CL Coatings & Linings

Electrochemical Impedance Spectroscopy: Testing Coatings for Rapid Immersion Service

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This article describes an innovative test program using electrochemical impedance spectroscopy to evaluate two high-build epoxy linings for rapid water immersion. The performance of a two-coat application of a low-temperature-cure 80% volume solids modified phenalkamine epoxy was compared with a one-coat application of a 100% volume solids polyamide epoxy. Each system was immersed in distilled and deionized water after only a 24- to 48-h curing time.

Touted as suitable for rapid water immersion, two epoxy coatings were selected for study based upon their different curing agent types and the presence, or absence, of solvent. The low-temperature-cure 80% volume solids modified coating (hereafter referred to as "phenalkamine epoxy" but also known as a modified aliphatic amine Mannich base) cures at temperatures as low as 0°F (–18°C).[1] An internal accelerator comprises part of the structure of the curing agent and eliminates the need for deleterious winter-grade catalysts, or accelerators, which could otherwise lead to premature coating failure. In comparison, the epoxy polyamide coating cures at temperatures as low as 50°F (10°C) and uses small amounts of the accelerator 2,4,6-tris(dimethylaminoethyl) phenol.

Electrochemical Impedance Spectroscopy (EIS)

EIS allows one to quantitatively determine several coating properties without affecting the coating and its performance. It also facilitates detection of changes in a coating's behavior at a small fraction of the exposure time required for those changes to be detectable by the traditional mechanical or visual methods.[2-3]

The barrier properties of organic coatings create a high electrical resistance across the coating thickness (Figure 1).[4] As coatings age, the interconnecting network of pores within the epoxy matrix eventually becomes saturated with water, salts, etc., exposing the metal substrate to a corrosive environment. The saturation of the pores also creates lower resistance paths through the coating itself.

Aged organic coating systems also possess other electrical properties. For instance, dielectric properties cause coatings to act as capacitors to an electrical current. Corrosion occurring at a metal surface possesses a polarization resistance related to the corrosion rate, and an electric double layer also behaves as a capacitor. Since Bacon, Smith, and Rugg released their pioneering work in the late 1940s, coatings with an impedance $>10^9$ Ωcm^2 at 0.1 Hz are said to provide excellent corrosion protection; in contrast, those possessing $<10^6$ Ωcm^2 are said to provide poor corrosion protection.[5]

Test Program

COATING SAMPLES

Each coating was applied by airless spray to several 4- by 8-in. (10- by 20-cm) cold-rolled steel panels previously abrasive blasted to a NACE No. 2/SSPC-SP 10[6] near-white-metal blast condition. The phenalkamine epoxy was applied in two coats, with final dry-film thicknesses (DFTs) ranging from 24 to 28 mils (607 to 711 μm). The polyamide epoxy was applied in a single coat, with final DFTs ranging from 35 to 45 mils (889 to 1,143 μm).

The coated steel panels were separated into different exposure streams:

- Stream 1—Hot water (40°C) immersion after 168 h cure
- Stream 2—Hot water (40°C) immersion after 48 h cure
- Stream 3—Hot water (40°C) immersion after 24 h cure
- Stream 4—Ambient water (25°C) immersion after 168 h cure
- Stream 5—Ambient water (25°C) immersion after 48 h cure
- Stream 6—Ambient water (25°C) immersion after 24 h cure

All test panels were allowed to cure at 25°C in 40 to 60% relative humidity before immersion in distilled, deionized water. Hot-water immersion at 40°C was used to accelerate the degradation of the coatings. Because higher temperature exposure also increased the possibility of accelerating the cure of an otherwise uncured coating, exposure in ambient temperature immersion was used to ensure that any beneficial effects were not the result of higher temperature.
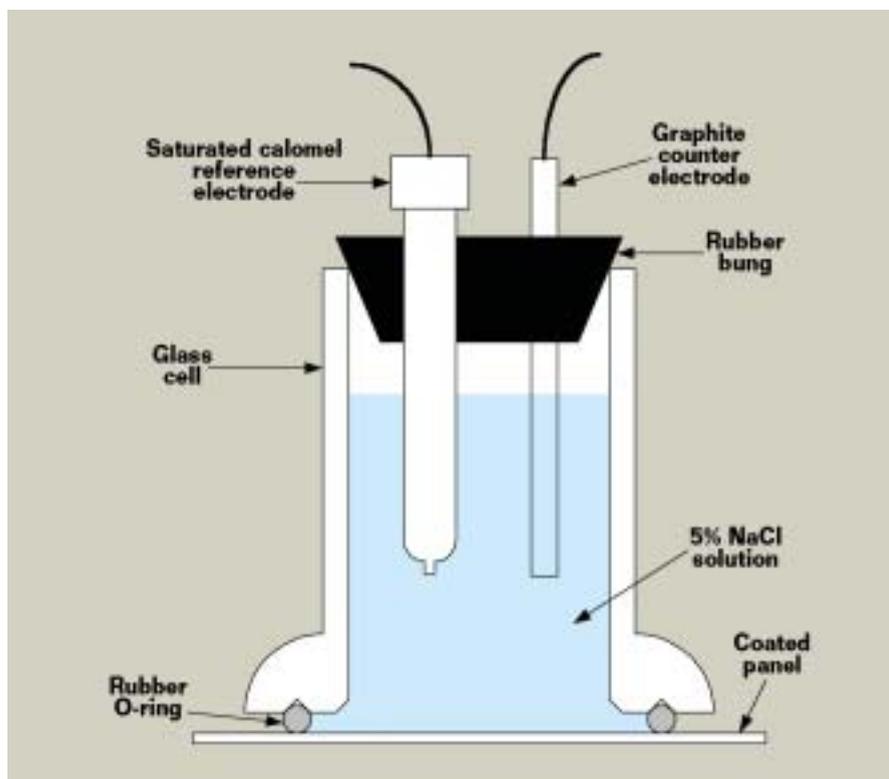
EIS MEASUREMENTS

Each coated panel was evaluated by EIS at 192 h (8 days), 528 h (22 days), and 1,000 h (~42 days). An impedance measurement was made by attaching a glass cell containing a counter electrode, a reference electrode, and a conductive solution (5% sodium chloride [NaCl]) to the coated metal panel (Figure 2). A small sinusoidal alternating current (AC) signal was applied be-

FIGURE 1
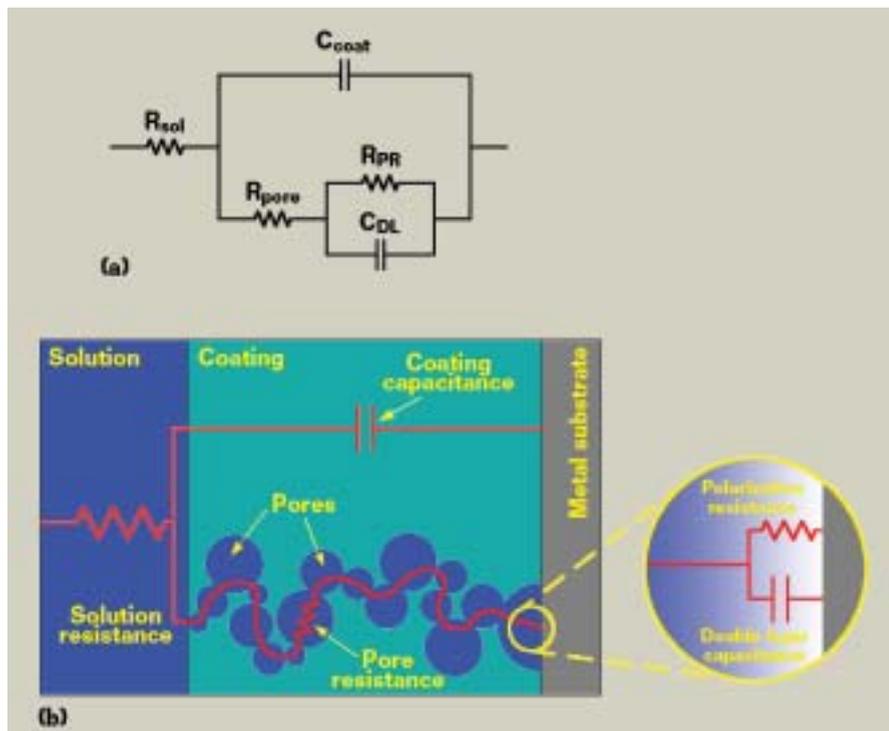
(a) Equivalent circuit model of fitting EIS data, (b) circuit model of coating physical properties.

FIGURE 2

Schematic of the EIS cell.

TABLE 1

EIS PARAMETERS

$Z_{0.1Hz}$ — Total coating impedance (Ωcm^2) at an applied signal frequency of 0.1 Hz. $Z_{0.1Hz}$ is a good general indicator of the protective capacity of the coating, with higher numbers indicating superior protection. In general, coatings with $Z_{0.1Hz} > 10^8$ Ωcm^2 are considered excellent providers of protection and coatings with $Z_{0.1Hz} < 10^6$ Ωcm^2 are considered poor providers of protection.

R_{pore} — The electrical resistance (Ωcm^2) to current traveling through the pore network in the coating. Higher values indicate higher resistance to penetration of corrosive species

R_{PR} — The polarization resistance (Ωcm^2) of the steel substrate to corrosion (inversely related to corrosion rate of the substrate). Higher values indicate lower rates of corrosion.

C_{coat} — The coating capacitance (F/cm^2) produced by the dielectric properties of the coating. C_{coat} is related to the dielectric strength of the coating and the water absorption by the coating, with higher values indicating higher dielectric strength or higher water content.

C_{DL} — The capacitance in F/cm^2 produced by the electric double layer at the water/substrate interface. A measurable C_{DL} value indicates that water is present at the substrate. Higher values of C_{DL} indicate a greater wetted area of substrate.

R_{sol} — The resistance of the test solution.

TABLE 2

EIS RESULTS FOR RAPID IMMERSION EPOXIES

Coating Age (h)		80% Solids Modified Phenalkamine Epoxy			100% Solids Modified Polyamide Epoxy		
		192	528	1,000	192	528	1,000
Stream 1 168 h cure, 40°C immersion	$Z_{0.1Hz}$	7.9×10^9	2.2×10^9	1.5×10^9	1.6×10^{10}	8.3×10^8	4.8×10^8
	R_{pore}	5.6×10^{10}	6.7×10^6	3.0×10^6	1.1×10^{11}	6.0×10^5	4.7×10^6
	R_{PR}	—	2.4×10^{10}	1.7×10^{10}	—	1.2×10^9	7.8×10^8
	C_{coat}	1.9×10^{-10}	3.1×10^{-10}	4.0×10^{-10}	9.8×10^{-11}	2.5×10^{-10}	3.9×10^{-10}
	C_{DL}	—	3.6×10^{-10}	5.5×10^{-10}	—	6.6×10^{-10}	9.8×10^{-10}
Stream 2 48 h cure, hot immersion	$Z_{0.1Hz}$	2.9×10^6	2.2×10^9	1.3×10^9	9.1×10^9	1.3×10^9	2.3×10^7
	R_{pore}	7.4×10^5	5.7×10^6	2.4×10^6	1.9×10^{10}	7.2×10^6	1.1×10^6
	R_{PR}	2.1×10^6	2.9×10^{10}	1.3×10^{10}	—	1.5×10^9	2.2×10^7
	C_{coat}	3.8×10^{-10}	2.9×10^{-10}	4.6×10^{-10}	1.4×10^{-10}	7.4×10^{-11}	9.6×10^{-11}
	C_{DL}	2.8×10^{-9}	3.7×10^{-10}	6.2×10^{-10}	—	2.4×10^{-10}	5.4×10^{-10}
Stream 3 24 h cure, hot immersion	$Z_{0.1Hz}$	1.4×10^6	1.7×10^9	1.2×10^9	3.0×10^9	9.1×10^8	2.1×10^5
	R_{pore}	2.4×10^5	5.1×10^6	3.0×10^6	3.5×10^9	1.8×10^6	5.5×10^4
	R_{PR}	1.1×10^6	2.3×10^{10}	1.4×10^{10}	—	1.9×10^9	1.6×10^5
	C_{coat}	6.9×10^{-10}	4.2×10^{-10}	5.9×10^{-10}	2.2×10^{-10}	1.8×10^{-10}	3.6×10^{-10}
	C_{DL}	4.8×10^{-9}	4.2×10^{-10}	5.9×10^{-10}	—	5.2×10^{-10}	1.7×10^{-8}
Stream 4 168 h cure, 25°C immersion	$Z_{0.1Hz}$	7.9×10^9	—	2.3×10^9	1.6×10^{10}	—	1.3×10^9
	R_{pore}	5.6×10^{10}	—	1.1×10^7	1.1×10^{11}	—	3.3×10^6
	R_{PR}	—	—	6.4×10^{10}	—	—	7.9×10^9
	C_{coat}	1.9×10^{-10}	—	3.4×10^{-10}	9.8×10^{-11}	—	1.9×10^{-10}
	C_{DL}	—	—	3.2×10^{-10}	—	—	7.7×10^{-10}
Stream 5 48 h cure, 25°C immersion	$Z_{0.1Hz}$	2.9×10^6	—	3.2×10^9	9.1×10^9	—	1.5×10^9
	R_{pore}	7.4×10^5	—	1.3×10^7	1.9×10^{10}	—	1.4×10^6
	R_{PR}	2.1×10^6	—	8.7×10^{10}	—	—	2.7×10^9
	C_{coat}	3.8×10^{-10}	—	2.3×10^{-10}	1.4×10^{-10}	—	1.4×10^{-10}
	C_{DL}	2.8×10^{-9}	—	2.3×10^{-10}	—	—	4.6×10^{-10}
Stream 6 24 h cure, 25°C immersion	$Z_{0.1Hz}$	1.4×10^6	—	2.9×10^9	3.0×10^9	—	9.3×10^8
	R_{pore}	2.4×10^5	—	1.1×10^7	3.5×10^9	—	5.9×10^6
	R_{PR}	1.1×10^6	—	8.3×10^{10}	—	—	1.5×10^9
	C_{coat}	6.9×10^{-10}	—	2.6×10^{-10}	2.2×10^{-10}	—	1.7×10^{-10}
	C_{DL}	4.8×10^{-9}	—	2.5×10^{-10}	—	—	7.0×10^{-10}

tween the counter electrode and the sample substrate. The resulting voltage response was monitored between the reference electrode and the sample substrate.
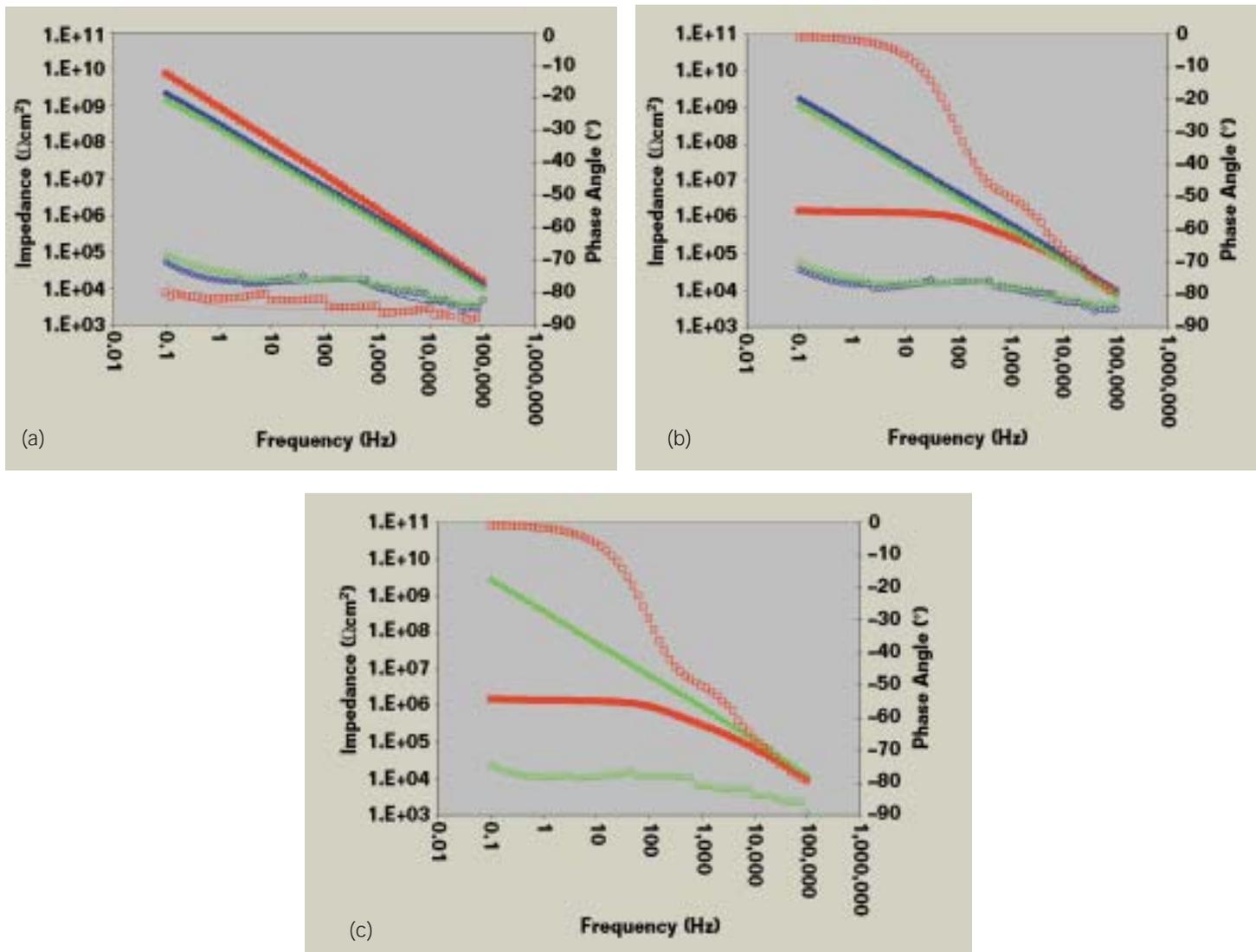
In EIS measurements, impedance in an AC circuit is analogous to resistance in a direct current (DC) circuit.

$$E = IZ \qquad (1)$$

where E is AC V, I is AC A, and Z (Ω) is impedance. The current (I) flows through the metal/coating system.

The parameters for each EIS measurement were as follows:

FIGURE 3

EIS results, phenalkamine epoxy, solid mark = impedance, hollow mark = phase angle. Thin line—circuit model fit. Red, blue, and green represent 192, 528, and 1,000 h exposure measurements, respectively. (a) 168-h cure, immersion at 40°C, (b) 24-h cure, immersion at 40°C, (c) 24-h cure, immersion at 25°C.

- Test area: 14.6 cm^2
- Frequency range: 100 kHz to 0.1 Hz
- Number of data points: five points per decade of frequency
- Induced DC potential: –0.7 V vs saturated calomel electrode
- Induced AC potential: ±0.01 V

Results

The data from each EIS scan were fit to the equivalent circuit model schematized in Figure 1. Table 1 describes the circuit model parameters. Table 2 and Figures 3 and 4 present the data from the circuit fitting of each scan.

80% SOLIDS PHENALKAMINE (MODIFIED) EPOXY

- The samples from streams 1 and 4 (168 h cure) showed aging behavior typical of a high-quality protective coating. The $Z_{0.1Hz}$ value decreased slowly with increased exposure time. The C_{coat} value slowly increased with time, indicating increasing water absorption. The R_{PR} and C_{DL} values were not present in the data until the 528-h measurement, indicating that water had not reached the substrate by 192 h. From 528 to 1,000 h, the R_{PR} value decreased slightly and the C_{DL}

value increased slightly; these changes indicated small increases in corrosion and pore filling at the metal substrate. Note that, although the corrosion rates increased, the measured rates are on the order of 10^{-8} mm/y. The R_{pore} value decreased significantly from 192 to 528 h because water penetrated through the pores; it decreased very slowly from 528 to 1,000 h, again indicating a slow degradation with increasing exposure.

- The Stream 2, 3, 5, and 6 (48 and 24 h cure) samples initially showed very poor results at the 192-h mark,

FIGURE 4
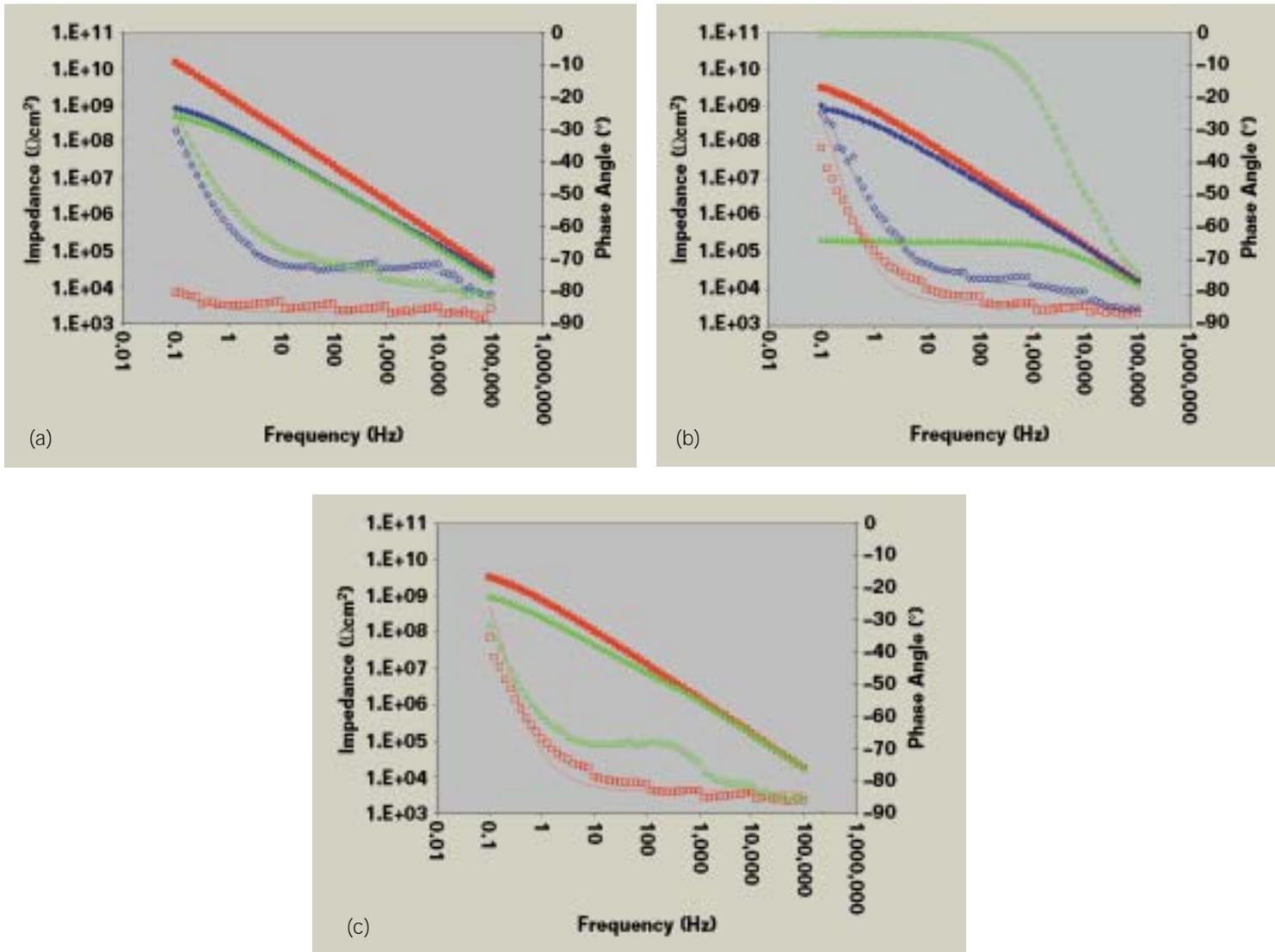
EIS results, polyamide epoxy. Solid mark = impedance, hollow mark = phase angle, thin line = circuit model fit. Red, blue, and green represent 192, 528, and 1,000 h measurements, respectively. (a) 168-h cure, immersion at 40°C, (b) 24-h cure, immersion at 40°C, (c) 24-h cure, immersion at 25°C.

indicating a significant undercure condition. The $Z_{0.1Hz}$ and R_{pore} values were marginal. The R_{PR} and C_{DL} values were present, indicating that water was present in the coating and at the substrate.

• The Stream 2, 3, 5, and 6 samples showed a dramatic improvement in protective capacity from 192 to 528 h. The 528-h results were now nearly identical to the Stream 1 and 4 samples. Of particular note is the fact that the C_{coat} values decreased, indicating either rejection of water or solvent from the coating or, more likely, an increase in the dielectric strength of the coating that resulted from increased polymer cross-linking.

• The aging characteristics of the samples in all exposure streams were identical from 528 to 1,000 h.

• No blistering was evident.

100% SOLIDS POLYAMIDE EPOXY

• The Stream 1 and 4 (168 h cure) samples showed aging behavior typical of a high-quality protective coating. The parameters followed the same aging patterns exhibited by the phenalkamine epoxy, with the exception that there was a slightly larger decrease in the R_{pore} value (indicating more degradation) as compared to the modified phenalkamine epoxy.

• The samples from Streams 2, 3, 5, and 6 (48 and 24 h cure) initially showed indications of excellent protection at 192 h. Only R_{pore} showed lower values and only C_{coat} showed higher values with decreasing cure time, thus indicating a slightly undercured condition.

• The Stream 2 and 3 (40°C immer-

sion) samples, like the phenalkamine epoxy, revealed a decrease in the C_{coat} values from 192 to 528 h. The decrease indicates that the polyamide epoxy still was either rejecting water or solvent from the coating or undergoing additional cross-linking reactions.

• The samples from Streams 2 and 3 also showed a rapid decrease in protective capacity, with increasing exposure time from 192 to 1,000 h as evidenced by large decreases in the $Z_{0.1Hz}$, R_{pore}, and R_{PR} values. The decreases indicated water penetration through the pore network to the substrate, with increasing corrosion and large increases in the C_{coat} and C_{DL} values. The latter indicated water absorption by the coating and its micro-blistering as it detached from the substrate.

• The samples from Streams 5 and 6 (25°C immersion) showed a lower rate of degradation compared to the Stream 2 and 3 samples. This finding was consistent with the less-aggressive lower-temperature exposure. However, the C_{coat} values did not significantly change from 192 to 1,000 h; hence no water or solvent rejection occurred from the coating and no additional cross-linking of the coating occurred (in contrast to the phenalkamine epoxy at 25°C, or itself at 40°C).

• No blistering was evident.

Discussion

The two rapid-immersion epoxy coatings discussed in this study (solvented and solventless) were expected to imbibe water in very different ways. Despite the fact that both were deemed suited for early water immersion, the question was: in rapid immersion, to what extent does water uptake prove deleterious to epoxy coating performance and thus undermine the projected in-service life expectancy of the coating?

Imbibed water can be absorbed in free-volume elements of polymer seg-ments, condensed in globular clusters at the polymer-substrate interface, or hydrogen-bonded to polar groups on the polymer. Irrespective of the micro-environment for the water in the polymeric matrix, water had a negative impact on coating performance for the polyamide epoxy yet had no unfavorable effects in the phenalkamine epoxy.

Although the cure of the 80% solids phenalkamine epoxy was somewhat retarded by early immersion, the underwater cure continued until full cure was reached after several days and with no deleterious consequences. In fact, the underwater-cure EIS signature was essentially the same as if the coating had cured in air. Significantly, these results also indicated that immersing the phenalkamine epoxy in water before full cure is achieved does not decrease its corrosion protection compared to when the coating is fully cured before immersion. Therefore, one would expect comparable life expectancies.

In contrast, the polyamide epoxy showed initial indications of high performance at early exposure times. Continued cure under water, however, demonstrated that the rate of degradation of the protective properties was pronounced—and accelerated—by the coating being placed into service before achieving a full cure.

Conclusions

• EIS measurements revealed significant nonvisual differences in the performance of rapid-immersion-grade coatings as they cured under water. The early onset of under-film corrosion processes beneath the 100% solids polyamide epoxy coating was readily detected using EIS. In contrast, a modified phenalkamine epoxy achieved full cure under water just as if it had cured under normal ambient conditions.

• The EIS technique provides specification authorities a judicious means for coating evaluation and selection where rapid immersion service is required.

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