ND Soybean Council – Year-End Report

Project: Ionic Liquid Soy-protein based Coating for Protection against Chloride-ion Attack

Objectives of the research

The objectives of this project are to synthesize soy-protein-based coating material and evaluate the corrosion inhibition performance of the soy protein-based coatings for mortar embedded rebars in an alkaline environment.

Completed work

The research tasks and the progress achieved in each of the research tasks are provided below.

Research Task-1 – Synthesis of Ionic Liquid-Soy Protein Coating: The research task aims to synthesize ionic liquid soy protein coatings. To achieve this task, aqueous soy protein coatings are synthesized that include soy protein isolate (SPI) as a base material and sorbitol as a plasticizing agent. The SPI concentrations in the soy protein coating formulations prepared in this task ranged from 5% to 15% (%wt. of deionized water). Moreover, each soy protein coating formulation further included 10%, 20%, or 30% of sorbitol (%wt. of SPI). Soy protein coatings are prepared by mixing SPI (with 90% protein content) in deionized water and stirring for 10 minutes to achieve uniform dispersion of soy protein in water. Sorbitol plasticizer is then added to the aqueous soy protein solution in varying concentrations (10%, 20%, 30% wt. of soy protein isolate) and stirred for further 20 minutes. The pH level of the resulting soy protein mixture is then adjusted to 12 by adding 1N NaOH solution. The soy protein mixture with adjusted pH level is then placed on an orbital shaker set at 210 rpm and 45 °C for 4 hours. Initial coatings are developed without using a cross-linker with an epoxy group and the coatings are cured at a temperature of 40 °C for 48 hours. The resulting soy protein coating material is stored at 5 °C before application on rebars. The soy protein coating synthesis process is depicted in Figure 1. In total, 12 soy protein coating formulations are prepared that include 4 combination each (0%, 10%, 20%, 30% Sorbitol) for 5%, 10%, and 15% SPI coatings. The synthesized coatings are labeled as S-#-*-$ where S refers to Soy Protein, # refers to wt.% of SPI isolate in deionized water, * refers to the pH level (alkalinity) of the soy protein suspension, and $ denotes the sorbitol weight in the mixture as a function of SPI. For instance, specimen S-5-12-20 has 5% SPI, a pH level of 12, and 20% wt. (% SPI) of sorbitol.

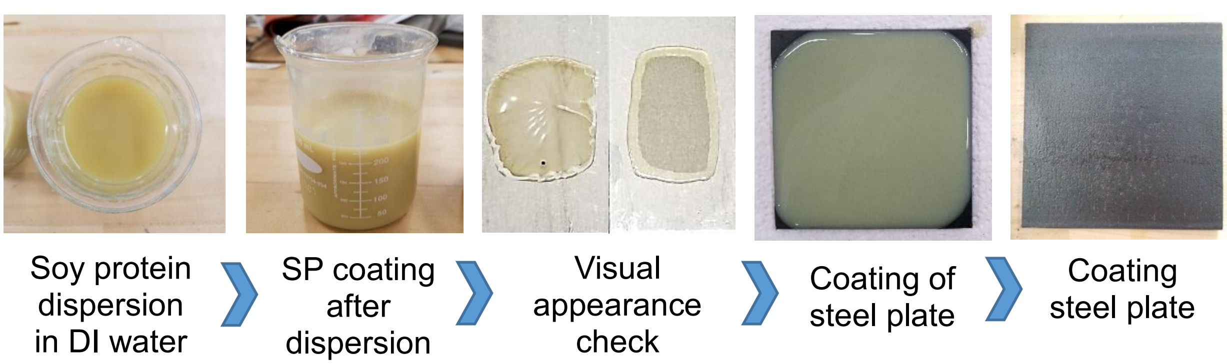

Figure 1. Typical workflow for each soy protein coating formulation trial.

Research Task-2 – Characterization of Corrosion Inhibition Potential of Ionic Liquid-Soy Protein Coating Material: In this task, the physical and chemical characteristics of soy protein coatings and their corrosion inhibition performance are evaluated through different experimental techniques. Specifically, the viscosities of the preliminary batches of the coating materials have been obtained and the presence of the functional groups in the preliminary batches of coatings materials have been determined using Fourier transform infrared spectroscopy. The materials required for conducted corrosion characterization of the soy protein coatings have been obtained. Two sets of steel specimens have been prepared to elucidate the corrosion protection performance of the soy protein coating materials. The first set of specimens are 3"×5" steel panels that are being used to determine the abrasion resistance of the coating material as well as the corrosion mitigation performance. The second set of specimens include #4 grade 60 rebars. The rebar samples have been thoroughly cleaned of dirt and grease with the help of acetone. The rebars are then coated with the soy protein coating batches and embedded in ordinary Portland cement mortar. The corrosion performance of the soy protein-coated rebars that are embedded in the cement mortar is determined using rapid macrocell corrosion tests.

Results

The results obtained from the work completed in Research Task-1 and Research Task-2 are as follows.

Chemical and Physical Characterization Results - Viscosity Tests: The viscosity tests are performed to determine the consistency and workability of the soy protein coatings containing varying amounts of SPI and Sorbitol plasticizer. The results obtained from the viscosity tests showed that increasing the concentration of polyol in the soy protein coating led to a slight reduction of viscosity of the resulting coatings (see Fig. 2). In this study, the viscosity of the bio-based deicing solutions and the reference deicing solution is determined using HAAKE Viscotester® 550. HAAKE viscotester® 500 consists of a standard cylindrical spindle and the data acquisition (DAQ) system that measures and records the shear stress and shear rate of a given fluid (see Figure 2). The results obtained from the viscosity tests are provided in Figure 3. As observed in Figure 3, the viscosities for 5% SPI coatings ranged from 1.15 m.Pa.s (corresponding to 30% sorbitol) to 1.43 m.Pa.s (corresponding to 0% Sorbitol in coating). The increase in the concentration of SPI in the coatings is observed to increase the viscosities of the coating formulations. In the case of 10% SPI coatings, the viscosities are observed to be in the range of 6.00-6.80 m.Pa.s. Similarly, the viscosities are observed to further increase in the case of 15% SPI coatings wherein viscosities are observed to be 24.8-26.4 m.Pa.s. It is further observed that the increase in the concentration of Sorbitol plasticizer in the coatings resulted in a minor reduction in their viscosities. These results showed that the 5% and 10% SPI coatings can be directly applied on the cracked concrete surface and hence can reach the rebar by virtue of their low viscosity. However, the 15% SPI coatings formulations need to be applied on the rebar surface directly for achieving desirable corrosion protection.

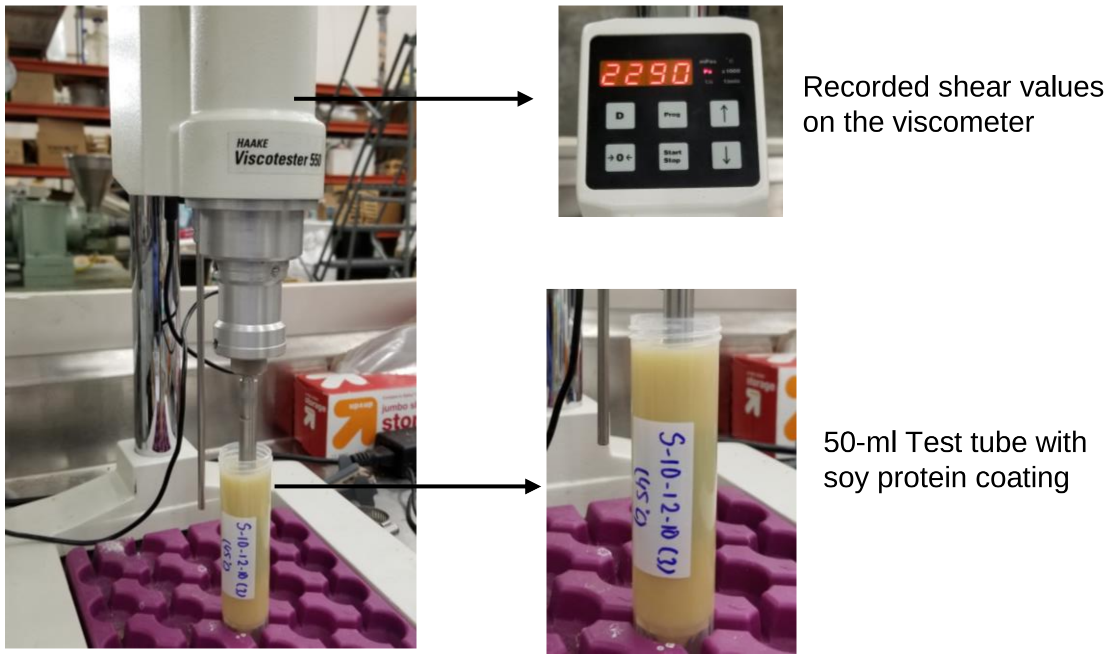

Figure 2. Viscosity test setup.

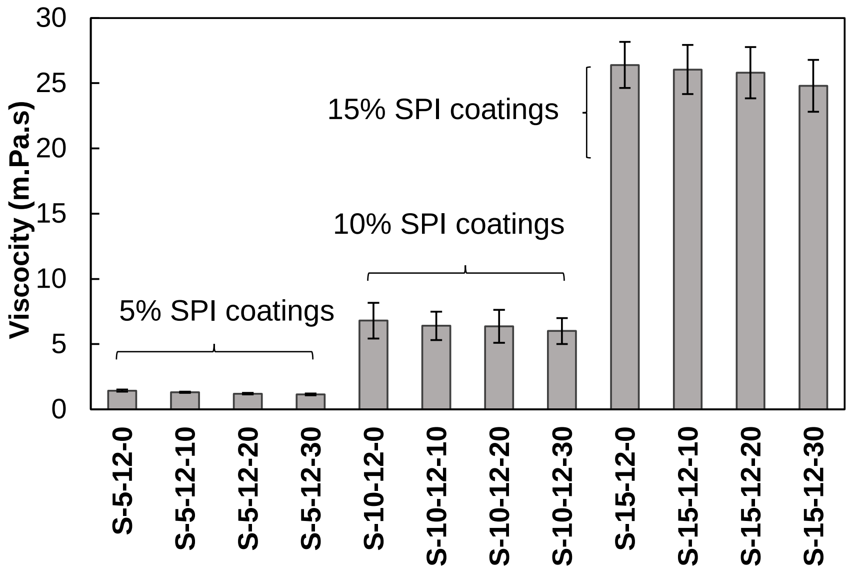

Figure 3. Viscosities of soy protein coatings with different SPI and Sorbitol content.

Chemical and Physical Characterization Results – FTIR Results: The functional groups present in the cured soy protein coating materials have been determined using Fourier transform infrared spectroscopy (FTIR). The FTIR spectra for the cured polyol soy protein coatings are provided in Figure 4. As shown in Figure 4, peaks corresponding to various stretching vibrations (such as O-H, N-H, C-H, C-O, C=O) are observed that indicate the presence of different functional groups (hydroxyl, amid, methyl, methylene, secondary amide, and carboxyl group). Almost identical functional groups are observed in all coatings. Moreover, it is observed that the –OH functional group almost vanished in the case of 15% SPI coatings. The presence of the observed functional groups in the FTIR spectra of the coatings exhibits the successful alkali modification of the soy protein mixture. Moreover, the disappearance of the hydrophilic groups (such as hydroxyl and carboxyl) in the spectra corresponding to the 15% SPI coatings shows that the addition of high sorbitol content improves the water resistance of the cured soy protein coatings.

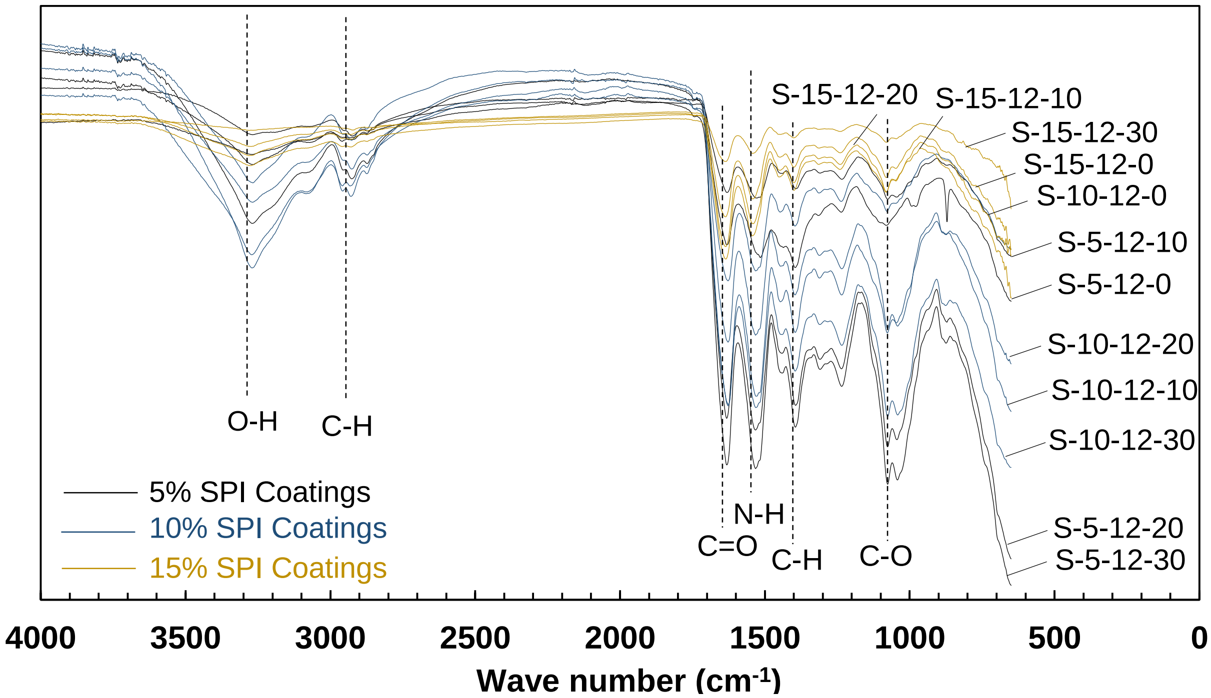

Figure 4. FTIR spectra of cured polyol-soy protein coating products.

Chemical and Physical Characterization Results – Visual Brittleness: The brittleness of the hardened soy protein coating is qualitatively assessed based on visual observation of the specimens. For this purpose, the soy protein coatings corresponding to each coating formulation (wt.% of SPI and wt.% of Sorbitol) are spread on mild steel plates and then cured for 48 hours. The cured coatings are then observed visually and the photograph of each coating is provided in Figure 5. As observed in Figure 5, the coatings with 0% Sorbitol plasticizer is visible brittle regardless of the wt.% of SPI in the coating. However, the addition of Sorbitol plasticizer is observed to significantly decrease the brittleness in the coatings. The highest improvement in the integrity (non-brittleness) is noted in the coatings corresponding to 30% Sorbitol content.

From these results, it can be concluded that the cured soy protein coatings proposed herein have the necessary functional groups, workable viscosity, and adequate plasticity for usage as a coating material. Consequently, two soy protein coatings are further investigated for corrosion mitigation performance in rebars that include 10% SPI coating with 30% Sorbitol (S-10-12-30) and 15% SPI coating with 30% Sorbitol (S-15-12-30). The procedure adopted for corrosion performance characterization (potentiodynamic polarization tests and rapid macrocell corrosion tests) and the results obtained are discussed in the next section.

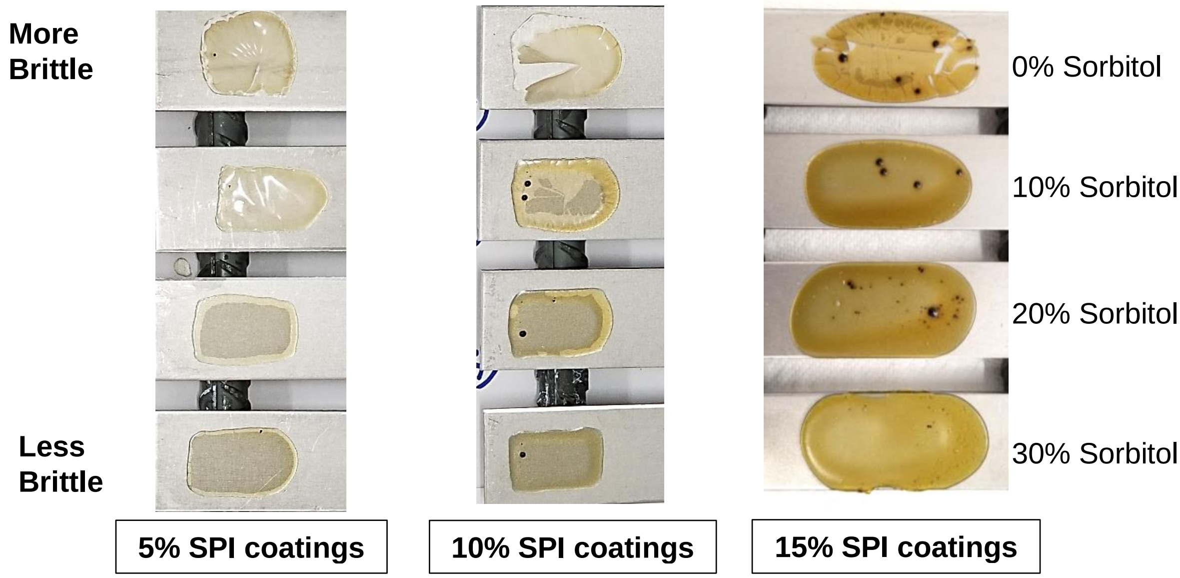

Figure 5. Visual brittleness of soy protein coatings with different concentrations of sorbitol.

Corrosion Performance Characterization: The corrosion mitigation performance of the soy protein coatings (S-10-12-30 and S-15-12-30) is determined using potentiodynamic polarization tests and rapid macrocell corrosion tests for coated rebars. For this purpose, double-coated rebar specimens and coated panels are prepared using each of the coating formulations (see Figure 6). Potentiodynamic polarization tests are then formed on the specimens using a standard 3-electrode electrochemical cell which included the coated specimens as working electrode, saturated calomel as reference electrode, stainless steel wire mesh as a counter electrode. During potentiodynamic polarization tests, the potential of the working electrode (coated specimen) is varied from cathodic to the anodic direction (anodic scan) within a range of ±500 mV with reference to the steady-state potential at a scanning rate of 2 mV/s. Tafel analysis is then performed on the polarization curves to obtained corrosion current densities and corrosion rates. For performing rapid macrocell corrosion tests, a test setup is prepared using the procedures specified in the Strategic Highway Research Program (SHRP) manual that consists of two containers (see Figure 7). One coated rebar embedded sample is immersed in container-1 which is filled with simulated concrete pore solution and 1.6 molal NaCl and acts as an anode whereas two rebar embedded samples are immersed in the second container that acts as a cathode and contains simulated concrete pore solution. The corrosion rates are then monitored for 90 days. The corrosion rates are determined using the following equation

$$Corrosion\ rate\ \left(\frac{\mu m}{yr}\right) = K\ \frac{V \cdot m}{n \cdot F \cdot D \cdot R \cdot A} \tag{1}$$

where, K = conversion factor (31.5×10^4), V = voltage drop across the resistor (mV), m = atomic weight of iron (55.8 g/g.atom), n = number of ion equivalents exchanged (for iron, n = 2), F = Faraday's constant (96485 coulombs/equivalent), D = density of iron (7.87 g/cm^3), R = resistance of the resistor (10 ohms), A = surface area of the immersed anodic rebar (approximately 39.9 cm^2).

Figure 6. Rapid macrocell corrosion test specimens preparation (uncoated and coated rebars embedded in OPC mortar with ~6% air entrainment.

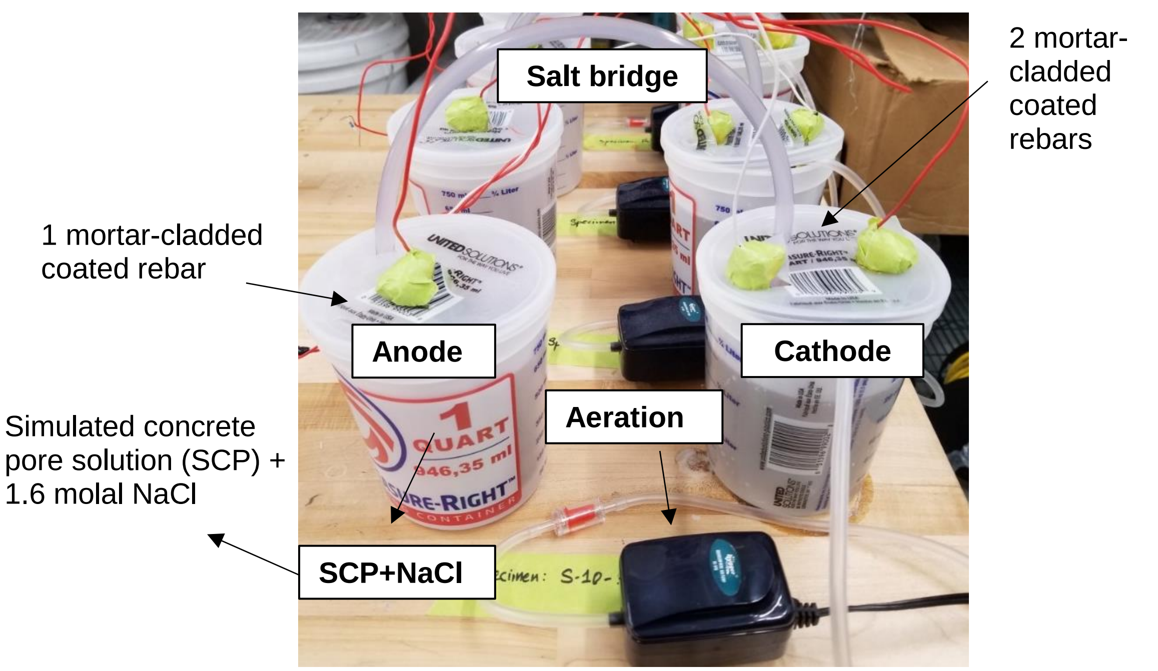

Figure 7. Rapid macrocell corrosion test setup.

The polarization curves obtained from the potentiodynamic polarization tests are provided in Figure 8. The Tafel analysis performance on these polarization curves showed that the application of 10% and 15% SPI coatings with 30% Sorbitol plasticizer content can reduce the corrosion current densities and corrosion current rates by 95% when compared to the corrosion current density and corrosion rate of bare steel specimens. Similarly, the corrosion rates obtained from rapid macrocell corrosion tests (using Eq. 1), as shown in figure 9, exhibited a considerable reduction in corrosion rates in the cement mortar embedded rebar specimens that are double-coated with 10% soy protein coating. The rapid macrocell corrosion tests for 15% SPI coatings are currently in progress. These results validate the effectiveness of the soy protein coatings in mitigating corrosion in rebars.

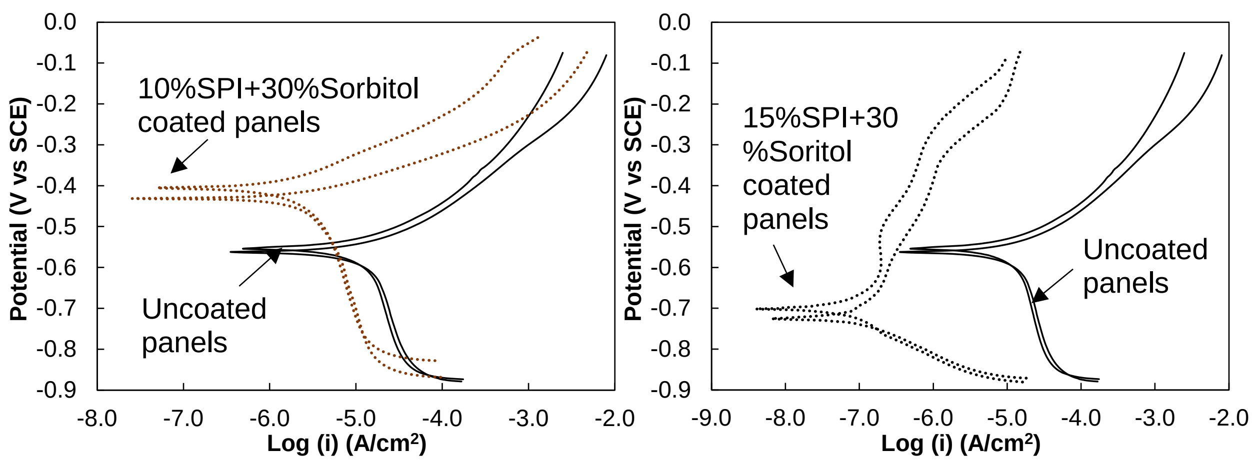

Figure 8. Potentiodynamic polarization curves of the uncoated panel and soy protein-coated panels.

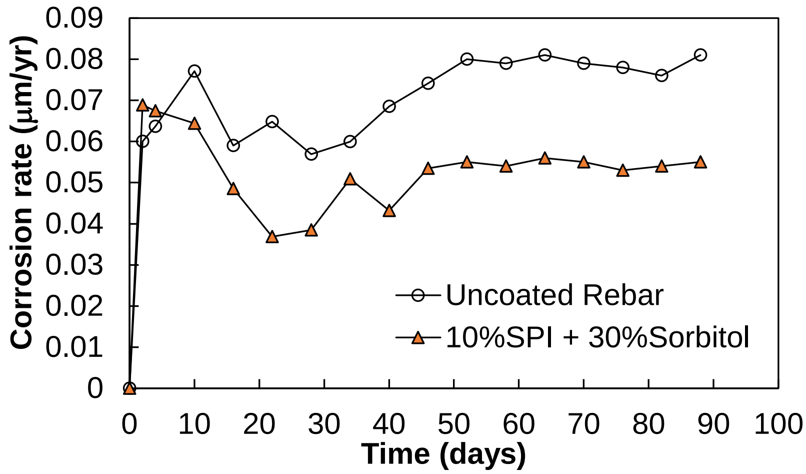

Figure 9. Corrosion rates obtained from rapid macrocell corrosion tests for uncoated rebars and soy protein-coated rebars that are embedded in Portland cement mortar.