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Polystyrene and cornstarch anti-corrosive coatings on steel

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Abstract: This work aims to evaluate the performance of anticorrosive thermoplastic coatings in cold rolled steel sheets. Two types of thermoplastic coatings were studied: polystyrene (PS) and cornstarch. These types of coatings are applied for protection against corrosion during transport and storage of steel plates after cold rolling until delivery to stamping or other processing. The good performance for these coatings is suitably standardized to ABNT NBR 5915-2: 2013 and ASTM A1008 / A1008M-2016. According to corrosion tests carried out in saline chamber, the coatings were satisfactory in different degrees of guarantee of corrosion protection on ASTM 1080 steel, in accordance with standards mentioned.

Keywords: aging, anti-corrosive coatings, polystyrene, cornstarch films.

1. Introduction

Coating metal surfaces with polymers is a protective method used as a physical barrier on metallic surfaces to protect against attack by corrosive species (e.g. O₂ and H⁺). However, polymeric coatings are not permanently impenetrable; once there are defects formed in the coatings, pathways will be created for the corrosive species to damage the metallic substrate, and localized corrosion will occur^[1].

According to ABNT NBR 5915-2:2013^[2], loads lower than 2 kbar are expected for the use of sheet steel coatings for stamping. In this case, polystyrene coatings become perfectly applicable, considering that its resistance is 4 kbar^[3].

According to the literature^[4], starch coatings with modified structures are renewable alternatives when compared with coatings of fossil sources, such as polystyrene. The starch coating presents hydrophilicity which can

be worked in terms of biodegradability of the coating. This type of coating may also be modified to a less hydrophilic condition^[5].

Starch is chemically composed of two polysaccharides, amylose and amylopectin^[6]. Starch may be converted into thermoplastic materials by conventional methods (extrusion, injection molding) in the presence of plasticizers, such as water and low molecular weight polyols. The casting technique can also be applied. In this case, starch is processed by heating in the presence of an excess of water, which causes irreversible swelling of the granules. Swelling is accompanied by disruption of the native crystalline structure and solubilization of amylose (gelatinization)^[7]. The advantages of thermoplastic starch when it is compared to other similar polymers are its renewability, low cost, and wide availability. It is also biodegradable and can be processed on common equipment of conventional plastics^[8].

The main aims of this work is to produce an anticorrosive coating for the Cold Rolled Steel According to the standard ABNT NBR 5915-2: 2013^[2] (ASTM A1008 / A1008M-16^[9]) using two types of thermoplastic coatings: starch and polystyrene.

2. Materials and Methods

2.1 Substrate cleaning of steel (ASTM 1080)

For the treatment of steel substrate samples used in the deposition of anti-corrosion polyester film, 6 samples of steel wire rod (ASTM 1080 standard) 11 cm long and 0.5 cm in diameter were selected. The samples were sanded by hand with grit sizes of sandpaper 220 #, 400 # and 600 # inline (unidirectional sanding). After sanding, the samples were cleaned by etching in sulphuric acid solution 2% in volume to remove possible oxides and hydroxides. Later, they were cleaned with neutral detergent and deionized water to remove grease and oils. After they were scrubbed and the clean substrate samples were dried in an oven at 150 °C over a period of 30 minutes^[10,11]. The applied time of 30 minutes also aimed at the removal of eventual organic residue on the surface.

2.2 Preparation of films

2.2.1 Cast cornstarch film

The biodegradable anti-corrosive layer was produced by gelling of cornstarch composed of 26-30% amylose and 74-70% amylopectin, and with less than 0.5% gluten, supplied by Corn Products Brazil (Sao Paulo, Brazil). Cornstarch (5 g) was dispersed in 50 mL distilled and deionized water at room temperature. The suspensions were diluted with 50 mL water previously heated to 95 °C and then held under stirring for 5 min. Glycerol (0.75 g) was added as a plasticizer^[12]. ASTM 1080 steel

substrates were immersed (dip coating) for 30 minutes in dispersion of starch-glycerol and held suspended for oven drying for 48 hours at 70 °C.

2.2.2 Cast polystyrene film

The film of PS were prepared by dip coating from 30 wt% toluene solutions (analytical grade) onto steel substrates (ASTM1080) at 2 minutes and held suspended for drying at room temperature^[12].

2.3 Test in saline solution

After a week the samples were dry and were withdrawn under the atmosphere temperature. All samples (ASTM 1080 steel coated with starch and polystyrene and not covered) were placed in a saturated solution of NaCl using two petri plates for storage. These samples were kept for a period of 6 months in saline solution for corrosive attack and evaluation by microscopy^[11,13,14].

2.4 Contact angle

The measurement of the contact angle was performed using the goniometer Ramé-Hart 100-00 NRL (operated in air and atmosphere temperature). Measurements were obtained in three different regions of the samples and the medium values evaluated. A drop of 2.5 μ l fluid was placed on the specimen surface, and a digital camera connected to the equipment captured the drop image. The contact angles were calculated automatically by the computer connected to the equipment, as shown schematically in Figure 1. The performance evolution of the drop was measured in the range of 15 seconds in a total time of 600 seconds^[12].

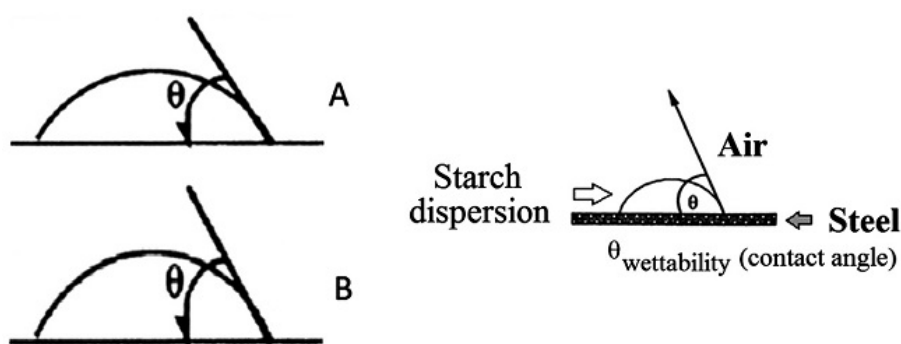


Figure 1.

Schematic contact angle dynamics of (A) polystyrene coating fluid on steel and (B) the starch coating fluid on steel.

2.5 Microscopic characterization of films

Optical microscopy was used for preliminary characterization of the morphology and texture of the thermoplastic polystyrene films. Used in this procedure was a Leica optical microscope (model DMRM) coupled with a digital camera.

High-resolution images of the surface of the films were obtained by atomic force microscope (AFM) for visualization of surface morphology and its texture (roughness was expressed in terms of root mean square roughness, RMS) with high lateral and depth resolution (nanometric ranges). The amplitude of deviation of RMS roughness of the oscillation varies per the morphological characteristics of the specimen surface and provides, in general, the most relevant information of the surface texture. The analyses were performed in air, in intermittent contact with a Micromesh NSC 16 rod (spring constant of 5 N/m), and on the atomic force microscope, model 1 M plus from JPK Instruments.

Also used was a scanning electron microscope that allows obtaining images of the surface with a great depth of field, high resolution, and easy interpretation of the three-dimensional looking images. Microscopy were obtained by scanning with energy-dispersive with an acceleration voltage of 20.0 kV spectrometer (Oxford Instruments), which provided the thickness and composition of the film on the steel wire (ASTM 1080). The samples were previously covered with 250 Angstroms of conductive gold-palladium alloy vacuum-evaporated (PVD) to provide a suitable microanalysis. Surface roughness and thickness of samples were measured with stylus roughness Sloan DekTak II surface profilometer (Dektak, Veeco Instruments Inc., Plainview, NY, USA).

3. Results and Discussion

Figure 1 shows the schematic contact angle dynamics from photos of water droplets of (A) polystyrene coating fluid on steel (about 45°) and (B) the starch coating fluid on steel (about 50°). All contact angles were similar and less than 90° (low contact angle), which indicated that the wetting of the surface was favorable, and the fluid would spread over a large area of the steel surface.

Figure 2 a shows the visual outcome by optical microscopy of ASTM 1080 steel covered with polystyrene which was attacked by corrosion in a saline chamber (after six months). The polystyrene-coated steel presented no signs of corrosion in its structure. Thus, the steel was protected against corrosion by the polystyrene film.

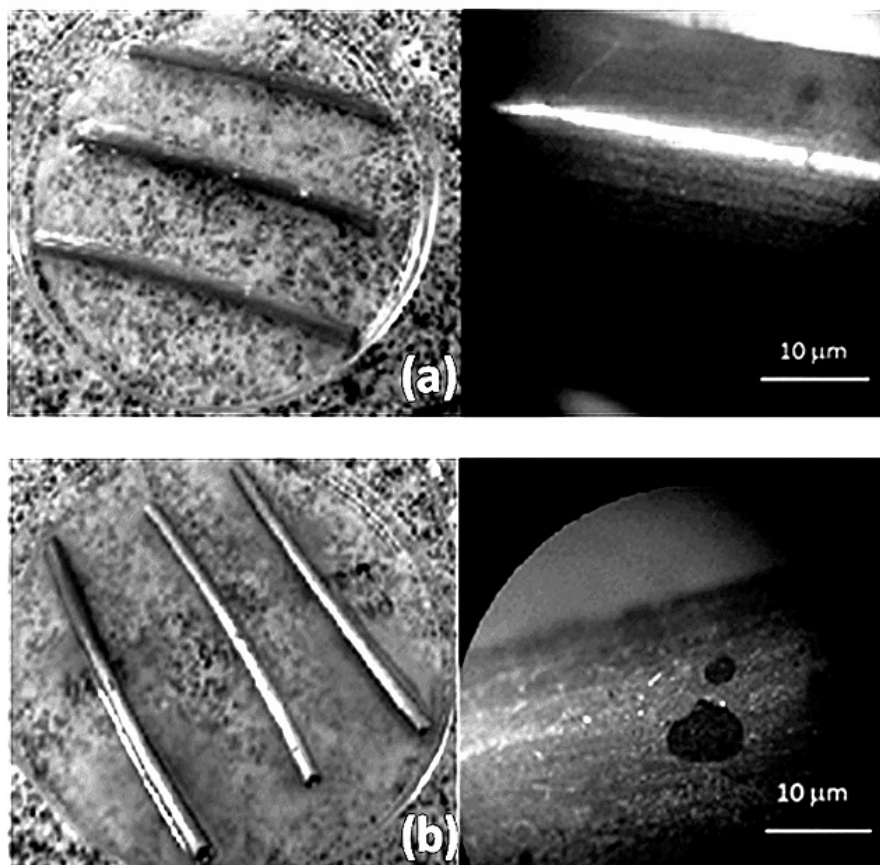


Figure 2.

(a) Visual outcome by optical microscopy of the surface of the steel with polystyrene (PS) coating after a six-month saline test for corrosion; (b) visual outcome by optical microscopy of the surface of the steel with starch after 2 weeks of analysis of saline corrosion.

Figure 2 b presents the visual outcome of the surface of the ASTM 1080 steel with the starch coating showed signs of corrosion after 2 weeks in the saline solution test, but it is important to note that the film dissolved differently on the surface. In the range of 2 weeks, there was no significant visual change in the starch film over the ASTM 1080 steel. Conclusively, it was observed by optical microscopy that there was collapse of the starch coating after 2 weeks of its application on the steel surface. There were no alterations in the PS coating until 6 months.

By ABNT NBR 5915-2:2013 standard and visual corrosion results, as shown in Figure 2 a and Figure 2 b, polystyrene on steel can cover a thin cold-rolled steel sheet forming the same quality as EEP grade (protecting until 6 months) and starch on steel can cover a thin cold-rolled steel sheet forming the same quality as EM grade (protecting until 2 weeks)^[2].

For the uniformity analysis of polystyrene film coating on the ASTM 1080 steel, an analysis of wettability was performed. Polystyrene wettability results indicated a contact angle of about 45.0° and a film thickness of about 40 μm (Figure 3 a, by scanning electron microscopy analysis). In Figure 3 a, the carbon sign in the steel was not revealed in the EDS spectrum due to its low intensity compared to the starch and

PS coatings. A good covering of polystyrene film-toluene was obtained on the surface of the ASTM 1080 steel (Figure 4 a). The Dektak II results of film thickness indicated a thickness between $34\text{ }\mu\text{m}$ to $43\text{ }\mu\text{m}$ with a low average roughness value of $(0.7 \pm 0.4)\text{ }\mu\text{m}$ and a diversion of RMS roughness by atomic force microscopy (AFM) of 35 nm (Figure 5 a).

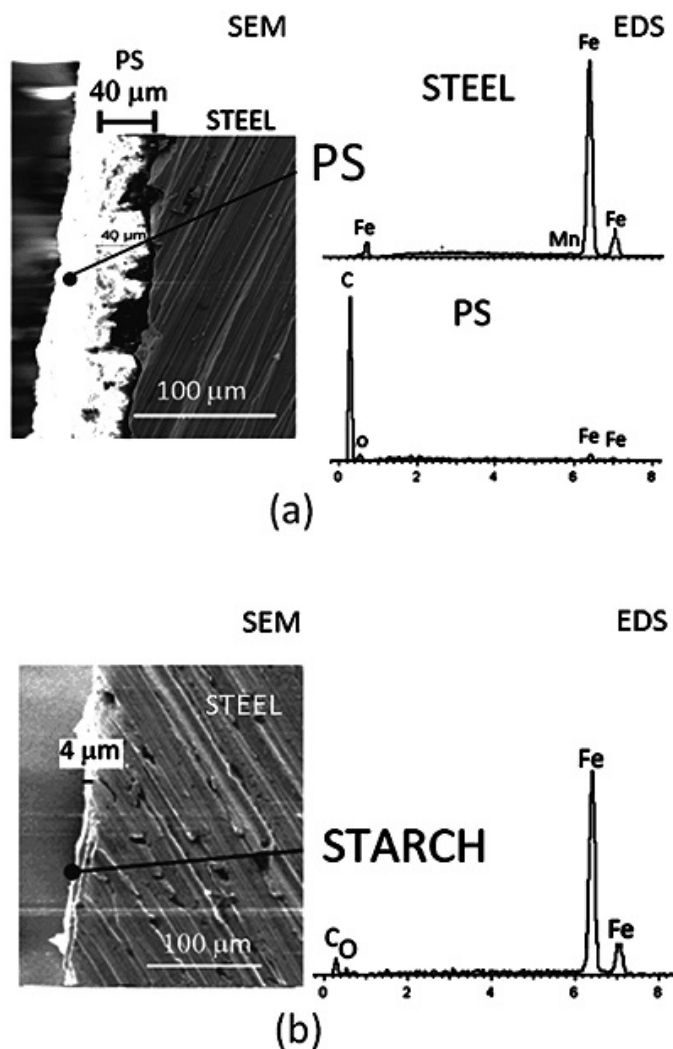
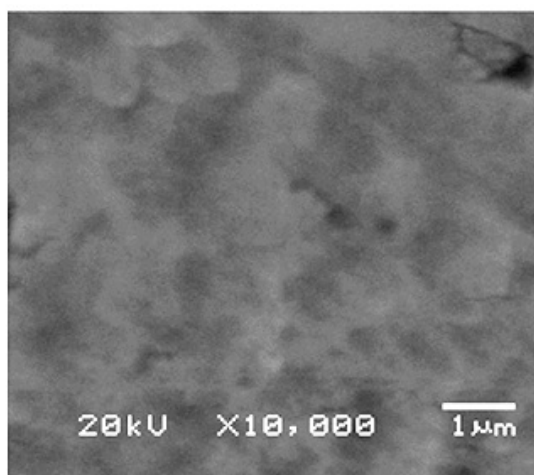
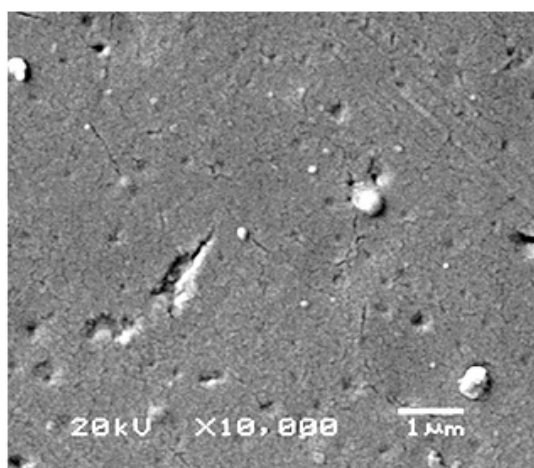


Figure 3.

(a) Photomicrography for secondary electrons $600\times$ substrate profile (SEM) of anticorrosive film of polystyrene (PS) on ASTM 1080 steel (Steel) and the energy-dispersive X-ray spectroscopy spectrum (EDS) for ASTM 1080 steel (Steel) and polystyrene (PS); (b) photomicrography for secondary electrons $600\times$ substrate profile (SEM) of anticorrosive film of starch (Starch) on ASTM 1080 steel (Steel) and the energy-dispersive X-ray spectroscopy (EDS) only to the spectrum for starch.



(a)



(b)

Figure 4.

(a) Photomicrography for secondary electrons 10,000× anticorrosive film of polystyrene (PS) on ASTM 1080 steel; (b) Photomicrography for secondary electrons 10,000× of anticorrosive film of starch (Starch) on substrate of ASTM 1080 steel.

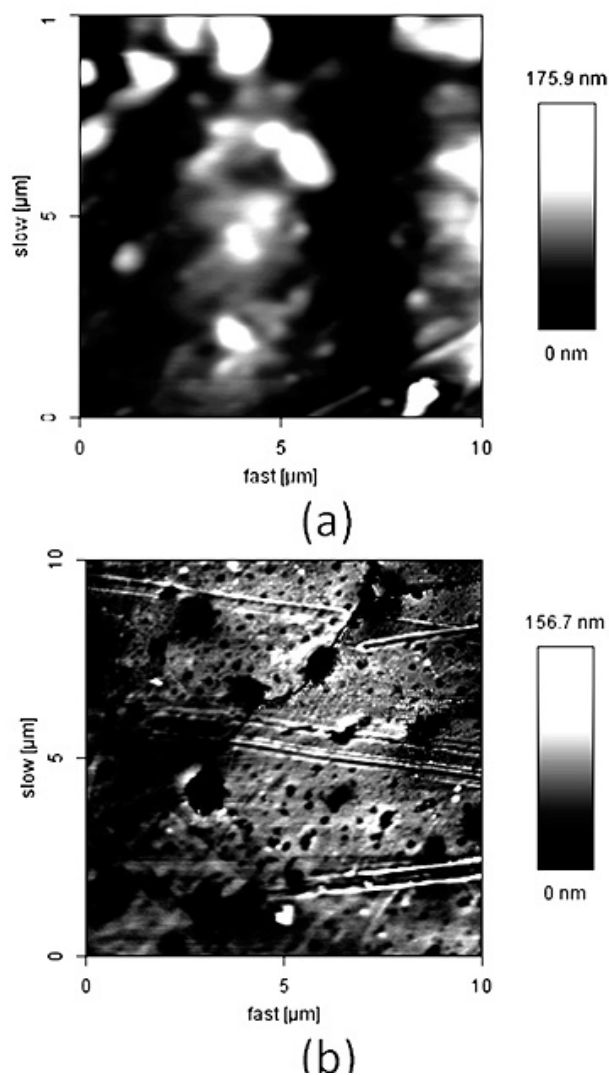


Figure 5.

- (a) AFM height image for polystyrene surface on steel;
- (b) AFM height image for starch surface on steel.

For the uniformity analysis of the starch-coated film on the ASTM1080 steel, it was made sure that the wettability analysis indicated a contact angle of about 50° (contact angle analysis) and a thickness of about $4 \mu\text{m}$ (Figure 3 b, analysis by electron microscopy by scanning). Then there was the possibility of a good spreading of starch film on the surface of the ASTM 1080 steel (Figure 4 b). The results of Dektak II indicated a thickness between 3 to $4 \mu\text{m}$ with a low average roughness value of $(0.7 \pm 0.4) \mu\text{m}$ and a range of RMS roughness by atomic force microscopy (AFM) of 150 nm (Figure 5 b).

4. Conclusions

As the optical and electronic microscopy results showed that the film was uniform and had a thickness of about $40 \mu\text{m}$, polystyrene film offers effective protection against corrosion and has good coverage on the

steel surface by saline chamber and results of contact angle (polystyrene presents good wettability on the ASTM 1080 steel). It also presented similar performance to that EEP grade of ABNT NBR 5915-2:2013 standard.

The starch-produced coating is attributed to the precipitation of amylose-lipid complexes that are formed after starch gelatinization and presents itself by microscopy results as uniform and with a thickness about 4 μm . Starch coating revealed effective corrosion protection for up to 2 weeks, as tested in saline solution. It also presented similar performance to that EM grade of ABNT NBR 5915-2:2013 standard.

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