The Study of Diffusion of Media in the Organic Coating Films by BAW Admittance Analysis

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ABSTRACT: The permeation of water and corrosive species in coating films is very important for the corrosion protection by organic coatings. As a new method for the study of diffusion of media in coating films, bulk acoustic wave (BAW) admittance analysis has been proposed in this article. Real-time information on the change of the film mass, mechanic property of the layer, and the permeation process of the media can be provided simultaneously by the parameters of BAW admittance analysis, f_s (series resonant frequency), ΔL_1 (inductance variance), R_1 (resistance), Q (quality factor), and C_s (film capacitance). The diffusion behavior of media and the corresponding film stability can be described by the following parameters: D (diffusion coefficient), P (permeation coefficient), S (the solubility of media), and SC (the swelling coefficient of the coating layer). © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2283–2290, 1998

Key words: diffusion; swelling; coating; bulk acoustic wave; admittance analysis

INTRODUCTION

Modern coatings possess the following two important actions: decoration and corrosion inhibition. The metal-polymer composites may fail by delamination of the metal-polymer interface due to the environmental attack of corrosive species. Blistering is the major mode of failure of coatings. The main cause of blistering is the osmotic pressure due to surface contamination or as a result of high ionic strengths resulting from the corrosion reaction. Blistering can be prevented when a certain rate of transport is taken into account.¹ However, the corrosion protection of organic coatings consists mainly of resistance inhibition and introduction of a barrier for the transport of water and corrosive species. When the transport rate through the coating film becomes too high, the effective resistance inhibition action of the coating will be diminished and corrosion of the sub-

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strate can probably not be prevented. Therefore, for a development of coatings, it is necessary to optimize the permeability of the coating for water and corrosive species. It is also necessary to get information about the interaction between the coating polymer and species taken up by the coating. For normal applications, water is the major component that can cause film swelling, which can result in loss of adhesion, deterioration of the mechanical properties,² and the start of the corrosion process.

For the transport of water and other species through a coating, diffusion is the major process. Many methods have been developed to study the diffusion of water and other species in a coating. The investigation of the water and other species uptake can be carried out on free films and supported coatings. Most of these methods are based on the permeation of the species in a coating (stationary flow), but there are also possibilities to determine the sorption of the permeant in the (supported) coating (nonstationary flow), as follows:

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- 1. Permeation methods³⁻⁶;
- 2. sorption methods^{7,8};
- 3. water in dielectric⁹;
- 4. impedance measurements.^{10–14}

For these methods mentioned above, the operations were complex, and the information about the permeation process of media and the change of mechanical properties of a coating caused by swelling could not be provided. Additionally, thick coating films were usually used. The result was that the experimental period was long.

In order to study rapidly the diffusion of water and other species in a coating layer, electrochemical quartz crystal microbalance (EQCM) technique was introduced and used to evaluate the diffusion of media in a coating layer in recent years.¹⁵ However, for the permeation process of media in a coating film, the relationship between the frequency shift of EQCM and the loading mass on the quartz crystal electrodes cannot be expressed exactly by Sauerbrey's formulation in most cases. The effects of the viscoelastic and dielectrical properties of the coating film on the frequency shift must be considered.

As described in previous works,¹⁶⁻²⁰ BAW admittance analysis can provide not only mass change but also surface chemical and physical process on a quartz crystal oscillator electrode. For the evaluation of coating performance, this method is very simple, rapid, and versatile. The curing behavior of coating films and the diffusion of organic solvents from the coating films during the curing process have been investigated successfully in our previous work.²¹ In this work, the solution uptake of the phenolic varnish films has been investigated. Information about the diffusion of water and other aqueous solutions $(H_2SO_4,$ NaOH) in the coating film and the real-time change of mass and mechanical properties of the coating films during media uptake period can be obtained.

THEORETICAL BACKGROUND

BAW Admittance Analysis

The same electrical equivalent circuit, parameters, and the corresponding treatments were used as described in our previous work.²¹ The parameters of BAW admittance analysis, f_s (series resonant frequency), ΔL_1 (inductance variance), R_1 (resistance), Q (quality factor), and C_s (film capacitance) can be obtained and used to describe

the permeation process of media in the coating films.

The Diffusion of Aqueous Solutions in Coating Films

Ideal Diffusion

It is assumed that the transport of aqueous solution in a coating film is described as ideal, and the corresponding diffusion coefficient is constant. Thus, Fick's law of diffusion can be written as follows:

$$\frac{\partial \phi}{\partial t} = D \cdot \frac{\partial^2 \phi}{\partial X^2} \tag{1}$$

where *D* is the diffusion coefficient $(m^2 s^{-1})$; ϕ is the volume fraction of aqueous solution taken up by the coating and is equal to the ratio V_s/V ; and V_s and *V* are the volume of aqueous solution taken up by the coating film and apparent volume of the coating film, respectively.

With the boundary conditions,²² (1) $t = 0 \Rightarrow \phi$ = ϕ_0 , X = 0 (for an initially dry film, $\phi_0 = 0$); (2) $t > 0 \Rightarrow \phi = \phi_t$, $0 \le X \le L_f$; and (3) at diffusion equilibrium $\Rightarrow \phi = \phi_{\infty}$, $0 \le X \le L_f$, the following equation can be obtained.

$$\frac{\phi_t}{\phi_{\infty}} = 1 - \left(\frac{8}{\pi}\right)^2 \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left[-\frac{(2n+1)^2 \pi^2 Dt}{4L_f^2}\right] \quad (2)$$

where $n = 0, 1, 2, 3, 4, \ldots$; ϕ_t and ϕ_{∞} are the volume fractions of the aqueous solutions taken up by the coating film, respectively, at t and $t = \infty$; and L_f is the film thickness.

On the other hand, the introduction of aqueous solution in a coating film results in an increase of the polarizability, which is reflected in an increase of the permittivity of the polymer. The permittivity of the polymer film due to the medium uptake can be expressed by the following equation²³:

$$\varepsilon = \varepsilon_p^{Vp/V} \cdot \varepsilon_s^{Vs/V} \cdot \varepsilon_a^{Va/V} \tag{3}$$

and

$$V = V_p + V_s + V_a \tag{4}$$

where ε is the total relative permittivity; ε_p , ε_s , and ε_a are the relative permittivities of the dry coating film, aqueous solution, and air, respectively; V is the total volume (that is, V is the apparent volume of the coating film); and V_p , V_s , and V_a are the actual volume of the polymer film, aqueous solution, and air taken up by the coating film, respectively.

Due to $\varepsilon_a = 1$, eq. (3) can be rewritten as follows:

$$\varepsilon = \varepsilon_p^{Vp/V} \cdot \varepsilon_s^{Vs/V} \tag{5}$$

 ε_p can be considered as a constant with respect to time. With the assumption that swelling of the coating film can be neglected, the variations of V_p and V are very small and can be neglected. Thus, the following equation can be obtained:

$$\frac{\varepsilon(t)}{\varepsilon(0)} = \frac{\varepsilon_s^{V_s(t)/V}}{\varepsilon_s^{V_s(0)/V}} = \frac{\varepsilon_s^{\phi(t)}}{\varepsilon_s^{\phi(0)}} \tag{6}$$

In this article, ϕ_0 is equal to zero. Thus, eq. (6) can be rewritten as follows:

$$\frac{\varepsilon(t)}{\varepsilon(0)} = \varepsilon_s^{\phi(t)} \tag{7}$$

At $T = 20^{\circ}$ C, the relative permittivity of water is equal to 80. Thus, eq. (7) can be rewritten as follows:

$$\frac{\varepsilon(t)}{\varepsilon(0)} = 80^{\phi(t)} \tag{8}$$

The relation between permittivity of the coating film and the capacitance can be given by

$$C_s = \varepsilon \cdot \varepsilon_0 \cdot A/L_f \tag{9}$$

where C_s is the capacitance of polymer or paint film (in Farad), ε is the relative permittivity, and ε_0 is the permittivity of vacuum (8.854 $\times 10^{-12}$ F m⁻¹), A is the surface area of coating or polymer film (in m²), and L_f is the thickness of coating or polymer film (in m). With the assumption that L_f is a constant due to the variation of V of coating film can be neglected, the following equation can be obtained from eqs. (8) and (9):

$$\phi_t = \frac{\log \left[C_s(t) / C_s(0) \right]}{\log 80}$$
(10)

By combining eqs. (2) and (10), the following expression can be derived:

$$\frac{\log \left[C_{s}(t)/C_{s}(0)\right]}{\log \left[C_{s}(\infty)/C_{s}(0)\right]} = 1 - \left(\frac{8}{\pi}\right)^{2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^{2}} \times \exp \left[-\frac{(2n+1)^{2} \pi^{2} Dt}{4L_{f}^{2}}\right]$$
(11)

To enable the use of the Levenberg–Marquardt algorithm using only the first two exponential terms of the expansion, the formula is rewritten to

$$F = k_1 [1 - (8/\pi^2) \exp(-\pi^2 k_2 t) - (8/9\pi^2) \exp(-9\pi^2 k_2 t)] + k_3 \quad (12)$$

where k_1 , k_2 , and k_3 are the fitting parameters; $k_1 = \log[C_s(\infty)/C_s(0)]; k_2 = D/4L_f^2; k_3 = \log[C_s(0)]; t$ is the independent variable (exposure time, s); F is the dependent variable [log $C_s(t)$]; $C_s(0)$ is the capacitance at t = 0 (in farad); and $C_s(\infty)$ is the capacitance at $t = \infty$ (in farad).

The diffusion coefficient follows directly from the expression and the solubility can be calculated from the following equation:

$$S = \phi_{\infty} \cdot \rho = \frac{\log[C_s(\infty)/C_s(0)]}{\log 80} = \frac{k_1 \cdot \rho}{\log 80} \quad (13)$$

where ρ is the specific density of the aqueous solution (kg m⁻³). Finally, the permeation coefficient can be calculated as follows:

$$P = D \cdot S \tag{14}$$

Nonideal Diffusion

In an ideal diffusion, it is assumed that aqueous solution enters the polymeric material at a constant rate, and no swelling of the polymer occurs. However, aqueous solution that is taken up by the coating film is not as inert, and swelling of the polymer occurs usually. Therefore, eq. (11) must be corrected, and a term is added,¹¹ as follows:

$$F = k_1 [1 - (8/\pi^2) \exp(-\pi^2 k_2 t) - (8/9\pi^2) \exp(-9\pi^2 k_2 t)] + k_3 + k_4 \cdot t \quad (15)$$

where k_4 is the fourth fitting parameter and presents the swelling coefficient (SC, in s⁻¹).

Sample No.	1	2	3
Aqueous medium	0.1 <i>M</i> NaOH	$0.1M \operatorname{H}_2 \operatorname{SO}_4$	Water
Content of phenolic varnish ^a (% W/W)	2.97	2.97	2.19
Evaporation rate of solvent ^b	0.70	0.70	0.32
Frequency shift Δf_s^c (Hz)	-1579	-1040	-3417
Film mass Δm_f^d (µg cm ⁻²)	8.608	5.668	18.623
Film thickness L_f^e (nm)	88.7	58.4	192.0
Diffusion coefficient $10^{18} \cdot D \ (\text{m}^2 \ \text{s}^{-1})$	1.51	1.38	60.64
Permeation coefficient $10^{18} \cdot P (\text{kg m}^{-1} \text{ s}^{-1})$	23.68	3.73	226.19
Solubility S (kg m ^{-3})	15.68	2.70	3.73
Swelling coefficient $10^7 \cdot SC$ (s ⁻¹)	1.82	1.01	0.83
Goodness of fit r	0.998	0.988	0.996

Table I Aqueous Solution Uptake of Phenolic Varnish Coatings and Some BAW **Admittance Analysis Data**

^a Solvent: dimethylbenzene for samples 1 and 2; 200# gasoline for sample 3.

^a Solvent: dimethylbenzene for samples 1 and 2; 200# gasonine for sample 5. ^b The evaporation rate of the solvent is relative to *n*-butyl acetate = $1.^{25}$ ^c $\Delta f_s = f_s - f_s^0$, where f_s^0 is the resonant frequency measured for the BAW sensor without coatings. ^d The dry film mass, Δm_f , is calculated according to the following Sauerbrey equation²⁶: $\Delta m_f = -K \Delta f_s$, where *K* is the proportionality constant for the crystal. For 9 MHz piezoelectric quartz crystal, K = 5.45 ng cm⁻² Hz⁻¹. ^e The film thickness, L_f , is estimated according to the following equation: $L_f = \Delta m_f \rho_f$, where ρ_f is the density of the dry coating $\Gamma_{12} = (2007 - cm^{-3})^{21}$

film (0.97 g cm^{-3}) .²

Thus, from the capacitance data of the BAW admittance analysis, the parameters related to the diffusion of media in the coating films, the diffusion coefficient (D), the solubility (S), the permeation coefficient (P), and the swelling coefficient (SC), can be obtained.

where

$$\overline{q(t)} = \frac{1}{M} \sum_{t} q(t)$$

Levenberg-Marquardt Algorithm

A nonlinear least squares technique, the Levenberg-Marquardt method,²⁴ is used for the fourparameter estimation $(k_1, k_2, k_3, \text{ and } k_4)$ of eq. (15) in this article. The program searches for the best set of parameters that allows the minimization of

$$\Delta q \ (k_1, \, k_2, \, k_3, \, k_4) = \sum_{t} \left[q(t) - q(t, \, k_1, \, k_2, \, k_3, \, k_4) \right]^2 \quad (16)$$

where q(t) represents the measured capacitance of the coating film to be fitted at time t, and term $q(t, k_1, k_2, k_3, k_4)$ is the expectation capacitance at time t based on the eq. (15). In order to assess the adequacy of the computed results, the F-statistical test was used as criteria, according to the following formula:

$$r^{2} = \sum_{t} [q(t, k_{1}, k_{2}, k_{3}, k_{4}) - \overline{q(t)}]^{2} / \sum_{t} [\overline{q(t)} - q(t)]^{2} \quad (17)$$

where *M* is the number of measured capacitance. When $r \rightarrow 1$, then residual sum of squares $Q \rightarrow 0$; this shows that the nearer r tends to 1, the better the goodness of fit is. Hence, r is the goodness of fit.

In this article, the corresponding values of rare listed in Table I. From Table I, a good fitness can be observed.

EXPERIMENTAL DETAILS

For the experiments presented in this article, the same coatings, equipment, and experimental procedures were used as described in the previous works.²¹ The thickness of the dry coating films was estimated as described in the previous work²¹ and listed in Table I.

All chemicals used were chemical pure. Double-distilled water were used throughout.

RESULTS AND DISCUSSION

Electrolytic Solution Uptake Monitoring

0.1M NaOH Solution

The electrolytic solution uptake of a phenolic varnish coating film has been investigated in a 0.1M NaOH solution. The results of BAW admittance analysis are shown in Figure 1. When water enters the coating, the overall mass increases. This is reflected by an increase of ΔL_1 and a decrease of f_s in Figure 1(a). Additionally, the introduction of water (with high ε) results in an increase of the permittivity of the coating, which is reflected by an increase of the capacitance of the coating, C_s , in Figure 1(c).^{9,11} From Figure 1(b), no obvious change of R_1 and Q can be observed. This implies that the viscoelastic property of the coating film does not change obviously during the uptake process of NaOH solution, and the insert of NaOH solution in the coating film don't destroy the binds between the coating molecules.

When the exposure time is more than 100 min, a decrease of ΔL_1 and an increase of f_s can be observed in Figure 1(a). This implies the loading mass on the working electrode decreases and part of the coating film is denuded from the electrode and enters in the solution. This indicates the adhesion is lost. In another article, the loss of adhesion will be discussed extensively.

As mentioned above, the aqueous solution uptake in a coating film can be described as a diffusion process. Therefore, according to eq. (15), the solution uptake can be investigated, and the results are summarized in Table I.

0.1M H₂SO₄ Solution

Figure 2 shows the uptake process of the acidic solution $(0.1M \text{ H}_2\text{SO}_4)$ in a coating film. In Figure 2, the change behavior of ΔL_1 , f_s , R_1 , Q, and C_s is very similar to that in Figure 1, but there are some differences, as follows.

- 1. The change magnitude of ΔL_1 and f_s appears to be smaller than that in Figure 1(a). This implies the mass of the solution adsorbed in the coating film is smaller, compared with that in 0.1*M* NaOH solution.
- 2. A decrease of ΔL_1 and an increase of f_s cannot be observed in Figure 2(a). This implies no adhesion loss occurs during the experimental period.

The above two differences imply that the coating film in acidic medium is more stable than that in alkaline solution. This is in good agreement with that quoted in previous works.²⁷

A same treatment for the diffusion of H_2SO_4 solution in the coating film was carried out, and the results are also summarized in Table I. The



Figure 1 The parameters of the BAW admittance analysis, f_s , [(a) left axis], ΔL_1 [(a) right axis], R_1 [(b) left axis], Q [(b) right axis], and C_s [(c) point, experimental data; line, fit result] as function of time during the uptake of 0.1*M* NaOH solution in an 88.7-nm coating film.



Figure 2 The parameters of the BAW admittance analysis f_s [(a) left axis], ΔL_1 [(a) right axis], R_1 [(b) left axis], Q [(b) right axis], and C_s [(c) point, experimental data; line, fit result] as function of time during the uptake of $0.1M \text{ H}_2\text{SO}_4$ solution in a 58.4-nm coating film.

further difference of the uptake of the electrolyte solutions with different pH values will be given below.

Nonelectrolytic Solution Uptake Monitoring (Double-Distilled Water)

The water uptake in a coating film has also been investigated by BAW admittance analysis, and the results are shown in Figure 3. From Figure 3, the change behavior of f_s and ΔL_1 is similar to that in Figure 1(a), except that adhesion loss, which is reflected by a decrease of ΔL_1 and an increase of f_s , does not occur. However, the curves of R_1 -t, Q-t, and C_s -t in Figure 3 are much different with that in electrolyte solutions (Figs. 1 and 2), as follows.

- 1. An obvious change of viscoelastic property of the coating film can be observed during the water entering process. This change can be reflected by a continuous increase of R_1 and a continuous decrease of Q in Figure 3(b). The reason for this change is the using of the solvent with a low evaporation rate (200# gasoline), which results in the fact that the curing of the coating film is not complete.²¹ That aqueous solution enters in the coating film makes the mobility of the unreacted paint molecules increase. This results in that the lost of energy increases, which is reflected by an increase of R_1 and a decrease of Q.
- 2. A decrease of C_s , which cannot be found in electrolyte solutions, can be observed in Figure 3(c). The uptake of water in the coating film causes an increase in the relative permittivity ε (relative dielectric constant) of the material. This results in an increase of the coating capacitance,^{9,11} which can be reflected by the increase of C_s . On the other hand, the uptake of water can cause the adhesion loss. This will yield an opposite effect, resulting in a decrease of the coating capacitance. With the exposure time increasing, the later effect is important, and a decrease of C_s can be observed. An extensive discussion about the lost of adhesion will be given in another article.

A similar treatment for the diffusion of water in the coating film was also carried out, and the results are also listed in Table I.

Comparison in Different Aqueous Solutions

From Table I, the order of parameters, diffusion coefficient (D), permeation coefficient (P), solu-



Figure 3 The parameters of the BAW admittance analysis f_s [(a) left axis], ΔL_1 [(a) right axis], R_1 [(b) left axis], Q [(b) right axis], and C_s [(c) point, experimental data; line, fit result] as function of time during the uptake of water in a 192.0-nm coating film.

bility (S), and swelling coefficient (SC), in different aqueous solutions are as follows.

$$D_{\rm H_{2}O} > D_{\rm NaOH} \ge D_{\rm H_{2}SO_{4}}$$
 (18)

$$P_{\rm H_{2}O} > P_{\rm NaOH} > P_{\rm H_{2}SO_{4}}$$
 (19)

$$S_{\rm NaOH} > S_{\rm H_{2}0} \ge S_{\rm H_{2}SO_{4}}$$
 (20)

$$SC_{\rm NaOH} > SC_{\rm H_2SO_4} > SC_{\rm H_2O}$$
 (21)

It is well known that the value of the diffusion coefficient D depends on the size of the transporting species, molecule and ion, and the porosity of the material. The using of the solvent with low evaporation rate (200# gasoline, in Sample 3) results in an increase of the porosity of the material.²¹ On the other hand, the water molecule is smaller than the hydrated Na⁺ and SO₄^{2-.28} Thus, the above order of the diffusion coefficients can be observed.

From the order of S and SC mentioned above, it can be obtained that phenolic varnish has a different stability in the aqueous solutions with different pH values. And the order of the stability of the coating film in different aqueous solution is as follows: alkaline solution < acidic solution < water.

This is in good agreement with that quoted in the previous work.²⁷

On the other hand, some differences can be observed in electrolytic and nonelectrolytic solutions. In nonelectrolytic solution, a decrease of C_s , which cannot be found in electrolytic solution, can be observed, and the adhesion loss starts at the turning point. A extensive explanation on the C_s-t curves in electrolytic and nonelectrolytic solutions will be given in another article.

From eqs. (18)–(21) and the curves of C_s –t, the following results can also be obtained: a low permeability of aqueous solution gives no guarantee for an optimal anticorrosion performance and a good adhesion, as this is likely to cause blistering when osmotic pressures occurs due to surface contamination.^{1,11}

Some Advantages of the BAW Admittance Analysis Method

The BAW admittance analysis method is based on the shift of the series resonant frequency of the BAW sensor to determine the film mass and estimate the thickness of the dry coating layer. As the BAW device is a mass sensor with very high sensitivity, a very thin coating film can be prepared. As described in Table I, the thickness of the coating film used in this article is 10^{-8} – 10^{-7} m. Compared with that in other methods $(10^{-6}-10^{-3} \text{ m}),^{11,15,29}$ this film is very thin. Therefore, in the evaluation of aqueous solution uptake of coating film by this method, the experimental period is about 2-2.5 h and is much shorter than that by other methods $(\geq 10 \text{ h})$. On the other hand, the multiple information about the real-time change behavior of the mechanical properties and film mass of the coating during the aqueous solution uptake process, and some parameters related to the aqueous solution diffusion in the coating film can be provided simultaneously. Compared with other methods, this method is very simple, rapid, and applicable.

CONCLUSIONS

Bulk acoustic wave admittance analysis as a new method for the study of diffusion of aqueous solutions in coating films has been proposed in this article. This method is very simple, rapid, and applicable. The aqueous solution uptake in the coating films and the corresponding variation of the film properties can be described by the parameters of the BAW admittance analysis, series resonant frequency (f_s), inductance variance (ΔL_1), resistance (R_1), quality factor (Q), and film capacitance (C_s). The diffusion of the media and the film stability can be represented by the parameters, diffusion coefficient (D), permeation coefficient (P), solubility (S), and swelling coefficient (SC).

For a phenolic varnish film immersed in a aqueous solution, the stability of the coating film varies with the pH values of the solutions. The order of the film stability is as follows: NaOH $< H_2SO_4 < H_2O$. This is in good agreement with that quoted in previous works.

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