Electrochemical Assessment of Spray-Applied Thermoplastic Coating Barrier Properties

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Flame-sprayed thermoplastic powder coatings act as barrier-type coatings for corrosion protection. Characteristic electrical properties for this type of coating are high resistance and capacitance, and low permeability to water and ions. Electrochemical impedance spectroscopy was used to evaluate the corrosion protection performance and electrical resistance of this type of coating during immersion in 3% NaCl solution.
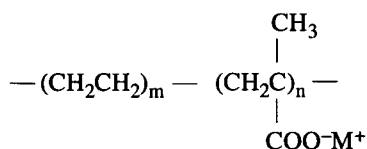
The variations with time of impedance and capacitance of two types of this coating, blue and black, were measured at three immersion temperatures (22, 50, and 80 °C). The impedance of both coatings remained consistently high when the solution temperature was maintained around ambient (22 °C). At the higher temperature of 50 °C, both coatings performed well initially, then showed signs of damage by a drop in the impedance. Both samples maintained at 80 °C failed after 12 and 25 days for the blue and the black coatings, respectively, with blistering occurring on both panels.

1. Introduction

Commercial applications for thermoplastic coatings have increased considerably. Applications vary from underground pipeline coatings (Ref 1) to pickup truck bed liners (Ref 2) to medical applications (Ref 3), all of which utilize the toughness, strength, and flexibility of these coatings.

The coatings investigated in this study, obtained from Flamecoat, (Plastic Flamecoat Systems, Big Spring, TX) are based on Du Pont's Surlyn, (Du Pont de Nemours, E.I., & Co., Inc., Wilmington, DE) a copolymer of ethylene and methacrylic acid (EMAA). The formulation of this copolymer incorporates carboxylic acid groups onto the backbone of the hydrocarbon chain. These acid groups can be neutralized by mixing the polymer with metal hydroxides, such as $Ca(OH)_2$. The resultant compound is known as an ionomer. As pure solids, ionomers, especially those with divalent cations, behave as reversibly cross-linked thermoplastics. The general formulation of the polymer molecule is shown below

$$-(CH_2CH_2)_m - \underset{\underset{COO^-M^+}{|}}{\overset{\overset{CH_3}{|}}{(CH_2C)_n}} -$$

where the ratio of m/n is usually on the order of 10 to 100, reflecting the overall low ionic content within the polymer (Ref 4).

The effects of plasticization of ionomers by water, despite their hydrophobic nature, are well known (Ref 5-7). A dramatic drop in

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the electrical barrier properties of an ionomer coating has been seen when the glass transition temperature of the Flamecoat has been exceeded in a conductive electrolyte (Ref 8).

2. Experimentation

Two coatings were examined, both from Flamecoat. The Flamecoat application involves fluidizing powdered polymer in a hopper and drawing the powder into a propane flame, which is then moved over the substrate. Detached coating samples were obtained by coating two glass panels by this method. The coatings were readily detachable from the smooth surfaces, with no release agent necessary. The first coating was black in color (and will be referred to as the black coating) and designed for ambient temperature and nonimmersion usage. The second coating, blue in color (referred to as the blue coating), was of similar composition but more flexible.

Both coatings were applied to 15 cm square, grit-blasted, mild steel panels via the Flamecoat technique. Table 1 gives the coating thickness for each panel. Small sections of the large panels were removed with an electronic guillotine for use in the smaller electrochemical cell (see the next section). All samples were holiday tested for pinhole defects.

Table 1   Coating thickness

Temperature of immersion, °C	Average thickness		Standard deviation	
	µm	mil	µm	mil
Blue coating				
80	462	18	61	2
50	277	11	72	2
22 (thin coating)	332	13	46	1
22 (thick coating)	411	16	54	2
Black coating				
80	769	28	106	7
50	367	14	48	1
22 (thin coating)	297	11	69	2
22 (thick coating)	846	33	57	2

The electrolyte used throughout the experimentation was 3 wt% NaCl (30 g/L). This provided a harsh environment for the coatings, simulating marine and burial conditions.

2.1 EIS Measurements

The primary mode of investigation was via electrochemical impedance spectroscopy (EIS). The EIS data were obtained using CMS 100 equipment (Gamry Instruments, Inc., Willow Grove, PA). The frequency range for these measurements was from 0.02 to 5 kHz, sampling at ten points per decade with alternating-current voltage of 10 mV (rms).

Two types of electrochemical cells were used. The first was a CorroCell (Fig. 1), a commercially available unit that incorporates a glass cylinder with open ends and three ground-glass ports along the body of the cylinder. The coated panels were clamped to these open ends by an external cast aluminum frame. A heating mat was wrapped around the body of the cylinder and the ground-glass ports used as access for a thermometer, a thermocouple, a reference electrode, and a platinum counterelectrode. For the high-temperature studies a silver/sil-
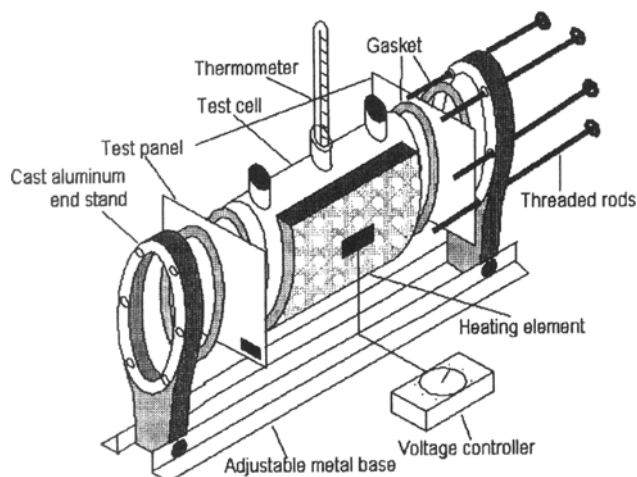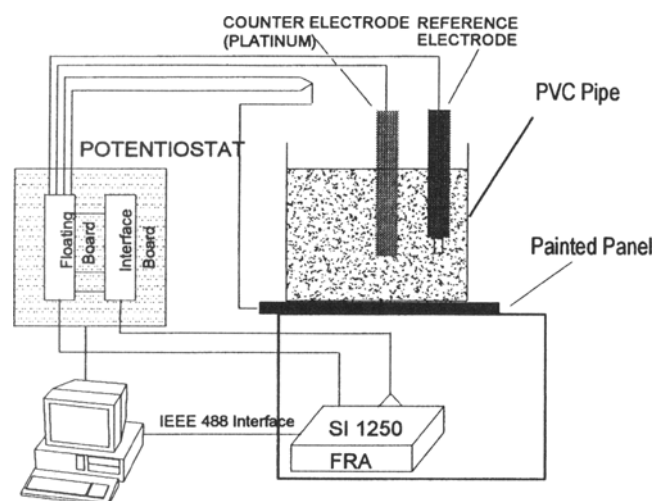

Fig. 1 CorroCell electrochemical cell

Fig. 2 Sample setup for EIS measurements of small panels at room temperature

ver chloride (Ag/AgCl) reference electrode was used; the ambient-temperature measurements used a saturated calomel reference electrode. The second type of cell, made in the laboratory, comprised a 5 cm section of polyvinyl chloride tubing with an internal diameter of 3.2 cm, which was sealed onto the surface of the coating with an acid-free silicone sealant and allowed to set overnight before use (Fig. 2).

The CorroCell (Fenner Associates, Houston, TX) setup was used to study the effect of maintaining the coating system at an elevated temperature and viewing the performance with time via EIS measurements. Two elevated temperatures were used, 50 and 80 °C. Both of these temperatures are below the glass transition temperature (T_g) of the coatings. Elevated-temperature studies were achieved by heating the electrolyte via the heating mat. Once the system was at the required temperature, it was held at that temperature for 10 min before the initial testing began. The EIS measurements were taken at regular intervals during the first day and the first week of immersion. Subsequent measurements were taken at weekly intervals up to 51 days from initial immersion.

Impedance measurements were performed in a manner described elsewhere (Ref 9). Throughout this paper, mention will be made of the impedance modulus. It is the measured impedance multiplied by the area of the coating. The units are ohm square centimeter $(\Omega \cdot cm^2)$.

2.2 Glass Transition Temperature

A Perkin-Elmer Series 7 (Perkin-Elmer Corp., Norwalk, CT) thermal analysis system in the differential scanning calorimetry (DSC) mode was used to assess the T_g of detached samples of the polymer coating. The temperature range studied was -60 to $+150$ °C at a scan rate of 10 °C/min.

3. Results and Discussion

3.1 Sample Preparation

Uniform coating thickness is difficult to obtain and is operator and process sensitive. A trained applicator is required for this particular coating technique, but even then film thickness can vary greatly over the surface of a given sample. Table 1 presents data for coating thickness on all samples. Excessive heat applied to a panel during spraying will also cause the coating to sag on the substrate, leading to lumps and thin areas and yielding a nonuniform coating thickness.

3.2 Black Coating

The maximum impedance modulus |Z| plotted with time (Fig. 3) shows the dramatic effect of maintaining the coating at elevated temperatures. The sample continually immersed in 80 °C electrolyte (with an apparent outlier point at 6 days) maintained a high impedance modulus for the first 25 days, comparable to the other samples. On exceeding this 25 day immersion period, the impedance modulus decreased rapidly to a value of $1 \times 10^8 \Omega \cdot cm^2$, indicative of the beginning of failure.

The remaining black coating samples exhibited high |Z| values greater than $1 \times 10^{11} \Omega \cdot cm^2$ for the first 35 days. After this period the 50 °C sample showed a continual reduction in

$|Z|$ to a value close to $1 \times 10^8 \cdot cm^2$. Both of the ambient-temperature samples remained stable over the immersion time, with the final values of $|Z|$ being within an order of magnitude of the initial immersion values obtained 50 days earlier.

After cooling the two high-temperature CorroCells at the end of the experimentation, a further impedance spectrum was taken. On cooling, the coating immersed in the 50 °C solution showed some reversibility, seen by the increase in the impedance modulus at low frequencies. The higher-temperature coating did not show this reversible property on cooling. The impedance modulus of the 80 °C immersion sample remained low, in the region of $1 \times 10^8 \Omega \cdot cm^2$ after cooling.

3.3 Blue Coating

Figure 4 shows that the thick blue coating sample maintained at ambient temperature failed after only 15 days of immersion. Blistering was also apparent on this sample after 20 days. On completion of the 50 day immersion, the coating was removed and large areas of disbondment were found both in the immersed area and on areas of the sample where coating was not exposed to the electrolyte. The surface finish of the metal was smooth, with no evidence of prior grit blasting. Failure of this sample at ambient temperature may have been due to poor surface preparation of the substrate.

The sample immersed in electrolyte maintained at 80 °C behaved similarly to the black coating: a high initial $|Z|$ maintained for the first 7 days of immersion, followed by a reduction in $|Z|$ from 1×10^{11} to 1×10^6 in a matter of 12 days. Blistering was observed on this sample after 18 days of immersion.

The remaining blue coating samples at 50 °C and the thin blue coating at ambient temperature behaved in a similar manner. The $|Z|$ values for the first 3 days for both samples were on the order of $1 \times 10^{11} \Omega \cdot cm^2$, dropping to about $1 \times 10^9 \Omega \cdot cm^2$ after 30 days of immersion, with this impedance maintained to the end of the study.

On cooling of both of the high-temperature blue samples, the impedance modulus remained consistent with the long-term data. No increase in value was seen for the 50 °C coating, unlike the black sample, and the 80 °C blue coating maintained the low impedance modulus of $1 \times 10^6 \Omega \cdot cm^2$ after cooling.

3.4 Both Coatings

Capacitance values obtained through high-frequency impedance measurements were consistent for both coating types. Low values of capacitance, on the order of $10 pF \cdot cm^2$, were measured for all samples on initial immersion. Only on samples where the $|Z|$ dropped below $1 \times 10^9 \Omega \cdot cm^2$ did the capacitance increase, indicative of water penetration into the coating (Ref 10).

The glass transition temperatures obtained are given in Table 2.

Table 2 Glass transition temperatures

Coating	Measured T_g temperature, °C
Black	91
Blue	90

4. Conclusions

Although the T_g of both coatings (91 and 90 °C) are above the highest-temperature Corrocell (80 °C), they both show signs of failure after prolonged exposure to 3 wt% NaCl electrolyte at this temperature. These experimental conditions are, admittedly, beyond the designed specifications for use. It is worth noting, however, that damage is largely irreversible, as demonstrated by the impedance data obtained after cooling the cell to 30 °C. Short-term exposure to higher-than-designed temperatures may have long-term effects on coating integrity.

Of the two sets of data obtained from the 50 °C Corrocell, the black coating performed better than the blue coating by maintaining a high maximum impedance modulus and a break-point frequency below 1 Hz with time up to 25 days. The blue coating exhibited continual decrease in the impedance modulus at low frequencies with time of immersion, falling to $1 \times 10^8 \Omega \cdot cm^2$ after 35 days of immersion at 50 °C, and would be expected to fail before the black coating. Clearly the standard black coating outperformed the more flexible blue coating.

The poor performance of the flexible coating in this study may have been caused by several factors. Poor preparation of the surface to ensure a good mechanical lock for the coating would certainly contribute to overall poor corrosion protection
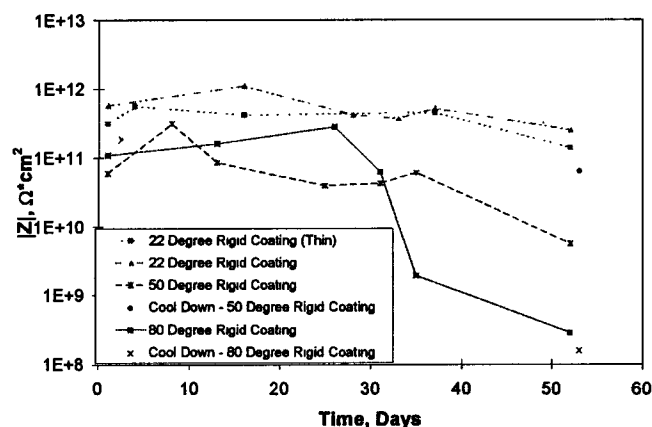

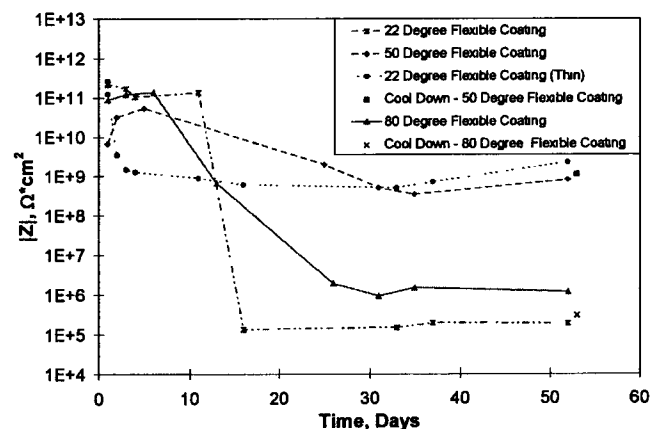**Fig. 3** Impedance modulus versus time for black coating

Fig. 4 Impedance modulus versus time for blue coating

performance. Water and oxygen will diffuse through a given coating. Poor adhesion would then contribute to the prevalence of corrosion and blistering at the coating/substrate interface.

Acknowledgments

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