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ELECTRODEPOSITION OF ADHERENT POLYANILINE-POLYPYRROLE COMPOSITE COATINGS ON LOW CARBON STEEL

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Uniform and adherent polyaniline-polypyrrole composite coatings were electrochemically polymerized on low carbon steel under aqueous conditions. The structure of the coatings was analyzed as a function of electrochemical deposition parameters (molar feed ratio of monomers and reaction time). X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition of the coatings and also the amount of dopants (oxalate ions) incorporated into the polymeric coatings. The morphology of the coatings was studied using scanning electron microscopy (SEM). The adhesion strength of the coatings was measured using simple lap joint tests. The composite coatings formed by an equimolar feed of the monomers were much more adherent than the homopolymeric coatings.

Keywords: Polyaniline; Polypyrrole; Composite coatings; Adhesion; Low carbon steel; Electrodeposition

INTRODUCTION

Conducting polymers such as polyaniline and polypyrrole have shown a wide range of applications due to their very interesting physical

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properties. Some of their important properties include electrical conductivity, electroactivity, electrochromism, environmental stability, chemical stability, and corrosion inhibition. Due to these properties, they are widely used in rechargeable batteries, electrochromic displays, ion-exchangers, pH sensors, gas sensors, and primers for corrosion protection of steel and aluminum.

Many metals such as steel, aluminum, copper, magnesium, etc. are very susceptible to corrosion. A commonly used technique to improve the corrosion resistance of metals involves passivating the metal surface by means of a heavy chromate treatment [1]. A phosphate conversion coating in conjunction with a chromate rinse is generally applied to improve paint adherence and provide corrosion protection. But such treatments are undesirable as they are highly toxic and carcinogenic.

There has also been a growing interest in the formation of special organic coatings with exceptional corrosion-resistant properties. Conducting polymers such as polyaniline and polypyrrole have shown a lot of promise. These polymers are coated on conductive substrates such as mild steel and aluminum using electrochemical methods [2–4]. The main advantages of these systems are that they are highly compatible with organic topcoats such as epoxy- and polyurethane-based coatings. It is believed that these coatings help in stabilizing a thin oxide layer on top of the metal, thereby causing prevention of corrosion [5]. Most of the work on conducting polymers has been done using inert metal electrodes. The major drawbacks of these polymers are that they are sparingly soluble in most common organic solvents and have very poor processibility. This difficulty can be overcome by directly forming these coatings on the desired substrates. The electrochemical method is a simple and easy way to form conducting polymeric coatings on steel and aluminum.

X-ray photoelectron spectroscopy (XPS) has been widely used as a characterization tool to study the structure of conducting polymers. In particular, XPS has been used as a quantitative tool to determine the amount of dopants incorporated in the conducting polymers. There have been numerous investigations of the structure of polyaniline and polypyrrole using X-ray photoelectron spectroscopy [6–11]. Kang et al. have shown that the N1s spectra of both polyaniline and polypyrrole contain four different components. The presence of amine ($-\text{NH}-$) and imine ($-\text{N}=\text{}$) components can be identified by the peaks at binding energies of 398.2 eV and 399.6 eV, respectively. The N1s spectrum also gives information about protonated amines (polaronic and bipolaronic form) by the presence of peaks at binding energies greater than 400 eV [11].

XPS analysis of polyaniline and polypyrrole formed using oxalic acid as the electrolyte has also been reported [12, 13]. The incorporation of oxalate ions as dopants can be detected by the presence of a peak at a binding energy of 288.6 eV (C_{ox}) in the C1s spectrum and also by a peak at a binding energy of 531.5 eV (O_{ox}) [12]. The incorporation of the oxalate ions is further confirmed by the fact that the ratio of these two peaks is exactly 0.5 (C_{ox}/O_{ox}) [13].

In our previous investigation, we reported a systematic investigation of the development of the passive layer (iron (II) oxalate) and showed that these coatings are formed by diffusion-controlled 3-d instantaneous nucleation [2, 14]. We have also reported a systematic investigation of the development of polyaniline-polypyrrole composite coatings on low carbon steel using aqueous oxalic acid as the supporting electrolyte [15]. In addition to this, it has also been demonstrated that polyaniline-polypyrrole composite coatings show much better corrosion performance than the homopolymeric coatings themselves [16].

In this investigation, we gained more insight into the surface structure of polyaniline-polypyrrole composite coatings using X-ray photoelectron spectroscopy. The adhesion of the polymeric coatings to the steel substrate was also measured by using lap joint tests.

EXPERIMENTAL

Chemicals

Two different kinds of monomers were used for the synthesis. Aniline (99.5% pure) and pyrrole (98% pure) were purchased from Aldrich Chem. Co., Milwaukee, WI. The supporting electrolyte that was used for the electropolymerization was oxalic acid (98% pure) and was also purchased from Aldrich Chem. Co. A known concentration of monomers and the supporting electrolyte were dissolved in aqueous media and used as the electrolyte for the electropolymerization.

Electrodes

The electrochemical polymerization was done using two counter electrodes or cathodes made of stainless steel. A 0.5 mm thick noninert electrode made of QD low carbon steel (99.9% Fe, 0.1% C), purchased from Q-Panel (Cleveland, OH), was used as the working electrode or anode to study the formation of polyaniline-polypyrrole composites. The low carbon steel purchased from Q-panel was ultrasonically cleaned for 15 minutes using methanol. The reference

electrode used was a saturated calomel electrode (SCE) purchased from Fisher Scientific.

Electropolymerization

A model 273A potentiostat/galvanostat purchased from EG&G Princeton Applied Research (Princeton, NJ) was used as the source to apply a constant potential difference between the working electrode and the counter electrodes. Aqueous electropolymerization was performed using a single compartment polypropylene electrochemical cell as shown in Figure 1. Controlled potential coulometry was used to form polyaniline-polypyrrole composite coatings on steel. The applied potential was varied from 0.8 V to 2.0 V *versus* SCE. The initial concentration of the comonomers (aniline and pyrrole) was varied from 1:9 to 9:1, respectively. The concentration of oxalic acid was kept constant at 0.2 M. The volume of the aqueous solution used for each experiment was 200 ml, and the area of the coated substrate was 20 cm². The coated samples were obtained by stopping the electrochemical reaction at predetermined reaction times. At the end of each experiment, the coated substrate was removed from the solution and rinsed thoroughly with methanol, so as to eliminate any loosely bound

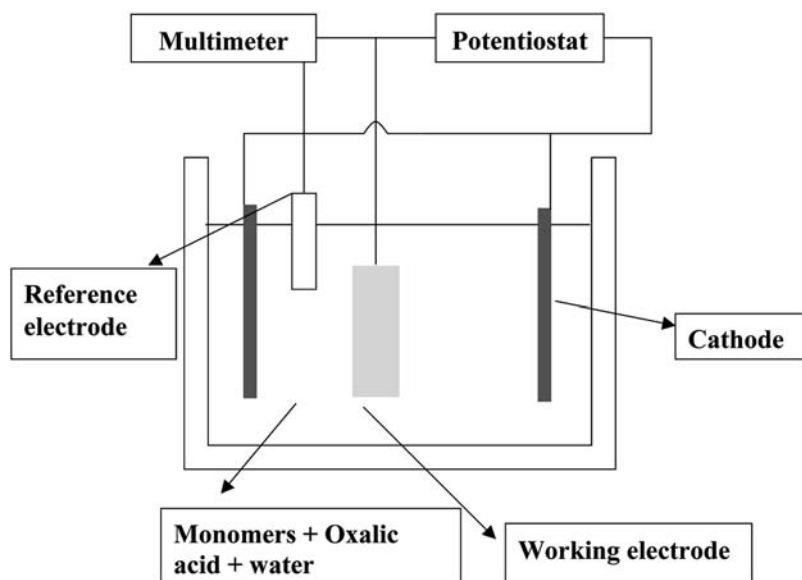


FIGURE 1 A single compartment electrochemical cell.

species. The sample was then dried in an oven at 100°C for about 2 hours.

Infrared Spectroscopy

The chemical structure of the electrochemical coatings that were formed was characterized using Fourier transform infrared (FTIR) spectroscopy. The coatings formed on low carbon steel were characterized using an FTS-40 BioRad reflectance absorption infrared spectroscopy (RAIR) instrument. All the RAIR spectra were taken at a resolution of 8 cm⁻¹, from 4000 cm⁻¹ to 400 cm⁻¹. The total number of scans done for each sample was 256. An angular specular reflectance attachment was set to an angle of 60°. A background spectrum of a bare-polished steel substrate was subtracted from the acquired spectra in all cases.

Scanning Electron Microscopy

The morphology of the coated samples was examined using a JEOL scanning electron microscope. All the micrographs were taken at an accelerating voltage of 15 KV, at a working distance of 25 mm from the detector. The morphology of the coatings was studied as a function of reaction time, applied potential, and feed ratio of monomers.

X-ray Photoelectron Spectroscopy

A Perkin–Elmer Model 5300 XPS spectrometer with Al K α X-rays, operating at 300 W and 15 KV DC, was used to obtain XPS spectra. An Apollo computer system with Perkin–Elmer software was used for data acquisition and processing. XPS spectra were recorded at take-off angles of 15°, 45°, and 75°. Surface elemental stoichiometries were obtained from the peak area ratios corrected with the appropriate experimentally determined sensitivity factors. The carbon 1s (C1s), oxygen 1s (O1s), and nitrogen 1s (N1s) spectra were fitted to Gaussian component peaks of equal full-width at half maximum (FWHM). The position and intensity of component peaks were optimized to give the best fit to the experimental spectrum. The binding energies are quoted relative to hydrocarbon C1s at 284.6 eV.

Lap Joint Tests

The adhesion of the polymeric coatings to the steel substrates was determined by lap joint tests. The adhesion strength was evaluated

according to ASTM standard procedure D1002-72. Pairs of coupons ($2.54 \text{ cm} \times 10.16 \text{ cm} \times 0.16 \text{ cm}$) were bonded together to form lap joints with an overlap length of 0.5 inches. The adhesive that was used to bond the two coupons consisted of an epoxy (EPON 828) and a polyamide-curing agent (EPI-CURE 3140). The tests were performed in an Instron machine with a speed of 1.27 mm/min.

RESULTS AND DISCUSSION

Infrared Spectroscopy

Figure 2 shows the comparison of the infrared spectra of polyaniline-polypyrrole composite coatings on steel with the homopolymeric coatings. Polyaniline shows characteristic peaks at 1600, 1500, 1300, and 830 cm^{-1} (Figure 2a), which are characteristic of the emeraldine form of polyaniline. These peaks are due to benzenoid groups, quinoid groups, aromatic NH deformation, and p-substituted benzene ring, respectively [17]. On the other hand, polypyrrole shows characteristic peaks at 1500 (C–N), 1400 (N–H def.), 1050, 960, and 790 cm^{-1} (Figure 2c). The assignment for the peaks are 1500 (C–N), 1400 (NH def.), 1050, and 790 cm^{-1} (pyrrole ring def.). The infrared spectrum of polyaniline-polypyrrole composite coatings shows very broad peaks in

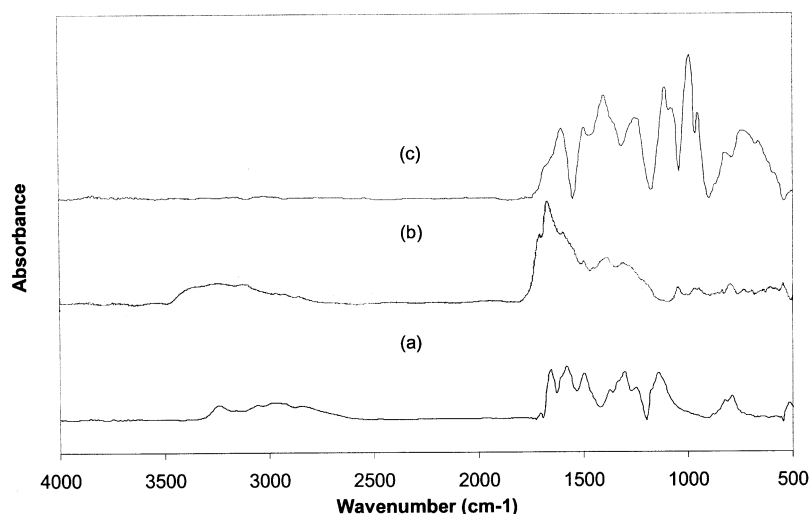


FIGURE 2 Infrared spectra of conducting polymeric coatings on low carbon steel using oxalic acid as electrolyte: (a) polyaniline, (b) polyaniline-polypyrrole, and (c) polypyrrole composite coatings.

the range of 1600–1500 cm^{-1} . The incorporation of both polyaniline and polypyrrole is confirmed by the presence of peaks at 1300 and 1400 cm^{-1} , respectively (Figure 2b). The incorporation of the dopant ions (oxalate) can be seen by the presence of a peak at 1675 cm^{-1} . A detailed description of the infrared study of the development of polyaniline-polypyrrole composite coatings on steel is given in our previous investigation [15].

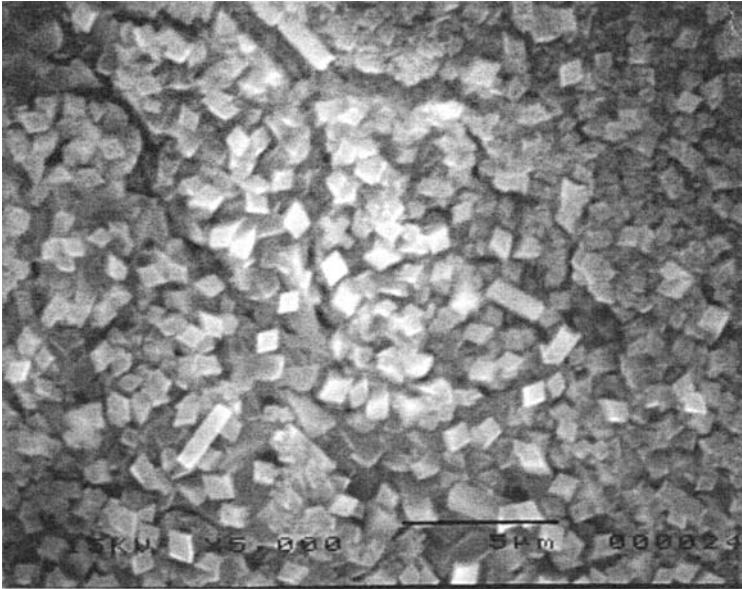
Scanning Electron Microscopy

At very short reaction times, inorganic crystals of iron (II) oxalate are formed on the surface of the steel as shown in Figure 3a. As the reaction time is increased, the inorganic crystals undergo dissolution and polymeric coatings are formed on the steel surface. A more detailed description of the development of the polymeric coatings on steel is given in our previous investigation [2, 14]. Figures 3b to 3d show the comparison of the SEM morphology of the composite coatings and the homopolymeric coatings. Polyaniline shows a granular morphology (Figure 3b) in contrast to polypyrrole, which has a globular morphology (Figure 3c). The composite coatings show distinct changes in morphology when compared with the homopolymeric coatings. The composite coatings have dense and compact structures, which may explain their superior adhesion and corrosion protection properties (Figure 3d).

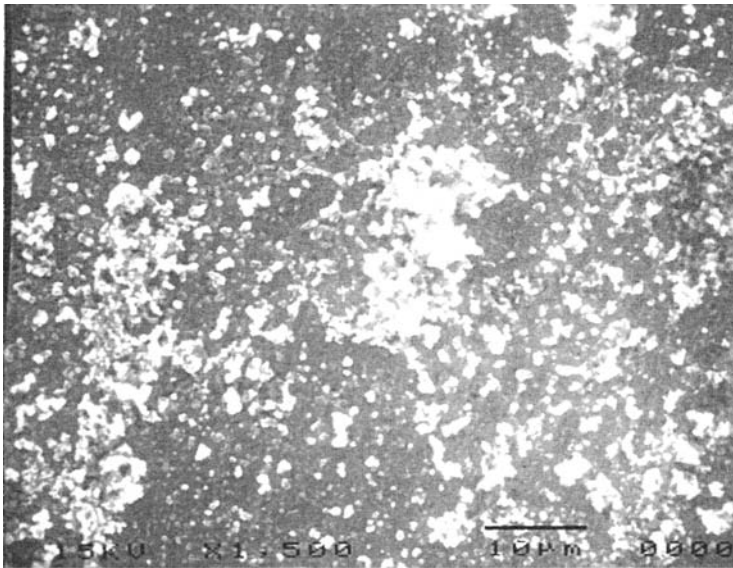
X-ray Photoelectron Spectroscopy

Figure 4 shows the survey spectrum of polyaniline-polypyrrole composite coatings. It was shown that C1s, O1s, and N1s signals are detected on the surface of the coatings. Figure 5 shows the atomic ratio as a function of the molar feed ratio of the monomers. When the concentration of aniline is higher, the ratio of C/N is very high. This suggests that the amounts of polymer formed under these conditions are less. It is also shown that the ratio of C/O is lower and Fe/N is higher. This suggests that there is partial dissolution of iron (II) oxalate and that some amount of iron (II) oxalate dihydrate is still present on the surface. As we increase the concentration of pyrrole in the solution, the ratio of C/N and Fe/N decreases, suggesting that the surface is fully covered by the polymer. On the other hand, the increase in the ratio of C/O and the presence of O are due to the incorporation of oxalate ions as dopants.

Figure 6 shows the deconvoluted high-resolution C1s spectrum of the composite coatings on steel. The XPS spectrum can be deconvoluted

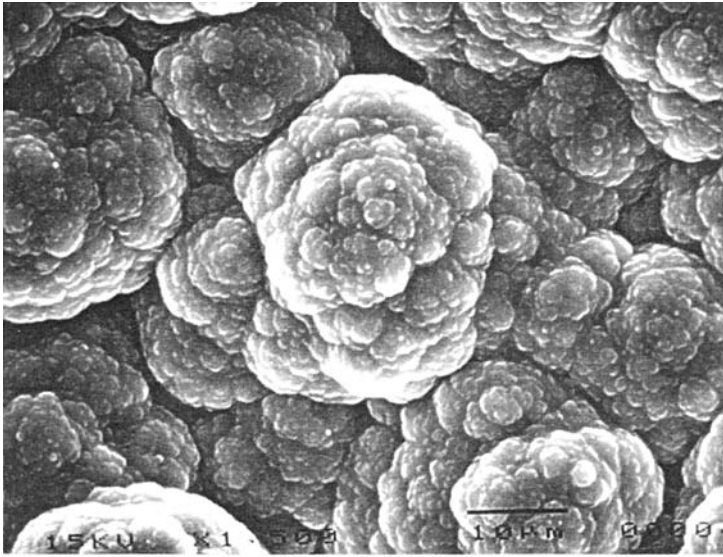


(a)

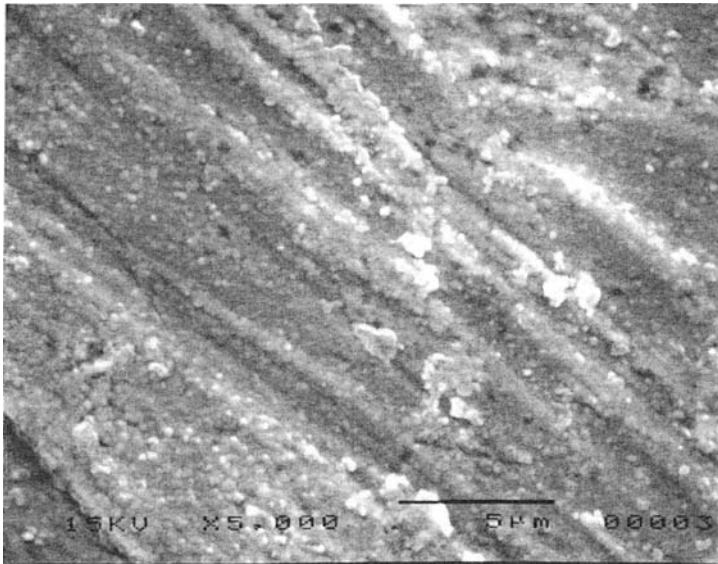


(b)

FIGURE 3 SEM micrographs of conducting polymeric coatings on low carbon steel using oxalic acid as electrolyte: (a) iron, (II) oxalate dihydrate, (b) polyaniline, (c) polypyrrole, and (d) polyaniline-polypyrrole composite coatings. (Continued.)



(c)



(d)

FIGURE 3 (Continued.)

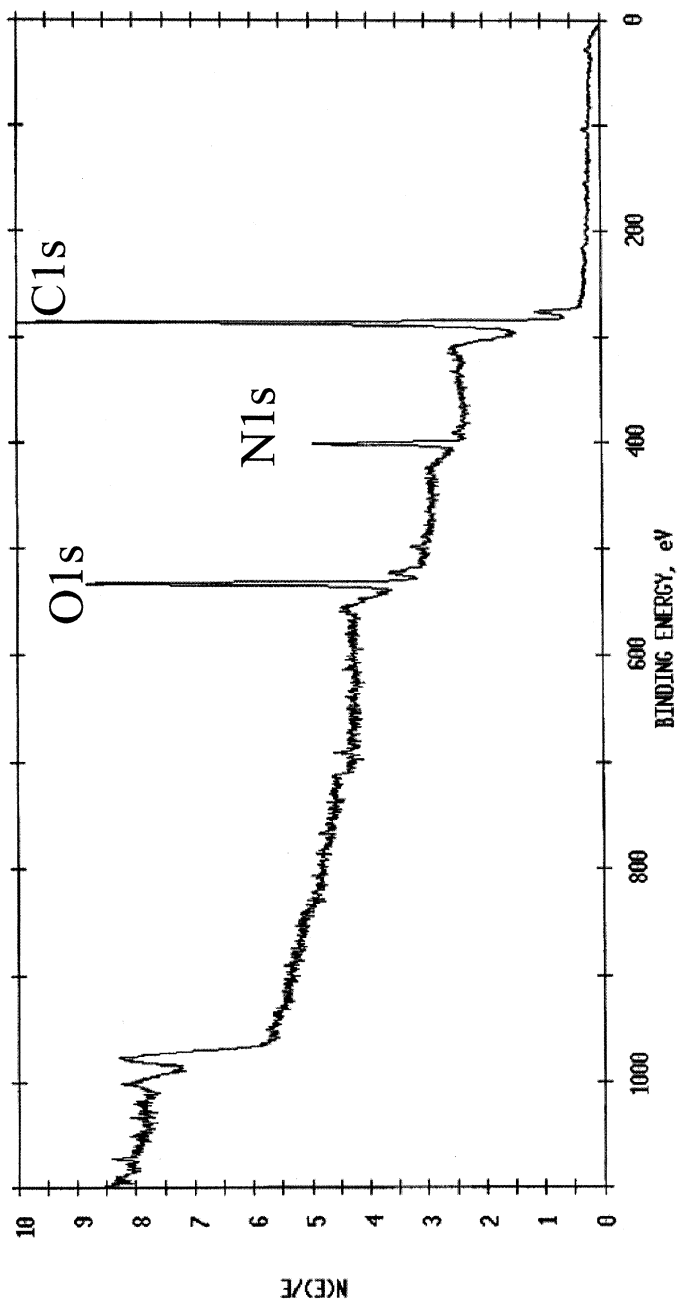


FIGURE 4 XPS survey spectrum of polyaniline-poly pyrrole composite coatings formed on low carbon steel using equimolar concentration (0.125 M) and oxalic acid (0.2 M) as electrolyte at an applied potential of 1.2 V *versus* SCE.

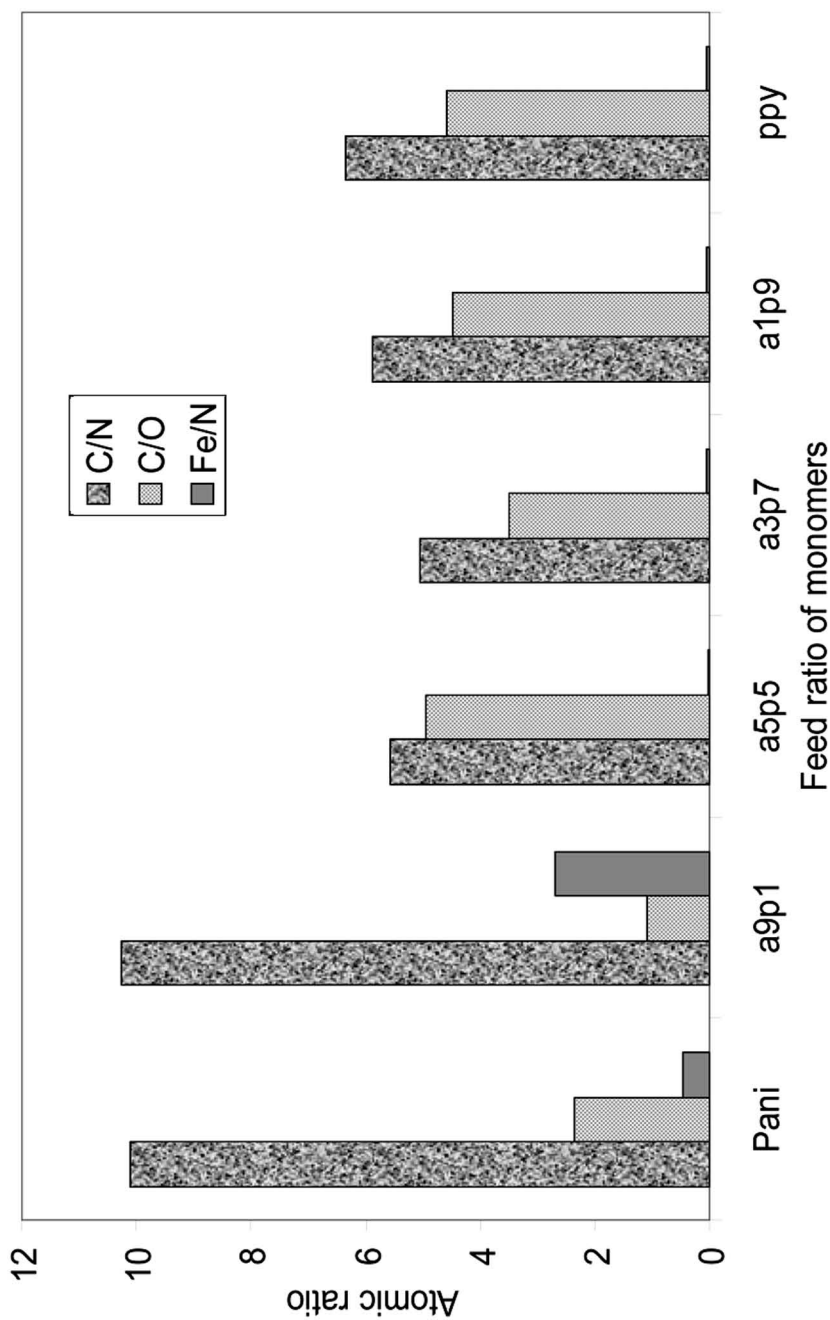


FIGURE 5 Atomic ratio as a function of molar feed ratio of monomers.

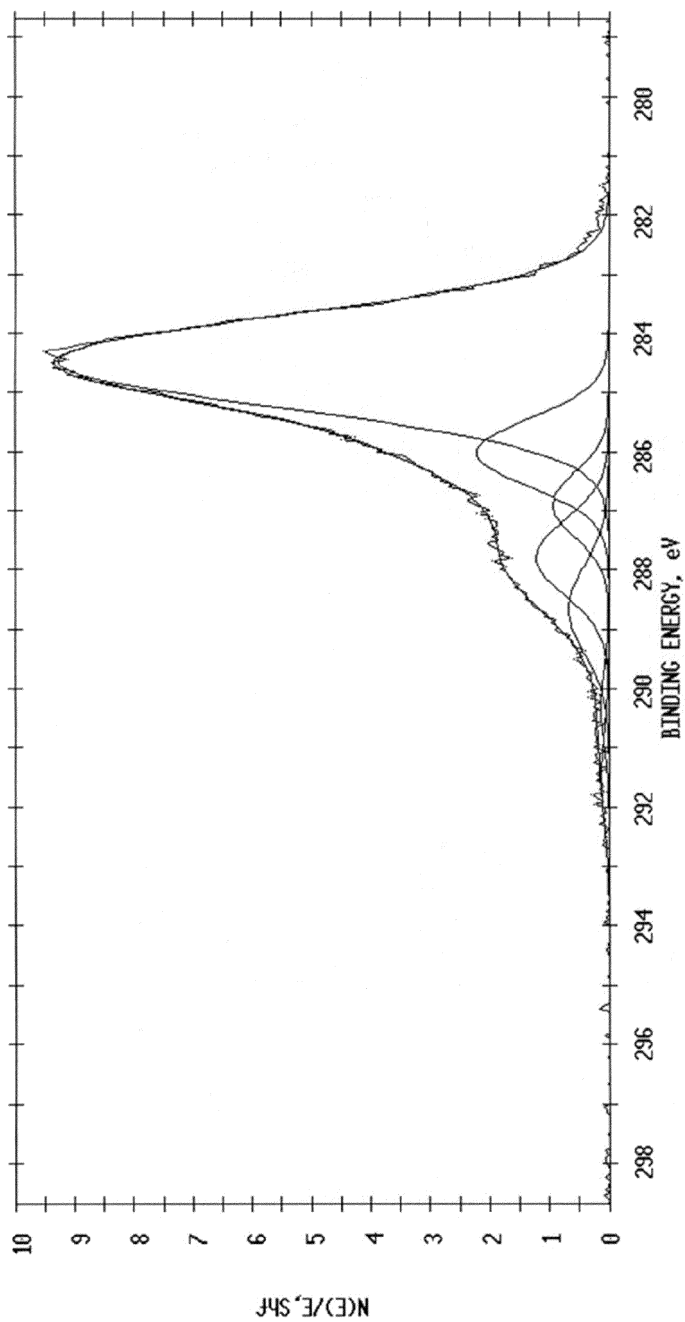


FIGURE 6 C1s spectrum of polyaniline-polypyrrole composite coatings formed on low carbon steel using equimolar concentration (0.125 M) and oxalic acid (0.2 M) as electrolyte at an applied potential of 1.2 V *versus* SCE.

into 7 components, at 284.6, 285.6, 286.2, 287.6, 288.6, 290, and 291.5 eV [17–23]. The main peak at 284.6 eV is attributed to the C–C/C–H groups present in polymer. The peaks at 285.6 eV and 288.6 eV (C_{ox}) are attributed to C–N groups and O–C=O groups, due to the oxalate which is incorporated in the film as a dopant. The peaks at 287.6 and 286.2 eV arise from contaminants in the polymer film and are due to the presence of C–O and C=O groups. There are two shake-up satellites at 290 and 291.5 eV, due to the presence of C–C groups and C–N groups, respectively.

Figure 7 shows the deconvoluted high-resolution O1s spectra of the coatings on steel. Figure 7a shows the O1s spectrum of the coatings

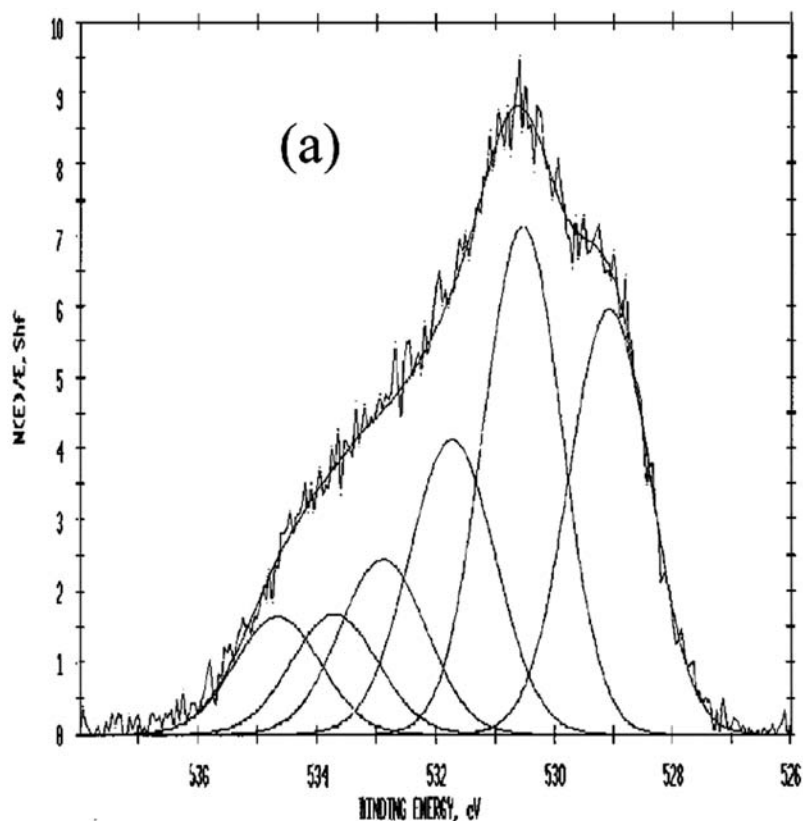


FIGURE 7 O1s spectrum of polyaniline-polypyrrole composite coatings formed on low carbon steel using equimolar concentration (0.125 M) and oxalic acid (0.2 M) as electrolyte at an applied potential of 1.2 V versus SCE. (Continued.)

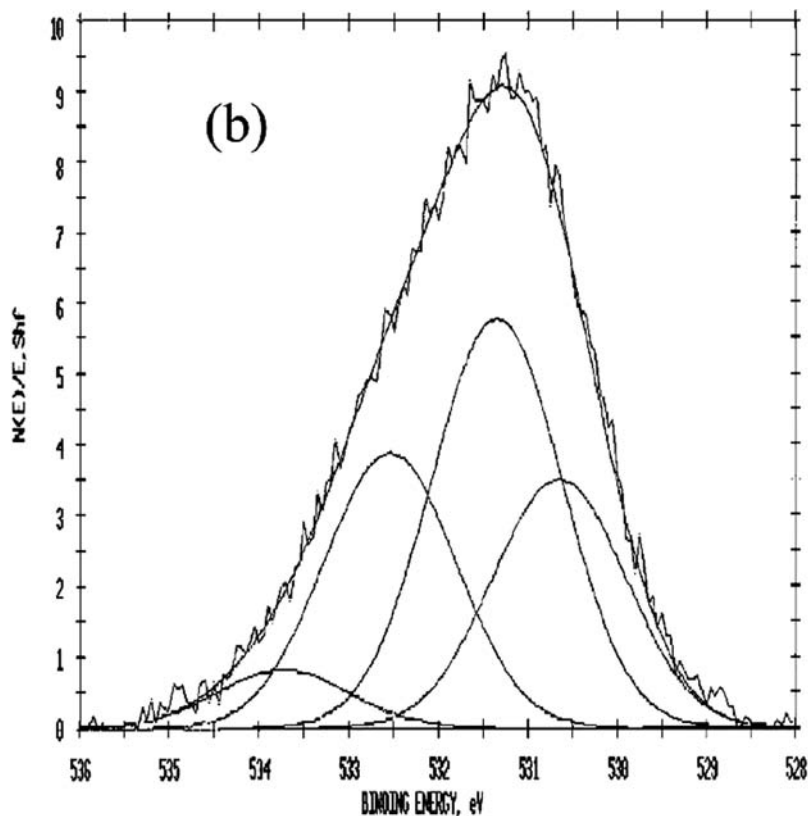


FIGURE 7 (Continued.)

formed on steel after 5 s of reaction. Infrared spectra (Figure 2) show that iron (II) oxalate dihydrate is formed under these conditions. The O1s spectrum was deconvoluted into 6 different components, at 529.2, 530.4, 531.4, 532.6, 533.6, and 534.5 eV, respectively. The peak at 531.4 (O_{ox}) and 533.6 eV is due to the presence of $O-C=O$ and $O-C=O$ groups present in the oxalate groups [12]. The presence of peaks at 529.2 and 530.4 eV shows the presence of impurities in the form of iron oxides (FeO , Fe_2O_3 , Fe_3O_4 , etc.), which is quite common when the reactions are done in aqueous conditions in a highly acidic environment in the presence of steel as an electrode. The presence of Fe is also detected from the survey spectrum, which shows an $Fe2p_{3/2}$ signal (Figure 8). The presence of peak at 532.6 eV is again due to the presence of contaminants and is attributed to the presence of $C=O$

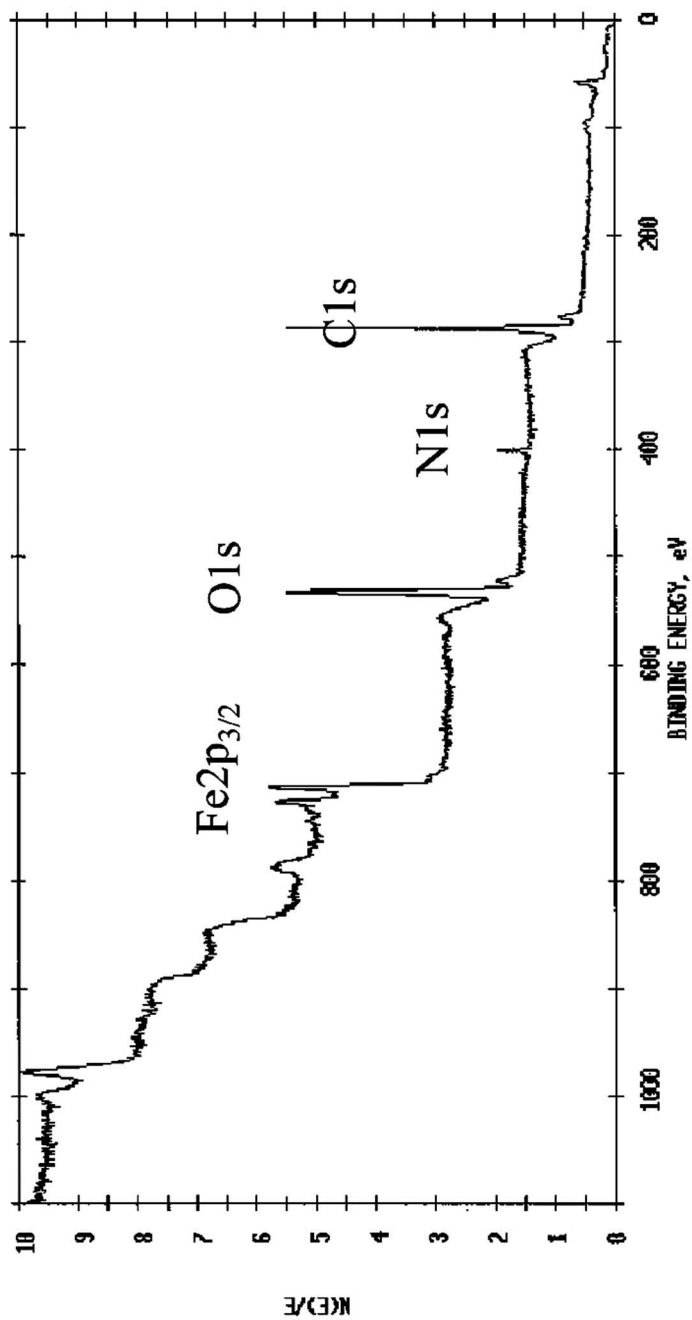


FIGURE 8 XPS survey spectrum of polyaniline-poly pyrrole composite coatings formed on low carbon steel using equimolar concentration (0.125 M) and oxalic acid (0.2 M) as electrolyte at an applied potential of 1.2 V *versus* SCE after 5 s of reaction.

groups. It was shown that the ratio of C_{ox}/O_{ox} was approximately 0.5 [13]. The peak at 534.5 eV is due to the presence of H_2O .

Figure 7b shows the O1s spectrum of the composite coatings formed on steel. The XPS spectrum can be deconvoluted into 4 components, namely 530.2, 531.4, 532.6, and 533.6 eV. The presence of these peaks indicates the incorporation of oxalate ions as dopants (531.4 and 533.6 eV) and presence of oxides and oxyhydroxides of iron.

Figure 9 shows the N1s spectrum of the composite coatings on steel. The XPS spectrum can be deconvoluted into 4 components, at 398.2, 399.6, 401.2, and 402.4 eV, respectively. These peaks are due to the presence of imine, amine, and protonated amine groups, respectively. It is interesting to note that the imine component of the N1s spectrum is much broader than the other two components. This is also in agreement with the results of infrared spectroscopy, which suggest broadening of the peaks in the region between 1500–1600 cm^{-1} . We believe that this broadening may be due to the presence of the imine groups of both polyaniline and polypyrrole. The individual components and their corresponding binding energies are summarized in Table 1.

Lap Joint Tests

From our previous investigation, we have shown that there are 4 distinct stages in the formation of polymeric coatings on steel, as follows [2, 14–16]:

- (a) dissolution of steel (Stage I),
- (b) formation of iron (II) oxalate dihydrate crystals (Stage II),
- (c) dissolution of iron (II) oxalate dihydrate crystals (Stage III),
- (d) formation of polymeric films (Stage IV).

Figure 10 shows the stress-strain curve of a lapjointed bare steel sample (control). It can be seen that the sample undergoes brittle failure and has an adhesion strength of 5.7 MPa. Figure 11 shows the stress-strain curve of the lapjointed samples as a function of feed ratio of monomers. It is shown that the samples undergo brittle failure for higher concentrations of both aniline and pyrrole. The sample prepared using an equimolar concentration of monomers showed ductile behavior. Figure 12 shows the adhesion strength of the coatings as a function of the feed ratio of monomers. The best results are obtained for coatings formed using a higher concentration of aniline. For an equimolar concentration of monomers, the adhesion strength of the

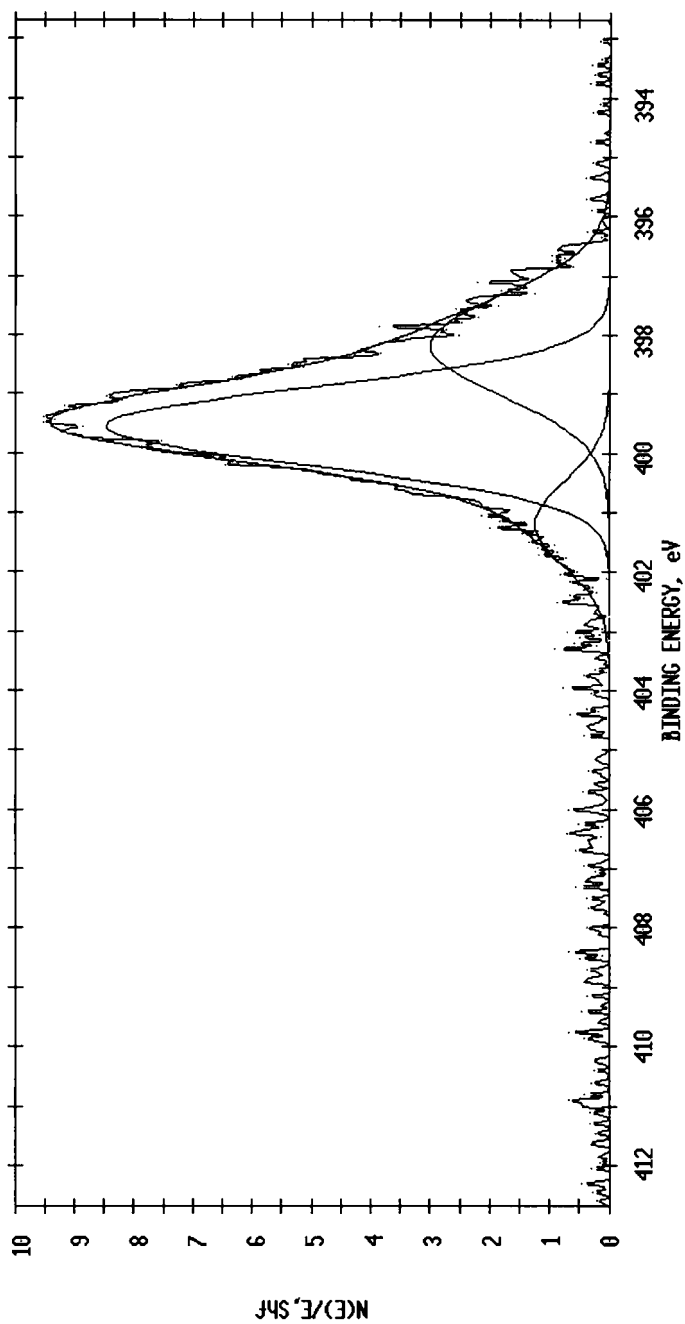


FIGURE 9 N1s spectrum of polyaniline-poly pyrrole composite coatings formed on low carbon steel using equimolar concentration (0.125M) and oxalic acid (0.2M) as electrolyte at an applied potential of 1.2 V *versus* SCE.

TABLE 1 Binding Energies and Their Components for Polyaniline-Polypyrrole Composite Coatings on Steel

Binding energies (eV)	Chemical composition
284.6	$\underline{\text{C}}-\text{C}$
285.6	$\underline{\text{C}}-\text{N}$
286.2	$\underline{\text{C}}-\text{O}$
287.6	$\underline{\text{C}}=\text{O}$
288.6	$\text{N}-\underline{\text{C}}=\text{O}$
398.2	$-\text{N}=\text{}$
399.6	$-\text{NH}-$
401.2	$-\text{N}^+$
530.2	Oxides of iron
531.4	$\underline{\text{O}}-\text{C}=\text{O}$
532.6	$\text{C}=\underline{\text{O}}$
533.6	$\text{O}-\text{C}=\underline{\text{O}}$

composite coatings is almost three times that of the control (uncoated samples).

The adhesion strength of the composites formed using an equimolar concentration of monomers was also studied as a function of reaction time. This was again done in an effort to understand the relationship between the chemical structure and the adhesion strength of the coatings. Figures 13 and 14 show the stress-strain curves, adhesion strength, and toughness of the composite coatings formed using an equimolar concentration of monomers as a function of reaction time. At very small reaction times (5 s) (Stage II), the adhesion strength of the coatings is even lower than the control and the sample undergoes brittle failure. This suggests that the iron (II) oxalate dihydrate crystals are not very adherent to steel. As the reaction proceeds, the adhesion strength and the fracture energy increases (Stages III and IV) and the sample starts to show ductile behavior. Thus, fully developed composite coatings show better adhesion performance than iron (II) oxalate dihydrate crystals.

Figure 15 shows the RAIR spectra of the fractured sample formed using an equimolar concentration of monomers. This is compared with the RAIR spectra of an epoxy-coated bare steel sample. It can be seen that the peaks due to the epoxy coating are clearly present on side 1 of the fractured composite coatings sample. It is also interesting to see that both sides have peaks in the region $3000\text{--}3400\text{ cm}^{-1}$ (secondary amine groups). The peaks due to the dopant and imine groups are clearly seen on side 2 (1670 and 1600 cm^{-1}).

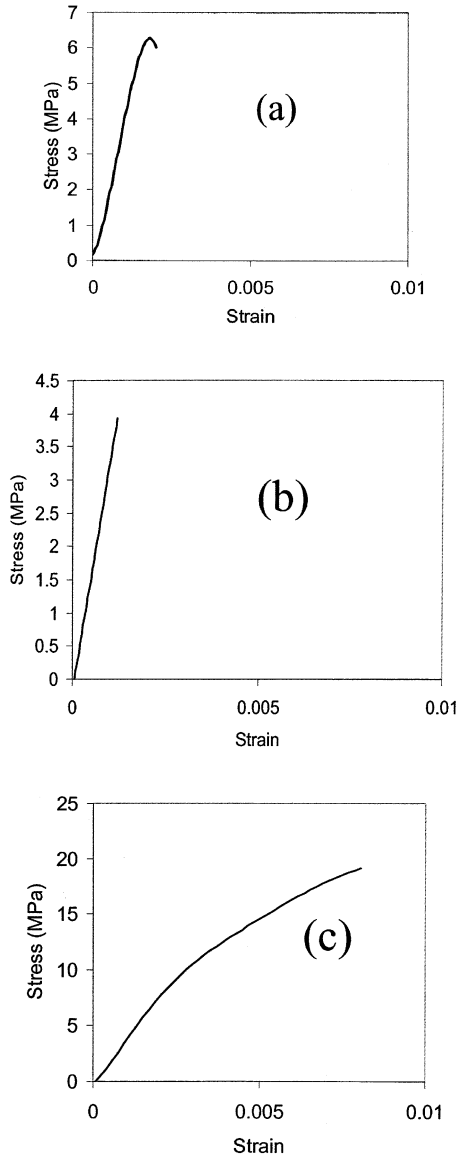


FIGURE 10 Stress-strain curves of lapjointed samples: (a) uncoated low carbon steel samples, (b) iron (II) oxalate dihydrate coated steel, and (c) polyaniline-polypyrrole composite coated steel.

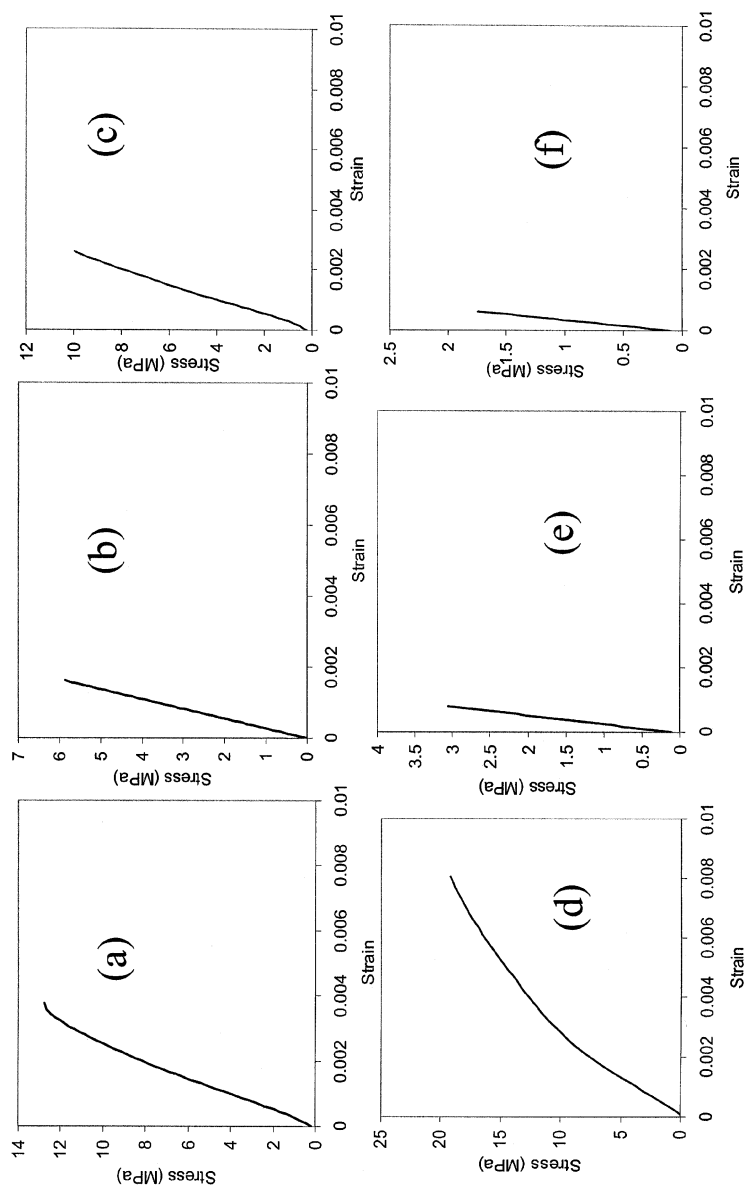


FIGURE 11 Stress-strain curves of lapjointed samples as a function of feed ratio of monomers for good corrosion-resistant properties: (a) polyaniline, (b) aniline-90% and pyrrole-10%, (c) aniline-70% and pyrrole-30%, (d) aniline-50% and pyrrole-50%, (e) aniline-30% and pyrrole-70%, and (f) polypyrrole.

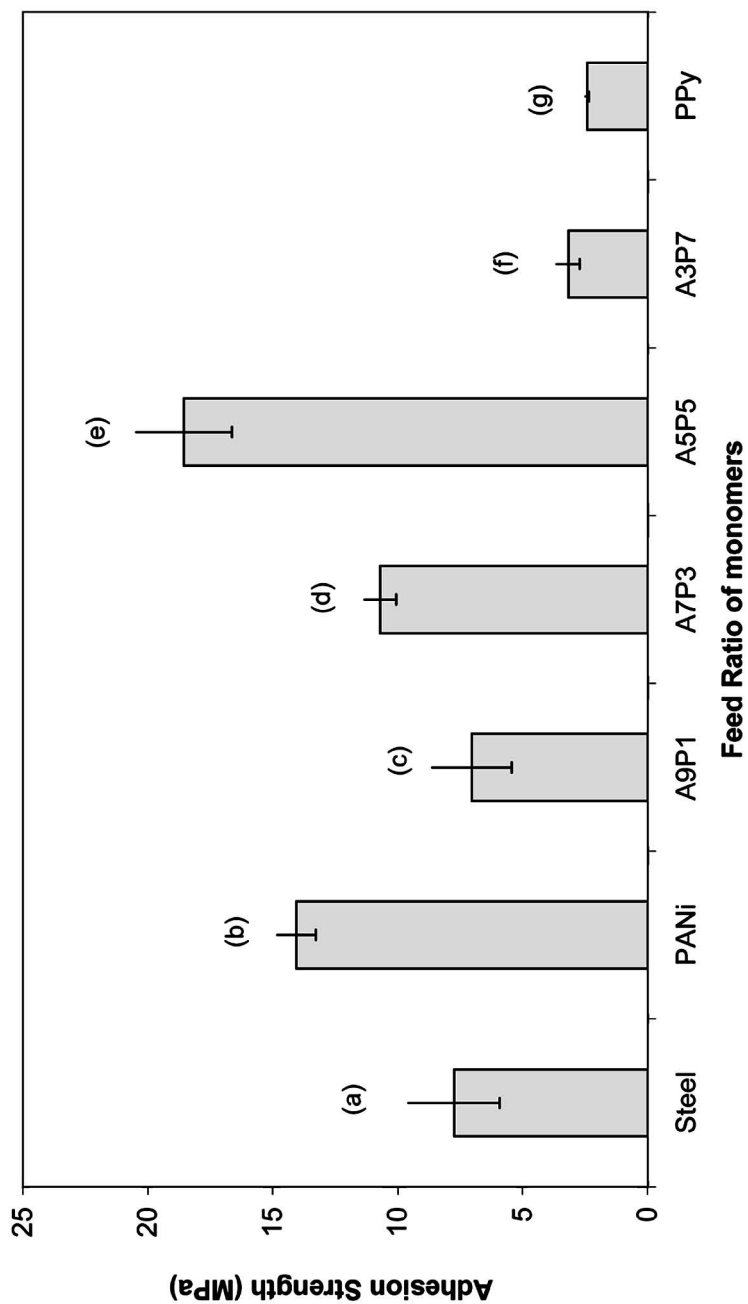


FIGURE 12 Adhesion strength of coatings formed as a function of feed ratio of monomers using oxalic acid as electrolyte: (a) low carbon steel, (b) polyaniline, (c) aniline-90% and pyrrole-10%, (d) aniline-70% and pyrrole-30%, (e) aniline-50% and pyrrole-50%, (f) aniline-70% and pyrrole-30%, and (g) polypyrrole.

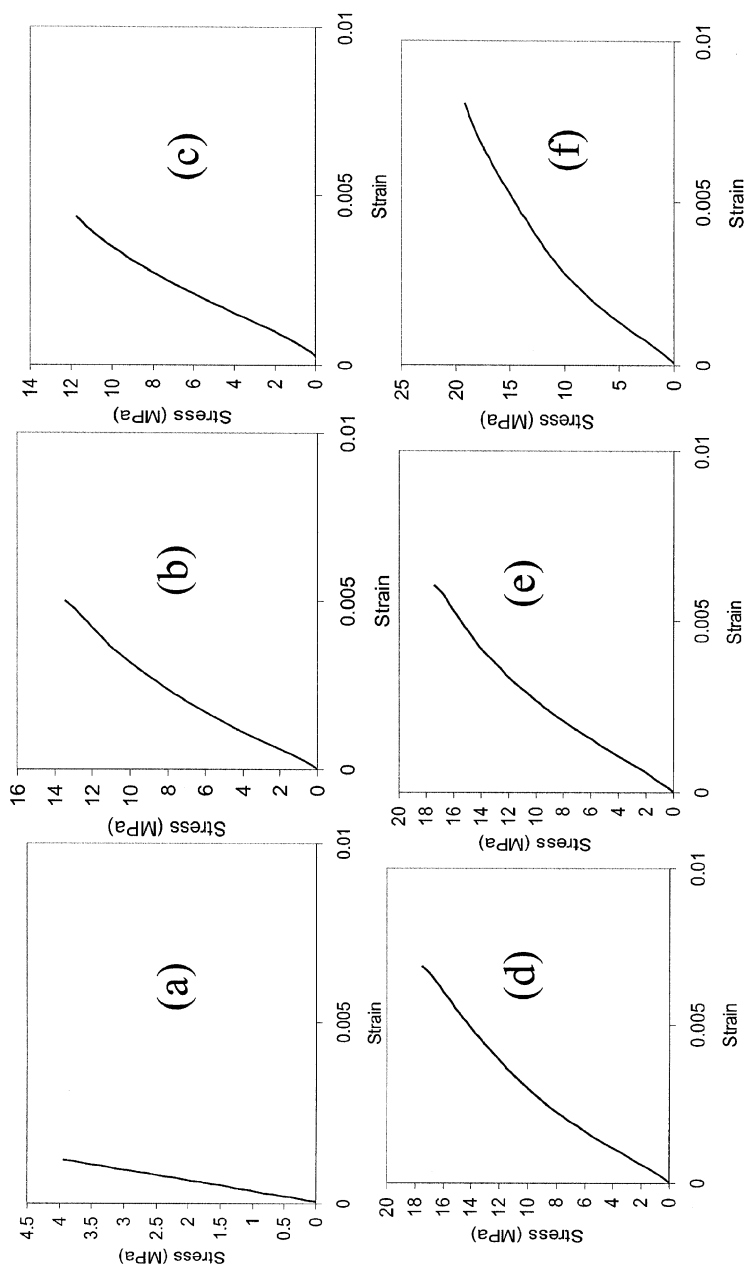


FIGURE 13 Stress-strain curves of lap-jointed samples formed using equimolar feed ratio of monomers at an applied potential of 1.2V versus SCE using oxalic acid as electrolyte: (a) 5 sec, (b) 100 sec, (c) 200 sec, (d) 400 sec, (e) 600 sec, and (f) 900 sec.

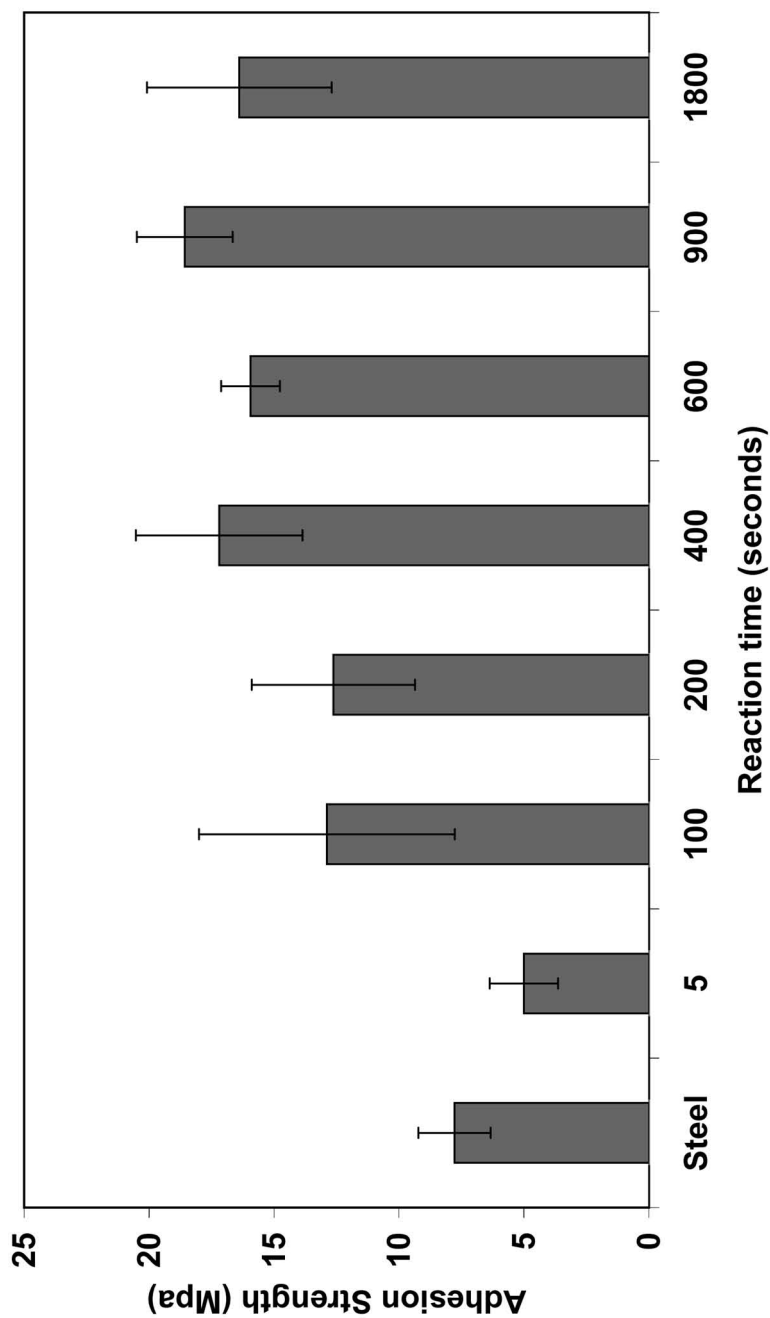


FIGURE 14 Adhesion strength of polyamine-poly pyrrole composite coatings formed with equimolar feed ratio of monomers at an applied potential of 1.2V *versus* SCE using oxalic acid as electrolyte as a function of reaction time.

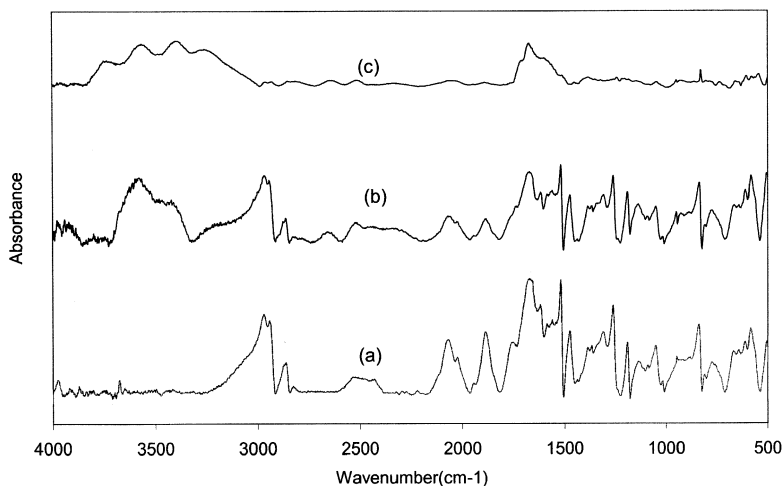


FIGURE 15 RAIR spectra of fractured sample formed with equimolar concentration of monomers at an applied potential of 1.5V *versus* SCE using oxalic acid as electrolyte: (a) fractured uncoated sample, (b) side 1, and (c) side 2.

This suggests that there is a cohesive failure of the coatings and the failure probably occurs in a mixed mode. Figure 16 shows the comparison of the micrographs of the fractured control sample and the composite coatings. It is clearly seen that the composite coatings undergo cohesive failure, not adhesion failure, at the substrate.

CONCLUSIONS

An inorganic passive layer of iron (II) oxalate dihydrate is formed prior to the formation of polyaniline-polypyrrole composite coating on steel. As we increase the reaction time, this layer starts to dissolve and the polymeric coating starts to form. Spectroscopic and morphological studies show that there is a significant difference in the chemical structure and the morphology of composite coatings when compared with the homopolymeric coatings. Adhesion studies show that the composite coatings formed using an equimolar feed ratio of monomers are much more adherent than the homopolymeric coatings.

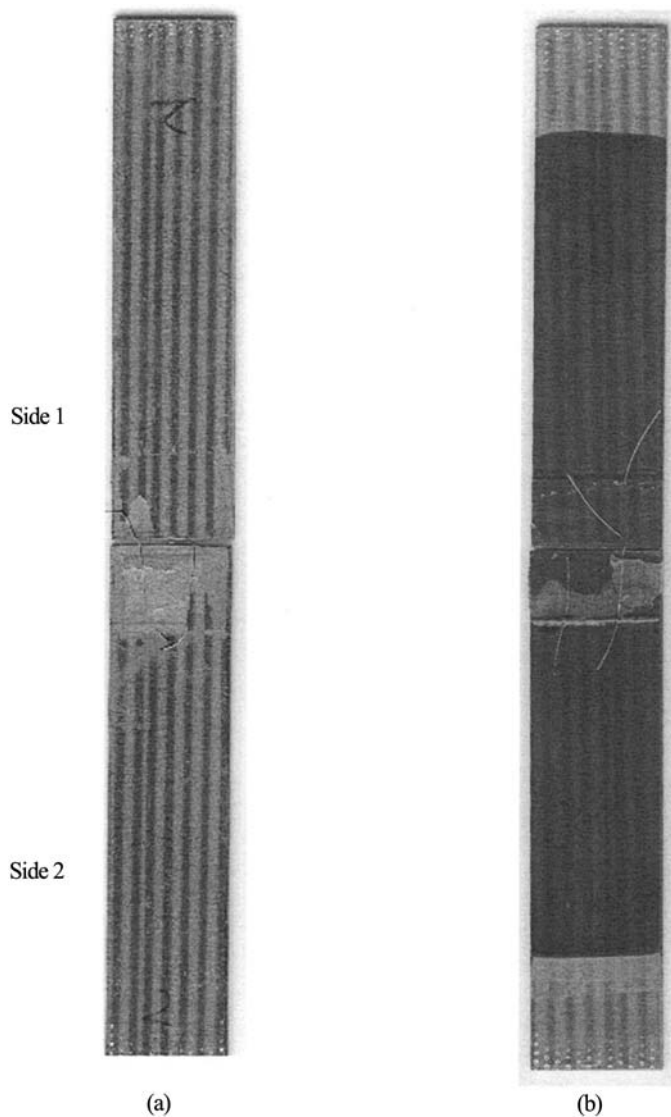


FIGURE 16 Micrograph of fractured lapjoint samples: (a) uncoated steel and (b) polyaniline-polypyrrole composite coated steel formed using equimolar feed ratio of monomers at 1.2V *versus* SCE.

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