Electrodeposition of Polyimides from Nonaqueous Emulsions

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Synopsis

A theoretical and experimental study was carried out to investigate the process of electrodepositing a polyamic acid film from a nonaqueous emulsion onto a metal surface (copper, aluminum) as well as the subsequent drying and imidization steps. The rate of film growth is controlled by the electrophoresis of the polymer emulsion particles to one of the electrodes and the concomitant film compaction due to the outflow of the solvent caused by electro-osmosis. Parameters affecting the coating process such as particle size, charge, ζ potential, viscosity of the liquid medium, conductivity of the deposited film, etc. were considered.

INTRODUCTION

Industrial electrodeposition of polymers is based primarily on aqueous systems. In the last ten years, however, considerable interest on nonaqueous electrodeposition has emerged. Nonaqueous electrodeposition does not have the drawbacks of an aqueous system, such as gas evolution at the electrode and low solubility of some high performance polymers. In a nonaqueous process, a polymer solution is first prepared by dissolving the polymer in a solvent. Then, an emulsion is formed by adding the solution into a precipitant, which is miscible with the solvent but immiscible with the polymer. The precipitated polymer emulsion particles are either positively or negatively charged, depending on the charge of the dissociated end groups on the polymer molecules and of any adsorbed ions. Electrophoresis of the emulsion particles occurs under an applied electric potential, resulting in the formation of a "wet" film made up of emulsion particles, the precipitant, and solvent at one of the electrodes. The polymer content in the wet film is much higher than that of the bath. Finally, a polymer coating is obtained by drying and curing the wet film.

The yield of a nonaqueous electrodeposition process is influenced by a host of parameters related to the characteristics of the emulsion (e.g., emulsion particle size), the electrodeposition cell (e.g., electrode material), and operating conditions (e.g., magnitude of applied voltage). Major investigations in this area were carried out by researchers at Westinghouse,[1-4] with the aim of optimizing the process before applying it on an industrial scale. Phillips[1] studied the electrodeposition of polyamic acids onto metal electrodes. In the presence of a base, triethylamine, the carboxyl group of polyamic acid carries

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a negative charge and the emulsion particles migrate to the anode in an electric field. Alvino and Scala[2] systematically varied the relative amount and types of solvent, base, and precipitant for a given polymer to determine the maximum yield of deposit for a constant voltage and deposition time. In two separate control experiments, they showed that dip coating with the nonaqueous emulsion provided no yield and that using water as the precipitant led to a poor, discontinuous coating because of considerable gassing at the electrodes. The rate of deposition as a function of time and voltage was studied by Alvino et al.[3] They reported an interesting observation that at any given deposition time, the polymer content in the wet film increased with higher voltages. A plausible explanation was suggested by these authors that electroosmosis caused the movement of the liquid—solvent and precipitant—in the wet film back into the bulk of the emulsion. In a recent review, Scala et al.[4] reported that nonaqueous electrodeposition has been successfully applied to aluminum, steel, brass, nickel, and platinum as electrode materials.

Thus, a comprehensive, qualitative view of the nonaqueous electrodeposition process is available. To aid in the design of a commercial process, however, it is essential to obtain a more quantitative understanding of how the wet film grows. The objective of this work was to develop such a model. Included is the presence of an adsorbed layer on the surface of a metal electrode, which was not considered previously. To confirm the theory, we need electrodeposition data for a system which is fully characterized.

EXPERIMENTAL

Design, Characterization, and Procedures

The deposition apparatus consisted of a glass beaker with aluminum or copper electrodes immersed 2.54 cm deep into the emulsion bath. The electrodes (2.54 cm wide) were held in a mounting device such that they were parallel to each other and their separation could be varied. The outward-facing side of each electrode was coated with an insulating layer of polyimide so that they did not participate in electrodeposition.

Emulsions were prepared with the composition suggested by Alvino et al.[3] 10 g Pyre ML RC-5057 (a 16.5 wt% polyamic acid dissolved in N-methyl-pyrrolidone (NMP); duPont), 62 g NMP (Aldrich), 0.4 g triethylamine (Aldrich), and 178 mL acetone (Fisher). The following steps were followed. Triethylamine was first mixed with acetone. The pyre ML solution, after dilution with pure N-methyl-pyrrolidone to a final 2.29 wt% polyamic acid, was slowly dripped at a constant rate from a funnel into the vigorously stirred acetone/triethylamine mixture. The resulting emulsion will be referred to as emulsion A. Alternately, the polymer solution was poured directly into the acetone/triethylamine mixture and then stirred for a period of time. The resulting emulsion was emulsion B.

The average emulsion particle size was measured with the laser light-scattering autocorrelation technique to be 0.068 μm for emulsion A and 0.146 μm for emulsion B. The zeta potential was -31.6 mV for emulsion A and -36.9 mV for emulsion B, as measured by a zeta potential meter (Pen Kem, Laser Zee 501). With a conductivity meter (Yellow Springs), both emulsions were found to have the same conductivity value of 23.3 μS/cm.

The results to be presented below were all based on potentiostatic experiments. Before each deposition experiment, the electrodes were cleaned of grease and dirt with acetone. A power source (Kepco, AT150-0.7M) supplied a constant voltage and a multimeter with a data storage option (Keithley, model 175) was used to monitor current decay at a rate of one reading per second. After the power had been switched off, the anode with its wet film was removed from the bath and as quickly as possible weighed with an analytical balance (Mettler, AE100). The drying rate in air due to evaporation of acetone and N-methyl-pyrrolidone was recorded every 10 seconds and then in increasing increments. Then the coated electrode was dried at 80°C for 30 minutes before curing it at 200°C for 40 minutes to achieve a substantial degree of imidization.

MODELING THE ELECTRODEPOSITION PROCESS

Consider an emulsion particle of radius, a_p, and net positive charge, q_p, under a potential gradient of $d\Phi/dx$ within the emulsion bath. The force due to the electric field on the particle is given by

$$F_E = \left(\frac{d\Phi}{dx}\right)_b q_p \qquad (1)$$

The oppositely directed drag force on the particle can be approximated by Stokes' equation

$$F_D = 6\pi\mu_b a_p v_p \qquad (2)$$

where μ_b is the viscosity of the continuous phase of the bath and v_p is particle velocity. In an electrodeposition bath with thousands of emulsion particles, the volumetric flow rate of polymer particles arriving at the anode due to electrophoresis is given by

$$\dot{V}_p = v_p A V_p n_p \qquad (3)$$

where A is the area of the electrode, V_p is the volume of an individual emulsion particle, and n_p is the number concentration of emulsion particles per unit volume. Equating eqs. (1) and (2) for v_p and subsituting it into eq. (3), we get

$$\dot{V}_p = \frac{q_p}{6\pi\mu_b a_p}\left(\frac{d\Phi(t)}{dx}\right)_b A V_p n_p \qquad (4)$$

Note that the potential gradient of the bath is a function of time. Although it is a potentiostatic experiment, the growing wet film and adsorbed layer reduce the potential drop for the bath. Also, diffusion is not considered in eq. (4) as it is small compared to electrophoresis. A volume balance for the particles in the deposit yields

$$A\frac{d}{dt}(\delta\beta_p) = \dot{V}_p \qquad (5)$$

where δ is the wet film thickness and β_p is the volume fraction of emulsion particles in the wet film.

Clearly, a certain amount of liquid from the continuous medium of the bath is dragged into the wet film with the emulsion particles. We assume that every particle brings in a fixed liquid volume so that the volumetric flow rate of liquid into the wet film can be expressed as

$$\dot{V}_{1,\text{in}} = \left[\frac{1 - \beta_o}{\beta_o} \right] \dot{V}_p \tag{6}$$

where β_o denotes the ratio of particle volume to the total volume of a particle and its associated liquid. A significant amount of the liquid in the wet film, however, migrates back into the bath due to electro-osmosis. The Smoluchowski[5] equation provides a simple model for this effect.

$$\dot{V}_{1,\text{out}} = \frac{\epsilon \zeta A}{4 \pi \mu_{wf}} \left[\frac{d\Phi(t)}{dx} \right]_{wf} \tag{7}$$

Here ϵ, ζ, μ_{wf}, and $(d\Phi/dx)_{wf}$ are dielectric constant, zeta potential, viscosity, and potential gradient of the wet film, respectively. A volume balance for the liquid medium in the wet film yields

$$A \frac{d}{dt} (\delta - \delta \beta_p) = \dot{V}_{1,\text{in}} - \dot{V}_{1,\text{out}} \tag{8}$$

An overall material balance for the wet film can be obtained by combining eqs. (5), (6), and (8).

$$A \frac{d\delta}{dt} = \frac{1}{\beta_o} \dot{V}_p - \dot{V}_{1,\text{out}} \tag{9}$$

Substituting eqs. (4) and (7) into eq. (9), we get

$$\frac{d\delta}{dt} = \frac{1}{6\pi} \frac{q_p V_p n_p}{\beta_o \mu_b a_p} \left(\frac{d\Phi}{dx} \right)_b - \frac{\epsilon \zeta}{4 \pi \mu_{wf}} \left(\frac{d\Phi}{dx} \right)_{wf} \tag{10}$$

In order to determine the time-dependent potential gradients in eq. (10), we need to examine the electrical resistances of the deposition apparatus. Clearly, we have the wet film and emulsion resistances between the electrodes. In addition, as discussed by Bard and Faulkner,[6] adsorption of electroinactive species or the formation of an oxide layer on the electrode is possible during electrodepositions. This was confirmed in our control experiments that current decay occurred with pure acetone or NMP as the only liquid in the electrodeposition bath (Fig. 1). Thus, the overall resistance is given by a series of individual resistances

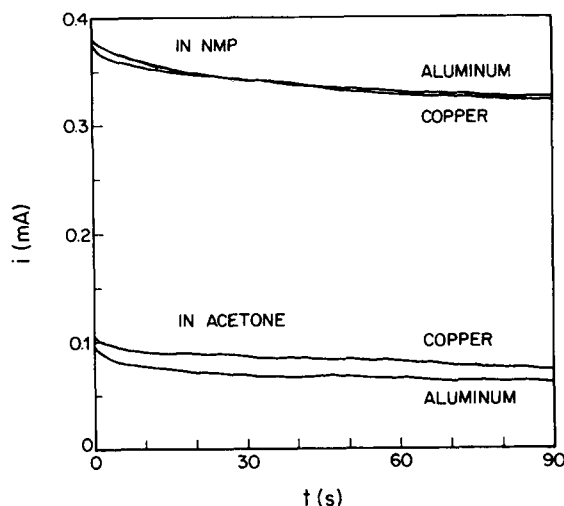$$R(t) = R_{wf}(t) + R_b(t) + R_{ad}(t) \tag{11}$$

Fig. 1.   Current versus time in pure acetone and pure NMP for copper and aluminum anodes. The applied voltage was 50 V and the electrode separation was 2 cm.

Here, R_{ad}, referred to as the adsorbed layer resistance is employed to represent the additional resistance regardless of its actual source. Equivalently, eq. (11) can be expressed as

$$R(t) = r_{wf}(t)\frac{\delta(t)}{A} + r_b\frac{L - \delta(t)}{A} + R_{ad}(t) \qquad (12)$$

where r_{wf} and r_b are the specific resistivities of the wet film and emulsion bath, respectively. L is the separation between the electrodes. Note that due to compaction of the wet film throughout the experiment, its specific resistivity increases with time. Applying Ohm's law, we get for the current decay

$$i(t) = \frac{U}{R(t)} \qquad (13)$$

where U is the applied voltage across the electrodes. Finally, assuming that the potential gradients across the wet film and emulsion bath are linear, we get

$$\left(\frac{d\Phi}{dx}\right)_{wf} = \frac{R_{wf}(t)i(t)}{\delta(t)} = \frac{r_{wf}(t)i(t)}{A} \qquad (14)$$

$$\left(\frac{d\Phi}{dx}\right)_b = \frac{R_b(t)i(t)}{L - \delta(t)} = \frac{r_b i(t)}{A} \qquad (15)$$

Method of Solution

Substituting eq. (12) into eq. (13) to get $i(t)$ for eqs. (14) and (15), we can in principle determine the wet film thickness as a function of time with eq. (10),

provided that all the parameters in these equations can be evaluated separately. Indeed, most parameters have been determined either experimentally or from various sources of material physical properties. The two exceptions are the wet film resistivity, $r_{wf}(t)$, and the adsorbed layer resistance, $R_{ad}(t)$.

In order to complete the analysis, we propose that $r_{wf}(t)$ and $R_{ad}(t)$ be expressed in terms of polynomials with adjustable coefficients. The strategy is to assume reasonable values for r_{wf} and R_{ad}, and then determine whether or not the overall theory is consistent with all the experimental data. Since the wet film thickness, δ, is expected to be a monotonic function of time [i.e., $\delta = f(t)$], we can obtain an inverse relationship [i.e., $t = f^{-1}(\delta)$]. Substituting this relationship into $r_{wf}(t)$ and $R_{ad}(t)$ and truncating after the quadratic term, we get

$$r_{wf}(t) = b_0 + b_1\delta + b_2\delta^2 \tag{16}$$

and

$$R_{ad}(t) = c_0 + c_1\delta + c_2\delta^2 \tag{17}$$

with the b's and c's being the adjustable coefficients.

Finally, the combination of eqs. (10), (12) to (17) gives

$$\frac{d\delta}{dt} = den\,2\,\frac{U}{den\,1} \tag{18}$$

where

$$den\,2 = \frac{1}{6\pi}\frac{q_p V_p n_p}{\beta_o \mu_b a_p}\frac{r_b}{A} - \frac{\epsilon\zeta}{4\pi\mu_{wf}}\frac{1}{A}\left(b_0 + b_1\delta + b_2\delta^2\right) \tag{19}$$

$$den\,1 = \frac{1}{A}\left[\delta\left(b_o + b_1\delta + b_2\delta^2\right) + r_b(L - \delta)\right] + c_0 + c_1\delta + c_2\delta^2 \tag{20}$$

An analytic solution to eq. (18) is given in Appendix A, eqs. (32) to (35).

In order to follow the compaction of the wet film, we need to know how the volume fraction of emulsion particles changes with time. Combining eqs. (4), (5), and (15), we get

$$\frac{d}{dt}\left(\delta\beta_p\right) = \frac{1}{6\pi}\frac{q_p V_p n_p}{\mu_b a_p}\frac{r_b}{A}i(t) \tag{21}$$

Integration of eq. (21) gives

$$\beta_p(t) = \frac{1}{6\pi}\frac{q_p V_p n_p}{\mu_b a_p}\frac{r_b}{A}\frac{Q(t)}{\delta} \tag{22}$$

where $Q(t)$ is the amount of charge passed through the system for a deposition time t, and is given by

$$Q(t) = \int_0^t i(t')\,dt' \tag{23}$$

Since we do not have an explicit relationship for $i(t)$, eq. (23) cannot be readily integrated. It is much easier to change the integration variable to δ through eq. (18). Note that the ratio $U/den\,1$ is $i(t)$. Therefore, eq. (23) can be rewritten as

$$Q(\delta) = \int_0^{\delta(t)} \frac{d\delta'}{den\,2} \tag{24}$$

An analytic solution to eq. (24) is given in Appendix A, eqs. (33) to (36).

Mass of the Wet Film

In order to match model and experiments, we must convert $\delta(t)$ and $\beta_p(t)$ predictions to the mass of the wet film, which was determined experimentally. Let us first assume that an emulsion particle consisted primarily of polyamic acid and a small amount of the solvent. The density of the emulsion particle is given by

$$\rho_p = \frac{\rho_{NMP}\rho_{PAA}}{\gamma_{PAA}\rho_{NMP} + (1 - \gamma_{PAA})\rho_{PAA}} \tag{25}$$

where ρ_{NMP} and ρ_{PAA} are the densities of NMP and polyamic acid, respectively, and γ_{PAA} is the mass fraction of polyamic acid in an emulsion particle. Similarly, the density of the liquid medium in the wet film is given by

$$\rho_1 = \frac{\rho_{NMP}\rho_{ac}}{\gamma_{ac}\rho_{NMP} + (1 - \gamma_{ac})\rho_{ac}} \tag{26}$$

where ρ_{ac} is the density of acetone and γ_{ac} is the mass fraction of acetone in the liquid phase of the wet film. The density of the wet film is given by

$$\rho_{wf} = \beta_p\rho_p + (1 - \beta)\rho_1 \tag{27}$$

The mass of the wet film can be readily calculated as

$$m_{wf} = \rho_{wf}A\delta \tag{28}$$

Finally, it should be mentioned that a modified form of Faraday's law[7] provides a basic relationship between the amount of chemical change and the change passed through the system

$$m_i = (\eta m_e)_i Q \tag{29}$$

Here, m_i is the mass of the deposited species i, η is an efficiency factor, and m_e is the mass equivalent to the chemical change per unit charge. The efficiency factor is included to account for possible side reactions. In practical systems, it is usually difficult to determine the exact value for m_e because systems with simple reactions are rare. Therefore, the product (ηm_e) is generally evaluated as a whole and termed Coulombic efficiency.
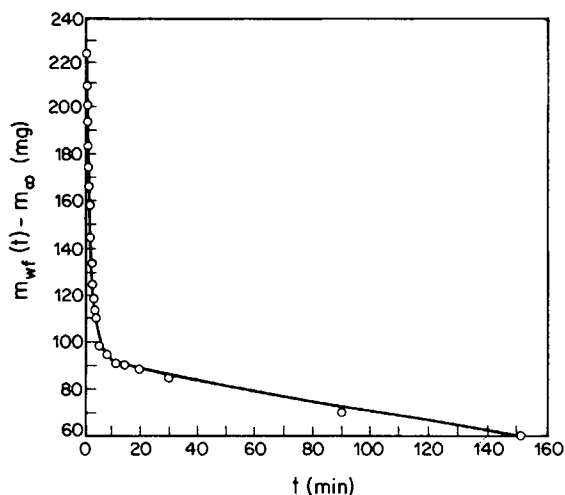
Fig. 2. A typical set of drying rate data. The mass of the wet film minus the same mass at the conclusion of air drying is plotted against time. ($\circ$) Experimental data; (—) fitted curve.

RESULTS

Drying Rate

We carried out a total of 81 experiments, with either aluminum or copper electrodes, at different voltages and for different deposition times. For each experiment, as mentioned in the section on the experimental system, the drying rate of the wet film in air was monitored before curing in oven. Figure 2 shows a typical set of drying data, which indicate two regions with significantly different drying rates. Apparently, absorption of moisture from the surrounding air was possible, and the precipitant (acetone) and solvent (NMP) did not evaporate separately. Nevertheless, if one assumes that the fast and slow evaporation processes are due to acetone and NMP, separately and respectively, the mass ratio of acetone to NMP in the wet film can be estimated to be about 1.34, which is lower than the value of 2.00 in the original emulsion composition. Anyway, extrapolation of the drying curve to zero time provides a better estimate of the wet film weight at the end of electrodeposition.

Coulombic Efficiency

The effect of voltage, emulsion type, and electrode material on Coulombic efficiency can be examined in Figure 3. The deposition time was fixed at 60 s. The mass of polyimide deposited, m_{PI}, depends linearly on the amount of charge passed, indicating a constant Coulombic efficiency. In fact, Coulombic efficiency was found to be independent of deposition time (Fig. 4) and the separation between the electrodes (Fig. 5). The average Coulombic efficiency based on the data in Figures 3 to 5 is 71.9 mg/C, which agrees well with the values (70.9 to 78.3 mg/C) reported by Alvino et al.[3] Since their electrodeposition cell is made up of a rod-shaped anode surrounded by a cathode in the
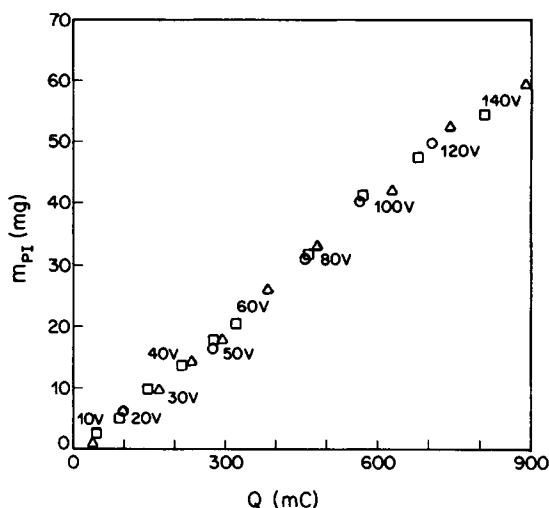
Fig. 3. Relationship between mass of polyimide deposited and charge passed through the electrodeposition cell. The effect of voltage, emulsion type, and electrode material on Coulombic efficiency is examined. (△) Copper anode, emulsion A; (□) aluminum anode, emulsion A; (○) aluminum anode, emulsion B.

form of a cylindrical sheath, the agreement lends support to our geometry of parallel electrodes.

Growth of the Wet Film and Current Decay

In the following, we compare two sets of experiments with model predictions. Aluminum electrodes and emulsion A were used in both cases. Electrode separation was kept constant at 2 cm. Model parameters, either taken from
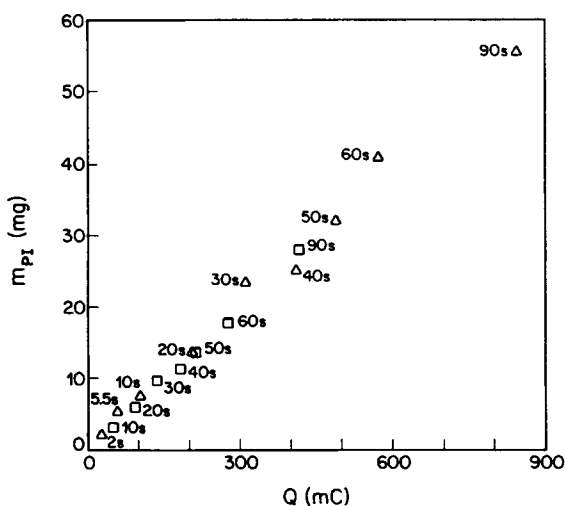

Fig. 4. Relationship between mass of polyimide deposited and charge passed through the electrodeposition cell. The effect of deposition time is examined. Emulsion A and aluminum electrodes were used. (□) 50 V; (△) 100 V.
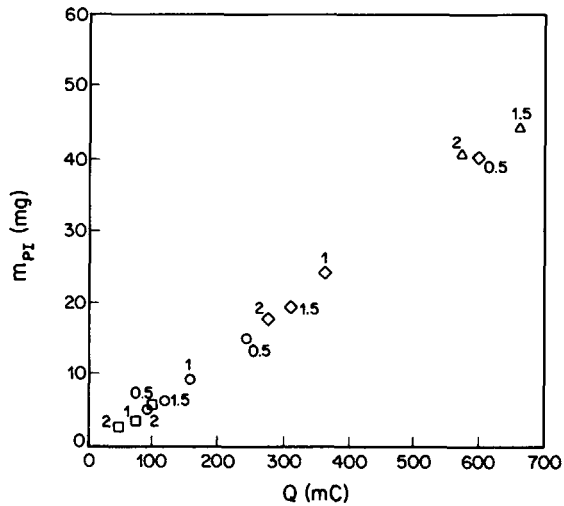
Fig. 5. Relationship between mass of polyimide deposited and charge passed through the electrodeposition cell. The effect of electrode separation is examined. Emulsion A and aluminum electrodes were used. The deposition time was fixed at 60 s. (□) 10 V; (○) 20 V; (◇) 50 V; (△) 100 V.

TABLE I
Values of Model Parameters

Densities:		
Acetone	ρ_{ac}	0.79 g/cm^3
NMP	ρ_{NMP}	1.03 g/cm^3
Polyimide	ρ_{PI}	1.42 g/cm^3
PAA	ρ_{PAA}	1.4 g/cm^3
Viscosities of the continuous phase:		
in wet film	μ_{wf}	6.6 Ns/cm^2
in emulsion	μ_b	5.6 Ns/cm^2
Dielectric constant in wet film	ϵ	1.8×10^{-10} As/Vm
Average emulsion particle radius	a_p	0.068 μm
Average emulsion particle volume	V_p	1.3×10^{-3} μm^3
Zeta potential of an emulsion particle	ζ	-30 mV
Charge on an emulsion particle	q_p	3×10^{-17} As
Mass fraction of PAA in an emulsion particle	γ_{PAA}	0.9
Coulombic efficiency	$(\eta m_e)_{PAA}$	77.2 mg/As
Number concentration of emulsion particles in bath	n_p	4×10^{18} 1/m^3
Resistivity of deposition bath	r_b	31000 Ω cm
Volume fraction of emulsion particle in the wet film at startup	β_o	0.04
Area for deposition	A	6.45 cm^2
Electrode separation	L	2 cm
Applied voltage	U	50 and 100 V

TABLE II
Values of the Coefficients for Wet Film Resistivity and Adsorbed Layer Resistance

	50 V	100 V
b_0, Ω cm	42,000	42,000
b_1, Ω	4.5×10^6	4.1×10^6
b_2, Ω/cm	-1.5×10^7	-1×10^7
c_0, Ω	10	10
c_1, Ω/cm	7×10^5	3.1×10^4
c_2, Ω/cm^2	-7.8×10^5	-3.4×10^5

various sources of physical properties, estimated by different means or determined in our own experiments, are listed in Table I. The viscosity value of an acetone–NMP mixture was estimated with the Kendall-Monroe equation.[8] The equations used to calculate the number concentration of emulsion particles, n_p, and charge on a particle q_p, are derived in Appendix B. The dielectric constant of the wet film, ϵ, for lack of better information is assumed to be that of acetone. The mass fraction of polyamic acid in an emulsion particle is assumed to be 0.9. The volume fraction of emulsion particles in the wet film at the startup of the experiment, β_o, was estimated by extrapolating the corresponding experimental data to zero time. Values of adjustable parameters, the polynomial coefficients in eqs. (16) and (17), are listed for the two sets of experiments in Table II. The coefficients b_o and c_o were kept constant as they represent the resistivities of an emulsion and that of an initial adsorbed layer before electrodeposition, respectively.

Figures 6 and 7 present the mass of wet film and polyamic acid deposited at applied voltages of 50 V and 100 V, respectively, as a function of deposition time. The amount of polyamic acid deposited depends almost linearly on time. Note that we actually measured the mass of polyimide deposited. However,
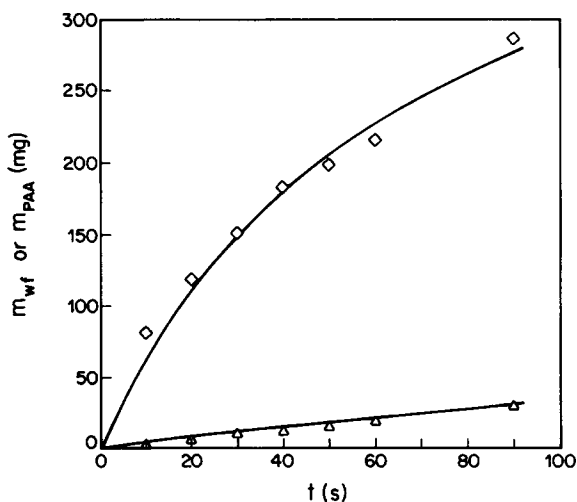

Fig. 6.   Mass of wet film ($\Diamond$) and polyamic acid ($\triangle$) deposited versus time. Model predictions (—) are compared with experimental data at a constant voltage of 50 V. The anode substrate was aluminum, electrode separation was 2 cm and emulsion A was used.
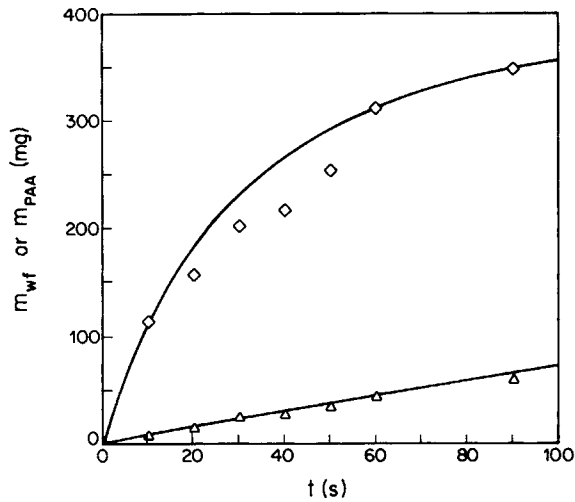
Fig. 7.   Same as Fig. 6 with the exception that the voltage was 100 V.

since every monomer unit of the polyamic acid produces two water molecules during imidization, the two masses are related by

$$m_{PI} = \left\{ 1 - \xi \frac{2M_w}{M_{PAA}} \right\} m_{PAA} \qquad (30)$$

where M_w and M_{PAA} are the molecular weights of water and polyamic acid, respectively. For our curing conditions, the extent of imidization, ξ, would be approximately 80%, as measured by Ginsburg and Susko.[9] Comparison of Figures 6 and 7 indicates that, as expected, the rate of polyamic acid deposition is higher at a higher voltage.
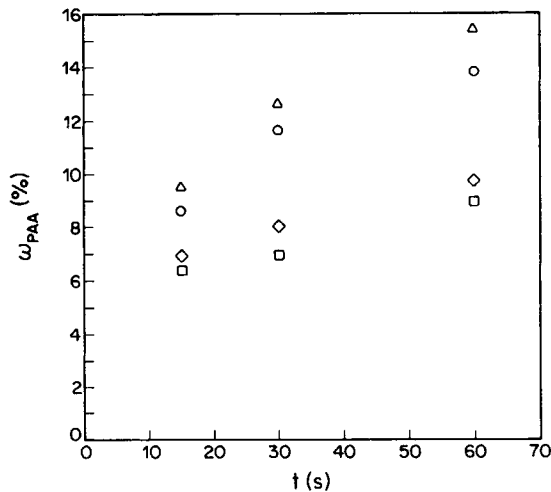

Fig. 8.   Mass fraction of polyamic acid in wet film versus deposition time. The experimental conditions correspond to those in Figs. 6 and 7. Emulsion A: (□) 50 V, (○) 100 V; Emulsion B: (◇) 50 V, (△) 100 V.
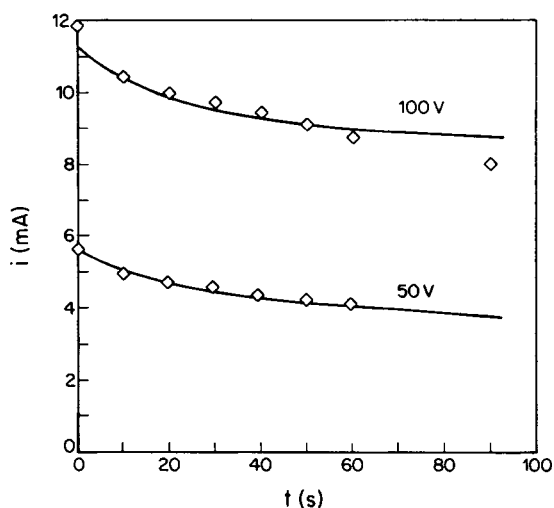
Fig. 9.   Current decay versus time. Model predictions (—) are compared with experimental (◇) data. The experimental conditions correspond to those in Figs. 6 and 7.

The mass of wet film depends nonlinearly on time, with the curve bending downward as time progresses. As discussed in the theory section, although the volume fraction of emulsion particles arriving at the anode, β_o, is expected to be approximately constant, the outflow of the liquid medium in the wet film due to electro-osmosis results in a reduced rate of wet film mass buildup. Figure 8 shows how the mass fraction of polyamic acid in the wet film, ω_{PAA}, increases with time at the two applied voltages.

Current decay for the same two sets of experiments are presented in Figure 9. The solid lines are calculated with eqs. (12) and (13). The combined increase
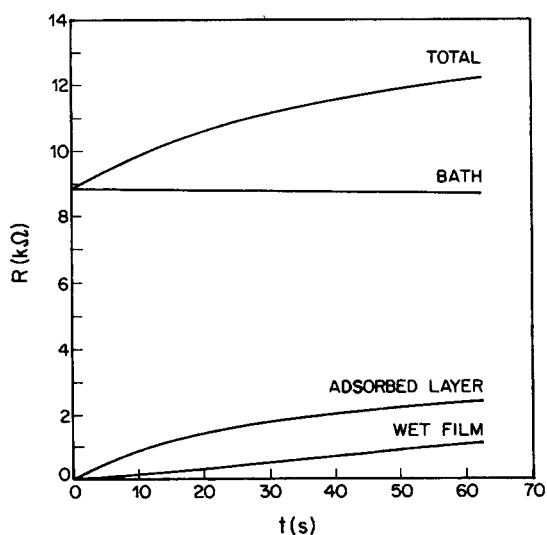

Fig. 10.   Resistance versus time in the electrodeposition process as predicted from the model. The experimental conditions correspond to those in Fig. 6.

in wet film and adsorbed layer resistances is larger than the decrease in resistance of the emulsion bath of a reduced length, thus leading to current decay. To illustrate this point, the resistances as a function of time for the 50 V experiment are presented in Figure 10. At the conclusion of electrodeposition, the sum of the wet film and adsorbed layer resistances constitutes 30% of the total resistance.

Other experimental results on wet film formation such as those for copper electrodes are given in Uebner.[10] Since the trends are similar for both cases, they are not reported here. It is, however, interesting to point out that, as expected, the wet film specific resistivity remains the same for aluminum and copper electrodes. The adsorbed layer resistance of copper is approximately half that of aluminum.

DISCUSSION

We carried out a systematic study to provide a more comprehensive and quantitative picture of electrodeposition from nonaqueous emulsions. Through a macroscopic model, the significance of electro-osmosis on wet film formation was established. It was shown that the major cause of current decay is due to the adsorbed layer resistance and the resistance of the wet deposit is secondary compared to that. Although every attempt was made to independently and accurately estimate all the system parameters, the wet film and adsorbed layer resistances were backed out from the deposition data. However, as can be seen in Figure 10, the increases of these resistances are reasonably smooth and their magnitudes remain low compared to the emulsion bath resistance. Future investigations of this process should focus on these parameters.

APPENDIX A: ANALYTIC SOLUTIONS TO EQS. (18) AND (24)

Let us first define the following quantities:

$$a = \frac{1}{6\pi} \frac{q_p V_p n_p}{\beta_0 \mu_0 a_p} \frac{r_b}{A} - \frac{\epsilon \zeta}{4\pi \mu_{wf} A} b_o$$

$$b = -\frac{\epsilon \zeta}{4\pi \mu_{wf} A} b_1, \qquad c = -\frac{\epsilon \zeta}{4\pi \mu_{wf} A} b_2$$

$$e = b_2, \qquad\qquad f = b_1 + c_2$$

$$g = b_o + c_1 - r_b, \qquad h = c_0 + r_b L$$

In terms of these symbols, we can rewrite the integral for eq. (18) as,

$$\int_0^\delta \frac{ex^3 + fx^2 + gx + h}{a + bx + cx^2} \, dx = \int_0^t A U \, dt' \tag{31}$$

We further define

$$Y = a + bx + cx^2$$

and
$$\Delta = 4ac - b^2$$

The general analytic solution to the definite integral of eq. (31) is

$$\left\{ \frac{b^2 e}{2c^3} - \frac{ae}{2c^2} - \frac{bf}{2c^2} + \frac{g}{2c} \right\} \ln\left| 1 + \frac{b}{a}\delta + \frac{c}{a}\delta^2 \right|$$

$$+ \left\{ h - \frac{b^3 e}{2c^3} + \frac{3abe}{2c^2} + \frac{b^2 f}{2c^2} - \frac{af}{c} - \frac{bg}{2c} \right\} \int_0^\delta \frac{dx}{Y}$$

$$+ \left\{ \frac{e}{2c} \right\}\delta^2 + \left\{ \frac{f}{c} - \frac{be}{c^2} \right\}\delta = \mathrm{AU}t \tag{32}$$

Depending on the value of Δ there are three cases for the remaining definite integral. For $\Delta > 0$,

$$\int_0^\delta \frac{dx}{Y} = \frac{2}{\sqrt{\Delta}} \left\{ \arctan\frac{b + 2c\delta}{\sqrt{\Delta}} + \arctan\frac{b}{\sqrt{\Delta}} \right\} \tag{33}$$

For $\Delta = 0$,

$$\int_0^\delta \frac{dx}{Y} = -\frac{2}{b + 2cx} + \frac{2}{b} \tag{34}$$

For $\Delta < 0$,

$$\int_0^\delta \frac{dx}{Y} = \frac{1}{\sqrt{-\Delta}} \left\{ \ln\left| \frac{2c\delta + b - \sqrt{-\Delta}}{2c\delta + b + \sqrt{-\Delta}} \right| - \ln\left| \frac{b - \sqrt{-\Delta}}{b + \sqrt{-\Delta}} \right| \right\} \tag{35}$$

In terms of the defined symbols, eq. (24) becomes

$$Q[\delta(t)] = \int_0^{\delta(t)} \frac{dx}{a + bx + cx^2} = \int_0^{\delta(t)} \frac{dx}{Y} \tag{36}$$

The solution for the definite integral is given in eqs. (33) to (35).

APPENDIX B: DETERMINATION OF n_p AND q_q

The number concentration of emulsion particles, n_p, can be estimated as the total mass of polyamic acid per unit volume of the emulsion m_{PAA} divided by the average mass of an emulsion particle. Thus we have

$$n_p = \frac{m_{\mathrm{PAA}}}{\gamma_{\mathrm{PAA}}\rho_p V_p} \tag{37}$$

The charge on a particle, q_p, is estimated as follows. According to the modified Faraday's law, eq. (29), we have

$$m_{\mathrm{PAA}} = \gamma_{\mathrm{PAA}}\rho_p A\delta\beta_p = (\eta m_e)_{\mathrm{PAA}}Q \tag{38}$$

Differentiating eq. (38) with respect to t, we get

$$A\frac{d}{dt}(\delta\beta_p) = \frac{(\eta m_e)_{\mathrm{PAA}}}{\gamma_{\mathrm{PAA}}\rho_p}i(t) \tag{39}$$

The L.H.S of eq. (39) is V_p [eq. (5)], which can be expressed through eqs. (4) and (15) as follows:

$$V_p = \frac{q_p V_p n_p}{6\pi\mu_b a_p} i(t) \tag{40}$$

Equating eqs. (39) and (40), we get

$$q_p = \frac{6\pi\mu_b a_p}{V_p n_p r_b} \frac{(\eta m_e)_{\text{PAA}}}{\gamma_{\text{PAA}}\rho_p} \tag{41}$$

Substitution of eq. (37) into (41) yields,

$$q_p = \frac{6\pi\mu_b a_p}{r_b m_{\text{PAA}}} \tag{42}$$

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