

The Study of Diffusion of Solvents from the Coating Films During the Curing Process by Bulk Acoustic Wave Admittance Analysis

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ABSTRACT: The diffusion of solvents from a coating layer and their evaporation at the surface of the coating film during the curing process of the coating are investigated by bulk acoustic wave (BAW) admittance analysis and can be expressed as change in the relative diffusion rate (J). The porosity and permeability of the coating film are related to the curing degree (η). The changes in J and the values of J_s (the relative diffusion rate at the surface dry time, t_s), Δt_p (the time difference between the surface dry time t_s and the turning point time t_p when the diffusion behaviour changes), and η can provide much useful information on selecting solvents and optimizing coating ingredients in the preparation of coatings. The effects of the coating film thickness, solvent content of the coating liquid, and the volatility of the solvent on the diffusion of solvent from the film are also discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 563–571, 1997

Key words: coating; bulk acoustic wave; admittance analysis; solvent diffusion; curing

INTRODUCTION

Organic coatings have been used for many years in the protection of metal structures against corrosion. Metal–polymer composites are of increasing importance for many areas of modern technology. Unfortunately, these composite materials may fail by delamination of the metal–polymer interface, owing to the environmental attack of corrosive species.^{1–4} Generally, coatings act like a barrier for the corrosive species from the environment and provide a high resistance between the sites of the cathodic and anodic reactions of the corrosion. The barrier properties of the coatings depend on their curing behavior and are determined by the rate of transport of water and ions

through their polymer matrix. The curing process of the coating can be divided into two stages: the film formation stage, in which the formation of a polymer network depends on the volatility of the solvent, and the curing stage, in which the curing degree of the dry film depends on the diffusion rate of the solvent through the film. In general, the volatility of solvents is expressed by their evaporation rates in the air. However, for the curing process of the coatings, the diffusion of solvents to the surface of the coating film is more important. For efficient development of new coatings it is necessary to study the curing behavior of the coatings and the transport rate of solvents in the coating polymer during the curing process.

Quartz crystal microbalance (QCM) is a kind of bulk acoustic wave (BAW) device. BAW admittance analysis is used widely^{5–9} and is commonly accomplished with impedance analyzers such as the Hewlett–Packard 4192 analyzer or the more

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sophisticated 4194A model. These instruments are capable of measuring impedance (Z), phase angle (θ), admittance (Y), conductance (G), and susceptance (B), as well as other parameters. The equivalent circuit components of the QCM (C_p , R_1 , L_1 , and C_1) can be calculated according to the corresponding relations (see Theoretical Background section), and much information about a coating can be obtained.

Detailed information about the curing process and the curing mechanism of the coatings has been described previously.⁹ This article is aimed at studying the diffusion behavior of the solvents in the coating polymer film during the curing process.

THEORETICAL BACKGROUND

BAW admittance analysis is an important method for studying the interface process. It can provide information not only about mass changes but also chemical and physical processes on a quartz crystal oscillator electrode, as demonstrated by many investigators.^{5,10–13} In general, the characteristics of the piezoelectric quartz crystal (PQC) oscillator can be represented by an electrical equivalent circuit, as shown in Figure 1(a). The parallel capacitance C_p originates from the capacitance between the electrodes and the stray capacitance to the supporting structure. The inductance L_1 corresponds to the inertial component of the oscillator, which is related to the vibrating mass. The capacitance C_1 corresponds to the mechanical elasticity of the crystal and surrounding medium. The resistance R_1 corresponds to the loss in mechanical energy dissipated to the surrounding medium and the supporting structures. A schematic depiction of conductance and susceptance spectra from which the circuit parameters can be evaluated is shown in Figure 1(b), where the frequency span covers the complete resonant region.

For the equivalent circuit shown in Figure 1(a), the admittance Y (the reciprocal of impedance Z) of the quartz crystal is complex: $Y = G + jB$, where the conductance, G , is the real part of Y and the susceptance, B , is the imaginary part of Y , and the following relations can be obtained:⁶

$$G = \frac{R_1}{R_1^2 + [\omega L_1 - 1/(\omega C_1)]^2} \quad (1)$$

and

$$B = \frac{-[\omega L_1 - 1/(\omega C_1)]}{R_1^2 + [\omega L_1 - 1/(\omega C_1)]^2} + \omega C_p \quad (2)$$

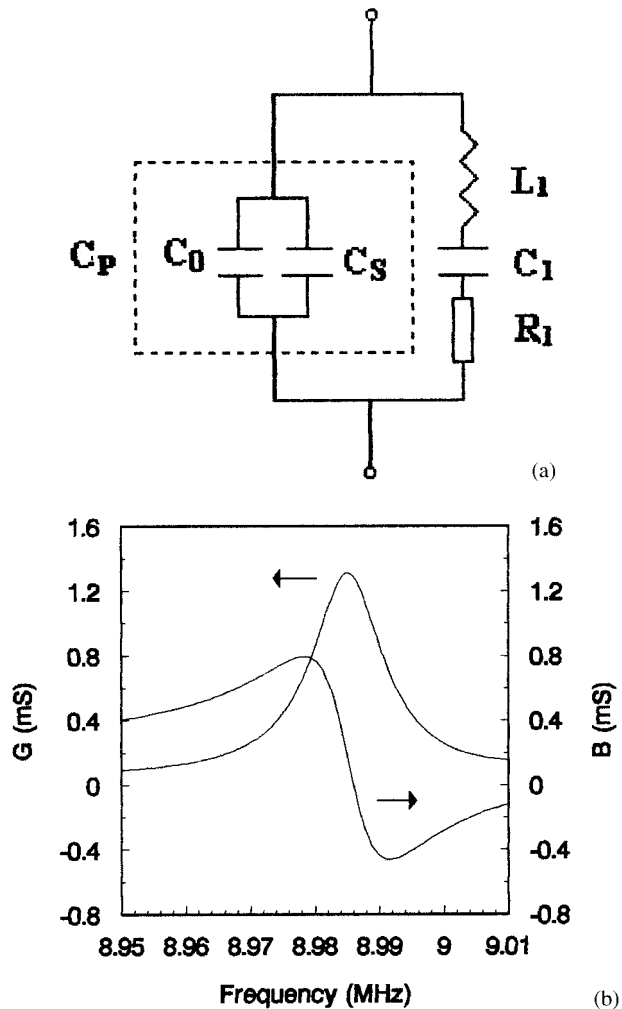


Figure 1 (a) Electrical equivalent circuit for a piezoelectric quartz crystal oscillator. (b) A schematic depiction of conductance and susceptance spectra.

The quantity, ω , is the angular frequency (in rad s^{-1}) and is defined by $\omega = 2\pi f$, where f is the frequency in Hz. From the measured data of G and B , four parameters (L_1 , R_1 , C_1 , and C_p) can be calculated simultaneously.

Since L_1 and C_1 are complementary, the fitting of admittance data with the above equation is not always a simple matter. Noël et al. found L_1 and C_1 varied greatly in opposite directions with time, but the resonant frequency f_0 , $f_0 = [2\pi(L_1 C_1)^{1/2}]^{-1}$, was quite stable.¹⁴ The variation of L_1 was so large that the real signal of L_1 could not be distinguished. Therefore, on the assumption that C_1 is a constant, the L_1 obtained from experiment is corrected (L'_1):

$$L'_1 = L_1(C_1/C_{\text{ref}}) \quad (3)$$

where C_{ref} is taken as the average of C_1 measured.

To express clearly the change of L'_1 , ΔL_1 is used in this article.

$$\Delta L_1 = L'_{1,t} - L'_{1,0} \quad (4)$$

where $L'_{1,t}$ and $L'_{1,0}$ are the values of L'_1 at time t and the beginning of the test, $t = 0$, respectively.

The curing behavior of the coating can be characterized by the multiple information (ΔL_1 , R_1 , C_s , f_s and Q), where f_s is the series resonant frequency, Q corresponds to the sharpness of the resonance and relates to L_1 and R_1 , and C_s is the capacitance of the coating film and solvents. The relation of Q , f_s , C_s and L_1 , C_1 , R_1 , C_p can be expressed as follows:^{6,14,15}

$$f_s = f_0[1 + C_p/(2C_1Q^2)] \quad (5)$$

$$Q = 2\pi f_0 L_1/R_1 \quad (6)$$

$$C_s = C_p - C_0 \quad (7)$$

where f_0 is the resonant frequency and is equal to $[2\pi(L_1C_1)^{1/2}]^{-1}$ and C_0 is the static capacitance of the PQC without any coatings.

During the curing process of the coatings, the decrease in C_s is caused by the following factors:⁹ (1) the evaporation of solvents and (2) the decrease in the number of polarizable groups owing to the curing reaction. When the curing time of the coating is larger than the surface dry time, t_s (see Results and Discussion section), the diffusion of solvents to, and evaporation at, the surface of the film are the dominant factors resulting in the decrease in C_s . Therefore, the diffusion behavior of the solvents can be investigated by the data of C_s (in $t \geq t_s$).

The permittivity of the polymer film caused by the diffusion of solvent in medium can be expressed by the following equations:¹⁶

$$\varepsilon = \varepsilon_p^{V_p/V} \varepsilon_1^{V_1/V} \varepsilon_a^{V_a/V} \quad (8)$$

and

$$V = V_p + V_1 + V_a \quad (9)$$

where ε is the experimental data of the permittivity and ε_p , ε_1 , and ε_a are the permittivities of the dry coating film, solvents, and air, respectively. V is the total volume (i.e., V is the apparent volume of the coating film) and V_p , V_1 and V_a are the actual volumes of the polymer film, solvents, and air, respectively.

Since $\varepsilon_a = 1$, eq. (8) can be rewritten:

$$\varepsilon = \varepsilon_p^{V_p/V} \varepsilon_1^{V_1/V} \quad (10)$$

ε_p can be considered to be constant with respect to time. During the curing process of the coating film, the variations in V_p and V are very small and can be considered as constants. Thus, the following equation can be obtained:

$$\frac{\varepsilon(\Delta t)}{\varepsilon(\infty)} = \frac{\varepsilon_1^{V_1(\Delta t)/V}}{\varepsilon_1^{V_1(\infty)/V}} \quad (11)$$

where $V_1(\Delta t)/V$ is the content of solvent at time Δt ($\Delta t = t - t_s$) and $V_1(\infty)/V$ is the solvent content in actual dry polymer film and is equal to zero. Thus, eq. (11) can be rewritten as follows:

$$\frac{\varepsilon(\Delta t)}{\varepsilon(\infty)} = \varepsilon_1^{V_1(\Delta t)/V} \quad (12)$$

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

$$C_s = \varepsilon A/L_f \quad (13)$$

where C_s is the capacitance of polymer or paint film (in farads), A is the surface area of coating or polymer film (in m^2), and L_f is the thickness of coating or polymer film (in m). With the assumption that L_f is a constant, since the variation of V of coating film can be neglected, the following equation can be obtained from eqs. (12) and (13):

$$\frac{\varepsilon(\Delta t)}{\varepsilon(\infty)} = \varepsilon_1^{V_1(\Delta t)/V} = \frac{C_s(\Delta t)}{C_s(\infty)} \quad (14)$$

Eq. (14) can be rewritten as follows:

$$\frac{V_1(\Delta t)}{V} \log \varepsilon_1 = \log \frac{C_s(\Delta t)}{C_s(\infty)} \quad (15)$$

Since $W_1 = \rho_1 V_1$,

$$\frac{\log \varepsilon_1}{V \cdot \rho_1} W_1(\Delta t) = \log \frac{C_s(\Delta t)}{C_s(\infty)} \quad (16)$$

where ρ_1 is the density of solvents and $W_1(\Delta t)$ is the mass of solvents in polymer. Therefore,

$$W_1(\Delta t) = \frac{V \cdot \rho_1}{\log \varepsilon_1} \log \frac{C_s(\Delta t)}{C_s(\infty)} \quad (17)$$

and

$$W_1(t_s) = \frac{V \cdot \rho_1}{\log \varepsilon_1} \log \frac{C_s(t_s)}{C_s(\infty)} \quad (18)$$

where $W_1(\Delta t)$ and $W_1(t_s)$ are the mass of solvents in polymer at time Δt and at $t = t_s$, respectively.

From eqs. (17) and (18), the following equation can be obtained:

$$\frac{W_1(\Delta t)}{W_1(t_s)} = \frac{\log C_s(\Delta t) - \log C_s(\infty)}{\log C_s(t_s) - \log C_s(\infty)} \quad (19)$$

Differentiating eq. (19) with respect to the curing time, Δt , yields an equation of the following form:

$$\begin{aligned} \frac{1}{W_1(t_s)} \frac{\partial W_1(\Delta t)}{\partial(\Delta t)} \\ = \frac{1}{\log C_s(t_s) - \log C_s(\infty)} \frac{\partial \log C_s(\Delta t)}{\partial(\Delta t)} \end{aligned} \quad (20)$$

The derivative $[\partial W_1(\Delta t)/\partial(\Delta t)]$ can be considered as the diffusion rate of solvent from the polymer layer to its surface. We define

$$J(\Delta t) = \frac{1}{W_1(t_s)} \frac{\partial W_1(\Delta t)}{\partial(\Delta t)} \quad (21)$$

$J(\Delta t)$ is the relative diffusion rate of solvent (i.e., the diffusion rate divided by the weight of solvent at the surface dry time) and depends on the porosity and permeability of the polymer layer. The negative sign implies solvent leaving the coating film and a decreasing of the solvent content. $J(\Delta t)$ is better suited to express the behavior of solvents in polymer during the curing process than the evaporation rate of solvents in air.

From eqs. (20) and (21), $J(\Delta t)$ can be expressed as follows:

$$\begin{aligned} J(\Delta t) \\ = \frac{1}{\log C_s(t_s) - \log C_s(\infty)} \frac{\partial \log C_s(\Delta t)}{\partial(\Delta t)} \end{aligned} \quad (22)$$

$$J(t) = -\frac{1}{\log C_s(t_s) - \log C_s(\infty)} \frac{\partial \log C_s(t)}{\partial t} \quad (23)$$

EXPERIMENTAL

Materials

The piezoelectric quartz crystals used were 9-MHz AT-cut crystals (12.5-mm diameter) having silver electrodes (6-mm diameter) on each side (JA-5 model; Peking Factory No. 707). One of the electrodes of the crystal was used as the working electrode. The geometrical surface area of the working electrode was 0.28 cm².

The specification of F01-1 phenolic varnish was in accordance with the standards of ZBG51018-87. The polymer material was abietyl-modified phenolic resin. A 200# gasoline was used as the original solvent, and the solid content of the coating liquid was 50%. The following solvents were used as diluents in this work: 200# gasoline (GB444-64) and dimethylbenzene. All chemicals used were pure.

Apparatus and Procedures

The admittance measurements of the PQC oscillator systems were performed by using a 4192A-LF impedance analyzer, which was connected through an HP-IB interface (Hewlett-Packard) to an IBM-compatible 486DX88 computer. The admittance data were transferred to the personal computer on which calculations were carried out and then graphically presented in the form of G versus frequency (conductance spectra) and B versus frequency (susceptance spectra). The parameters R_1 , ΔL_1 , C_p , F_s , and Q could then be calculated.

To study the diffusion behavior of solvents on the surface of the coating films, we investigated the $C_s \sim t$ curves after surface dry time, t_s ($t \geq t_s$); then, the relative diffusion rate of solvents were determined from C_s data according to eq. (23). Factors such as coating film thickness, solvent content, and the volatility of solvent are discussed.

Phenolic varnish was diluted by a solvent. The PQC oscillator was connected to the impedance analyzer, and the admittance of the PQC oscillator without any coating film was measured. The prepared coating liquid was then coated on one of the electrodes of the PQC oscillator. At the same time, the data of the BAW admittance analysis

were monitored. All the admittance measurements were carried out at laboratory temperature ($27 \pm 1^\circ\text{C}$).

Estimation of the Density of the Dry Coating Film

A certain amount of phenolic varnish was diluted by dimethylbenzene and then coated on one surface of aluminum foil with dimensions of $0.0075 \times 2.0 \times 2.0$ cm. The mass of the aluminum foil was 0.0778 g. After the coating film was dry, the total mass and the thickness of the aluminum foil with coating film were measured and were found to be 0.093 g and 0.114 mm, respectively. Therefore, the density of the dry phenolic varnish film (ρ_f) could be calculated and was found to be 0.97 g cm^{-3} .

RESULTS AND DISCUSSION

Monitoring of the Curing Behavior of Coatings

The typical behavior of the curing of a coating (coating thickness is 166.814 nm) obtained from the BAW admittance analysis is plotted in Figure 2. From Figure 2, multiple data about the curing process, such as surface dry time (t_s), mass change, solvent evaporation, solvent diffusion to the surface of the coating film, and state change of the coating can be derived.

The progressive curing of the coating and the evaporation of the solvents from the coating are reflected in the BAW admittance analysis parameters: f_s , ΔL_1 , R_1 , C_s , and Q . The curing process can be divided into the following four stages:

1. During the first stage of the curing ($t \leq 4$ min), the evaporation of the solvents results in an increase of viscosity of the coating liquid and the loss of energy of BAW, which is manifested by an increase of R_1 . The maximum of R_1 implies the coating state is changed from liquid to paste. On the other hand, with the evaporation of solvents from the varnish, the network is formed at specific places and clusters—nodules are formed on the electrode surface of BAW, which are reflected in the increase of ΔL_1 and the decrease of f_s .
2. In the second stage of the curing ($4 \text{ min} \leq t \leq 10 \text{ min}$), the coating on the electrode of the BAW is being changed from paste to a complete film with elastic property. This

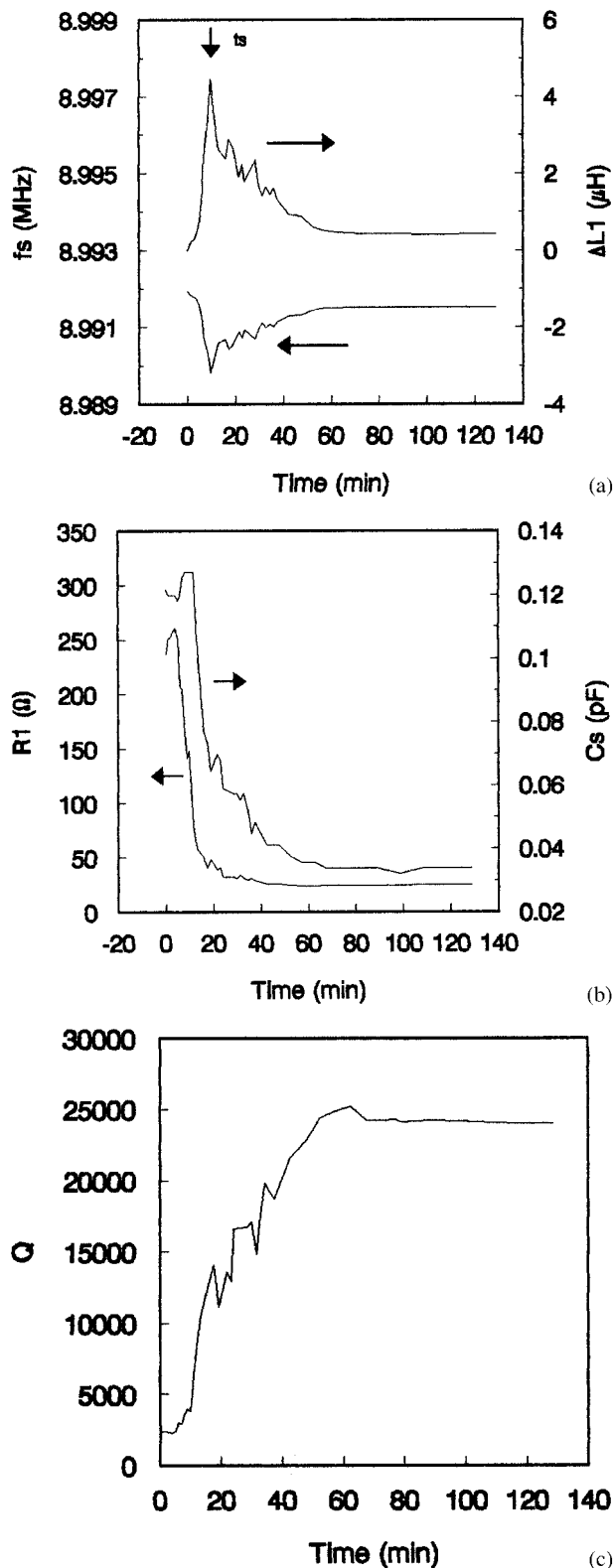


Figure 2 The parameters of the BAW admittance analysis: (a) f_s (left axis), ΔL_1 (right axis); (b) R_1 (left axis), C_s (right axis); and (c) Q as a function of time during the curing period of a 166.814-nm coating (Sample 3).

results in a sharp decrease in the curve of R_1 , an increase of ΔL_1 , and a decrease in the curve of f_s . When the curing time is equal to 10 min, a minimum of f_s and a maximum of ΔL_1 exist. We can conclude that an elastic coating film has formed, and this time can be defined as surface dry time (t_s).

3. In the third stage of the curing ($10 \text{ min} \leq t \leq 65 \text{ min}$), the solvents evaporate from the coating film, and drying of coating film continues. This results in a decrease of mass of coating film, which is reflected in an increase of f_s and a decrease of ΔL_1 . C_s decreases continuously owing to the evaporation of solvents (with high ε), as mentioned in previous work.⁹
4. In the fourth stage of the curing ($t \geq 65 \text{ min}$), a stationary situation is reached, and the coating film is actually dry. The parameters of BAW admittance analysis (f_s , ΔL_1 , R_1 , C_s , and Q) do not change any more.

In these four stages of the curing mentioned above, the overall effects of R_1 and L_1 are represented by Q and shown in Figure 2(c).

The Diffusion Behavior of Solvents

The regressed equation of a group of typical experimental data ($t \geq t_s$) was subjected to eq. (23) and a plot of $J \sim \Delta t$ was obtained as shown in Figure 3, which represents the typical behavior of the diffusion of solvents on the surface of a coating film (coating film thickness is 166.814 nm). The diffusion rate, J , varies with curing time. At the beginning ($t - t_s = 0$), a maximum of J , J_s (the relative diffusion rate at the surface dry time, t_s), exists due to the low curing degree of the coating film. With increasing curing time ($t > t_s$), the curing degree of the coating film increases, and the diffusion of solvents to the surface of the coating film becomes more difficult. Therefore, the diffusion rate, J , decreases with time (t). This also implies that the curing process begins at the outer layer of the polymer and then extends to the inner layer. From Figure 3, the change of J can be divided into two cases (t_p is the turning point time): when $\Delta t \leq \Delta t_p$ ($\Delta t_p = t_p - t_s$), J falls suddenly because of the obvious change of the curing degree of the coating film; when $\Delta t > \Delta t_p$, J decreases slowly. This implies that the curing process of the coating film is almost complete, and the curing degree of the coating film does not change consid-

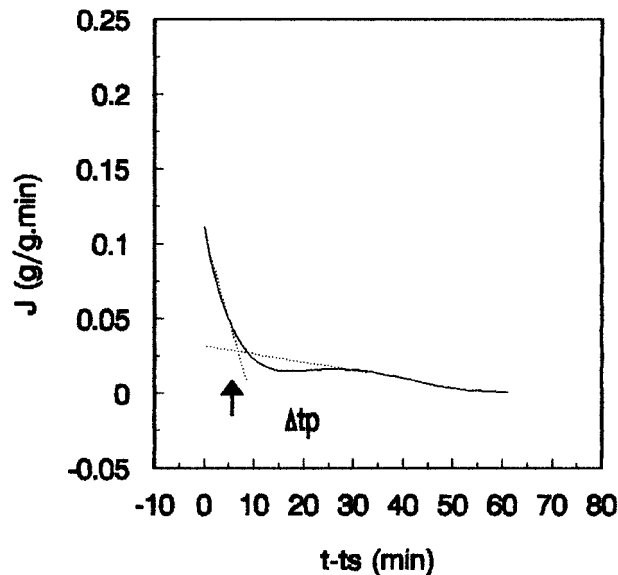


Figure 3 Typical diffusion behavior of solvents during the curing period of a 166.814-nm coating layer (Sample 3); (—) calculated from C_s in Figure 2(b) ($t \geq t_s$); (----) linear fit of the $J \sim t$ curve.

erably. The dominant process is the solvent diffusion to, and evaporation at, the surface of the coating film. With the curing degree of coating film increasing, the porosity and permeability of the coating film decrease, and the diffusion of solvents to the surface of the coating film becomes more difficult. To express clearly the porosity and permeability of a coating film, a parameter, η , is introduced.

$$\eta = \frac{J_s - J_p}{J_s} \quad (24)$$

where J_p is the diffusion rate of solvents at the turning point time, t_p and η is the relative drop in the relative diffusion rate in the $t_s \sim t_p$ time interval and can be referred to as the curing degree. The larger the value of η , the higher the curing degree. The value of η is from 0 to 1. When the porosity and permeability of the coating film decrease, η increases. Therefore, the curing behavior of a coating and the quality of the coating film can be described by J_s , Δt_p , and η . The corresponding data of the coating film with 166.814-nm thickness are listed in Table I. On the other hand, according to the data of J_s , Δt_p , and η , and the dependence of J on time, one can select and optimize the solvents and the ingredients of paint liquid in preparing new coatings with good properties.

Table I The Diffusion Behavior of Solvents from the Coating Films with Different Conditions and the Corresponding BAW Admittance Analysis Data

Sample No.	w/w ^a (%)	v^b	Δf_s^c (Hz)	Δm_f^d ($\mu\text{g cm}^{-2}$)	L_f^e (nm)	$J_s \times 10^{3f}$ (g/g min)	Δt_p^g (min)	$J_p \times 10^{3h}$ (g/g min)	η (%)	$10^{-4} \times Q_s^i$
1	1.35	0.70	-140	0.763	7.866	202.8	4.73	7.89	96.0	1.36
2	1.35	0.70	-1096	5.973	61.577	191.0	6.32	11.37	94.0	1.60
3	5.09	0.70	-2969	16.181	166.814	110.8	6.67	29.95	73.0	2.40
4	2.58	0.70	-3178	17.320	178.557	157.3	6.00	8.64	94.5	2.52
5	2.19	0.32	-3417	18.623	191.990	54.4	15.16	5.89	89.2	2.43

^a W/W is the content of phenolic varnish in percent. The following solvents are used: dimethylbenzene for samples 1, 2, 3, and 4; 200# gasoline for sample 5.

^b The evaporation rate of the solvent, v is relative to n -butyl acetate = 1.¹⁹

^c $\Delta f_s = f_s - f_s^0$; f_s^0 is the resonant frequency measured for the PQC oscillator without coatings.

^d The dry film mass estimated according to the Sauerbrey equation¹⁷; $\Delta m_f = -K \Delta f_s$; K is the proportionality constant for the crystal. For 9 MHz PQC, $K = 5.45 \text{ ng cm}^{-2} \text{ Hz}^{-1}$.

^e The thickness of the coating film estimated according to the following equation: $L_f = \Delta m_f / \rho_f$; where, ρ_f is the density of the dry coating film (= 0.97 g cm^{-3} ; See Experimental section).

^f The diffusion rate of solvents at time $t = t_s$ (surface dry time).

^g $\Delta t_p = t_p - t_s$, t_p is the time at which the diffusion behavior of solvents changes.

^h The diffusion rate of solvents at time $t = t_p$ (at turning point).

ⁱ The quality factor of PQC at steady state.

Factors Influencing the Diffusion of Solvents

In order to study their influence on the diffusion of solvents, some factors, such as coating film thickness and the contents and volatility of solvents have been investigated. The $J \sim \Delta t$ curves are shown in Figure 4. These curves show similar features to that of the 166.814-nm coating film (Fig. 3). The corresponding data of J_s , Δt_p , and η are summarized in Table I. From Table I, the dependence of J_s , Δt_p , and η on these factors can be observed.

1. J_s : The volatility of solvent is the dominant factor for J_s . When the evaporation rate of the solvent decreases, J_s clearly decreases (see Sample 5). On the other hand, the thickness of the coating layer and the solvent content of the coating liquid also have a definite effect on the diffusion behavior of solvents in the polymer film. J_s decreases slightly with the thickness of the coating film increasing and increases slightly with the solvent content increasing (see Samples 1, 2, 3, and 4).
2. Δt_p : The value of Δt_p in Table I corresponds to the solvent type. For Samples 1, 2, 3, and 4, the same solvent, dimethylbenzene, was used, and the data of Δt_p are very similar to each other, although the thickness of the coating films are very different. When the solvent has a lower evap-

oration rate, the value of Δt_p is larger (see Sample 5). Additionally, for a very thin film, Δt_p decreases slightly with the drop in the thickness of the coating film (see Samples 1 and 2). From Table I, an interesting phenomenon can also be observed, for Δt_p is independent of the solvent content.

3. η : As mentioned above, η corresponds to the porosity and permeation property of the coating film. Therefore, during the preparation of coating liquid and coating film, η is an important parameter. For the data of η , the content and volatility of solvent in the coating liquid are the dominant factors. η decreases with the decrease of solvent content (see Samples 3 and 4) and the decrease of the evaporation rate of solvent (see Samples 4 and 5). This implies that the porosity and permeability of the coating film increase with the decrease of solvent content and the decrease of the evaporation rate of the solvent. In other words, increasing the solvent content and using the solvent with high volatility benefit the complete curing of the coatings¹⁸ and the preparation of the coating film with lower porosity and permeation. On the other hand, η can be affected slightly by the thickness of the coating film. With the thickness of the coating film increasing, η falls slightly. This can be observed

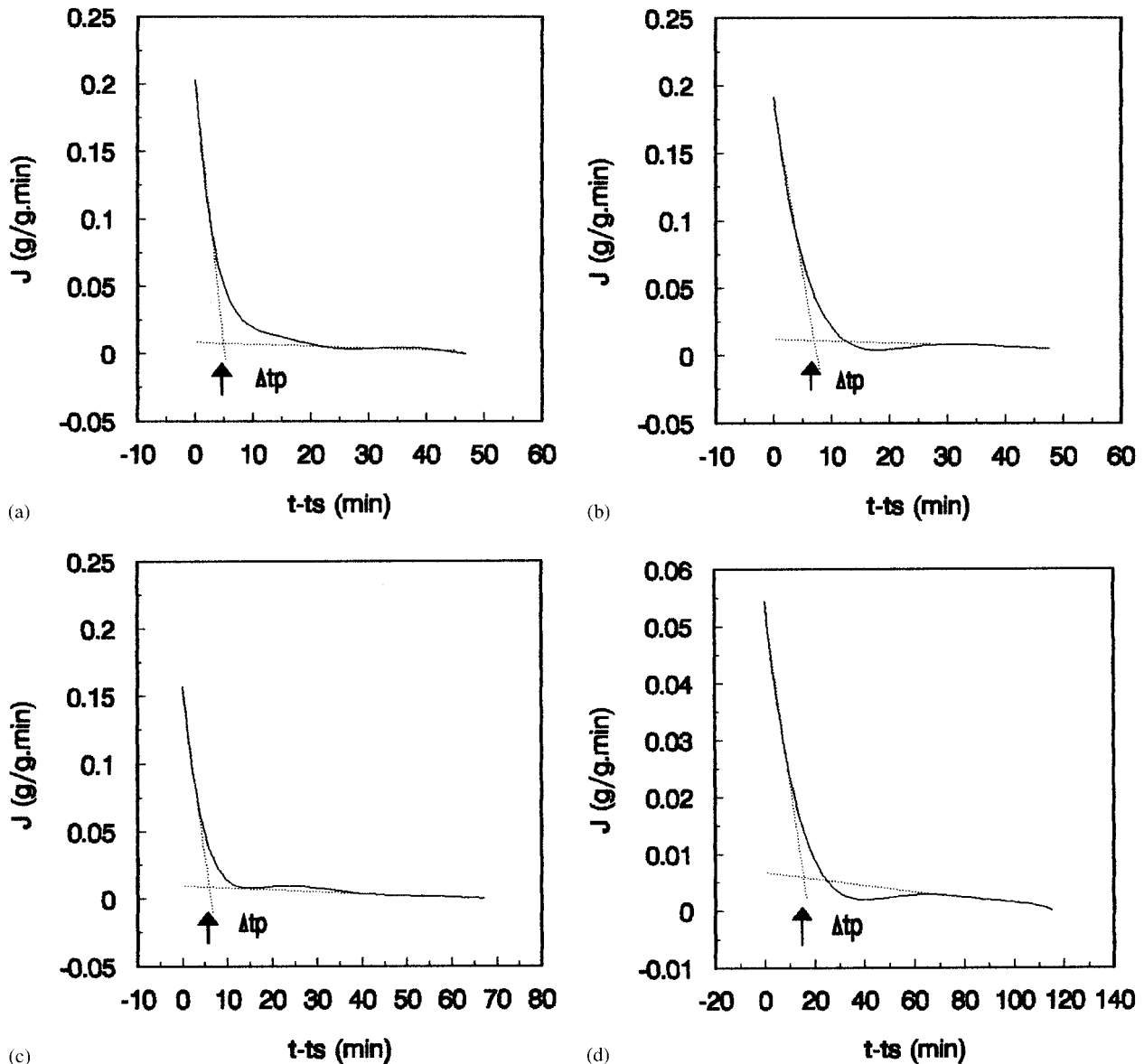


Figure 4 The diffusion behavior of solvents during the curing period of the coating films: (a) Sample 1, 7.866 nm; (b) Sample 2, 61.577 nm; (c) Sample 4, 178.557 nm; (d) Sample 5, 191.990 nm.

clearly from the results of Samples 1 and 2, which have the same solvent (dimethylbenzene) and solvent content.

As mentioned above, a coating film with good properties needs a suitable thickness of coating film and suitable volatility and contents of solvents in coating liquid. According to the values of J_s , Δt_p , and η and the rate of change of J , one can select and optimize the sorts and contents of solvents for preparing a definite thickness of coating film. For the porosity and permeation of

a coating film, among many affecting factors, the solvent content and the volatility of solvent are important.

CONCLUSIONS

A coating film with good properties needs suitable diffusion and evaporation of solvents from the coating film layer. The diffusion and evaporation of solvents from the coating film can be studied by BAW admittance analysis and can be ex-

pressed by the changes in the diffusion rate of the solvents (J). The porosity and permeability of the coating film can be expressed by the curing degree η , which is the relative drop in the diffusion rate. With both the solvent content in the coating liquid and the evaporation rate of solvent increasing, η increases. The thickness of the coating film has a definite effect on the two parameters of solvent diffusion behavior: J_s (the relative diffusion rate at the surface dry time) and η . However, for the parameter Δt_p (the time difference between the surface dry time t_s and the turning point time t_p when the diffusion behavior changes), the influence of the thickness of the coating film and the solvent content is not obvious.

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