification.

Equipment and Instruments

Reactor Assembly

A four-necked round bottom glass flask (1 L capacity) equipped with a mechanical stirrer, a thermometer, a reflux system, a dropping funnel and an inert gas inlet were used as the basic reactor unit for resin preparation. The heating was carried out in a 1 L heating mantle up to reaction temperatures of 180°C.

Electrodeposition (ED) Cell

The electrodeposition cell consisted of a 500-mL glass vessel containing 350 mL of depositable solution. The anode was made of a rectangular stainless steel plate (8 × 3) cm equal in size and shape to the cathode, a bare mild steel panel. The anode and the cathode were connected to the respective terminals of a DC power supply (0-450V, 4A, from Eamen Tablo Co.). The distance between the anode and the cathode was about 8 cm. The solution was magnetically stirred during the whole electrodeposition process.

Analyzing Instruments

The analyzing instruments used in this study were: pH-meter (MeterLab/pH M240 from RADIOMETER-Copenhagen), conductivitymeter (Sheen Instrument, 4071), viscometer (Abbelohde suspended level viscometer (DIN 562, Part 1)), particle size analyzer (SEM-633 from SEMATech).

Practical Work

The cataphoretically applicable epoxy-amine adduct dispersions were prepared by reacting the stoichiometric amounts of diglycidyl ether bisphenol A (DGEBA) with different molecular weights of 350-400(A), 900-1100(B), 1600-1800(C) and 3200-3600(D) mentioned previously, with diethanolamine. In order to improve the corrosion resistance of the resin, they were then reacted with Cardura E-10 [11]. Dispersions of the resins in deionized water were prepared using a homogenizer at 85% neutralization level of ionizable groups by adding different amounts of 10% acetic acid [12-13]. The cross-linking of the resins were made to occur by using 20% HMMM (based on the epoxy amine adduct solids). The prepared dispersions were further diluted by distilled water (i.e., to about 10% solid content), the mean particle size, pH and conductivity of each dispersion were measured subsequently.

Each dispersion was electrodeposited at a constant current and /or at constant voltage. The coulombic efficiency and the throwing power of each were then determined.

RESULTS AND DISCUSSION

Figure 1 shows the variation of mean particle size with changing the molecular weight of the resin. As it could be seen, an increase in the molecular weight of the resin

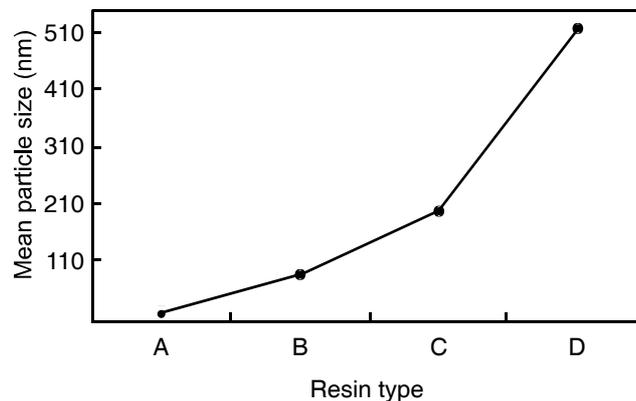


Figure 1. Variation of mean particle size with molecular weight of the resin.

leads to an increase in the particle size of the dispersed resin in water. For the resin with a molecular weight = 360 (dispersion A in Figure 1) the ionic strength per unit area is at the highest level, so this resin is the most hydrophilic and it can, therefore, disperse in water at a molecular level. The appearance of the dispersions confirms it optically (dispersion A: clear solution, B: translucent, and C&D: opaque).

Figure 2 shows the variation of pH and conductivity with changing molecular weight. As it can be noticed, increasing the molecular weight has led to an increase in the pH of the dispersion. In the case of dispersion D the amount of neutralizing acid is not enough to stabilize the resin dispersion in the water. Figure 3 shows the miliequivalent gram of quaternary amine value (QAV) in 100 grams of solid resin (QAV measured based on ASTM- D2074-92). It is also seen that the QAV decreases with increasing molecular weight, this is because of the lower amount of tertiary amines present in the higher molecular weight resins. The

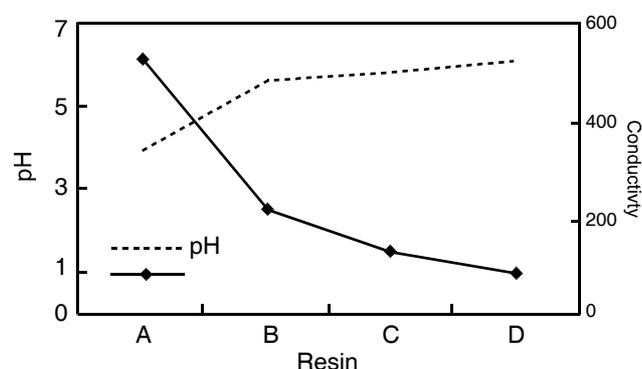


Figure 2. Variation of pH and conductivity with molecular weight of the resin.

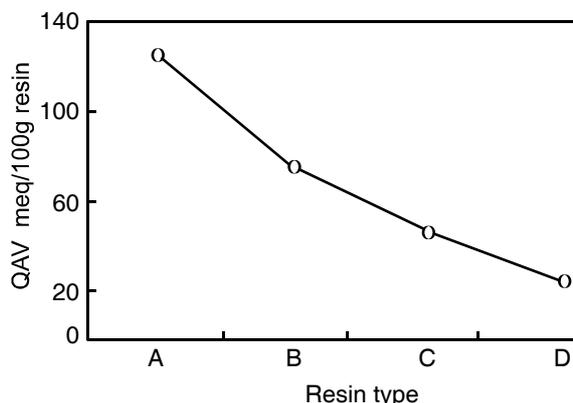
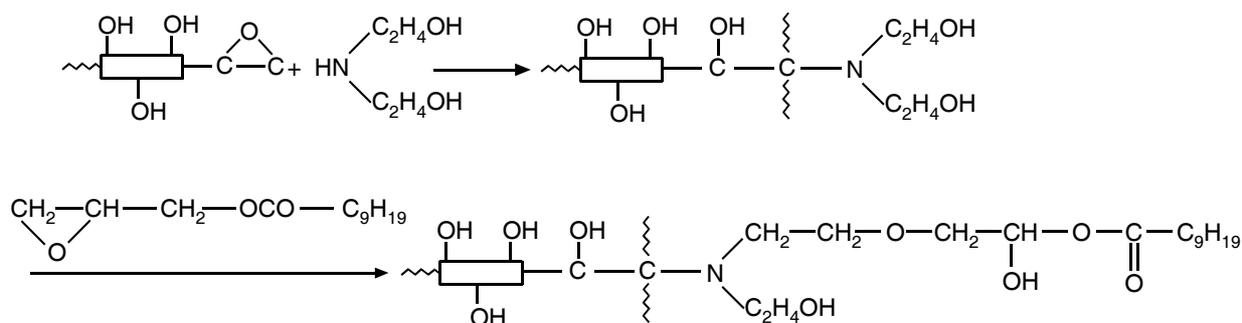


Figure 3. Variation of quaternary amine value with type of resin.

resins with higher molecular weights have lower epoxy groups in their structure for reacting with diethanol amine, therefore, lower amine sites per unit weight (the sites responsible for carrying a charge) will be available in the epoxy-amine adduct structure and when these adducts are further neutralized with acid lower ionic groups (QAV) would result. Reaction 1 (Scheme I) shows the different stages of reaction between epoxy resin and a secondary amine. Resins with higher molecular weight will contain lower numbers of prepared tertiary amine groups.

The more the available ionic sites, the lower will be the pH of the aqueous phase, which demonstrates that there is more free acid present in the aqueous phase. Figure 2 also shows that the conductivity increases by decreasing the molecular weight. The number of ionic groups per unit area of the resin determines the conductivity of the electrodeposition bath. Decreasing molecular weight results in a higher ionic strength per unit area and unit weight of the resin leading to enhanced conductivity.



Scheme 1- (1) Epoxy resin and diethanol amine, (2) epoxy amine adduct and CE10.

Figure 4 shows the variation of voltage during the electrodeposition of epoxy adducts at constant current density i.e., 0.85 mA/cm^2 . As it is observed the voltage rises after a very short time in case of the prepared adduct from C, while no increase in voltage can be seen for the adducts prepared from A and B. In these cases the voltage needed to maintain the current density at 0.85 mA/cm^2 was very small. But the voltage rises to a value of nearly 350 V in case of C for the same current density. In the case of D, dispersion was not stable enough and it was not possible to obtain an acceptable film, as the film was too rough and full of bubbles.

Figure 5 shows the coulombic efficiency and throwing power of different types of resin (with different molecular weights).

The tube penetration test [14] was used to measure the throwing power of the epoxy-amine adduct resin dispersions. In the measurement procedure, the epoxy-amine adduct resin dispersion was poured into a stainless steel cylindrical vessel up to a height of 26 cm from the bottom, and the bath was maintained at 25°C by the aid of uniform magnetic stirring.

The test strips ($8 \times 220 \times 0.8 \text{ mm}$) and the hollow glass tube were immersed to a depth of 23 cm. The coating time was constant at 180 s and the voltage was set at a predetermined desired value (200 V). The distance from the bottom of the strip upwards and measured in cm is the throwing power of each epoxy-amine adduct dispersion.

Coulombic efficiency is the sum of the coulombs needed to deposit one gram of the dispersed material on the electrode.

It seems that by increasing molecular weight the throwing power and the coulombic efficiency will also increase. In the case of resin A, there was a patchy film

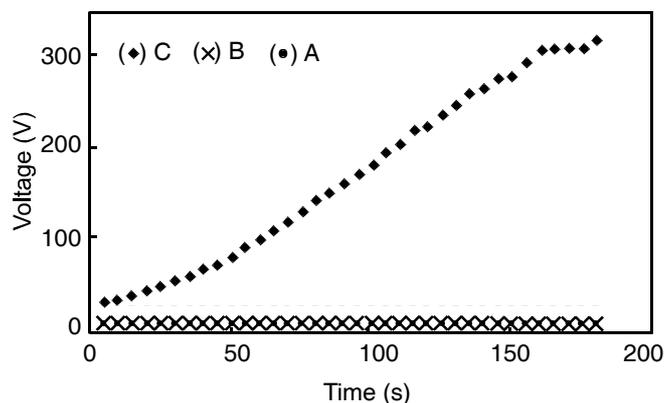


Figure 4. Variation of the voltage during the electrodeposition of the resin A,B and C.

which could not be considered as a protective film. In case B, a smooth and pore free film was obtained, but in case C there were some pores in the film, this is because the film cannot easily release the gas bubbles which are being formed.

This means that these bubbles are confined within the film which produce some pores as they leave the film. In case D an acceptable film could not be prepared, it was very rough although it was cured for 20 min at 180°C. The phenomena of forming porous and pore-free films and the basic concepts behind these are described elsewhere [15]. A porous film is anticipated to be produced when dispersions of C are electrodeposited on steel substrates.

As expected, the hydrophilicity of the modified resin was greatly changed by the variation of molecular weight relating to the water solubility of the resin. Lowering molecular weight results in a decrease of area per unit charge at the surface of the formed

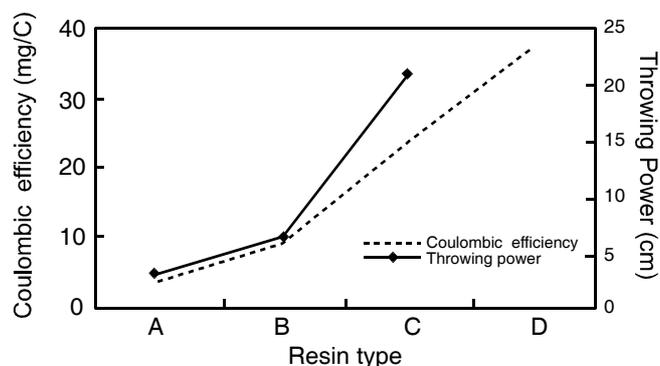


Figure 5. Variation of coulombic efficiency and throwing power of the resin dispersion with different molecular weights.

micelles and hence it leads to micellar breakages due to the increased repulsion between like charges giving smaller structures. By increasing the molecular weight, the modified resin showed different colloidal states ranging from a solution to emulsion. The colloidal state of the system is of utmost importance. The colloidal state of the system itself could influence many properties of the electrocoatings such as the stability of the dispersion, the kinetics of film growth and the throwing power.

The results of the electrodeposition experiments showed that in the cases C and D, porous films were formed on the steel substrate.

The porous film will only form if the polymer is either poorly coalesced or the soluble electrolyte leads to excessive gassing at the cathode [9]. In our case, since poor coalescence did not occur (i.e., T_g of the deposited films were measured to be well below the bath temperature), therefore, the porosity could only result from the gas evolution. If the characteristic time of the gas evolution is much less than the characteristic time for the deposition of the electrocoagulates on the surface of the growing film, the bubbles are interlocked within the film.

We could in effect define a dimensionless time factor which, is defined as the ratio of the characteristic time of the gas bubble growth to the characteristic time ($\phi = \tau_g/\tau_d$, τ_g is gassing characteristic time and τ_d is deposition characteristic time) of the deposition of the electrocoagulates. If ϕ is less than one, then there is a strong possibility that the pores would be filled in by new electrocoagulates and so a porous film would result, however if ϕ is more than 1, the pores will continue to be imbedded in the film. If ϕ equals one an intermediate state results depending on the size and the rate of evolution of gas in addition to the size of the electrocoagulates[15].

Assuming the characteristic time of the formation and growth of the hydrogen gas bubbles to be constant (at constant current density); the determining factor for the value of ϕ will be the characteristic time of the deposition of the electrocoagulates. The deposition of the electrocoagulates will take place if the size of the electrocoagulates is greater than a certain value, otherwise the gas bubbles leaving the cathode surface will prevent the deposition of the electrocoagulates. Therefore, the electrocoagulation process should proceed at such a

high rate that it would be impossible for the gas bubbles to prevent the attachment of the electrocoagulates to the surface. One main factor determining the rate of formation of the electrocoagulates is the rate by which the charged sites are removed from the micellar surface causing coalescence to occur. On the other hand, the stability of the particles would be determined by a certain [critical] charge/ weight ratio of the resin micelles. This critical ratio could be approximately constant for samples having different degrees of neutralization. Since in this case the electrocoagulation begins from larger particles (i.e., less charge/weight ratios) the ripening and reaching the critical charge/weight ratio will take place in a much shorter time; hence a fast rise in voltage is observed. However, as the molecular weight increases, the electrocoagulation will start with larger particles (having less charge/weight ratios). During this achievement period, the smaller electrocoagulates under the influence of the gases evolved will have difficulties to electrodeposit on the surface. This means that they will only be able to reach the surface through a limited number of routes, not occupied by the outgoing gas bubbles. In other words, the process of the film growth can be imagined as competitive phenomena between gas bubbles evolution and electrocoagulates deposition. During the latter stages of bubble confinement, the gas flow rate through the bubbles is so high that no continuous film is permitted to form easily and even if such film is formed it is easily torn off.

When a porous film is formed, since the conductance of the resin is so much lower than the conductance of the electrolyte, most of the conduction can only take place through the pores in the film and the polymer conduction could be neglected [10]. The film growth at the higher degrees of neutralization clearly shows a porous behaviour.

As the electrodeposition continues, the fraction of cathode area covered by pores diminishes and the voltage starts to rise. Eventually, the electrode will seal itself off and the voltage rises rapidly.

CONCLUSION

It can be concluded from the present study that the molecular weight of the resin drastically affects many properties of the electrodeposited coatings. By increas-

ing the molecular weight, the ionic sites on the surface of the particles will decrease leading to higher particle sizes. Some characteristics of the resins such as particle size, viscosity and appearance of such systems confirm this conclusion.

The molecular weight has also very important effects on the electrodeposition behaviour of such electrocoatings. By increasing the molecular weight, the film grows in a porous like manner, which can be attributed to the fact that the rate of hydrogen gas evolution is much higher than the rate of electrocoagulate deposition of the particles on the surface. The evolution of hydrogen gas will prevent the electrocoagulates to easily reach the surface, so that the formed pores through the passages of gas bubbles could not be rapidly filled in causing porosity in the film and the conduction occurring only through these pores. It is only after the completion of the gradual filling of these pores (i.e., sealing) that the voltage begins to rise steeply.

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