Time-Temperature Effects in Polymer Coatings for Corrosion Protection as Analyzed by EIS

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Summary: More information is contained in Electrochemical Impedance Spectroscopy (EIS) results at steady-state vs. Temperature data sets than just the low frequency limit/polymer coating film resistance data most often cited. We have analyzed various EIS-Temperature data sets for several coating films in immersion and present the results considering the coating film dielectric constant vs. frequency and temperature. Water up-take can be analyzed by these methods and can be used to estimate the role of this process in the failure of corrosion protective coatings. For coating films that have been subjected to cyclic exposure, analysis of the dielectric constant vs. frequency data resulting from EIS data on these films indicate that cyclic exposure contributes significantly to 'physical aging' of the coating polymer.

Introduction

Barrier properties are a key factor in organic coating to protect the metal substrate from the corrosion. In general it means the ability of the intact organic coating to prevent corrosive species such as water, ion and other reactants to penetrate down to the coating layer. The quantitative measurement of these barrier properties is of interest of the coating scientist to evaluate the protection performance of the organic coating under corrosive environment. For corrosion of a metal substrate to occur, corrosive species such as water, oxygen and electrolyte must be present at metal/coating interface. Organic coatings provide much of their protection against corrosion by blocking the other species necessary for the corrosion process from the metal surface.

Electrochemical impedance spectroscopy (EIS) has been widely used in the characterization of the organic coating in exposure to a corrosion causing environment. The low frequency impedance modulus ($|Z|_{\text{low f}}$) has been considered as almost equivalent to the coating resistance in the stages of exposure of a coating/metal system prior to any significant metal

 CCC 1022-1360/00/$ 17.50+.50/0

damage, and therefore one measure of the barrier properties of the film.[1] By the method, the changes in coatings during prolonged exposures can be monitored to evaluate the life time of the coating.[2] Moreover, through some assumption on the physical processes involved in the film degradation and corrosion, equivalent circuit fitting can be performed on EIS data so that one can calculate intrinsic properties of the coating such as the such as coating resistance, coating capacitance, charger transfer resistance and double layer capacitance.

Recently, our laboratory has begun to explore the interpretation of the EIS frequency data besides using solely the low frequency regime characterize to the barrier properties of coatings by examining EIS data with respect to coating polymer dielectric properties over the entire measurement frequency range. First, we will describe how dielectric constant measurement characterizes the barrier properties and the changes in the polymer during thermal cycling testing, second, we try to introduce how dielectric constant information can be extracted from EIS data.

The dielectric constant of a material can be represented by a complex quantity is given in the following equation:

1. $\varepsilon^* = \varepsilon' + j\,\varepsilon''$

where ε' is referred to the real or storage part of the dielectric permittivity, which measures the amount of the alignment of the dipoles and ε'' is referred to loss factor which represents the energy required to align the dipoles and move the ions. ε' is proportional to the capacitance and ε'' is proportional to the conductance. Tan δ is the ratio of ε'' to ε', and the ionic conductivity can be derived from the ε''.[3]

In the previous work, we have observed that the barrier properties have an abrupt decrease when the temperature was over T_g of the coating through thermal cycling EIS testing.[4] The relaxation process of the polymer reflects the mobility of the polymer chain, which is also highly dependent on the temperature, through the dielectric constants measurement under various the temperature, the relationship between the barrier properties and the relaxation process of the coating and the influence of the temperature can be well related.

Impedance data can be related to the dielectric constant[5] through the following equations. The complex impedance is given by

2. $Z = Z' + jZ''$

Using the relation between admitance and impedance as functions of frequency, and defining ω as the angular frequency and ε_0 as the dielectric constant of free space, one has the following equations for calculating the real and complex parts of the dielectric constant from the complex impedance as:

3. $$\varepsilon'(\omega) = \frac{-Z''(\omega)}{Z'(\omega)^2 + Z''(\omega)^2} \bullet \frac{1}{\omega\varepsilon_0}$$

4. $$\varepsilon''(\omega) = \frac{Z'(\omega)}{Z'(\omega)^2 + Z''(\omega)^2} \bullet \frac{1}{\omega\varepsilon_0}$$

These calculations of the real and imaginary part of the dielectric constant are most accurate in the high frequency regime because at the high frequency range, the impedance behavior is dominated by the capacitance values, and the influence from the ionic or electric conductance could be minimized. We will use them for the entire range of ω assuming the high resistance values

Experimental

Sample Preparation

Aluminum alloys 2024-T3 panels from Q-Panel Lab Products of size 7.62 x 7.62 x .864cm were used as the substrate. There were three coatings applied to the substrate, the first one examined was a BASF e-coat with plasma polymer pretreatment (e-coat) and the second coating studied was a $SrCrO_4$ pigmented epoxy-polyamide primer(PEPP), the detail of how to make coating samples could be referred in our previous paper[6]. The thirdtwo packages clear epoxy coating comprising Epon 1001 CX-75 (Shell Chemicals) and Ancamide 2353(Air Product) were cast on the panel using a drop-down bar. Before the application of the coatings, the panels were pretreated by alkaline cleaner Turco 4215-S. After air dry for one week, the film final thickness was 26.6±1.2 , 28.0±0.9 and 300±30 μm respectively measured by an electromagnetic digital coating thickness gauge Elcometer 345 (Elcometer Instrument Ltd.).

Experimental Procedure

The thermal cycling testing protocol and the experimental set-up can be found in our previous paper[6]. The protocol has been modified a little to fit the requirement of the experimental, which is shown as in following schematic. There were total three runs applied to the samples. For thermal EIS testing, a Gamry CMS300 System with PC4 Potentiostat was used for the impedance measurements. A three electrodes system is use by with a platinum counter electrode and a silver/silver chloride reference electrode in the Corrocell™, and the test samples as working electrode. The scanning frequency range is from 5,000 Hz to 0.01 Hz with 10mV (rms) applied AC voltage in open circuit mode. The testing solution is dilute Harrision's solution (0.05% NaCl and 0.35% $(NH_4)_2SO_4$) and the exposure area for testing is 8.30cm^2. The major differences of two protocols used in this study lie on (1) the testing temperature of the first and the second coating samples were rt, 35, 55, 75 and 85^{o}C, the more testing temperatures were set for the third coating including rt, 35, 45, 55, 65, 75 and 85^{o}C. (2) The testing frequency for the first and second coating was from 0.1Hz to 5000Hz, and the testing frequency was lower down to 0.01Hz to 5000Hz for the third coating system. DSC measurements by a Perkin-Elmer 7 Series Thermal Analyzer were also performed on the samples before and after thermal cycling testing. In these measurements, the temperature scan was conducted under N_2 from -50^{o}C to 150 ^{o}C with a heating rate of 10 ^{o}C /min.

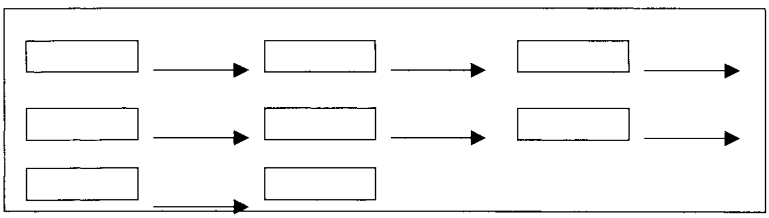

Figure 1. Schematic of Thermal Cycle Test Protocol

Results and Discussions

Wet State T_g and Dry State T_g

The initial purpose of the thermal cycling testing to develop a fast and reasonable corrosion accelerated evaluation protocol for organic coatings, and the results can be found in the previous paper.[6] As we had observed before in our laboratory,[4] the glass transition temperature, T_g, for wet coating films could be determined from the EIS data. To do this, we examined plots of $|Z_{low\ freq}|$ vs. $1/T_{absolute}$ (^{o}K), and determined the T_g from the break point in the slopes of the data.

The low frequency impedance modulus $|Z|_{0.01Hz}$ was considered as the barrier properties index, usually, the temperature dependent properties showed an Arrhenius relationship. Thee plot of the log ($|Z|_{0.01Hz}$) vs. 1/T*1000 for three runs of thermal EIS results shows a discontinuities at a very specific temperature, as shown in figure 2, and these points are identified as the T_g transition.

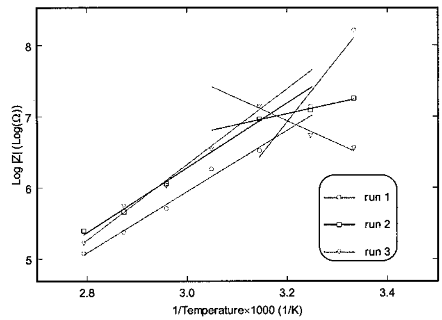

Figure 2. T_g determination from EIS results: low frequency |Z| vs 1/Temperature for 2K epoxy coating

The T_g obtained from the EIS testing was about 43.72 ± 1.76°C, which was about 20°C lower than the T_g of dry film measured by DSC, which was 66.°C. This was attributed to the water absorption and plasticization during the thermal cycling testing. The T_g depression was also considered as the index to evaluate the barrier properties of the coating because the T_g depression was proportional to water intake until the sample was saturated with water.[6] By this method, the fast evaluation of the protective coating could be made upon the T_g depression during the thermal cycling testing.

Roll-off Frequency and Polymer Relaxation

As mentioned before, the barrier properties are often characterized by the low frequency impedance modulus $|Z|_{0.01Hz}$. If one assuming a simple Randles circuit model, the $|Z|_{0.01Hz}$ is roughly equal the resistance of the coating. It decreases during the thermal cycling testing because the mobility of the polymer chain increases sharply with heating over T_g. At same time, the water diffuse into the coating system and the ingress of water causes strong plasticization of the polymer, which improve the polymer mobility even further, making the water diffusion easier. For samples exposed under thermal cycling testing, the polymer chain mobility and water absorption/plasticization both influence the barrier properties of the coating. To properly consider these mutual effects, a parameter which include both the effect of coating resistance and capacitance should to be considered.

In thermal cycling testing, the impedance modulus |Z| is changes from being primarily resistive behavior to capacitive behavior as the testing frequency increases. It also decreases as the immersion temperature increases. To identify the transition from resistive to capacitive behavior, the break point frequency (f_{45}^{o} - the frequency that the phase angle between the real and imaginary components of the impedance reaches 45°), sometimes also defined as the roll-off frequency, is used to identify where the transition behavior changes in the Bode plots.

In Figure 3 an example of a Bode plot of the samples under thermal cycling testing is shown, in which the inflection points/break point frequencies are marked.

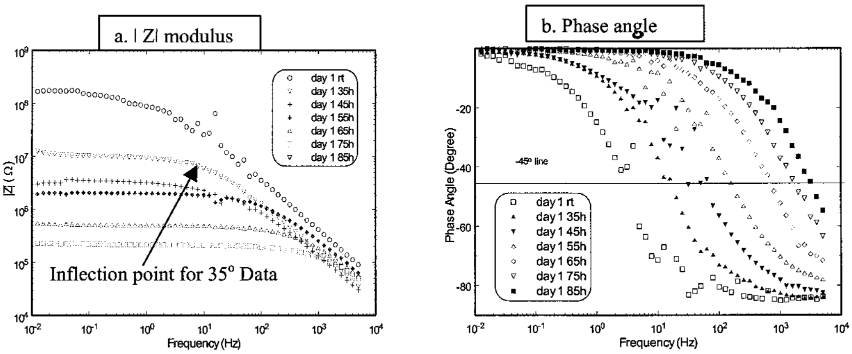

Figure 3. The Bode plots of a.)impedance modulus and b.) phase angle to show the Inflection point

By this method, we can obtain a series of break point frequency values under various exposure temperatures during thermal cycling testing. The plot of the break point frequency vs. 1/T of three coating systems also identifies the discontinuity at the T_g transition, at which the frequency was called the roll off frequency, three thermal runs are summarized as shown in figure 4. We can calculate directly the frequencies at which the phase angle is 45° for each individual temperature run.

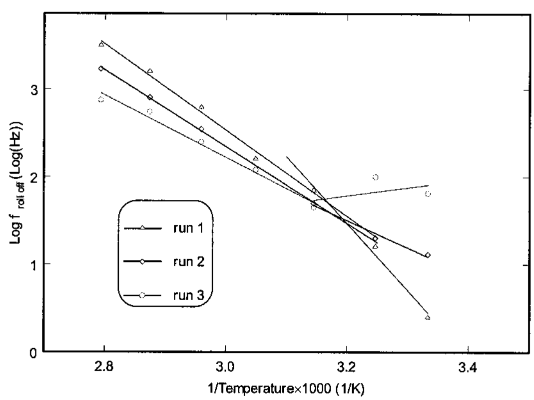

Figure 4. Log (break point)(Hz) vs 1/ $T_{Absolute}$ (1/K) for 2K epoxy coating systems

Analysis of Results from e-coat and PEPP coat

There were only four roll off frequency data points obtained for the e-coat, at 35,55,75,and 85°C, and no roll off frequency could be found on the EIS data measured at room temperature. It is very difficult to find the transition point by this data. Taking the temperature where roll-off frequency is 1Hz was found tobe a good estimate of the T_g of a good coating system tested in our lab.[7] When the frequency reached 1 Hz, the temperature obtained was close to the T_g result estimated from the EIS $|Z|_{low\ f}$ vs. 1/T data. Similarly, the transition point which corresponded the wet state T_g of PEPP coat could be observed. They are pretty close to the EIS results. The relaxation frequency for three runs were found to be 2000, 560 and 500 Hz respectively. The large value of relaxation frequency demonstrated the poor barrier properties of PEPP coating although the decrease of relaxation frequency implied the improvement of barrier properties of PEPP coat during thermal cycling testing. We have measured the T_g of the samples prior to immersion (dry state) and after immersion (wet state), the thermal cycling by DSC and we have used $|Z|_{0.01Hz}$ to calculate the T_g of the wet stage of samples. T_g results of three coating systems from these three different methods are shown in Table 1 below.

Table 1. Comparing T_g results for e-coat, PEPP coat and 2K epoxy coat from different methods

e-Coat				
T_g from the DSC (°C) (Average of three runs)	Prior testing (dry): 61.9 No wet state data			
T_g from the plot $\|Z\|_{0.01Hz}$ vs. 1/T(°C)	1st run 45.5	2nd run 46.5	3rd run 45.5	Average 45.8
T_g from the plot $f_{roll\ off}$ vs. 1/T(°C)	1st run 48.5	2nd run 48.5	3rd run 50.6	Average 50.0
PEPP Coat				
T_g from the DSC (°C) (Average of three runs)	Prior testing (dry): 85.7 No wet state data			
T_g from the plot $\|Z\|_{0.01Hz}$ vs. 1/T(°C)	1st run 66.0	2nd run 56.0	3rd run 49.6	Average 57.2
T_g from the plot $f_{roll\ off}$ vs. 1/T(°C)	1st run 64.8	2nd run 52.7	3rd run 51.7	Average 56.4
2K plain epoxy coating				
T_g from the DSC (°C) (Average of three runs)	Prior testing (dry): 66		After testing (wet): 44	
T_g from the plot $\|Z\|_{0.01Hz}$ vs. 1/T(°C)	1st run 42.06	2nd run 44.36	3rd run 44.76	Average 43.72
T_g from the plot $f_{roll\ off}$ vs. 1/T(°C)	1st run 43.15	2nd run 40.28	3rd run 45.37	Average 42.93

The T_g results from both EIS calculations were close to the T_g of wet film after thermal cycling measured by DSC. Thermal cycling EIS has been proved a powerful technology to detect the T_g of wet state sample by identifying the abrupt change in barrier properties as measured by |Z|. There are some differences between the T_g results obtained from $|Z|_{0.01Hz}$ and $f_{roll\ off}$ or f_{45^O}, the possible reason for which is the contribution of coating capacitance incorporated into $f_{roll\ off}$ calculation. Besides the wet state T_g obtained from the thermal EIS results, the roll-off frequency at wet stage, which was 60Hz for run 1 testing of clear epoxy coating, 1Hz for E-coat and 2000Hz for run 1 testing of PEPP coat respectively provides the information about polymer chain relaxation. As in the previous studies[8,9] , a 1Hz roll off frequency was found for epoxy coatings tested by thermal cycling, its reciprocal was proportional to the polymer relaxation time and it was a characteristic of the barrier property of coating system.

Barrier properties and physical ageing

In this section, the dielectric constant results from thermal EIS testing of three different coatings used for corrosion protection were discussed.

The dielectric constant data calculated from EIS results vs. frequency at various temperatures are presented in Figure 5 (real portion and imaginary portion of dielectric constant) for e-coat data, the rest of the data is discussed in summary form below. Among these coating systems, the e-coat shows superior corrosion protection because of its excellent barrier properties, the PEPP coating had poor performance because its high pigment volume concentration. The plain epoxy coating did not provide much corrosion protection as it only a polymer that was not designed for corrosion protection use in un-pigmented form. For dielectric constants data, the dot curves stand the first thermal run data, the dot-line curves stand for the second run data and the line curves stand the third run data. The data measured at same temperature was drawn in same color in the plots.

There is no significant change in the dielectric constant data between runs for e-coat sample, which implied barrier properties of the coating kept constant during three thermal runs. The ε' and ε'' increased significantly for PEPP coating after first run when temperature was below 55°C.. The increase of dielectric constants could be attributed to the plasticizing effect on molecular chain by H_2O and the increase caused by water uptake[10]. When the temperature reached 75°C, no increase was found because the system was saturated with water, but an obvious plateau was observed that is often related to the appearance of the delaminated area. An increase of ε' and ε'' is also observed for plain epoxy coating when temperature was below 45°C. No apparent increase was found when temperature was over 45°C. No shoulder or plateau is found for this sample. We are still seeking an explanation for these observations.

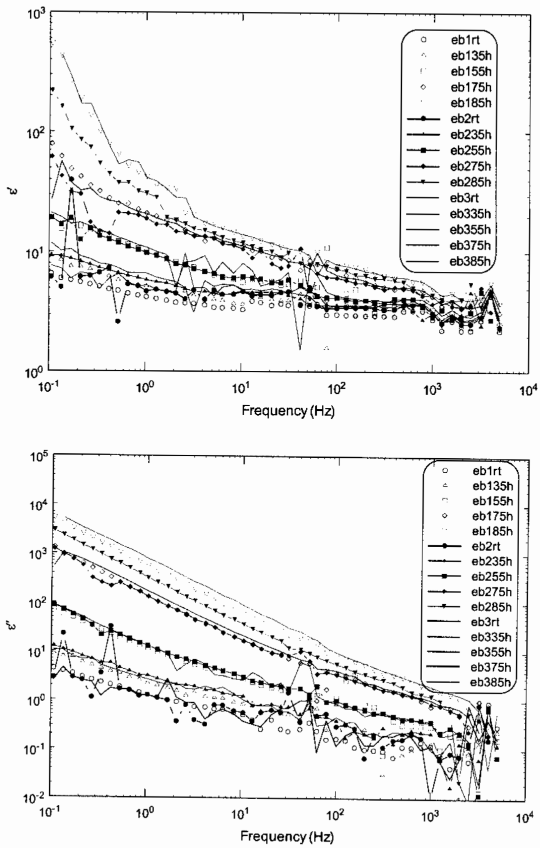

Figure 5. Real Portion (ε′) and Imaginary Portion (ε″) of Dielectric Constant of e-coat vs. Frequency for Various Thermal Conditions.

The barrier properties of samples could be clearly measured by ε′ and ε″ derived from EIS , and the changes on barrier properties due to temperature cycling in immersion were mainly affected by the plasticising effect of water on molecular chain and the water uptake. Further, the thermal cyclic exposure contributed significant of physical ageing of the coating sample.

Conclusions

The barrier properties of corrosion protective organic coatings during the thermal cycling testing were measures by EIS. The $|Z|_{0.01Hz}$ and roll-off frequency from EIS testing can be used as indexes to evaluate the barrier properties of the coatings. The plot of them against the reciprocal of the temperature showed discontinuity, which represented the T_g of the polymer plasticized by the diffused water The roll-off frequency which includes the effects came from both the resistance and capacitance seems to be a characteristic index of coating barrier properties. Analyzing the EIS data via the dielectric constant data clealy illustrates the effect of water plasticization and water uptake on barrier properties of coatings.

Acknowledgements

This project was supported by US Air Force Office of Scientific Research under Grant No. F49620-99-1-0283, Lt. Colonel P. Truelove - Program Manager.

References

1 Delucchi, S. Turri, A. Barbucci, M.Bassi, S.Novelli and G.Cerisola, *J. Polymer Science: Part B: Polymer Physics* **2002**, 40, 52-64

2 Gordon Bierwagen, Junping Li, Lingyun He, and Dennis Tallman "Fundamentals of the Measurement of Corrosion Protection and the Prediction of Its Lifetime in Coatings," Chapter 14 in *Proceedings of the 2nd International Symposium on Service Life Prediction Methodology and Metrologies*, Monterey, CA, Nov. 14-17, 1999, ACS Symposium Series # 805, J. Martin and D Bauer, ed., ACS Books, Washing ton, DC (2001) 316-350

3 D.Kranbuehl, D. Hood, LmcCollough, H. Aandahl, N. Haralampus, W. Newby & M. Eriksen, "Frequency Dependent Electromagnetic Sensing for Life Monitoring of Polymers in Structural Composites During Use," *Progress in Durability Analysis of Comosite Systems,* A.H. Cordon, K.Reifsnider, Eds., A.A.Balkema Publ., Rotterdam (1996) pp.53-59

4 J.Li, C.S.Jeffcoate, G.P.,Biewagen, D.J.Mills & D.E.Tallman, *Corrosion,* **1998**, *54*, 763-771

5 J.R. Macdonald, ed., "*Impedance Spectroscopy",* Wiley, NY (1989)

6 Gordon P. Bierwagen*, L. He, J. Li, L. Ellingson & D.E.Tallman, *Prog. Organic Coatings,* **2000**,*39* 67-78

7 Private communication, S. Duval

8 Gordon Bierwagen, "EIS Studies of Coated Metal in Accelerated Exposure," presented at EIS 2001, Marilleva-Trento, Italy, June 17-22, 2001; to be published in *Prog. Organic Coatings*

9 Junping Li, Ph.D. Dissertation North Dakota State University, Fargo, ND USA (2001)

10 S.Duval, Y. Camberlin, M.Glotin, M.Keddam, F.Ropital and H. Takenouti , Abstract n331, 198th Meeting of The Electrochemical Society, Phoenix, October 2000