Constant Voltage Electrodeposition of Poly(vinylidene chloride) Emulsions

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ABSTRACT: In the field of organic coatings, electrodeposition is a technique that holds many advantages over traditional methods of immersion and dispersion, such as low levels of contamination, ease of control and automatization, and high penetration capacity. In this article, the results of the electrodeposition of poly(vinylidene chloride) emulsions on galvanized steel are presented. The operating conditions to form thin, uniform, and adherent films were established. A mathematical model was also developed to predict film growth with time as a function of the process parameters. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2479–2486, 1998

Key words: electrodeposition; emulsion; polymerization; PVdC emulsions

INTRODUCTION

Poly(vinylidene chloride) (PVdC)

The double bond in the vinylidene chloride (VdC) makes it highly reactive and susceptible to oxidation and polymerization reactions. PVdC contains a repeated symmetric unit that permits the polymer to pack efficiently in the solid state, which is represented accordingly by its high crystallinity.

The crystalline structure of PVdC has been extensively studied, but not totally resolved. However, studies have reported important aspects, such as the distribution of molecular weight, length, ramification, and morphology of the solid state. Due to its chemistry of polymerization, VdC polymers can show the same range of molecular weights and the same type of distribution observed with other monomers, such as methyl methacrylate. PVdC possesses several characteristics that make it commercially of interest: it maintains a highly crystalline structure in the normal range of operating temperatures (0–100°C), and it can be adapted to obtain fibers and films with high mechanical resistances.

The properties of a crystalline polymer like PVdC change drastically when the material is heated or cooled. The majority of these changes take place at two well-defined temperatures: the melting point ($T_m = 200$°C) and the glass transition temperature ($T_g = -13$°C). The polymer is transformed from a strong and flexible material to a rigid and brittle solid when it is cooled below T_g and to a rubber or viscoelastic fluid when it is heated above T_m. The nature of the material is defined by the relative location of these temperatures with respect to the use of the polymer. Due to its low permeability to a wide range of gases and liquids, PVdC is used as an organic coating, being generally applied as a lacquer or by immersion. However, the polymer is highly thermally unstable and cannot be heated until it melts, because in a short span of time it begins to degrade with a consequent release of large quantities of hydrochloric acid, which in turn catalyzes the decomposition process. The type of polymerization process is selected, depending on the final use of the polymer. For example, the need for a polymer in granulated form for injection molding is as-

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sisted if the polymerization process is conducted in suspension; in the case of paint and adhesive manufacture, polymerization is completed in emulsion or in solution.[1]

Electrodeposition

Electrodeposition is a process used to produce organic and inorganic coatings on metals. For organic coatings, this technique holds several advantages over conventional methods, such as: (1) production of thin, uniform, and electrically resistant films; (2) high penetration capacity, which allows that areas of metal with access difficulties can be covered; and (3) ease of control and automation.

The development of polymeric emulsions with an aqueous base has also contributed to the rapid adoption of electrodeposition by industry, because the levels of contamination and fire risks are considerably reduced during the process. The electrodeposition process can be anodic or cathodic, according to the charge of the solubilizing groups present on the surface of the particles. Among the functional groups commonly used are weak acids (carboxylic), strong acids (sulfonic), weak bases (amine), and strong bases (tertiary and quaternary compounds of ammonium).[2]

Entering in detail into the dynamics of the process, the flow of current initially creates an electric double layer in the outskirts of the metallic surface to be coated (anode or cathode accordingly); after this has stabilized (in a few milliseconds), the deposition of the polymer commences. The film growth depends on the number of electrochemical equivalents required to neutralize the solubilizing groups and finishes when this exerts a resistance sufficiently high to impede the passage of current or with the establishment of a limiting thickness.[3–5]

Electrodeposition can be conducted at constant current or voltage. Studies reported in the literature suggest the following conditions[3,4]: voltage, 50–500 V; solid concentration, 10–20%; current density, 1–10 mA cm^{-2}; and deposition time, between 30–120 s.

If electrodeposition is conducted in aqueous emulsions, electrochemical decomposition of the water occurs:

$$\text{cathodic } 2H_2O + 2e- \rightarrow H_2 + 2OH- \quad (1)$$

$$\text{anodic } 2H_2O \rightarrow 4H+ + O_2 + 4e- \quad (2)$$

In addition, provided that the metal substrate used as the electrode is not inert, the dissolution of the metal should be considered. This process is more significant in anodic than in cathodic electrodeposition.

Kinetics of Electrodeposition

The relationship between the mass deposited and the amount of current passed is defined as the coulombic efficiency (C) or, in other words, the mass deposited per coulomb of charge transferred. This factor is related to the number of dissociated groups on the surface of the latex particle, as well as the amount of additional electrolytes (salts and surfactants) present in the system. Theoretically, it is represented by M/nF, where M is the molecular weight of the deposited species, n is the number of equivalents per mole of this species, and F is Faraday's constant (96,487 C/equivalent). This factor can be obtained experimentally.[4] Generally, the coulombic efficiency is considered independent of the deposition time and the voltage applied; however, it has been found in some cases to increase with voltage.[6]

Constant Voltage Models

General Model

The rate of change of film thickness with time is related to the coulombic efficiency C (mg-coul) and the current density, by the following equation:

$$d\delta/dt = Cj/(1000\rho_p) \quad (3)$$

where δ is the film thickness, j is the current density, and ρ_p is the density of the deposited film.

Many electrodeposition systems (anodic and cathodic) produce films that exhibit Ohmic conduction characteristics. That is, the current density is directly proportional to the field strength across the film (the relation between applied voltage and film thickness). Other systems, such as some types of metal oxides, show a nonlineal dependence between current density and field strength, for example:

$$j = A^*\exp(BV/\delta) \quad (4)$$

$$j = A^*\sinh(BV/\delta) \quad (5)$$

In the specific case when field strength is small, it is possible to consider that:

$$\sinh(BV/\delta) = BV/\delta \qquad (6)$$

and

$$j = A\ BV/\delta \qquad (7)$$

where, according to Ohm's law, the product $AB = \sigma_p$; thus:

$$\delta = (2C\sigma p V)^{1/2} t^{1/2} = K t^{1/2} \qquad (8)$$

where σ_p is the specific conductivity of the film.

In general, it is not possible to predict if an electrodeposition film is ohmic or nonohmic in its conduction characteristics. The current density and field strength determine the type of behavior.[3]

Redissolving Films

The rate of film growth is described by:

$$d\delta/dt = C(j - jd)10^{-3}/\rho_p \qquad (9)$$

where, j_d is the dissolution current (i.e., the minimum current density under which no deposition occurs) and can be determined by the rate of ion transfer (H^+ and Me^{n+}) outward from the film by diffusion, electrophoresis, and convection.

If the electrodeposition process follows Ohm's law, the current density is described by:

$$j = V_{ap}/[(d/\sigma_b) + (\delta/\sigma_p)] \qquad (10)$$

where, V_{ap} is the applied voltage, d is the distance between electrodes, and σ_b is the specific conductivity of the bath.[4]

EXPERIMENTAL

Materials and Equipment

The power source was 12–800 V DC, with automatic control. A rectangular cell made of acrylic was $10 \times 7 \times 7$ cm. One of the faces of the cell had a 3-cm diameter orifice. Working electrodes were of galvanized steel with dimensions of 4×4 cm. The stainless-steel (AISI 304) electrodes had dimensions of 3×6 cm (cathode). Thickness meter

model was a Positector 6000 FNSI (DeFelsko). Software was required to control the power unit.

The emulsion used for electrodeposition was an anodic aqueous emulsion of PVdC supplied by Zeneca Resins of England (Haloflex 202), with a 60% weight of solids. The average molecular weight (M_w) of Haloflex 202 was 74,750.

Preparation of Working Electrodes

The electrodes were initially washed with soap to remove any dirt and then degreased with an alkaline solution (NaOH, carboxymethyl-cellulose, nonionic surfactant, and water). The plate was then activated by acid immersion (hydrochloric acid, sulfuric acid, and water) to eliminate all oxides. Each of these steps was followed by a distilled water rinse.[7]

Electrodeposition Procedure

Polymeric baths were prepared by diluting the emulsion standard. Once the galvanized plate was prepared, it was fixed in the cell as the anode on the lateral orifice, whereas a stainless-steel (AISI 304) sheet that remained within the bath was used as the cathode.

On connecting the electrodes to the source, the voltage and the test duration time were noted, and the cell was powered up. After the experiment was completed, the plate was removed, washed in distilled water, and dried at room temperature (25°C). Parameters such as the pH and conductivity of the bath were measured before and after each test run.

The film was weighed in the dry state to obtain the deposited mass and thus determine film thickness. In addition, the coulombs of current transferred in each test were determined (by integrating the i-t curve); this data was necessary to calculate the coulombic efficiency, density of the film, and the field magnitude based on the coating deposited at the end of the run.

RESULTS AND DISCUSSION

To establish the variables that control the electrodeposition process and their appropriate effects, a factorial experimental design was used at two levels (type II).[3] The parameters of study were voltage, concentration, and deposition time; eight experimental runs were conducted, with a duplicate for each one.[8,9] Film weight and thick-

Figure 1 Variation of current with time at 200 V for 60 s.

ness were measured as the response variables, whereas film appearance was also observed (rugosity and continuity).

Preliminary tests were initially conducted using % solid weight concentrations of 1, 30, and 60 wt %, with voltages from 50 to 500 V and deposition times of 30–60 s. It was observed that, with 1% concentrations and voltages <150 V, the film produced did not totally cover the predetermined deposition area (i.e., formation of noncontinuous films), whereas at voltages exceeding 300 V, wrinkled films were produced. Moreover, with high concentrations (30–60 wt %), thick and poorly adherent films were obtained, up to the point when detachment of the film from the metal occurred in the dry state.

Based on these preliminary trials, experimental design was established such that voltage was set at 200 and 300 V, and deposition time at 30 and 60 s, with variation in the solid concentrations used. In the first set of runs, 5 and 10 wt % concentrations were used. At 200 V, thick (thicknesses >350 μm), wrinkled, and poorly adherent films were formed; at 300 V, the film detached from the metal surface.

The second set of experiments was conducted at low concentrations (0.1 and 1 wt %). With the 0.1 wt % concentration, no film development was observed. However, in the area established for deposition, a white opaque surface was noted,

indicating possible chemical attack of the metal substrate. With concentrations of 1 wt %, thin (thicknesses between 17 and 60 μm), uniform, and smooth films were formed.

A third set of experiments was conducted, with a concentration range of 0.5 to 2 wt % to determine the quality of the films formed under these conditions. The films obtained with 0.5 wt % concentrations are very thin (thicknesses between 5 and 20 μm) and discontinuous; those formed with 2 wt % are wrinkled and thick (thicknesses between 64 and 225 μm).

Taking into account these sets of experiments, the behavior of the current during the process was determined. Figures 1 and 2 show the variation of current with time at 200 V–60 s and 200 V–30 s, respectively. As can be observed, for the 0.1 wt % concentration and concentrations >5 wt %, the current drops to 0 after a certain time; different phenomena can be attributed to both cases. In the first case, as has been described, chemical attack of the metal substrate could cause the inactivation of the electrode. In the second case, the drop in current is attributed to the high resistance of the thick film that is formed. On the contrary, for low concentrations

Figure 2 Variation of current with time at 200 V for 30 s.

Figure 3 Variation of current with time at 200 V for 5 min at 1 wt %.

(0.5–1 wt %), the current does not tend toward zero; but, as with concentrated baths, it oscillates between a small range of values exhibiting peaks. This behavior can be explained by one of two phenomena: a continuous dissolution of the film[3] or because of electric discharges within the film resulting from the large electric field across it.[10]

For concentrations >10 wt %, the films tend to be smooth and uniform. Due to the increase in the concentration of electroactive species, the initial current is high, which promotes an increase in the electrophoretic transport of the particles. Hence, the electrical resistance of the film increases rapidly, causing a heating of the electrode that promotes the particles to pack more uniformly and form smooth films.

An additional test was completed for the 1 wt % concentration at 200 V and with process times >1 min. An increase in electrosmosis was observed. The current tended to a residual value with time, and it also maintained an oscillating pattern, which is indicative of the redissolving of the film. Figure 3 presents the variation of current with time for the run: 200 V for 5 min at 1 wt %.

The effect of each of the process variables was evaluated using the experimental data. Table I presents an estimation of the effects and typical deviations for the thickness variable. The effects and typical deviations for the weight variable are given in Table II.

The concentration–time relationship, followed by the concentration–voltage relationship, was found to be the most important in determining film weight and thickness. As can be expected, an increase in the amount of active species and an increase in the electric field strength favor the electrophoretic phenomenon, thus accelerating the migration rate of the *micelles* toward the electrode and consequently the amount of polymer deposited.

With a 1 wt % concentration, time (5–60 s) and voltage (50–500 V) sweeps were completed to select the optimum operating conditions. Thin, adherent, and smooth films were obtained using a 1 wt % concentration, a 30-s process time, and a 200-V applied voltage. Under these conditions, additional tests were conducted to establish the behavior of parameters, such as bath conductivity and pH, with successive depositions in it. These results are given in Table III.

Conductivity decreases and pH increases with the number of tests. Moreover, a drop in the amount of polymer deposited and the initial current were observed for each deposition. Figure 4 shows the variation of weight and thickness with a number of tests (200 V for 30 s at 1 wt %). Figure 5 presents the variation of current with time for successive depositions.

Table I Effects and Typical Deviations for the Thickness Variable

Average	65.973 ± 0.789
Principal effects	
Voltage (V)	37.5913 ± 1.5791
Time (t)	49.3912 ± 1.5791
Concentration (C)	103.379 ± 1.5791
Interactions	
Vt	27.146 ± 1.5791
tC	38.433 ± 1.5791
VC	35.433 ± 1.5791
VtC	26.578 ± 1.5791

Table II Effects and Typical Deviations for the Weight Variable

Average	64.275 ± 0.8179
Principal effects	
Voltage (V)	25.4 ± 1.6359
Time (t)	40.475 ± 1.6359
Concentration (C)	101.75 ± 1.6359
Interactions	
Vt	18.175 ± 1.6359
tC	33.275 ± 1.6359
VC	24.25 ± 1.6359
VtC	18.325 ± 1.6359

Table III   Variation of Parameters with Successive Depositions

No. of Tests	pH	Conductivity (ms cm^{-1})	Weight (mg)	Thickness (μm)
1	3.04	311	22.1	22
2	3.12	281	21	21
3	3.20	255	19.5	20
4	3.32	237	18.2	19
5	3.49	215	17.6	18
6	3.63	198	17.3	18
7	3.78	185	15.7	16
8	3.93	170	15.3	16

The increase in bath pH is caused by the neutralization of a proportion of the hydrogen ions (H^{+}) produced by the electrolysis of the water by the charged species present on the surface of the *micelle.* Similarly, the decrease in bath conductivity results from the decrease in the amount of electroactive species, either by parallel reactions at the electrodes or their incorporation in the film.[6]

Tests were conducted to determine the behavior of current density with field strength (Table IV). The field strength across the film was found to be considerable, of the order of 10E5, which conforms to reported values.

From the weight/area *vs.* charge/area curve (Fig. 6), it was concluded that the process obeys Faraday's law, because the amount of polymer deposited is proportional to the amount of coulombs transferred. The curve does not pass through the origin; this phenomenon has been reported in the literature. Even though its exact

Figure 4   Variation of weight and thickness with the number of tests (200 V for 30 s at 1 wt %).

Figure 5   Variation of current with time for successive depositions.

origin and significance is unknown, it is accepted that the behavior can vary significantly with the type of polymer and the operating conditions used.[4] The slope of the curve represents the coulombic efficiency, which was calculated as 3.1281 mg coulomb^{-1}. The intersection of the curve with the x axis represents the dissolution current density (j_d). This can vary significantly, depending on the type of system and polymer used.

From the thickness against weight/area curve presented in Figure 7, the film density was obtained as $\rho_p = 1.64$ g cm^{-3}; this corresponds to the reciprocal value of the slope.

Values of the current density were correlated with the field strength to determine the conduction characteristics of the film. The following logarithmic-type equation was obtained:

$$J = 0.07 \, \text{Ln}(V/\delta) - 0.7758, \quad r = 0.991 \quad (11)$$

It can be concluded that the film presents nonohmic characteristics, because the current density is not directly proportional to voltage. Figure 8 shows the relationship between current density and field strength.

Using experimental data (coulombic efficiency and film density) and eq. (11), it is possible to develop a mathematical model of the variation of thickness by the Runge–Kutta method. As previously described, the film was found to redissolve; thus, the process can be represented by eq. (9). Experimentally, a negative dissolution current was obtained that was probably due to electrical discharges or a possible adsorption of the polymer on the metal surface before the electrodeposition process was initiated. With the aim of resolving

Table IV   Variation of Parameters with Voltage (for 30 s at 1 wt %)

Voltage (V)	Weight (mg)	Thickness (μm)	Charge (coulomb)	Field Strength (V cm^{-1})	Current Density (A cm^{-2})
50	2	5	0.279	71,428	4.25E-03
100	8.4	10	1.994	80,956	5.47E-03
150	14.8	17	3.682	81,082	1.62E-02
200	18.6	20	5.719	93,023	2.57E-02
250	21.9	22	7.096	98,039	3.28E-02
300	24.4	26	7.958	109,091	3.62E-02
350	26.2	28	8.592	114,754	3.85E-02
400	29.3	30	9.177	123,077	4.49E-02
450	33.6	32	9.884	132,353	4.70E-02
500	36.8	34	10.940	136,986	5.36E-02

the problem of not knowing j_d and the effect of the discharges on growth kinetics, the model was adjusted by introducing a proportionality constant ($K = 0.4$). The following model was thus obtained:

$$d\delta/dt = 5.3312 \text{ E-5 } \text{Ln}(V/\delta) - 5.9085 \text{ E-4} \quad (12)$$

The results from this mathematical model were used to compare the experimentally obtained thicknesses at different deposition times. Variation of weight and thickness are given in Table V for the 200-V 1 wt % test conditions. Similarly, Figure 9 presents the thickness against time curve.

As can be observed, the model describes very approximately experimental results. The average, standard deviation, and variation coefficient of the deviations are 1.1 μm, 1 μm, and 90.9%, respectively.

CONCLUSIONS

- The electrodeposition of PVdC obeys Faraday's law of electrolysis. It is important to point out that not all polymeric emulsions follow this behavior.
- The decline in conductivity after each run, as well as corroborating the neutralization of the charged species, indicates that the surfactant is incorporated in the film.
- No comparative studies exist in the literature related to the evaluation of the transport, and morphological and physicochemical properties of PVdC using conventional methods and electrodeposition.
- Based on a factorial experimental design, it was found that uniform, thin ($\cong 20$ μm), and adherent films were formed by using the following operating conditions: 200 V for 30 s at 1 wt % solid concentration.
- The coulombic efficiency (which is related to the number of dissociated groups on the surface of the polymer particle) is independent of the operating voltage.
- Successive depositions using the same emulsion gave a decrease in the weight and thickness of the film.

Figure 6   Weight/area against charge/area curve.

Figure 7   Thickness against weight/area curve.

Figure 8 Relationship between current density and field strength.

- The film exhibited nonohmic conduction characteristics and showed a logarithmic relationship between current and field density; therefore, a rapid drop in film growth rate was experienced as time increased.
- The increase in film thickness and weight was directly related to the increment in concentration, process time, and applied voltage.
- The films produced by this method were smooth, continuous, and had very good adhesion.
- A mathematical model for the rate of film growth was obtained from the experimental data and is expressed by the following equation:

Table V   Variation of Weight and Thickness (200 V at 1 wt %)

Time (s)	Weight (mg)	Experimental Thickness (μm)	Thickness from Model (μm)
5	2.3	5	6.8
10	5.2	8	10.2
15	6.0	11	12.8
20	9.4	14	14.9
25	10.2	16	16.7
30	18.0	19	18.2

Figure 9 Prediction of the thickness against time curve.

$$\frac{d\delta}{dt} = 5.3312 * 10^{-5} \, \mathrm{Ln}\!\left(\frac{V}{\delta}\right) - 5.9085 * 10^{-4}$$

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