Adhesion of Electrochemically Formed Polypyrrole Coatings to Low Carbon Steel

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ABSTRACT: The lap shear strength of polypyrrole coatings formed on low carbon steel ($\sim$ 23 MPa) is shown to be significantly higher (by $\sim$ 60%) than that obtained using uncoated steel as the adherend. The lap shear (adhesion) strength of polypyrrole-coated steel varied with the pH of the monomer–electrolyte solution and the applied current. The low carbon steel-containing polypyrrole coatings formed at low pH (pH $\leq$ 2.4) have higher adhesion strength than those coated with polypyrrole at higher pH (pH $\geq$ 6.0). However, poly(*N*-methyl pyrrole)-coated steel showed significantly lower adhesion strength. Increasing the applied current density decreased the adhesion strength. The surface free energies of polypyrrole coatings, $\sim$ 49–53 mJ/m^2 are similar to that obtained for uncoated low carbon steel, $\sim$ 53 mJ/m^2, indicating that polypyrrole will effectively wet low carbon steel. The extent of wetting of low carbon steel by the coatings was additionally confirmed by an interaction parameter, ϕ, of unity. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2757–2763, 2002

Key words: adhesion; polypyrrole coatings; electrochemical polymerization; work of adhesion; surface free energy; lap joint shear strength

INTRODUCTION

Adequate wettability of a substrate is a prerequisite for the formation of uniform and strongly adherent coatings. A combination of low contact angle (<30°) and high surface free energy ($\geq$45 mJ/m^2) are sufficient criteria for wetting. The reversible work of adhesion, W_A, can also be used to predict the wettability of a solid by a liquid. The relationship between the work of adhesion, W_A, the liquid surface tension, γ_1, and contact angle, θ, is given by the expression $W_A = (1 + \cos\theta)\gamma_1$. The dispersive and polar surface energies, γ^d and γ^p, respectively, can be obtained from the geometric (eq. 1a) and Harmonic mean (eq. 1b) equations[1]:

$$W_A = 2[(\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2}] \qquad (1a)$$

$$W_A = 4\left[\frac{\gamma_s^d \gamma_l^d}{\gamma_s^d + \gamma_l^d} + \frac{\gamma_s^p \gamma_l^p}{\gamma_s^p + \gamma_l^p}\right] \qquad (1b)$$

where the subscripts l and s represent the liquid and the substrate, respectively. If we substitute a polymeric coating for the liquid, the work of adhesion, $W_A = W^d + W^P$ can be related to the interfacial shear strength, τ, exerted at the coating–substrate interface by combining the Schultz and Nardin[2,3] and modified Cox[4] expressions:

$$\tau = kW_A = k(W^d + W^p) = \left(\frac{E_c}{E_s}\right)^{1/2} \frac{W_A}{\lambda} \qquad (2)$$

where λ is the equilibrium intermolecular distance, with a value of $\sim$ 0.5 nm,[5] and E_c and E_s are the elastic modulii of the coating and the

substrate, respectively. As shown by eq. 2, the higher the work of adhesion, the higher the interfacial shear strength.

The work of cohesion of the coating, W_c, can easily be determined from the surface free energy of the coating; that is, $W_c = 2\gamma_c$.

The nature of the interaction between the coating and the substrate can also be estimated by comparing the work of adhesion with the work of cohesion. If the work of adhesion is larger than the work of cohesion, then interfacial failure of the coatings will not occur. The difference between W_A and W_C gives the spreading coefficient, S (i.e., $S = W_A - W_C$), which is defined as the decrease in free energy due to formation of a coating of unit interfacial area.[1,6,7]

For spreading to occur, the work of adhesion must be higher than the work of cohesion ($W_A - W_C > 0$). It is expected that high applied current will lead to high deposition rate resulting in more porous coatings with increased roughness.

The extent of interaction between the coatings and the substrate can be determined by using the interaction factor, ϕ, which is associated with the intermolecular forces acting on the coatings–substrate interface. The mathematical expression for ϕ is derived by Good and Girifalco[8–10]:

$$\phi = \left[\frac{W_A}{(W_{C1}W_{C2})^{1/2}} \right] \quad (3)$$

where W_{c1} is the work of cohesion for the coatings and W_{c2} is the work of cohesion for the substrate. If the volume of the interacting components is unity, the interaction parameter has a value of 1 as long as the coatings and the substrate have similar polarities (i.e., $x_s^P = x_c^P$). The value of the interaction parameter decreases with increased disparity in the polarities of the components (i.e., $\phi \leq 1.0$).

According to the interfacial defect model, the optimum condition for wetting and adhesion is the equalization of the polarities of the adhesive and the adherand; that is, that the spreading coefficient, $S = 2\phi(\gamma_1\gamma_2)^{1/2} - 2\gamma_1$, should be maximized.[11–14] Note that if the ratio γ_1/γ_2 and x_s^P are constant, ϕ has maximum value of unity for the geometric mean model, $d\phi/dx_s^P = 1$ and $d\phi/dx_s^P = 2(\gamma_1 + \gamma_2)^{1/2}$ for the Hamonic mean model. Both S and W_A are maximized at maximum ϕ. However, additional increase in the adhesive or coatings surface tension at constant ϕ will lead to a decrease in S in accordance with the fracture energy model.

The adhesion strength obtained from such a test can be compared with the calculated thermodynamic interfacial strength. The load–displacement curve from the lap shear test can be related to the adhesion energy as follows[15]:

$$\frac{\text{Adhesion energy}}{\text{Unit volume}} = \int_0^{\varepsilon_{\max}} \sigma \, d\varepsilon \quad (4)$$

The adhesion energy can give a good measure of the quality of the coatings and the adhesion between the coatings and substrate. A high adhesion energy is indicative of the existence of strong bonds between the substrate and coatings. It is also indicative of the coating toughness and uniformity. The converse will imply weak interfacial bonds resulting in coatings delamination due to the presence of flaws and cracks.

A correlation between the adhesion energy and the thermodynamic work of adhesion W_A can be made, taking into consideration the viscoelasticity of the coatings. According to the fracture energy model, $W_A = 2\phi(\gamma_1\gamma_2)^{1/2}$ should be maximized.[16–20] By combining the predictions of the interfacial model and that for the fracture energy model, one can obtain the optimum condition for wetting, which results in spontaneous spreading (i.e., $S = 0$ at $\gamma_1 = \phi^2\gamma_2$ and $W_A = 2\phi^2\gamma_2$). It has been shown that the maximum lap shear bond strength occurs when the surface free energies of the adhesive, γ_1, and the adherand, γ_2, are equalized (i.e., $\gamma_1 = \gamma_2$).

EXPERIMENTAL

Materials

Pyrrole (98%), *N*-methyl pyrrole (reagent grade), and oxalic acid (98%) were obtained from Aldrich Chemical Company. The reagents were dissolved in deionized water.

A $4'' \times 1'' \times 0.02''$ low carbon steel (99.9% Fe, 0.1% C) obtained from QD Panel Company Company was used as the working electrode. Two titanium alloy plates were used as the counter electrodes. The electrodes were degreased with tetrachloroethylene for ~ 1 h prior to electrochemical polymerization. A saturated calomel electrode (SCE) manufactured by Corning Company was used as the reference electrode.
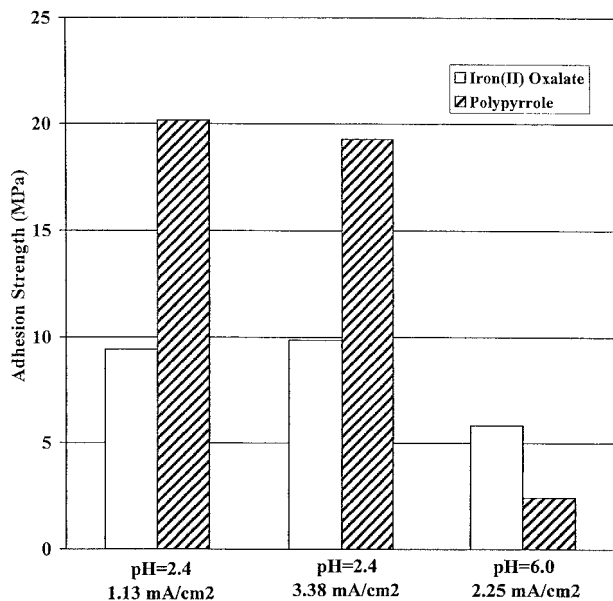
Figure 1 The adhesion strength of steel coated with the passive interlayer and steel coated with polypyrrole as a function of pH and applied current.

Electrochemical polymerization was performed by an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273 A.

Electrochemical Polymerization

Electrochemical polymerization was was carried out in a one-compartment electrochemical cell. The applied current density was varied from 0.22 to 11.26 mA/cm^2. The initial concentration of oxalic acid and the monomers were maintained at 0.1 and 0.25M, respectively. Electropolymerization was performed for $\sim$ 30 min.

Contact Angle Measurement

Contact angle measurements were performed by using a VCA 2000 Video Contact Angle System from Advanced Surface Technology, Inc., Billerica, MA. The sessible drop method was used, with deionized water and methylene iodide as the probing liquids. The contact angles were averaged for five drops. The Harmonic-mean model was used to calculate the dispersive and polar components of the surface energy. The values of the dispersive and polar components of the surface tension of deionized water and methylene iodide used in our calculations are 22.1 and 50.7 and 48.5 and 2.3 mJ/m^2, respectively.

Lap Shear Test

The lap shear strength of the coated and uncoated (control) samples was determined in accordance with the ASTM standard test procedure D-1002-72.[21] The standard test coupons (2.54 $\times$ 10.2 cm^2) were provided by the Q-Panel Company. The samples were dry polished and subsequently electrochemically coated with iron(II) oxalate passive coatings, polypyrrole, and poly(N-methyl pyrrole) coatings, respectively. Pairs of the test coupons were bonded together to form lap shear joints with an overlap length of 1.27 cm (Figure 1). A 0.25-mm diameter wire was used as a spacer to set the thickness of the bondline. The adhesive consisted of an epoxy resin EPON 828 and a polyamide curing agent (EPI-CURE 3140 from Shell Chemical Company). The resin and the curing agent were mixed in a 1.0 : 0.75 epoxy-to-polyamide ratio. The bonded joint was cured at room temperature for 18 h followed by vacuum oven curing at 50°C for 5 h. Lap shear tests were performed with an Instron Universal Mechanical tester model 4206 at a crosshead speed of 1.27 mm/min. Five tests were performed per specimen, and the average lap shear strength was reported.

Table I Surface Free Energies for the Coatings and Low Carbon Steel

Sample ID	γ^d (mJ/m^2)	γ^p (mJ/m^2)	γ^T (mJ/m^2)
Bare steel	29.8	23.4	53.2
PPy, pH = 1.4, i = 1.13 mA/cm^2	40.0	7.9	47.9
PPy, pH = 2.4, i = 1.13 mA/cm^2	38.1	10.8	48.9
PPy, pH = 2.4, i = 3.38 mA/cm^2	40.2	9.1	49.3
PPy, pH = 4.1, i = 1.13 mA/cm^2	38.9	10.7	49.6
PmPy, pH = 1.4, i = 1.13 mA/cm^2	41.7	10.2	51.9
PmPy, pH = 2.7, i = 1.13 mA/cm^2	42.1	6.3	48.4

Table II Comparison between the Work of Adhesion and Work of Cohesion for the Coatings

Sample ID	W_A (mJ/m^2)	W_C (mJ/m^2)
PPy, pH = 1.4, i = 1.13 mA/cm^2	96.3	95.8
PPy, pH = 2.4, i = 1.13 mA/cm^2	99.2	97.8
PPy, pH = 2.4, i = 3.38 mA/cm^2	98.4	98.6
PPy, pH = 4.1, i = 1.13 mA/cm^2	100	99.2
PmPy, pH = 1.4, i = 1.13 mA/cm^2	101.4	103.8
PmPy, pH = 2.7, i = 1.13 mA/cm^2	95.1	96.8

Reflection-Absorption Infrared Spectroscopy (RAIR)

Reflection-absorption infrared spectroscopy (RAIR) of the coatings was performed with a BIO-RAD FTS-40 FIIR spectrometer. An angular specular reflectance attachment was set to an incident angle of 65°. Spectra were obtained using a resolution of 4 cm^{-1} and were averaged over 128 scans. A background spectrum of a bare polished steel substrate was subtracted from the acquired spectra in all cases. In the case of transmission IR, the spectra were obtained with potassium bromide(KBr) pellets.

RESULTS AND DISCUSSION

The surface free energies of low carbon steel, polypyrrole (PPy)-coated steel, and poly(N-methyl pyrrole) (PmPy)-coated steel are shown in Table I. PPy- and PmPy-coated steel have similar surface energies of ∼ 50 mJ/m^2. The dispersive component of the surface free energy for uncoated low carbon steel is ∼ 29.8 mJ/m^2, which is lower than the 38–42 mJ/m^2 obtained for PPy- and PmPy-coated steel. However, the polar component of of the surface free energy of steel of ∼ 23 mJ/m^2 is significantly higher than the 6–11 mJ/m^2 ob-

tained for PPy- and PmPy-coated steel. The polar component of the surface free energies for common commercial polymers (0–5 mJ/m^2) are significantly lower than those of PmPy and PPy, indicating that the latter polymers can be effectively wetted by the commercial polymers when used either as top coating or as paint.[22] Adequate wettability of the polymer coatings or primers is required for subsequent application of uniform and adherent top coating. The first step in the formation of an adhesive bond is establishment of interfacial molecular contact by wetting.[1] Insufficient wetting results in interfacial defects, thereby lowering the adhesive bond strength. Also adequate wetting can increase the adhesive bond strength by increasing the work of adhesion, which is directly proportional to the fracture energy.[1]

The reversible work of adhesion is compared with the work of cohesion in Table II. Both W_A and W_C lie between 95 and 104 mJ/m^2, and the difference between them ($S = W_A - W_C$) ranges from −2.4 to 0 (Table III). This result indicates that the PPy coatings will spontaneously wet the steel substrate. These data also satisfies the optimum condition for spontaneous spreading as predicted by the interfacial and fracture energy models (i.e., $S = 0$ when $\gamma_1 = \phi^2 \gamma_2$ and W_A

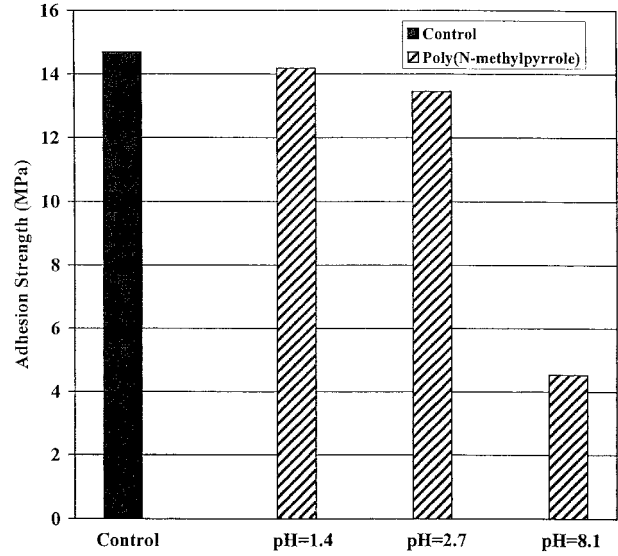**Table III Effect of the Process Variables on the Interaction Parameter and Spreading Coefficient**

Sample ID	ϕ	S
PPy, pH = 1.4, i = 1.13 mA/cm^2	0.95	0
PPy, pH = 2.4, i = 1.13 mA/cm^2	0.97	1
PPy, pH = 2.4, i = 3.38 mA/cm^2	0.97	−0.2
PPy, pH = 4.1, i = 1.13 mA/cm^2	0.97	0.8
PmPy, pH = 1.4, i = 1.13 mA/cm^2	0.97	−2.4
PmPy, pH = 2.7, i = 1.13 mA/cm^2	0.93	−1.7
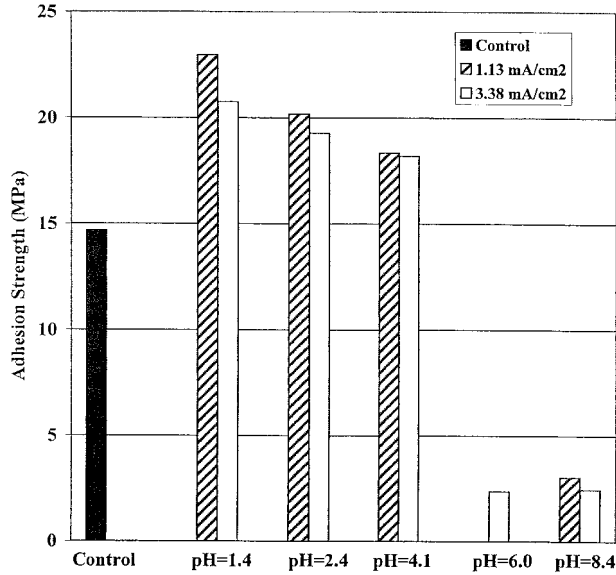
Figure 2 The adhesion strength of steel coated with polypyrrole as a function of pH and applied current.

Figure 3 The adhesion strength of steel coated with poly(N-methylpyrrole) as a function of pH.

$= 2\phi^2\gamma_2$). Substituting $\gamma_2 = 53$ mJ/m^2 and $\phi = 0.95$, into these equations, we obtain 96 and 48 mJ/m^2, for W_A and γ_1, respectively. Compared with commercial and polar polymers such as epoxy resin ($\gamma = 46$ mJ/m^2), PMMA ($g = 40$ mJ/m^2), and nylon 6.6 (40 mJ/m^2),[22] PPy and PmPy coatings have slightly higher surface free energies (48–53 mJ/m^2). PPy and PmPY could be used as primers for epoxy ($\gamma = 46$ mJ/m^2) resin and polyimide ($\gamma = 44$–53 mJ/m^2) adhesives and topcoats.

The adhesion strengths of PPy coatings formed on low carbon steel as a function of the electrochemical process variables are shown in Figures 1 and 2. The adhesion strength of PPy-coated steel decreased slightly with increased applied current density. The adhesion strength of PPy-coated steel is dependent on the pH of the monomer–electrolyte solution. A significant improvement in the adhesion strength over the control sample (of about ≤ 60%) was obtained for PPy coatings formed at pH ≤ 4. The adhesion strength of PPy coatings formed at pH ≥ 6.0 were significantly lower than that of the control (uncoated) sample ($\sim$ 14.5 mJ/m^2).

The comparisons of the adhesion strength of PmPy-coated steel and the uncoated steel are shown in Figures 3 and 4. The variation of the adhesion strength with pH of the electrolyte–monomer solution is also shown in Figure 3. As the pH of the electrolyte–monomer solution was changed from 1.4 to 8.1, the adhesion strength decreased from $\sim$ 14 MPa to 4.5 MPa. The PmPy-coated steel had significantly lower lap joint shear strength ($\sigma_{max} \sim$ 14 MPa) than the PPy-coated steel ($\sigma_{max} \sim$ 23 MPa). Considering the fact that the surface energies of PPy- and PmPy-coated steel are similar ($\sim$ 50 mJ/m^2), one would expect the two systems to have similar lap joint shear strength. It is likely that PPy-coated steel can

Table IV   Dependence of the Interfacial Energy, Thermodynamic, and (Lap Joint) Interfacial Shear Strength on the Process Variables

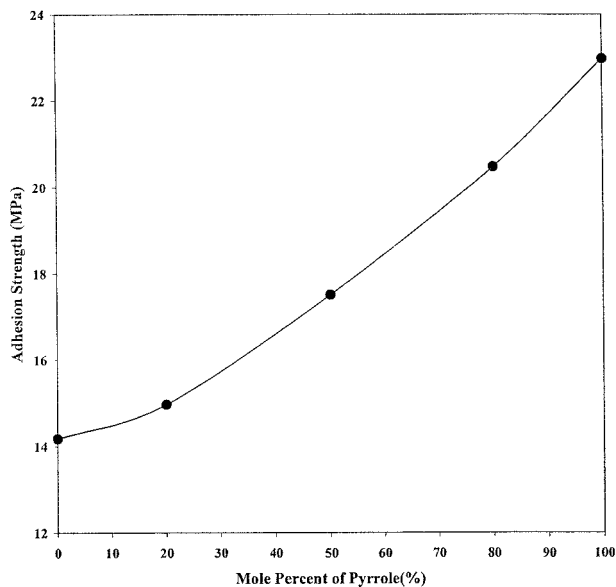| Sample ID	γ_{SC} (mJ/m^2)	τ (MPa)
PPy, pH = 1.4, i = 1.13 mA/cm^2	32	0.019 (23)
PPy, pH = 2.4, i = 1.13 mA/cm^2	35	0.02 (20)
PPy, pH = 2.4, i = 3.38 mA/cm^2	34	0.019 (19)
PPy, pH = 4.1, i = 1.13 mA/cm^2	35	0.02 (18)
PmPy, pH = 1.4, i = 1.13 mA/cm^2	34	0.02 (14)
PmPy, pH = 2.7, i = 1.13 mA/cm^2	31	0.018 (13)
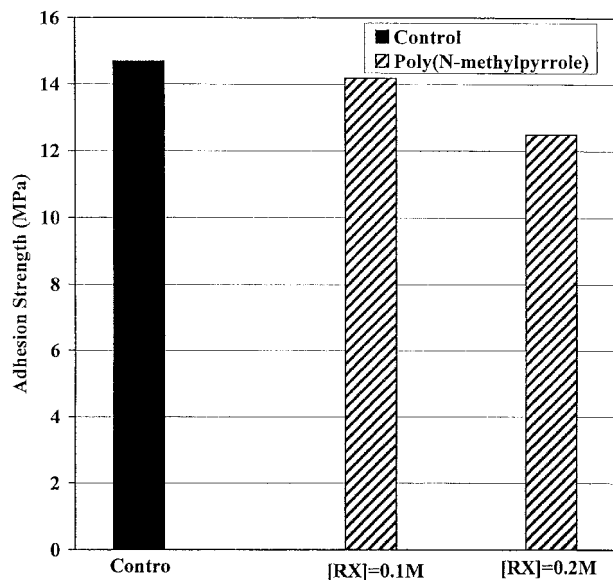
Figure 4 The adhesion strength of steel coated with poly(*N*-methylpyrrole) as a function of oxalic acid concentration.

Figure 5 Dependence of the adhesion strength of steel coated with polypyrrole-*co*-poly(*N*-methylpyrrole) as a function of mol % of pyrrole in the feed.

interact with the substrate via the —NH group, which is absent in PmPy. It is also possible that the bulky —CH3 group may impede the interaction between the phases. Note that increasing PPy composition in a PPy–PmPy copolymer increases the adhesion strength (Figure 2), indicating that the mechanism of adhesion may not solely be due to mechanical interlocking.

A comparison of the adhesion strength of both iron(II) oxalate passive interlayer and PmPy-coated steel (Figures 1, 3, and 4) show that both systems have lower adhesion strength than the control sample. However, increasing the PPy composition in a PPy–PmPy copolymer increases the adhesion strength (Figure 5), indicating that the mechanism of adhesion may not solely be due to mechanical interlocking.

Analysis of the Coatings by RAIR

The IR spectra for pyrrole, the passive coatings, and PPy coatings obtained at pH 1.4 are shown in Figure 6. The IR spectrum of pyrrole was obtained by transmission mode. IR analysis confirm that the passive coatings and PPy coatings have different chemical structure. However, the N—H and O—H stretch peaks associated with pyrrole and oxalic acid, respectively, were absent in the RAIR spectrum of PPy. This phenomenon is consistent with the findings of other researchers,[23]

and may be due to the fact the —NH group may be located at the interface where it may be involved in chemical bonding. Evidence from RAIR
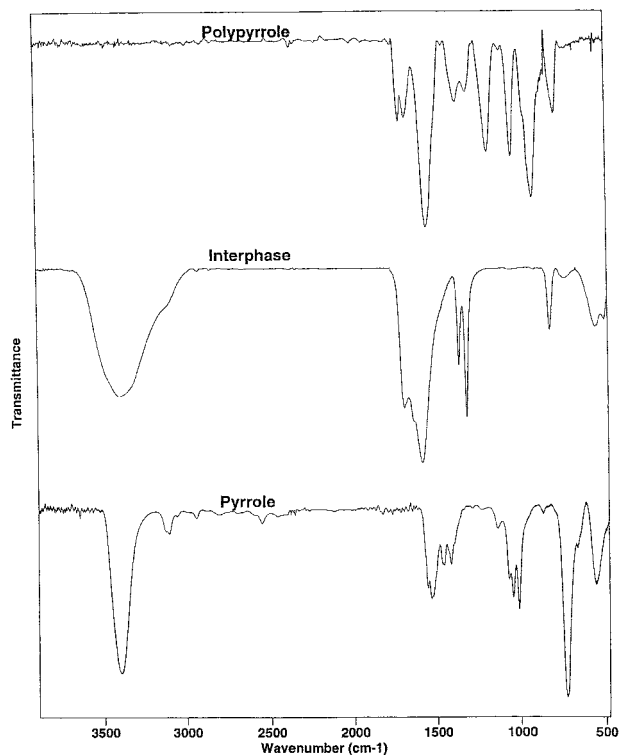
Figure 6 RAIR spectra for polypyrrole, passive coatings, and pyrrole.

shows that the absorption peak characteristic of the —NH group is missing.

CONCLUSIONS

Polypyrrole coatings were successfully formed on low carbon steel from an aqueous solution containing pyrrole and oxalic acid. Low carbon steel coated with polypyrrole at pH 2.4 has a lap joint shear strength of $\sim$ 23 MPa, which is $\sim$ 60% higher than that obtained by using uncoated steel as the adherand. The adhesion strength of polypyrrole coatings to steel varied with the pH of the monomer–electrolyte solution and the applied current. The polypyrrole coatings formed at low pH (pH $\leq$ 2.4) have higher adhesion strength than the polypyrrole coatings formed at higher pH (pH $\geq$ 6.0). Increasing the applied current density also decreases the adhesion strength.

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