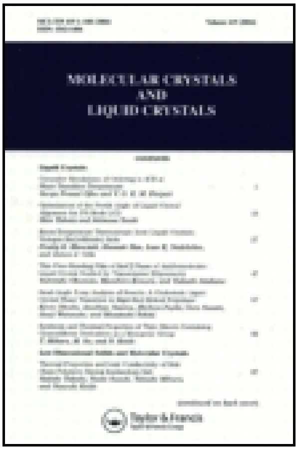

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Iron Corrosion Protection by Ultra-thin Conductive Films Based on Polypyrrole/Poly(methyl methacrylate) Composite

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*The metallic surfaces can be protected from the corrosive media by conducting polymer coating which provides passivation mechanism by redox chemistry. Their poor solubility and processibility were improved by the use of soluble polypyrrole (PPy) and composite with poly(methyl methacrylate) (PMMA). Soluble PPy was synthesized by controlling the monomer-to-oxidant ratio in the presence of dodecylbenzenesulfonic acid (DBSA) as a dopant. And then MMA was mixed with PPy/**m**-cresol solution to spin-coat onto iron. The 4-probe method was used to measure electrical conductivity and FTIR spectra were used to study the conjugation length of PPy. Scanning electron microscopic (SEM) images were obtained to observe the surface morphology. Tafel plots showed that the PMMA/PPy composite film caused a positive shift of around 200 mV in the corrosion potential and the anodic current decreased by two orders of magnitude compared with bare iron.*

Keywords: cyclodextrin porogen; dielectric materials; nanoporous dielectrics; reactive porogen; ultra-low dielectrics

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INTRODUCTION

Most industrial corrosion protection relies on a very thin layer, ~50 nm, of chromate conversion coatings to provide the anodic protection against the corrosive environment [1], but the use of chromates and other chromium containing compounds has been limited since 1982 due to their carcinogenic effect. It is, therefore, highly desirable to develop a chromate-replacing inhibitor that is environmentally benign. In recent years intrinsically conducting polymers such as conjugated polyaniline (PANi) and polyprrole (PPy) have attracted much attention as a novel corrosion inhibitor because of the easy synthesis, oxidative stability and mass productivity [2,3]. De Berry first reported that PANi film electrochemically polymerized on the stainless steel protected the bare alloys by anodic protection [4] and Camelet *et al*. found the homogeneous PANi film can be electrochemically deposited on the iron substrate in oxalic acid solution [5]. In addition, Wessling *et al*. found that the repetitive immersion coating of doped PANi solution on metallic substrates such as iron, carbon steel and copper made the metallic surfaces much more passive [6]. It is believed that the high redox potential of conjugated polymers allows iron or carbon steel to be maintained in the passive state. When a metal substrate is in contact with a conducting polymer film, an electrochemical process takes place at the metal-coating interface, which leads to the oxidation of the metal substrate by conducting polymer to produce a metal hydroxide (initial step of passivation). The reduced conducting polymer is likely to be oxidized at the polymer coating/corrosive environment interface [7]. As a result, conducting polymers are able to act as a redox mediator between metal and corrosive solution.

On the other hand, thin and protective films prepared from chemically or electrochemically polymerized conducting polymer are mechanically brittle and less adhesive to substrates [8].

Thus, we prepared the soluble PPy [9] in organic solvents with the use of dodecylbenzenesulfonic acid (DBSA) as a dopant and studied the polymerization yield, solubility and conductivity of PPy at different initiator concentration. To improve the brittleness and the processiblity of the chemically polymerized PPy its solution in *m*-cresol were mixed with methyl metacrylate (MMA) and then applied on an iron by spin-coating. The conductivity, surface morphology and potentiodynamic polarization of the composite films were investigated.

EXPERIMENTAL

Pyrrole monomer (ACROS) was distilled under vacuum prior to use. Ammonium persulfate {APS, $(NH_4)_2S_2O_8$, Aldrich} were used as an oxidant without further purification. PPy was prepared by following procedures: pyrrole monomer and DBSA were dissolved in deionized water and then aqueous APS solution was slowly added into the aqueous pyrrole/DBSA solution. Dropping time of oxidant solution was controlled by Master Flex L/S pump drive. The reaction temperature was maintained at 0°C in a circulation bath (Lauda RM 20 S). The polymerization reaction was terminated by pouring the excess methanol into the reactor. The precipitated powder was sequentially washed with distilled water, methanol and acetone until the filtered solvent became colorless, and then dried in a vacuum oven at room temperature for 24 h. The polymerization yield was estimated by the weight ratio of polymer to initially charged monomer.

PPy powder was dissolved in *m*-cresol (Junsei Chemical) and filtered through 0.45 µm Teflon membrane syringe filter (Whatman Paper Ltd.). The filtered solution was mixed with MMA and azobissisobutyronitrile (AIBN). The solution was cast onto an iron by spinning and then polymerized at 80°C in vacuum. The standard 4-probe method was used to measure electrical conductivity (σ) of PPy powders and films. FTIR spectra were obtained for PPy powders by Midac Prospect IR at transmission mode in the resolution of 4 cm^{-1}. SEM images were obtained on the coated iron surfaces. Electrochemical corrosion measurements were performed at room temperature in 3% NaCl, 0.1 M HCl and 0.1 M H_2SO_4 solutions. Potentiodynamic polarization experiments were started from the open circuit potential at the scan rate of 2 mVs^{-1}.

RESULTS AND DISCUSSIONS

Because the properties of conducting polymers were quite dependent on the concentration of initiator [10], we studied the effect of monomer-to-oxidant ratio on the yield, conductivity and solubility of PPy. Figure 1 shows the polymerization yield and electrical conductivity of PPy as a function of monomer-to-oxidant ratio. The conductivity of each sample was measured with pelletized powder. Both conductivity and polymerization yield decreased with increasing monomer-to-oxidant ratio. As Kim *et al*. [11] reported, smaller molecular weight would be expected at the lower oxidant concentration due to fewer generated radicals. In addition, the yield was also lower at higher monomer-to-oxidant ratio since more oligomeric PPy was not recovered from the polymerization product.

When the solubility was compared by preparing 3 wt% of solution, the solubility in *m*-cresol was highly improved only if the monomer-to-oxidant ratio was equal to or greater than 7.5. Therefore, the ratio of

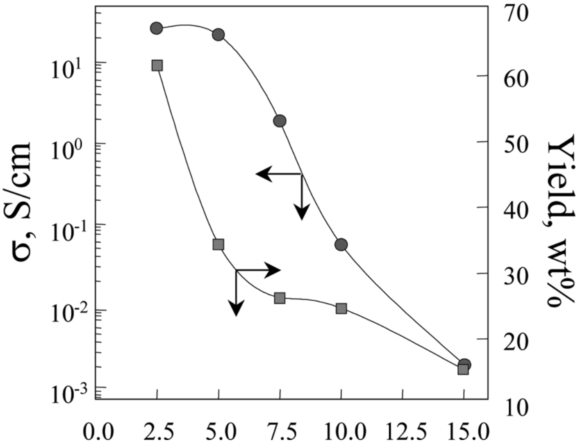

FIGURE 1 Conductivity and polymerization yield of PPy/DBSA at different [Mo]/[Ox].

7.5 was chosen for later polymerization, where the balanced conductivity and solubility were obtained.

In general the smaller molecular weight of conducting polymers might result in the lower conductivity due to shorter conjugation length. We measured the conjugation length and doping level of PPy/DBSA, which are directly related to the electrical conductivity.

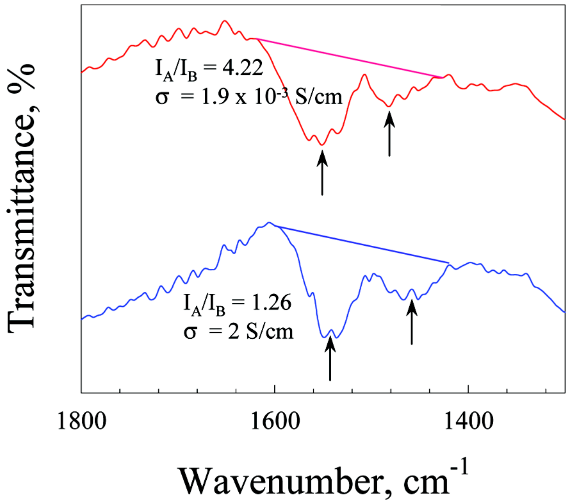

FIGURE 2 FTIR spectra of PPy/DBSA powders.

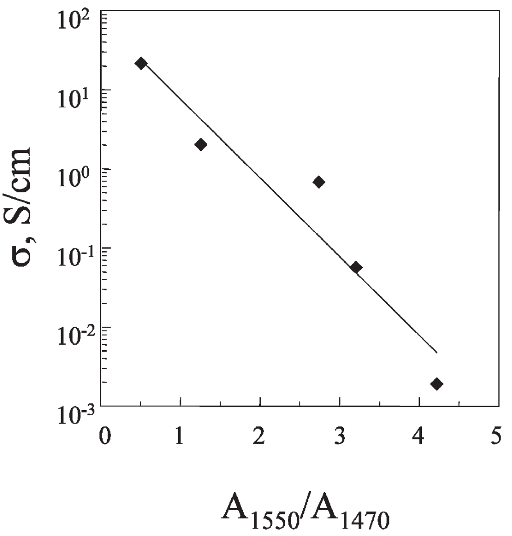

FIGURE 3 Conductivity vs. A_{1550}/A_{1470} of PPy/DBSA powders.

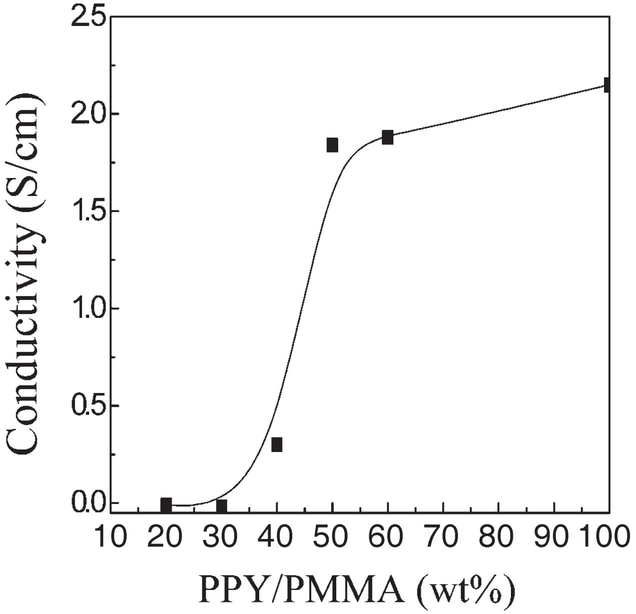

FIGURE 4 Conductivity of PMMA/PPy composite film as a function of PPy content.

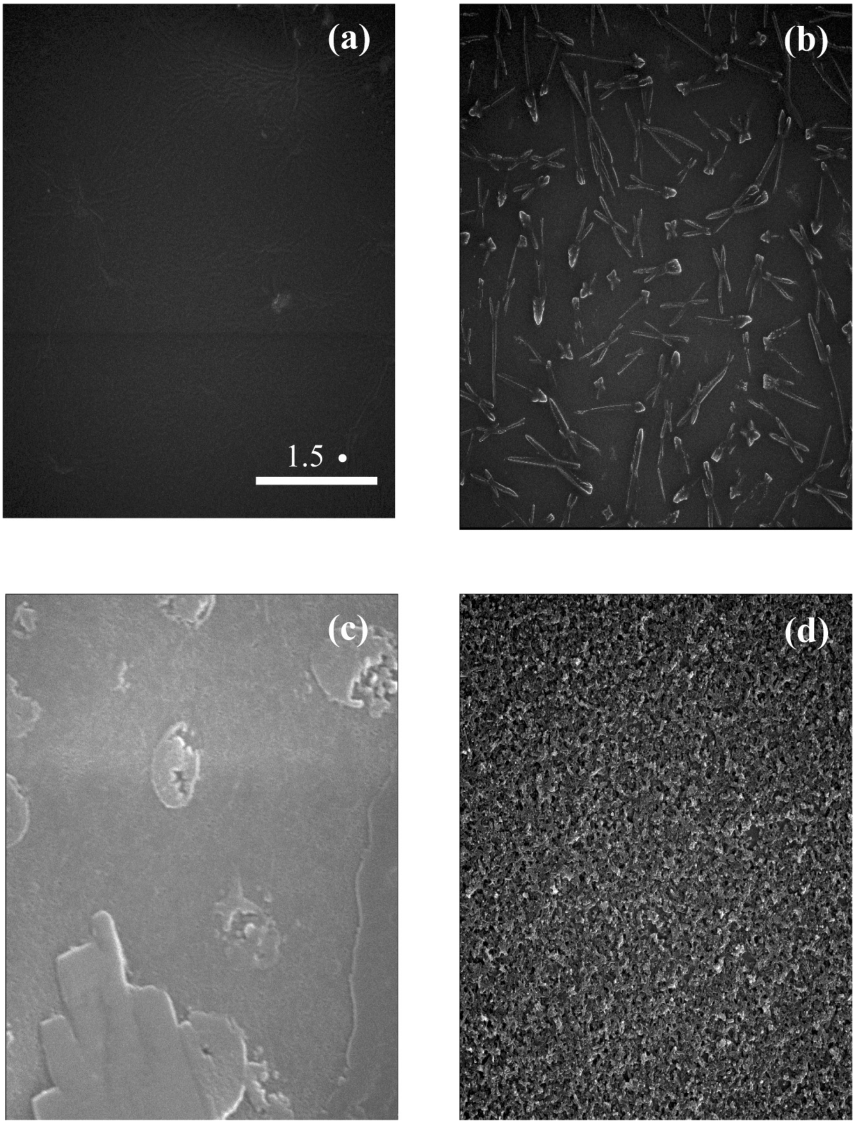

FIGURE 5 SEM images of (a) PMMA, (b) PMMA/PPy 50 wt%, (c) PMMA/PPy 20 wt% and (d) PPy.

The doping level was obtained from the molar ratio of sulfur/ nitrogen by elemental analysis. Irrespective of the monomer-to-oxidant ratio, the doping level was nearly constant ranging from 21 to 22%, close to the theoretical value of 25% [12]. The conjugation length was estimated by measuring the degree of delocalization according to Tian and Zerbi's method [13]. The typical FTIR spectra of PPy/DBSA powders are shown in Figure 2 and the measured A_{1550}/A_{1470} was plotted with conductivity as an ordinate in Figure 3. There existed linear relationship between conductivity and $A_{1550}/A_{1470.}$ The degree of delocalization was inversely proportional to the ratio of FTIR peak area at 1550 cm^{-1} and 1470 cm^{-1} (A_{1550}/A_{1470}). Thus, the elemental analysis and FTIR results implied that the conductivity was closely related to the conjugation length of PPy/DBSA.

Figure 4 shows the proton conductivity of PMMA/PPy composite films. The conductivity was directly related to the ratio of PPy used in the composite membranes, but there appears to be sharp increase in conductivity from 0.3 to 1.84 S/cm when the weight of PPy was increased from 40 to 50 wt%. However, a further increase in PPy content to 60 wt% did not change the conductivity appreciably.

The SEM image of PPy on an iron revealed very rough and nonhomogenous surface (Fig. 5(d)) but the surface morphology of PMMA was smooth (Fig. 5(a)). The PMMA/PPy (50 wt%) composite film showed lots of crack on the surface but the other composite (20 wt% of PPy) resulted in homogeneous and smooth surface (Fig. 5(b, c)). Therefore, we chose the PPy content of 20% in the composites for corrosion protection film.

The potentiodynamic polarization curves are plotted (Fig. 6) for the bare iron and the coated iron in the corrosive solution. Corrosion rate

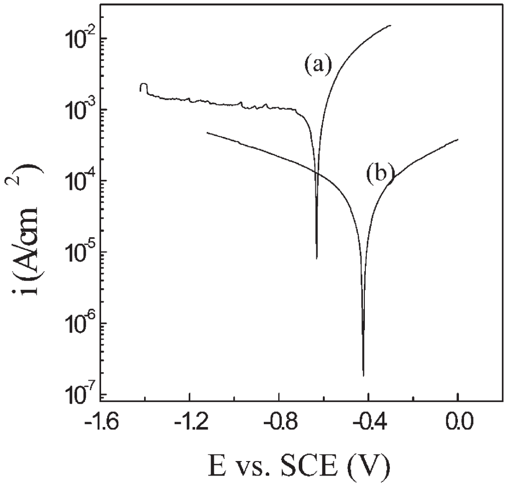

FIGURE 6 Potentiodynamic curves in the electrolyte solution for (a) bare iron and (b) the iron coated with PMMA/PPy composite.

information could be obtained by Tafel extrapolation method, where the intersection point of a cathodic and anodic polarization curve provides both the corrosion potential and the corrosion current. Tafel extrapolations showed that the PMMA/PPy composite film caused a positive shift of around 200 mV in the corrosion potential compared with the bare iron. Tafel measurement also showed that the anodic current (corrosion current) decreased by two orders of magnitude. This result indicated that PMMA/PPy composite film would be an good alternative to chromate coating for corrosion protection of iron.

CONCLUSIONS

Soluble PPy doped with DBSA was synthesized and PMMA/PPy composite film was applied on an iron surface to protect efficiently from the corrosion. The properties of the PPy such as solubility and conductivity depended on the initiator concentration. The soluble PPy was obtained at monomer-to-oxidant ratio 7.5 and PPy/*m*-cresol solution was mixed with MMA, and then this mixture was spin-coated onto iron substrate to protect corrosion. Tafel extrapolations showed that the PMMA/PPy composite film caused a positive shift of around 200 mV in the potential and the decrease in anodic current by two orders of magnitude compared with bare iron. These results showed that PMMA/PPy composite film played a role as both corrosion barrier and redox mediator and could be an environmentally benign candidate for the corrosion protection of metal surfaces.

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