# Smart acrylic coatings for corrosion detection

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## ARTICLE INFO

## ABSTRACT

Corrosion detecting coating was prepared using acrylic polymer chemically modified with 5-acrylamido-1,10-phenanthroline (AMP). Modified polymers having varied AMP content were synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetric (DSC) and thermo gravimetric (TGA) analysis. The modified polymer after complex formation with $Fe^{2+}$ ions showed additional absorption peak at 359 nm in UV–vis spectrum confirming the polymer-Fe (II) complex formation. Corrosion sensing ability of these polymers was evaluated by immersing the coated mild steel panels in 3.5% NaCl solution and visually monitoring the color change of coating. Electrochemical impedance spectroscopy (EIS) was used to measure the polarization resistance ($R_{PR}$) of coated steel specimens and correlated with the color change of coating. Coating from the point of color change was removed and bare metal was analyzed by scanning electron microscopy (SEM) to reconfirm that the point of color change was the corrosion site. Results reveal that these new sets of polymers can be used for corrosion detection.

## 1. Introduction

Early detection of underfilm corrosion facilitates the maintenance of the metal structures to enhance their service life and reduce the risk of accidents. Several strategies have been suggested to sense early under-film corrosion [1]. Many types of sensors have been used in variety of applications to understand and track the parameters related to corrosion. Such parameters include pH, humidity, oxygen level, ionic concentrations, corrosion potential, corrosion current, electrochemical impedance, electrochemical noise etc [2,3]. Instrumental techniques such as ultrasonic, radiographic, thermal imaging, electromagnetic and electrochemical are being used to detect the onset of underfilm corrosion [1–3]. The existing methods for corrosion inspection and detection entail large amounts of money, time and efforts to combat corrosion.

Over the last few decades, researchers are continuously focusing on development of smart corrosion detecting coatings as an alternative method for corrosion detection. These coatings respond to pH, metal ions and other electrochemical changes during corrosion [4], and show color or fluorescence change in the coating at the sites of corrosion as an early warning for corrosion initiation [5,6]. Such coating systems typically contain a primer and a topcoat, and the corrosion indicator is usually added in the primer formulation.

Zhang and Frankel [7] reported the use of coating with color changing compounds that respond to pH change during corrosion. Coatings that change from non-fluorescent to fluorescent state as a result of pH change, oxidation or metal ion interactions are reported by Johnson and Agarwala [8,9]. Incorporation of fluorescent dyes in coating formulations in the form of pH-triggered dye-filled micro (or nano) capsules that release dyes when the coating is damaged due to the change in pH during corrosion is reported by Kumar and Stephenson [10]. Augustyniak et al. [11,12] have reported the use of chelation enhanced fluorescence indicator, spiro [1H-isoindole-1,9'-[9H] xanthen]-3(2H)-one,3',6'-bis(diethylamino)-2-[(1-methylethylidene) amino] in paint composition for the detection of corrosion on steel and aluminum.

Maia et al. [13] have used nanocontainer based coating to sense corrosion of aluminum and magnesium alloys. They have synthesized mesosphere silica and loaded with phenolphthalein indicator. The silica as a filler material was used in the water-based epoxy coating formulation to sense hydroxyl ions released at the cathodic reaction sites during corrosion. This coating has shown pink color due to the onset of corrosion. More recently, Maia et al. [14] have also developed corrosion sensing polyurethane coatings for aluminum and magnesium alloys. These coatings have polymeric microcapsules containing pH-indicator and are reported to indicate the onset of corrosion through a pink coloration because of pH change at cathodic areas.

The use of pH indicator or pH sensitive fluorescent dye based

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coatings are effective in sensing corrosion in neutral or near neutral pH conditions. These chemicals have found ineffective when used in epoxy resin due to their sensitivity toward alkaline hardener. Hardeners are alkaline in nature and used for curing of epoxy resin. The small amount of unreacted hardener can lend these chemicals to change their color leading to false corrosion alarm. To overcome the above difficulty, the corrosion sensing coatings based on color or fluorescence chemicals responding to metal ions generated during corrosion reaction are reported. However, these chemicals have the limitation related to their dispersion, stability and leaching during service life of the coating. In this study, an attempt has been made to modify the acrylic polymer with corrosion sensing moiety in their backbone to overcome the above problems.

In this work, a corrosion sensing coating based on an acrylic polymer modified with phenanthroline has been reported as a simple, practical and more reliable technique for early detection of corrosion at metal-coating interface in neutral or near neutral pH conditions. 1,10-phenanthroline is reported in the literature to form red color complex with ferrous ions and is being used for detecting ferrous ions in water, food and biological samples [15]. Therefore, 5-acrylamido-1,10-phenanthroline (AMP) was synthesized and used for the modification of acrylic polymer to make corrosion sensing coating. AMP was chemically attached to the acrylic polymer through amide linkage at various concentrations ranging from 1.5 to 3% w/w. These polymers have ability to change from light yellow to intense red color after complex formation with ferrous ions. Mild steel specimens coated with modified acrylic polymers were evaluated for corrosion resistance and sensing property by immersing them in 3.5% NaCl solution. The polarization resistance of coated panels was measured periodically using electrochemical impedance spectroscopy (EIS) and correlated with color change of coating. This approach avoids non-uniform distribution of sensing material at the time of dispersion and leaching during the service life of coating.

## 2. Experimental

### 2.1. Materials

All chemicals were obtained from Sigma Aldrich (USA). Triethylamine and other solvents were dried and distilled before use. Benzoyl peroxide was purified by recrystallization in chloroform-methanol (1:1) mixture.

### 2.2. Synthesis of 5-acrylamido-1,10-phenanthroline (AMP)

AMP was synthesized [16] as follows: 5-amino-1,10-phenanthroline (2 g, 1 mol) was taken in a two-necked round bottom flask with 50 ml dry and distilled chloroform. Dry triethylamine (4.28 ml, 3 mol) was slowly added to the reaction mixture with constant stirring under nitrogen atmosphere. The reaction mass then cooled to 0 °C and acryloyl chloride (1.21 g, 1.3 mol) along with 10 ml dry and distilled chloroform was added drop wise for 30 min. After the addition of acryloyl chloride solution, reaction mixture was maintained at 0 °C for 1 h. Thereafter, the reaction mixture was kept at 27 °C with constant stirring for 24 h. The progress of reaction was monitored by thin layer chromatography (TLC). Product formation was confirmed by the disappearance of 5-amino-1,10-phenanthroline spot in TLC of reaction mixture.

The formed product was dissolved in 200 ml chloroform and washed with distilled water (200 ml × 2) and 10% NaHCO$_3$ distilled water solution (200 ml × 2) to remove the unreacted acryloyl chloride. Organic phase was collected and dried over 100 gm anhydrous sodium sulphate. Sodium sulphate was removed by filtration. 5-acrylamido-1,10-phenanthroline was recovered as a pale yellow crystalline solid from organic phase by removing chloroform in rotary evaporator under vacuum at 27 °C. Synthesized AMP was further purified by column
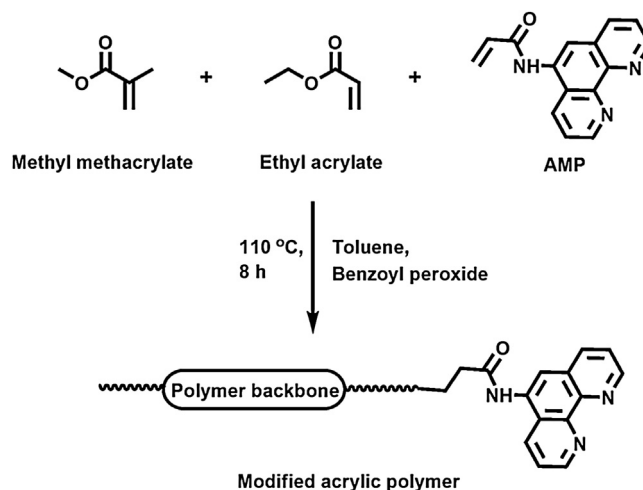


**Fig. 1.** Scheme for the synthesis of modified acrylic polymer.

chromatography. Silica column (size 200 × 25 mm) was used as stationary phase, and distilled methanol and chloroform solution as the moving phase. The pale yellow crystalline product (75% yield) was recovered after removing the solvent under reduced pressure at 27 °C; the product was preserved at 0 °C.

### 2.3. Synthesis of modified acrylic polymers

Fig. 1 shows the scheme for synthesis of modified acrylic polymer. The procedure for the synthesis of modified polymer with 2.5% AMP is as follows. 50 ml toluene was taken into a four-necked reaction flask fitted with a stirrer, inlet for nitrogen gas, thermometer and condenser, and heated to 110 °C. The solution containing 58.50 g methyl methacrylate (MMA), 39 g ethyl acrylate (EA), 2.5 g AMP and 0.6 g benzoyl peroxide in 125 ml toluene was added drop wise for 2 h under nitrogen atmosphere. The reaction mixture was maintained at 110 °C and stirred continuously. After 5 h, solution having 0.2 g benzoyl peroxide and 25 ml toluene was added drop wise for half an hour. Stirring was continued at 110 °C for another 3 h to obtain viscous polymer. Polymer was cooled to room temperature and crystallized in chilled methanol. The crystallized polymer was again washed thrice with chilled methanol to remove unreacted monomers and dried under vacuum to obtain as a solid (80% yield). Polymer compositions, AR-0, AR-1, AR-2, AR-3 and AR-4 were synthesized with MMA to EA ratio of 60:40 and AMP content of 0, 1.5, 2, 2.5 and 3% w/w, respectively. The estimation of AMP content in the polymer was calculated on the basis of quantity of AMP used for the synthesis as there was no unreacted AMP in the methanol washings.

### 2.4. Surface preparation and coating application

Burnished mild steel panels conforming to IS 513 and UNS G10100 (size 150 × 100 × 1.5 mm) were cleaned with toluene and one coat of 60% w/w solid polymer in toluene was applied by a brush to obtain total coating thickness of 60 ± 5 μm. The coated panels were kept in dust free cabinet for drying. The application of coating was done as per the directives given in IS 1477 and IS 384.

### 2.5. Evaluation of corrosion sensing property

Corrosion sensing property of coated panels was evaluated by immersing them in 3.5% NaCl solution. Corrosion sensing ability of coating was determined with respect to the number of developed red color spots in the coating due to the onset of corrosion.