Electrochemical Deposition of Polyaniline–Polypyrrole Composite Coatings on Aluminum

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ABSTRACT: The electrodeposition of polyaniline–polypyrrole composite coatings on aluminum was successfully performed by using cyclic voltammetry. Oxalic acid was used as the electrolyte. Electrodeposition was carried out at a scan rate of 20 mV/s by varying the number of cycles. An anodic peak current at around -0.1 V versus saturated calomel electrode (SCE) was observed in the cyclic voltammograms. This peak is due to the oxidation and adsorption of hydrogen. The cyclic voltammograms also show another anodic peak current at around 1.0 V versus SCE, which is the characteristic peak of the polyaniline–polypyrrole composite. The behavior of this peak with respect to the number of cycles is discussed in detail. A corresponding cathodic peak current at around -0.7 V versus SCE was also observed in the cyclic voltammograms. The infrared spectra of the composite coatings revealed the infrared peaks of both polypyrrole and polyaniline. The scanning electron micrographs of the coatings indicate a morphology completely different from its homopolymers. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1970–1977, 2002

Key words: electrodeposition; conducting polymeric composite coatings; aluminum; polyaniline; polypyrrole

INTRODUCTION

Conductive polymers are being extensively researched for their application in a lot of new technologies. There is a lot of literature concerning the synthesis and characterization of conducting polymers. A few popular examples of conducting polymers are polyacetylene, polyaniline, polypyrrole, and polythiophene. They have potential applications in electronic displays,[1] as electrode materials in batteries,[2] as molecular electronic circuit elements,[3] in restoration of data,[4] as indicators of gasometers,[5] and in biochemical analysis.[6] The conductivity of doped conducting

polymers can be attributed to the delocalization of Π-conjugated systems.

Conducting polymers containing two compounds can be prepared as copolymers, composites, bilayers, or blends. This is done for the improvement of the physical, chemical, mechanical, and electrical properties of the homopolymers. Polyaniline and polypyrrole are two of the most promising conducting polymers. Both of them have a relatively high conductivity and good environmental stability.[7] The synthesis of polyaniline has been extensively carried out on various substrates such as Pt, Au, Fe, Al, stainless steel, and carbon fibers, by both chemical and electrochemical methods.[8–11] It also has been successfully copolymerized with other polymers by chemical and electrochemical polymerization.[12–14] Polypyrrole can also be synthesized chemically[15] and electrochemically.[16] It has been synthesized on various substrates such as iron,[17] steel,[18] Al,

brass, mild steel,[19] and zinc. It has also been copolymerized extensively with polyaniline.[20,12] The nature of the working electrode plays an important role in the electrodeposition of polyaniline and polypyrrole films. Thermodynamic study predicts that the metal will start to dissolve even before the electropolymerization potential of the monomer is reached.[9] Thus, the right conditions are to be found where the passivation of the metal occurs without any hindrance to electropolymerization.

Electropolymerization is a very effective technique for the deposition of polymer coatings onto various substrates.[21] Because of its advantage over the traditional coating techniques, preparation of polyaniline/polypyrrole conductive polymer films by electrochemical methods[1,3,12,22,23] is preferred.

In this article, we report the electrochemical polymerization of polyaniline/polypyrrole composite coatings on Al 2024 substrate in aqueous oxalic acid solution. Cyclic voltammetry is the technique used to electropolymerize the polyaniline/polypyrrole composite coatings.

EXPERIMENTAL

The electrochemical deposition of polyaniline–polypyrrole composite coatings was carried out by using a Potentiostatic/Galvanostatic Model 273A (EG&G Princeton Applied Research) in a one-compartment electrochemical cell. Two stainless steel rectangular sheets were used as the counter electrodes (cathode) and a 2024 T3 bare aluminum alloy of dimensions $4 \times 1 \times 0.063''$ was used as the working electrode (anode). The aluminum samples were purchased from Q-Panel Lab Products. The reference electrode was a saturated calomel electrode, which was purchased from Fischer Scientific Co.

Aniline (99.5%) and pyrrole (98%) taken at a concentration of $0.25M$ and a feed ratio of 3 : 7 were mixed with oxalic acid (98%), taken at a concentration of $0.3M$, and deionized water to prepare an aqueous solution of the mixture. Aniline and oxalic acid were purchased from Aldrich Chemical Co. A 100-ml solution was used for each reaction. The concentrations of aniline and oxalic acid were kept constant at 0.1 and $0.25M$, respectively. The reactions were carried out at a scan rate of 20 mV/s and by varying the number of cycles. All the reactions were carried out in the scan range of -1.0–3.0 V versus saturated calomel electrode (SCE). The cyclic voltammograms, I–E curves, for the reactions were obtained by using the Potentiostatic/Galvanostatic Model 273A. The aluminum samples were ultrasonically cleaned in acetone for 15 min before the reaction. The coated aluminum samples were washed with methanol and dried at room temperature.

The reflection absorption infrared (RAIR) spectra of the polyaniline coatings were obtained by using a Bio-Rad FTS-40 spectrometer. The angular specular reflectance attachment was set to an incident angle of 50°. The spectra were obtained by using a resolution of 8 cm^{-1} and averaged over 256 scans for a scan range of $4000-400$ cm^{-1}. A background spectrum of bare aluminum was subtracted from the acquired spectra in all cases. The surface structure and composition of the coatings were determined by scanning electron microscopy (SEM). The SEM micrographs were obtained by using a Jeol JSM-T220A scanning microscope.

RESULTS AND DISCUSSION

Polyaniline Coatings on Aluminum

Cyclic Voltammetry

Figure 1 shows the cyclic voltammograms of the polymerization of aniline as a function of the number of cycles. At shorter reaction times, an anodic peak occurs at around -0.1 V versus SCE. This peak reduces in intensity with an increase in the number of cycles. This peak is due to the oxidation and adsorption of hydrogen.[24] As we increase the number of cycles, another anodic peak appears at around 0.3 V versus SCE, which is characteristic of polyaniline coatings and corresponds to the formation of emeraldine form of polyaniline. However, as the number of cycles is increased further, a sharp anodic peak appears at around 1.0 V versus SCE along with a sharp cathodic peak at around -0.5 V versus SCE. This peak is attributed to the redox peaks of the polymeric coatings. It was shown that thick, darkish-green coatings of polyaniline were formed on aluminum only when the scan range was from -1.0 to 3.0 V versus SCE.

Infrared Spectroscopy

Figure 2 shows the infrared spectra of polyaniline coatings formed on aluminum as a function of the number of cycles. Polyaniline coatings show char-
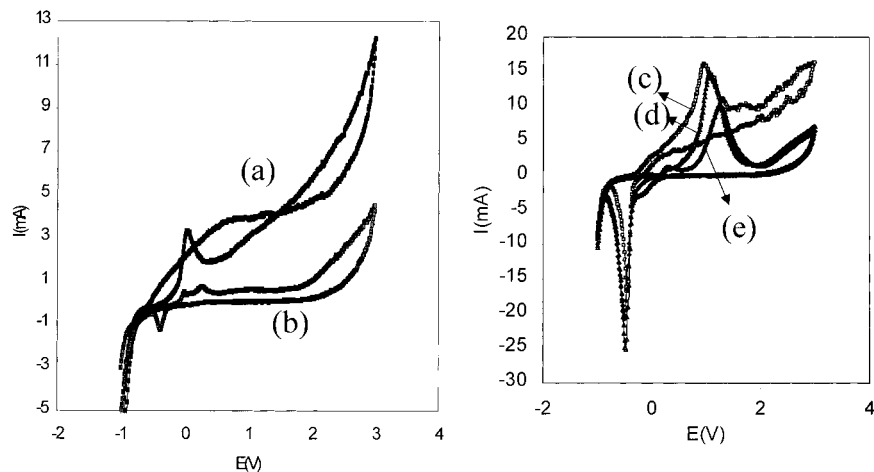
Figure 1 Cyclic voltammograms for the polymerization of aniline [0.1M] using oxalic acid [0.25M] as electrolyte at 20 mV/s. (a) 1st cycle, (b) 3rd cycle, (c) 15th cycle, (d) 20th cycle, and (e) 25th cycle.

acteristic peaks at 1600 and 1500 cm^{-1} because of the presence of quinoid and benzenoid groups. The presence of aromatic NH groups is confirmed by the presence of a peak at 1300 cm^{-1}. The peak at 830 cm^{-1} confirms the presence of p-substituted benzene rings. These peaks are in agreement with the characteristic peaks of polyaniline reported in the literature.[25]

Polypyrrole Coatings on Aluminum

Cyclic Voltammetry

Figure 3 shows the cyclic voltammograms of the formation of polypyrrole coatings on aluminum as

a function of the number of cycles. Unlike polyaniline coatings, polypyrrole coatings were formed at very high scan rates to trap the initial adsorption of hydrogen process. This was possible when the coatings were formed by using a scan rate of 750 mV/s. As the number of cycles was increased, the peak starts to disappear and polypyrrole does not show any major peak in the scanned region.

Infrared Spectroscopy

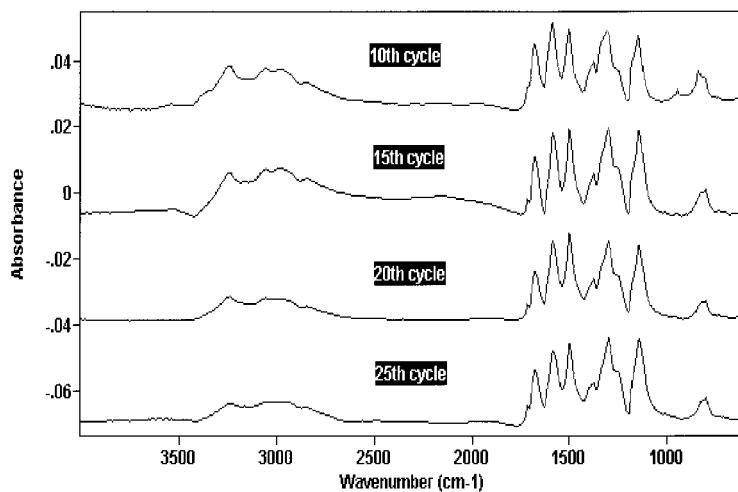Figure 4 shows the infrared spectra of polypyrrole coatings formed on aluminum as a function of the

Figure 2 Infrared spectra of polyaniline formed at 20 mV/s for long cycles using aniline (0.1M) and oxalic acid (0.25M) as electrolytes.
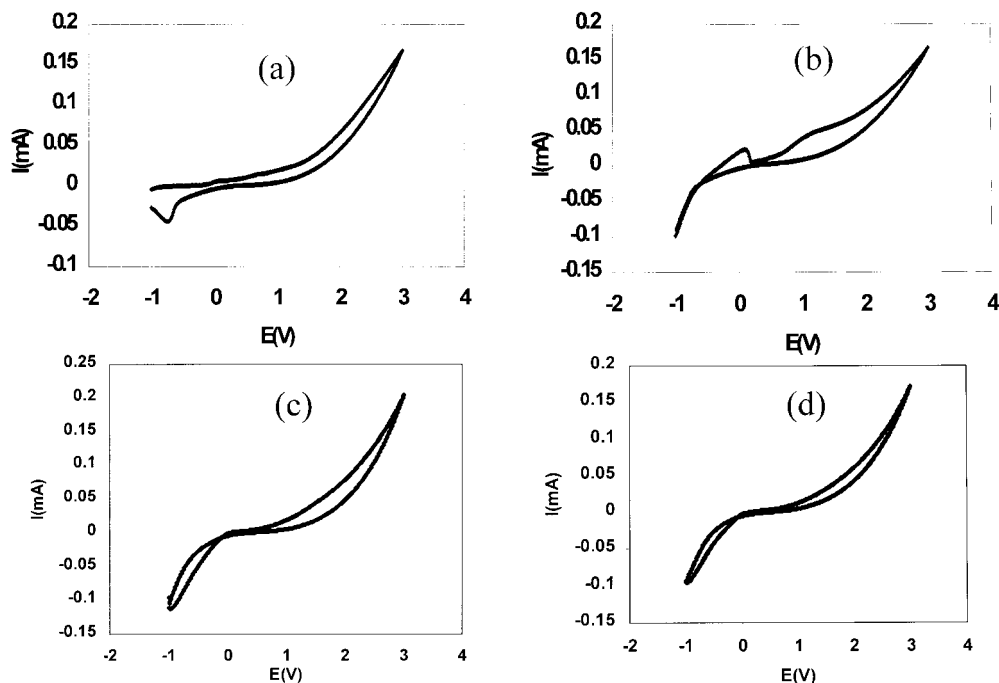
Figure 3 Cyclic voltammograms of the polymerization of pyrrole (0.1*M*) and oxalic acid (0.25*M*) at 750 mV/s. (a) 1st cycle, (b) 3rd cycle, (c) 10th cycle, and (d) 20th cycle.

number of cycles. Polypyrrole shows characteristic peaks at 1550 and 1500 cm^{-1} due to C=N stretch and C—N stretch. It also shows peaks at 1040, 960, and 790 cm^{-1} due to ring vibrations of pyrrole.[26] It can be clearly seen that the chemical structure of polypyrrole is different from that of polyaniline. The presence of the peak at 1720 cm^{-1} suggests overoxidation of polypyrrole under these conditions.

Formation of Polyaniline–Polypyrrole Composite Coatings on Aluminum

Cyclic Voltammetry

Figure 5 shows the cyclic voltammograms of the polymerization of aniline and pyrrole after the second, third, and fifth cycles, respectively. There are two prominent peaks in the cyclic voltammograms, an anodic peak current at around 1.0 V
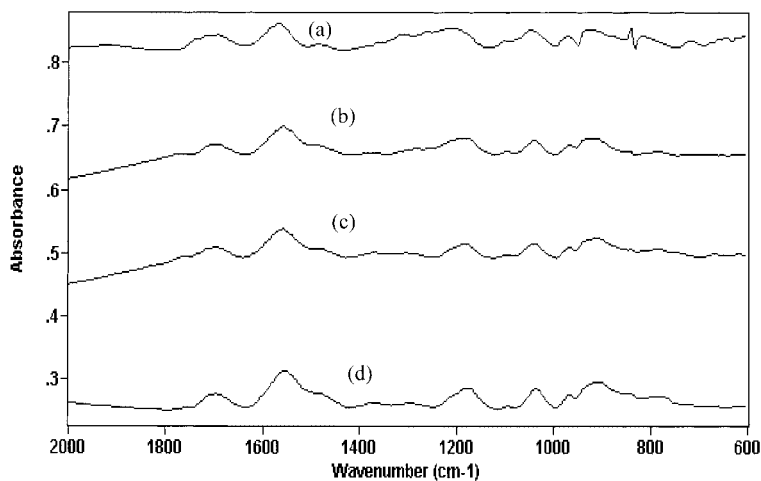

Figure 4 Infrared spectra of the formation of polypyrrole at 750 mV/s using oxalic acid (0.25*M*) as electrolyte. (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle, and (d) 4th cycle.
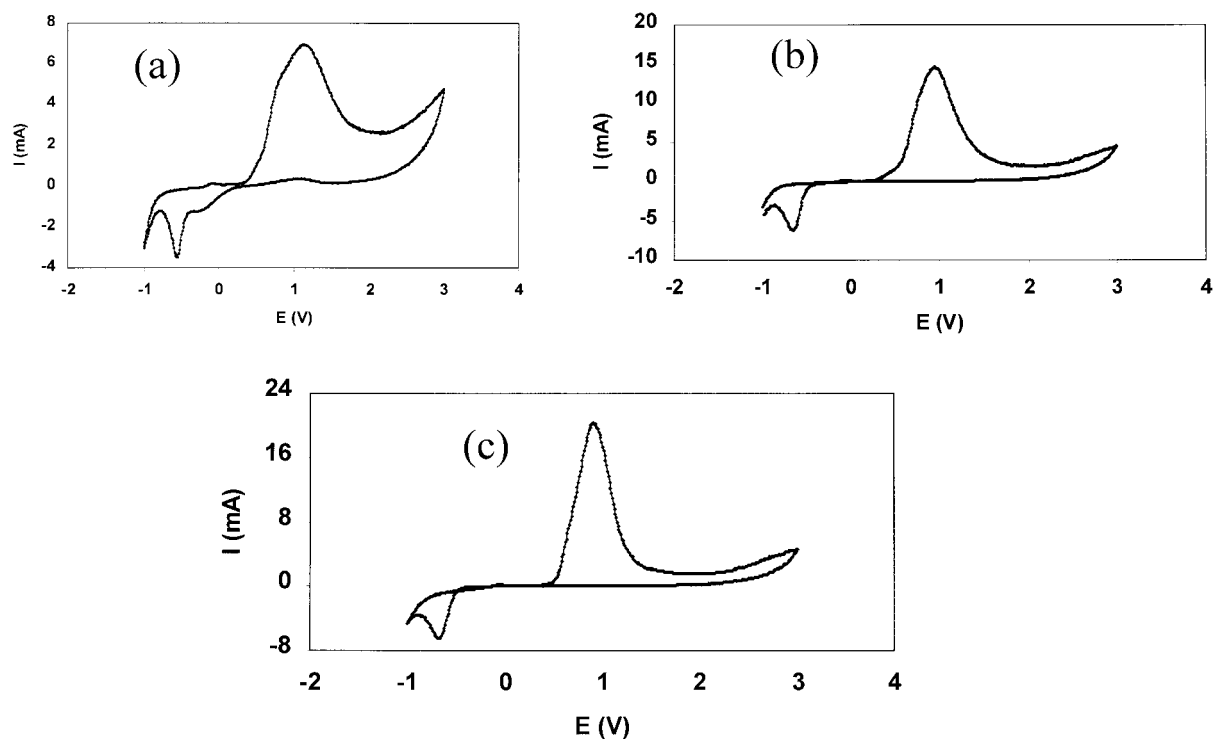
Figure 5 Cyclic voltammograms for the polymerization of polyaniline–polypyrrole composite coatings at 20 mV/s using oxalic acid (0.25M) as electrolyte and aniline (0.1M) and pyrrole (0.1M) as monomers. (a) 2nd cycle, (b) 3rd cycle, and (c) 5th cycle.

versus SCE, which is due to the oxidation of the composite. A corresponding cathodic peak current at around −0.7 V versus SCE is due to the reduction of the oxidized composite. There is also an anodic peak current at around −0.1 V versus SCE. This peak reduces in intensity with the increase in number of cycles. This is due to the oxidation and adsorption of hydrogen as seen in the formation of both polyaniline and polypyrrole coatings on aluminum. This particular anodic peak current is a dominant reaction prior to the formation of the composite coatings.

Figure 6 shows the cyclic voltammograms of the polymerization of aniline and pyrrole after the 10th, 15th, and 25th cycles, respectively. Here also, the peak due to the oxidation and adsorption of hydrogen can be seen around −0.1 V versus SCE, but it is further reduced in intensity. The prominent anodic peak current around 1.0 V versus SCE, which increases in intensity until the first five cycles, decreases in intensity from the 10th to the 25th cycles. It becomes broader to extend over a range of 1.0–1.8 V versus SCE. Similarly, the corresponding cathodic peak at around −0.7V versus SCE also reduces in intensity from the 10th to 25th cycle. Comparing Fig-

ures 1, 3, and 6, it can be clearly seen that the shape of the cyclic voltammogram is influenced by the nature and concentration of the monomers in the solution.

Infrared Spectroscopy

Figure 7 shows the comparison of the infrared spectra at longer reaction times for the composite coatings and the homopolymeric coatings. The composite coatings show characteristic peaks at 1600, 1400, 1300, 1040, 960, 790, and 830 cm^{-1} due to C=N, NH deformation from pyrrole ring, aromatic NH, ring deformations of pyrrole, and p-substituted benzene rings. The presence of characteristic peaks of both polyaniline and polypyrrole confirms the formation of polyaniline–polypyrrole composites.

Scanning Electron Microscopy

Figure 8 shows the comparison of the SEM micrographs of polyaniline–polypyrrole composite coatings and the homopolymeric coatings formed on the aluminum substrate. It can be seen that the morphology of the composite coatings are dis-
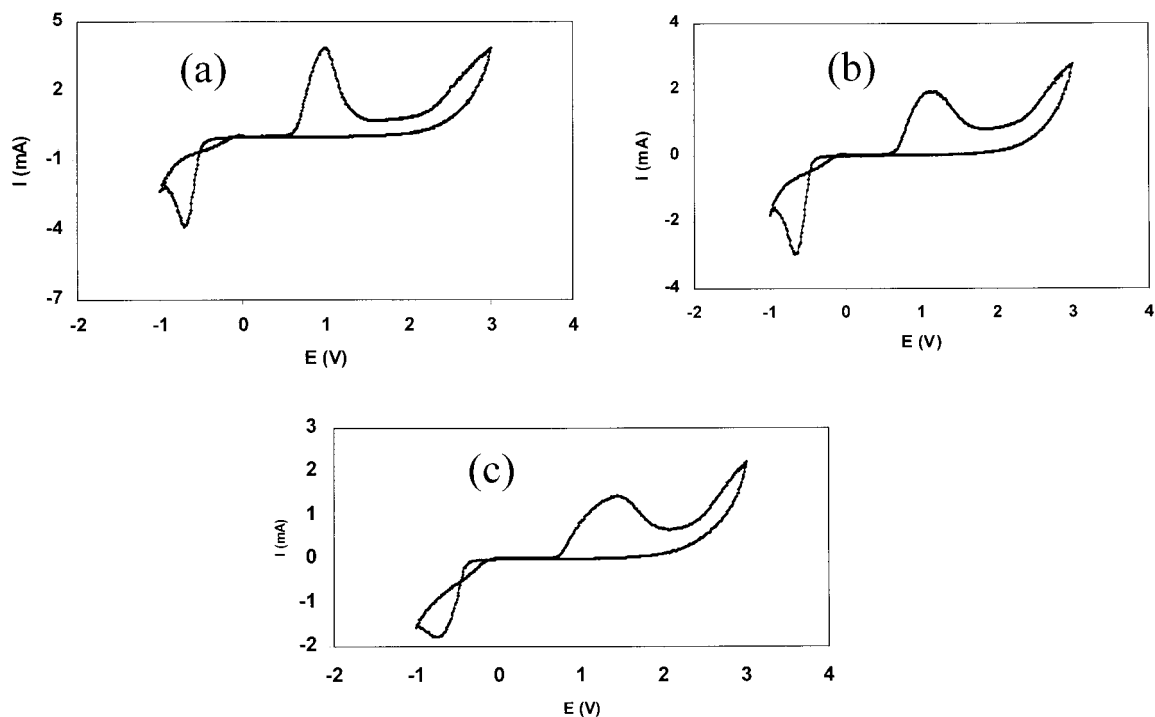
Figure 6 Cyclic voltammograms for the polymerization of polyaniline–polypyrrole composite coatings at 20 mV/s using oxalic acid (0.25M) as electrolyte and aniline (0.1M) and pyrrole (0.1M) as monomers. (a) 10th cycle, (b) 15th cycle, and (c) 25th cycle.

tinctly different from that of the homopolymers. Polyaniline has granular structure when compared to that of polypyrrole, which has globular structure. When the composite coatings of these two homopolymers are formed, we see a dense, compact flaky morphology.

CONCLUSIONS

The formation of polyaniline–polypyrrole composite coatings on aluminum substrate was successfully achieved by using oxalic acid as the electrolyte. The technique used for the electrochemical
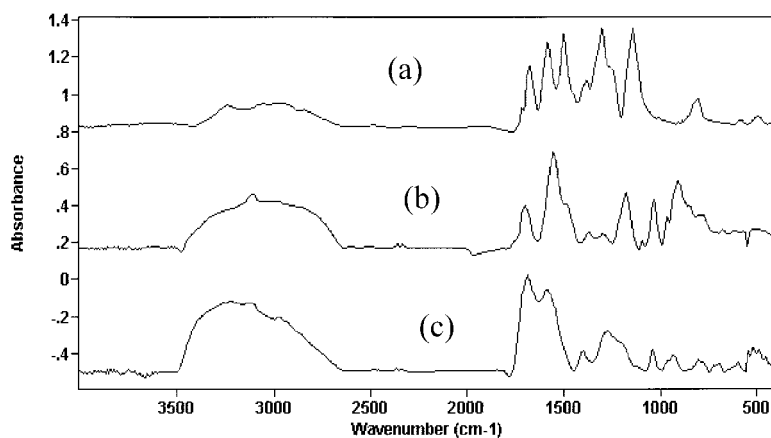

Figure 7 Comparison of the infrared spectra of the coatings formed on aluminum. (a) Polyaniline coatings, (b) polypyrrole coatings, and (c) polyaniline–polypyrrole composite coatings.
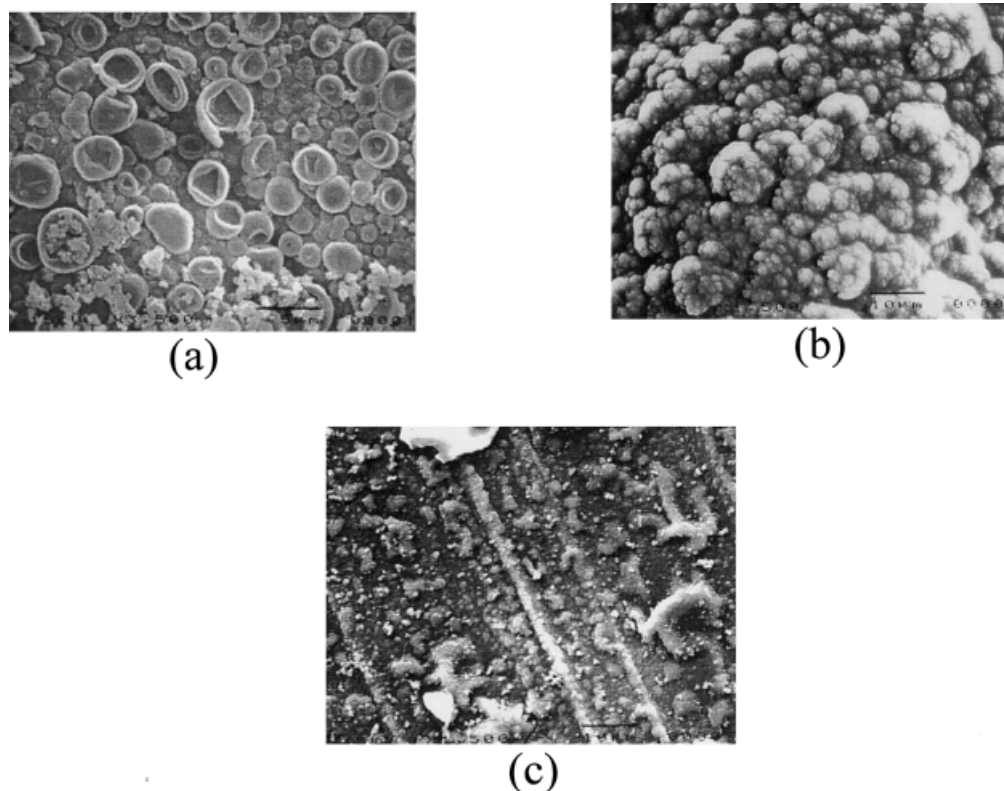
Figure 8   Comparison of the SEM micrograph of the coatings formed on aluminum. (a) Polyaniline coatings, (b) polypyrrole coatings, and (c) polyaniline–polypyrrole composite coatings.

deposition was cyclic voltammetry. An anodic peak at around -0.1 V versus SCE is present at shorter reaction times. This is due to the oxidation and adsorption of hydrogen. The cyclic voltammograms of the composite coatings shows the presence of an anodic peak current (around 1.0 V versus SCE) and a cathodic peak current (around -0.7 V versus SCE). Infrared analysis of the coatings reveal that composite coatings of polyaniline and polypyrrole can be formed on aluminum substrate by using cylic voltammetry. The SEM micrographs of the composite coatings also show distinct changes in morphology from that of the homopolymeric coatings.

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