

Study of the Chemical Polymerization of Pyrrole onto Printed Circuit Boards for Electroplating Applications

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SYNOPSIS

We have studied the deposition of thin films of a conducting polymer, polypyrrole, onto printed circuit boards (PCBs). Film formation occurs as a result of the *in situ* polymerization of pyrrole monomer using a 1 : 1 FeCl₃/5-sulfosalicylic acid oxidant complex in aqueous solution. We have optimized the polymerization conditions in order to coat a large number of PCBs with a *single* polymerization bath, while at the same time maintaining the *quality* of the conducting polymer coating (i.e., keeping its surface resistance below 10⁴ Ω per square). These improvements were achieved simply by controlling the initial oxidant–monomer mole ratio such that the oxidant is always present in significant excess. We have also examined the formation of thick polypyrrole layers obtained from the progressive buildup of thin layers. The morphology and film thickness of these polypyrrole coatings have been studied by scanning electron microscopy. Some preliminary electroplating experiments using these polypyrrole–PCB composites are also described. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Current industrial technologies employed for the metallization of printed circuit boards (PCBs) utilize colloidal precious metals (e.g., Pd or Pt) and known carcinogens such as formaldehyde.¹ Thus, for both economic and environmental reasons there is considerable interest in developing alternative “clean” technologies for such processes. In the last few years several groups have demonstrated the potential utility of conducting polymers for the metallization and through-hole plating of PCBs.^{2–6} In this general approach a thin film of conducting polymer is first deposited onto the surface of the PCB. Once this electrically conductive layer has been formed, the PCB can be subsequently metallized by conventional electroplating technologies.⁷ In the case of polypyrrole, deposition onto the PCB has been achieved via a two-step chemical synthesis in which either the pyrrole monomer or oxidant are located (adsorbed) at the surface of the PCB in a pretreatment step.^{2,3}

This treated PCB is subsequently immersed in a solution containing the other reagent, and the resulting polymerization occurs almost entirely at the PCB surface. In the case of polyaniline the preformed conducting polymer is solution-cast or dip-coated from acetic acid solution onto the PCB.^{4,5} This conducting polymer layer is then dried in an oven prior to electrolytic metallization. The only drawback of this latter method would appear to be the use of a highly corrosive acidic solvent.

In collaboration with a research group at Los Alamos National Laboratory one of us (S.P.A.) recently described a facile one-step method for coating PCBs with an insoluble polypyrrole film of submicron dimensions.⁶ The general protocol was first described by Kuhn et al. of the Milliken Research Corporation for the preparation of conducting polymer–textile composites.^{8,9} Thus, the PCB was simply immersed into an aqueous reaction solution containing pyrrole monomer, a near-stoichiometric amount of FeCl₃ oxidant (i.e., an initial FeCl₃–pyrrole mole ratio of 2.40 : 1), 5-sulfosalicylic acid, and 1,5-naphthalenedisulfonic acid (disodium salt). The 5-sulfosalicylic acid acts as a bidentate ligand to form a 1 : 1 complex with the Fe³⁺ oxidant; this oxidant

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complex is less reactive toward pyrrole than the Fe^{3+} species alone.^{8,9} The resulting slower polymerization rate appears to favor *surface* polymerization over *solution* polymerization. The role played by the 1,5 naphthalenedisulfonic acid salt is less clear. However, it has recently been established that, at least in the case of textile substrates, *both* these aromatic sulfonic acid species subsequently become incorporated into the polypyrrole coating as dopant counterions.¹⁰ In our initial experiments at Los Alamos using the Milliken methodology outlined above, the polypyrrole was deposited directly onto the surface of the PCB substrate within 60 min at room temperature. At first sight this procedure is rather attractive as a means of obtaining a sufficiently conductive coating on PCBs so as to allow subsequent metallization via electroplating. However, the polypyrrole deposition process is very inefficient: less than 4% by mass of the conducting polymer (based on the initial charge of pyrrole monomer) is actually adsorbed onto the PCB. Furthermore, in their subsequent independent experiments, the Los Alamos group encountered problems in developing the polypyrrole deposition process so as to be able to coat multiple PCBs with a single polymerization bath.¹¹ Achieving such multiboard coating capability would considerably enhance the commercial viability of this new process.

In the present work we describe an improved recipe for the chemical deposition of polypyrrole layers onto PCBs. Unlike the previously reported "Los Alamos" recipe, this "Sussex" recipe is particularly well suited for the treatment of many PCBs using a *single* polymerization bath. The resulting polypyrrole-PCB composites have been characterized by both gravimetry and surface resistance measurements. The morphology and thickness of the polypyrrole coatings have been examined by scanning electron microscopy and some preliminary electroplating experiments are also described.

EXPERIMENTAL

Chemicals

The PCBs were all FR-4 single-laminate epoxy-glass composites obtained from LeaRonal (U.K.) Ltd. They were used as received in all experiments apart from one when they were subjected to a methanol rinse pretreatment (*vide infra*) prior to use. For identification purposes each PCB sample was stamped with an identification number using a hand-held punch.

The pyrrole, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 5-sulfosalicylic acid (5-SSA) and 1,5 naphthalenedisulfonic acid (disodium salt) (1,5 NDSA) were supplied by Aldrich Chemical Co. All were used as received except the pyrrole monomer, which was purified by passing through a basic alumina column immediately prior to use. Deionized water was used in all experiments. Methanol (e.g., Fisons) was used as received.

Chemical Deposition of Polypyrrole onto PCBs

Effect of Immersion Time

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.330 g), 5-SSA (2.222 g), and 1,5-NDSA (0.634 g) were co-dissolved in 34 mL water at room temperature with the aid of an ultrasonic bath. A piece of PCB (0.48–0.54 g) was immersed in this purple solution and finally 10.0 μL ($\pm 2\%$) pyrrole (corresponding to an initial oxidant-monomer mole ratio of 60 : 1) was injected via micropipette. The polymerization vessel was placed on a roller mill for the required time period (5–60 min) and then the PCB was removed from the solution bath and dried using a fast-flowing nitrogen stream at room temperature. Weight uptake (due to polypyrrole deposition) and sheet resistance values were recorded for each PCB sample.

Multiple Deposition of Polypyrrole Coatings onto a Single PCB

The above procedure was adopted using a constant immersion time of 20 min. The resulting polypyrrole-coated PCB sample was subsequently immersed in a further seven fresh polymerization baths in turn (each with an initial oxidant-monomer mole ratio of 60 : 1) in order to build up a thicker polypyrrole coating on the PCB surface. Weight uptake and sheet resistance measurements were carried out on the dried PCB between each bath treatment.

Multi-PCB Coatings from a Single Polymerization Bath

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.167 g), 5-SSA (1.111 g), and 1,5 NDSA (0.317 g) were co-dissolved in 17 mL water at room temperature using an ultrasonic bath. A piece of PCB (0.30–0.40 g) was immersed in this solution and then 5.0 μL ($\pm 2\%$) pyrrole (corresponding to an initial oxidant-monomer mole ratio of 60 : 1 for this first PCB sample) was added via a micropipette. The polymerization vessel was placed on a roller mill for 20 min at room temperature. At the end of this time period the coated PCB was re-

moved and a new "virgin" PCB was immersed in the same "old" polymerization bath and a further $5.0 \mu\text{L}$ ($\pm 2\%$) pyrrole was injected into the reaction mixture. This procedure was repeated in order to treat up to 15 PCB boards *using the same polymerization bath*. During the course of these experiments the oxidant complex is progressively depleted, but even for the final fifteenth PCB sample, the "initial" oxidant-monomer mole ratio is still as high as 25 : 1 (assuming all the pyrrole monomer from each of the previous experiments has been used up). After drying in a nitrogen stream, the weight uptake and sheet resistance values were recorded for each PCB sample. This experiment was repeated three times to check reproducibility.

The above experiment was repeated with a methanol rinse pretreatment of each of the 15 PCB samples. Thus, all the PCBs were completely immersed in methanol for 10 min, initially dried in a nitrogen stream, and then finally dried in a 40°C oven overnight. After this pretreatment each PCB was weighed prior to the experimental procedure described above.

Finally, the above experiment (*without* the methanol rinse pretreatment) was repeated in the *absence* of (a) 5-SSA and (b) 1,5 NDSA. In all of the experiments described above due care was taken to ensure that all of the PCB samples were dried under identical conditions in order to minimize random errors in the gravimetric analyses.

Copper Electroplating of Polypyrrole-coated PCBs

Effect of Immersion Time

A piece of polypyrrole-coated PCB (sheet resistance = $1500 \pm 150 \Omega$ per square for each sample) was drilled at one end and a piece of copper wire was passed through the drill hole to form a loose loop. This PCB was then immersed in a proprietary cleaning agent, Ronaclean PC590, at 40°C for 3 min before being rinsed with deionized water. It was then etched using proprietary Ronaetch PS at 25°C for 1 min followed by a water rinse. A hot-air dryer was then used to dry the PCB before leaving it in a desiccator for 30 min. The loop of copper wire was then removed and the initial mass of the PCB was measured. The copper wire was then re-inserted through the hole and an extremely tight contact between the PCB and the copper loop was achieved using a pair of pliers. The PCB was then immersed in 10% H_2SO_4 for 1 min. It was then placed just below the surface of a proprietary Copper Gleam 2001 solution (a proprietary copper sulfate solution containing various

additives [e.g., LeaRonol (U.K.) Ltd.] so as to be equidistant between two copper electrodes. The battery power supply was switched on and a current of 0.34 mA (corresponding to a current density of 2 A dm^{-3}) was passed through the solution. After the desired time interval (5–40 min), the current was switched off and the copper-coated PCB sample was rinsed with deionized water. It was then dried using a hot-air stream and placed in a desiccator for 30 min. Once the copper wire loop had been removed, the final mass of the PCB was recorded, and hence the mass of copper deposited onto the PCB was calculated.

Effect of Current Density

The same electroplating procedure as outlined above was utilized for various PCB samples, each with sheet resistances of $1600 \pm 350 \Omega$ per square. A fixed immersion time of 30 min was utilized and the current density was varied over the range $1\text{--}3 \text{ A dm}^{-3}$ by adjusting the power supply to the required value prior to inserting the polypyrrole-coated PCB sample between the two electrodes. After the electro-deposition of copper, the metallized polypyrrole-PCB samples were cleaned and dried prior to removal of the wire loop and recording the final mass of each composite as described above.

Effect of Sheet Resistance

The same electroplating procedure outlined above was employed with a fixed immersion time of 30 min and a constant current density of 2.0 A dm^{-3} . Various polypyrrole-coated PCB samples of differing sheet resistances obtained from our earlier multi-layer deposition experiments (*vide supra*) were utilized. Their sheet resistance values lay in the range 8×10^1 to $9 \times 10^3 \Omega$ per square.

Synthesis of "Bulk Powder" Polypyrrole

The polymerization of pyrrole at an initial oxidant-monomer mole ratio of 60 : 1 was carried out in the *absence* of any PCB substrate so as to obtain polypyrrole as a precipitated "bulk powder" rather than as a thin film. The synthesis was scaled-up by a factor of 60 in order to obtain a sufficient quantity of polypyrrole for subsequent characterization. Thus, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (70.1 g), 5-SSA (66.7 g), and 1,5-NDSA (19.0 g) were co-dissolved in 1020 mL deionized water prior to the addition of pyrrole ($300 \mu\text{L} \pm 2\%$) via micropipette. This reaction solution was then stirred for 60 min at room temperature. The precipitated polypyrrole bulk powder was separated

by filtration under gravity and washed with water. This black powder was further washed with copious amounts of methanol (until the washings were clear) in order to remove any excess iron salts still remaining in the precipitate. The precipitate was then dried in a 40°C oven for 48 h (final yield = 0.275 g) prior to characterization by elemental microanalyses, four-point probe conductivity measurements, thermogravimetric analysis, FTIR spectroscopy, atomic absorption spectroscopy, and scanning electron microscopy.

Instrumentation

Perkin-Elmer TGA-7 and 2380 spectrophotometer instruments were used for the thermogravimetric analyses and atomic absorption assays, respectively (in the former experiments runs were made in air at a scan rate of 40°C per minute and in the latter experiments the polypyrrole bulk powder sample was dissolved in a commercial bleach solution as described by Kuhn et al.^{9b} prior to analysis in the 5–30 ppm range). An FTIR spectrum of the bulk polypyrrole (KBr disk) was recorded using a Perkin-Elmer 1700 spectrometer in the range 1800–600 cm^{-1} at a spectral resolution of 4 cm^{-1} (256 scans). Elemental microanalyses (C, H, N, and S) of the polypyrrole bulk powders were determined in-house at the University of Sussex using both Carlo-Erba 1106 and Perkin-Elmer 2400 analyzers. All weight uptake measurements (for both polypyrrole and copper deposition) were made using an OHAUS GA2000 five figure balance ($\pm 20 \mu\text{g}$). Surface resistance measurements (estimated experimental uncertainty $\pm 5\%$) were made using a Keithley 195 digital multimeter in the “ohmmeter” mode. Two clean copper plates were applied to the polypyrrole-coated PCB sample under investigation so that the edges of each plate formed a “square” of 4 cm^2 surface area. The sheet resistance for both sides of the PCB sample was measured and an average value was recorded. Our control experiments on uncoated PCB samples indicated sheet resistances greater than $10^8 \Omega$ per square.

Scanning electron microscopy studies were carried out at LeaRonald (U.K.) Ltd. using a JEOL JSM-35 instrument at an operating voltage of 20 kV. All samples were sputter-coated with gold prior to examination in order to prevent sample charging.

RESULTS AND DISCUSSION

Most chemical syntheses of conducting polymers described in the literature are carried out under

nonstoichiometric conditions, with the monomer usually present in excess relative to the chemical oxidant. This method is believed to reduce the possibility of overoxidation of the conducting polymer. In contradistinction, in our research program on conducting polymer colloids^{12–15} we have generally synthesized conducting polymers such as polypyrrole and polyaniline using *stoichiometric* initial oxidant–monomer mole ratios (e.g., 2.33 : 1 for the polymerization of pyrrole by FeCl_3). These reaction conditions were selected in order to *minimize* the rate of polymerization (which increases with both increasing oxidant and monomer concentration¹⁶) for a given *yield* of conducting polymer. If the rate of polymerization is too high, stable colloids are not formed and the conducting polymer is instead obtained as an unprocessable macroscopic precipitate.

There have been relatively few studies of conducting polymer syntheses using oxidant–monomer ratios in *excess* of the stoichiometric amount. As far as we are aware, Myers was the first to point out that high initial oxidant–monomer mole ratios were actually desirable for the synthesis of polypyrrole in certain nonaqueous solvents.¹⁷ We share the view expressed by Nicholau et al. that, regardless of the solvent, such syntheses should suppress the formation of soluble pyrrole oligomers and favor the formation of insoluble high-molecular-weight polymer.¹⁸ Recently, in an attempt to verify this hypothesis we synthesized polypyrrole using ammonium persulfate at three oxidant concentrations, which were in excess, stoichiometric, and deficient with respect to monomer. The postreaction supernatant solutions from each of these polymerizations were examined by UV/visible absorption spectroscopy, and we observed a decrease in absorbance in the pyrrole oligomer peaks with increasing oxidant concentration.¹⁹ Thus these preliminary experiments suggested that oligomer formation can indeed be suppressed by using higher initial oxidant–monomer mole ratios for the polymerization of pyrrole. Moreover, we also noted a sharp decrease in conductivity ($< 10^{-5} \Omega^{-1} \text{cm}^{-1}$) for the polypyrrole powders obtained from the two syntheses with stoichiometric and higher than stoichiometric oxidant concentrations. Clearly for *some* oxidants the use of high (or even stoichiometric) oxidant–monomer ratios is impractical for the synthesis of high-quality conducting polymers. On the other hand, Martin’s group has reported that surprisingly good-quality polypyrrole bulk powders can be prepared with oxidant–monomer ratios as high as 50 : 1 provided *mild* oxidants such as FeCl_3 are utilized.²⁰

Accordingly, in the present work we modified the

near stoichiometric oxidant–monomer ratio of 2.40 : 1 used in the Los Alamos recipe in favor of a much higher initial oxidant–monomer ratio of 60 : 1 (based on the first 5.0- μL aliquot of pyrrole). We calculated that this new Sussex recipe would enable us to treat up to 15 PCBs sequentially using the same polymerization bath while remaining at relatively high oxidant–monomer ratios for each individual PCB treatment. This “excess oxidant” approach also means that the coating process is easily controlled: each PCB sample is simply immersed in the reaction solution containing the oxidant and the required aliquot of pyrrole monomer is added last to the solution. We anticipated that the *overall* rate of pyrrole polymerization would be similar to that obtained using the Los Alamos recipe since the effect of increasing the oxidant concentration by a factor of 5 would be compensated by the concomitant fivefold decrease in monomer concentration. We considered that any *modest* increase in polymerization rate due to the decreased solution pH (resulting from the higher concentrations of the acidic FeCl_3 and 5-SSA reagents) would be potentially beneficial since it should lead to a reduced immersion time for each PCB sample relative to that used in the Los Alamos recipe. However, since it is well known that highly acidic media ($\text{pH} < 1$) can be detrimental to the formation of highly conductive polypyrrole,²¹ we were careful to avoid excessively high initial concentrations of these two reagents.

In our first experiment using the Sussex recipe we examined the effect of immersion time on the mass of deposited polypyrrole and the sheet resistance of this conducting polymer coating (see Fig. 1). Although there is some scatter in the experimental data, it is nevertheless evident that increasing the immersion time results in a monotonic increase in the weight uptake of polypyrrole. On the other hand, there is relatively little decrease in the sheet resistance of the polypyrrole-coated PCBs for immersion times longer than approximately 20 min. Obviously for commercial production the immersion time should be as short as possible. Thus, as a compromise we decided to maintain the immersion time at 20 min in all our subsequent experiments, even though the pyrrole monomer is clearly not completely consumed in this time period. This immersion time is considerably less than the 60-min immersion time utilized for the Los Alamos recipe,⁶ but it is achieved at the expense of sheet resistance. Thus, the average sheet resistance for the Sussex polypyrrole-coated PCB samples is approximately 1200 Ω per square after 20 min (see Fig. 1), whereas sheet resistances as low as 380 Ω per square were

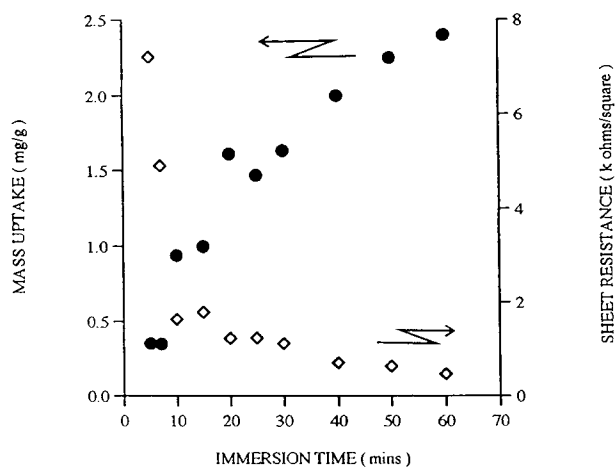


Figure 1 Effect of PCB immersion time on the normalized weight uptake of polypyrrole (per gram of PCB) and average sheet resistance of the polypyrrole–PCB composites using the Sussex recipe (see text).

obtained after 60 min using the Los Alamos recipe.^{6a} However, the normalized weight uptake of polypyrrole for these two samples is 1.5 mg g^{-1} for the Sussex recipe (see Fig. 1) vs. 1.1 mg g^{-1} for the Los Alamos recipe.^{6b} It is not clear whether these values actually reflect some difference in the *quality* of the deposited polypyrrole; they may simply reflect differences in surface area and/or porosity between the two types of PCB substrate (FR-4 and G-10) used in these independent investigations.

In our second experiment we examined the effect of repeated deposition of up to eight polypyrrole coatings on the weight uptake and sheet resistance of a single PCB sample. This experiment was carried out for two reasons. First, we wanted to investigate whether there were any changes in the morphology of the polypyrrole coating with increasing coating thickness. Using the Los Alamos recipe Gottesfeld et al. have shown that the polypyrrole was initially deposited onto the PCB substrate as a compact thin film of 100–300 nm thickness.⁶ However, further polypyrrole deposition resulted in a profound change to a less dense, globular conducting polymer morphology. Therefore we felt it would be of interest to examine whether the increased oxidant–monomer mole ratio used in the Sussex recipe (which should suppress the formation of soluble pyrrole oligomers) had any affect on the morphology of the deposited polypyrrole. Second, these experiments were expected to produce polypyrrole-coated PCB samples over a wide range of sheet resistances, which could be subsequently utilized in our electroplating experiments (*vide infra*). The results are depicted in Figure 2. The weight uptake due to polypyrrole de-

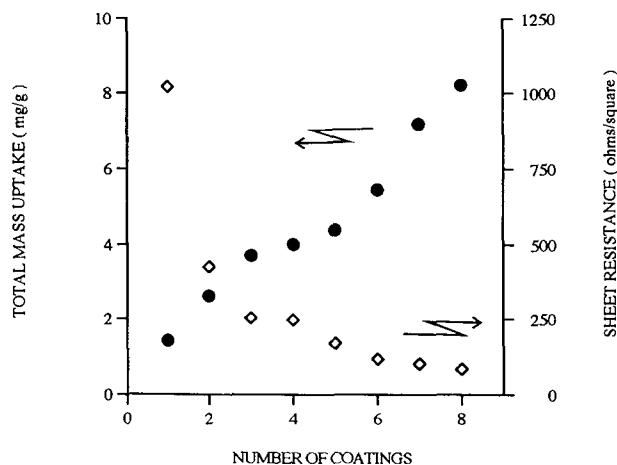


Figure 2 Cumulative effect of repeated polypyrrole deposition onto a single PCB substrate in terms of the increase in normalized polypyrrole weight uptake (per gram of PCB) and the decrease in average sheet resistance of the polypyrrole-PCB composites using the Sussex recipe (see text).

position is almost linear, with an average weight uptake of approximately 1 mg g^{-1} per coating treatment. This weight uptake is accompanied with a concomitant near-exponential decrease in the sheet resistance from approximately 1000Ω per square initially down to 84Ω per square for the eighth sample.

The morphology of a virgin uncoated FR-4 PCB sample is shown in Figure 3. A cross section through the same PCB sample is shown in Figure 4. Clearly the PCB substrate has an appreciable surface roughness factor on a microscopic scale. Figure 5 depicts a similar cross section of a PCB which has been coated with eight consecutive polypyrrole lay-

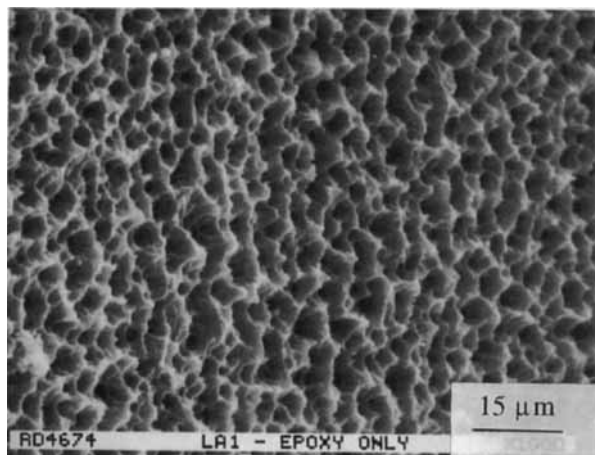


Figure 3 Scanning electron micrograph of an uncoated FR-4 PCB substrate (birds-eye view).

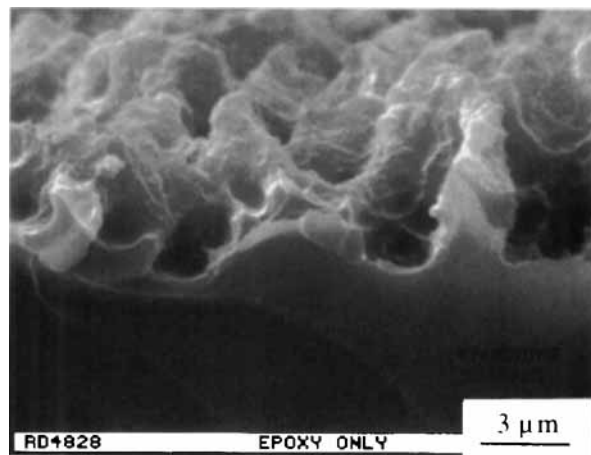


Figure 4 Scanning electron micrograph of an uncoated FR-4 PCB substrate (cross-section view).

ers. Initially, a continuous thin film of polypyrrole is formed over the surface of the PCB, but subsequently the conducting polymer is deposited with a more globular morphology. We have recently observed very similar changes in morphology for polypyrrole-quartz composite fibers of increasing conducting polymer coating thickness.²² Thus it seems that the Sussex recipe offers no obvious advantages over the Los Alamos recipe in terms of controlling the morphology of the polypyrrole coating.

In our third series of experiments we examined the efficiency of the polypyrrole coating process. Specifically, we asked the following question: How many PCB samples can be successfully coated with polypyrrole using a *single* polymerization bath? The results of our first study are illustrated in Figure 6. Although there is considerable scatter on the ex-

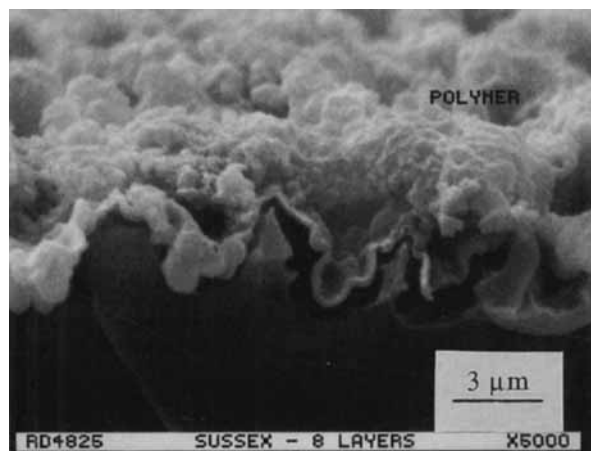


Figure 5 Scanning electron micrograph of a polypyrrole-coated PCB composite after eight successive coatings using the Sussex recipe (cross-section view).

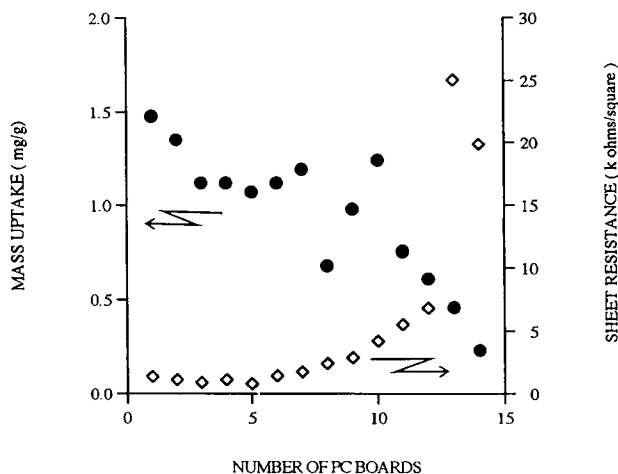


Figure 6 Normalized polypyrrole weight uptake (per gram of PCB) and average sheet resistance for each of 14 PCB samples treated with the same polymerization bath using the Sussex recipe (see text).

perimental points, there is nevertheless a dramatic decrease in the mass of polypyrrole deposited onto each of the PCB samples from 1.50 to 0.25 mg g^{-1} during the course of the experiment. The sheet resistance for the first 12 polypyrrole-coated PCB samples remained below 10^4 Ω per square but then increased dramatically ($> 10^4$ Ω per square) for the thirteenth and fourteenth PCB samples. This single polymerization bath experiment was repeated twice with essentially the same results and no discernible improvement in experimental scatter. It was also repeated in the absence of (a) 5-SSA and (b) 1,5 NDSA and in both cases significantly higher sheet resistances were obtained. This latter observation suggests that both these aromatic sulfonate species are indeed incorporated as dopant anions into the polypyrrole film.

A remarkable improvement in coating performance was achieved by a simple methanol-rinse pretreatment of the PCB samples (see Fig. 7). Much higher weight uptake of polypyrrole was obtained (initially as high as 4.0 mg g^{-1} and remaining above 2.7 mg g^{-1} even for the fifteenth PCB sample), and this in turn resulted in consistently lower sheet resistances (less than 10^4 Ω per square for *all* 15 PCB samples). We believe that this methanol-rinse pretreatment is an effective method for the removal of surface contaminants (e.g., dirt, grease, etc.) from the PCB surface. The resulting *clean* PCB surface is probably more easily wetted than the original contaminated PCB surface, which in turn leads to a more efficient deposition of the polypyrrole coating.

We note that the Sussex recipe leads to a comparable mass of polypyrrole deposited on the PCB substrate to the Los Alamos recipe (1.5 vs. 2.0 mg g^{-1} for the same immersion time of 20 min,²³ even though the latter method utilizes *five times as much* pyrrole monomer. We conclude that polypyrrole deposition onto a given PCB substrate is much more efficient for the Sussex recipe.

If we compare the weight uptake values and sheet resistances observed for the “clean” PCB samples (see Fig. 7) with the “dirty” PCB samples (see Fig. 6), it is evident that high weight uptake alone is not a sufficient condition for low sheet resistances. For example, a sheet resistance of less than 10^3 Ω per square was obtained with a loading of only 1.1 mg g^{-1} polypyrrole for the fifth “unwashed” PCB sample, whereas the sheet resistance of the fifteenth “methanol-washed” PCB sample was 8.5×10^3 Ω per square even though this latter sample’s polypyrrole loading was more than twice as high (> 2.7 mg g^{-1}). This observation suggests that there is a gradual drift in polypyrrole *quality* with successive PCB coating treatments. This is consistent with the expected increase in acidity of the polymerization bath during the course of the experiment due to the loss of protons from the 2- and 5-positions of the polymerizing pyrrole monomer.²⁴ Nevertheless, we believe these experiments have confirmed that our new Sussex recipe can greatly improve the overall efficiency of the polypyrrole deposition process. In particular, we have *significantly* increased the number of PCB samples which can be treated from a single polymerization bath. Very recently, we have

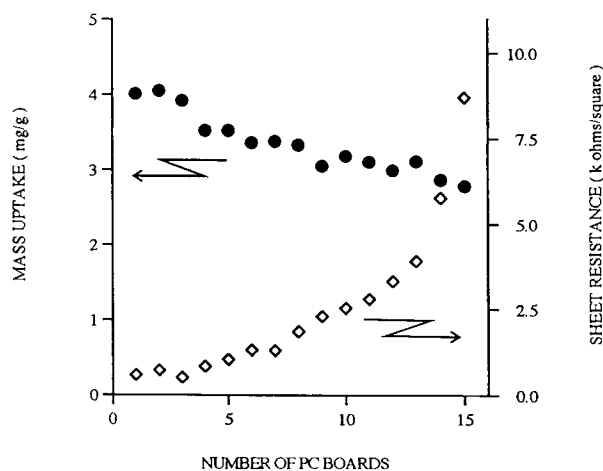


Figure 7 Normalized polypyrrole weight uptake (per gram of PCB) and average sheet resistance for each of 15 *methanol-rinsed* PCB samples treated with the same polymerization bath using the Sussex recipe (see text).

found that up to 30–40 PCBs can be coated with a high-quality polypyrrole overlayer from a single polymerization bath.²⁵ This further improvement can be achieved simply by immersing three PCBs in the bath for each addition of pyrrole monomer.

In this regard it is worth emphasizing that our own attempts²³ to increase the oxidant–monomer mole ratio of the Los Alamos recipe (by simply maintaining the original concentration of FeCl_3 and decreasing the pyrrole monomer concentration by a factor of 10) produced only very patchy polypyrrole coatings of very high sheet resistance (10^5 – 10^6 Ω per square) using immersion times of 20 min. We believe that this poor coating performance is due to the greatly reduced rate of polymerization obtained at this lower monomer concentration. Similarly, the Los Alamos group have attempted to coat large numbers of PCB samples by adding aliquots of *both* the FeCl_3 oxidant *and* the pyrrole monomer (such that the oxidant–monomer mole ratio was 2.40 : 1) to the polymerization bath for each successive PCB treatment.¹¹ In addition, for optimum results the bath liquor had to be filtered between each PCB treatment in order to remove excess solution-polymerized polypyrrole. This modified Los Alamos recipe also produced markedly inferior results to those obtained with the Sussex recipe: After only eight PCB samples the sheet resistance had risen to nearly 10^6 Ω per square. The authors suggest that this loss in coating quality is due to the progressive buildup of soluble pyrrole oligomers in the polymerization bath. They showed that the sheet resistance of the coated PCBs could eventually be reduced to below 10^4 Ω per square again by modifying the redox potential of the polymerization bath solution with the addition of KMnO_4 solution.¹¹ Thus, implementation of the Los Alamos recipe on a commercial basis would be feasible if the redox potential of the bath were continuously monitored prior to the judicious addition of KMnO_4 solution. On the other hand, the polypyrrole deposition achieved with the Sussex recipe is both reasonably rapid and relatively efficient at room temperature and the quality of the polypyrrole coating is acceptable for subsequent copper electroplating even up to the fifteenth PCB treatment (*vide infra*). The relatively high oxidant–monomer mole ratio used in this latter formulation *minimizes* the formation of soluble pyrrole oligomers, thus no KMnO_4 addition is required to modify the redox potential of the bath solution. There is also significantly less solution-polymerized polypyrrole (since the surface polymerization is more efficient) so the bath liquor does not require periodic filtration. Moreover, the Sussex formulation is facile:

it requires only the addition of a fixed quantity of pyrrole monomer with each new PCB sample.

In our electroplating experiments we examined the effect of immersion time, current density, and sheet resistance on the extent of copper deposition. The mass of copper deposited onto the polypyrrole-coated PCB samples increased linearly for immersion times up to 40 min (see Fig. 8). A similar linear increase in mass of copper was observed for current densities in the range 1 – 3 A dm^{-3} (see Fig. 9). The effect of increasing the sheet resistance on the efficiency of the electroplating process is illustrated in Fig. 10. The mass of deposited copper is not particularly sensitive to the sheet resistance of the polypyrrole-coated PCB. For example, a near 70-fold increase in sheet resistance from 84 Ω per square to 5700 Ω per square results in only a 2-fold reduction in mass of electrodeposited copper. Thus even the sample with the highest sheet resistance (ca. $9,400$ Ω per square) could be successfully coated with copper, albeit less efficiently. We conclude that all 15 polypyrrole-coated PCB samples from our “methanol-rinse” single polymerization bath experiments (sheet resistances $\leq 8,700$ Ω per square) were sufficiently conductive for the subsequent electrodeposition of copper.

Since the Sussex recipe utilizes even higher initial oxidant–monomer mole ratios than those reported by Martin’s group,²⁰ we decided to synthesize polypyrrole as a bulk powder precipitate in the *absence* of any PCB substrate in order to establish the quality

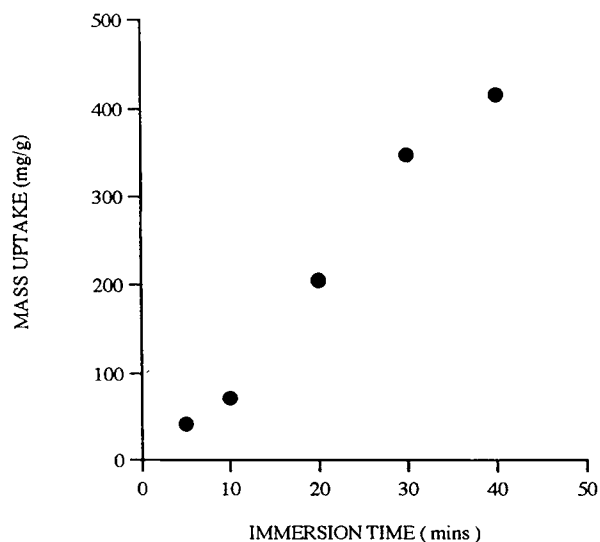


Figure 8 Effect of immersion time on the mass of copper deposited onto a polypyrrole-coated PCB sample during electroplating process (current density = 2 A dm^{-3} ; average sheet resistance = 1500 ± 150 Ω per square).

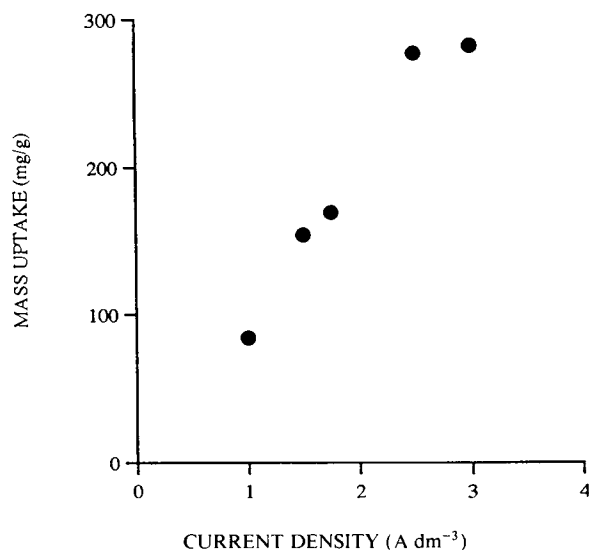


Figure 9 Effect of current density on the mass of copper deposited onto a polypyrrole-coated PCB sample during electroplating process (immersion time = 30 mins; average sheet resistance = $1600 \pm 350 \Omega$ per square).

of the material obtained under these rather unusual conditions. Our four-point probe measurements on this dried precipitate gave compressed pellet conductivities of approximately 1 S cm^{-1} . In addition, its FTIR spectrum was consistent with that previously reported for doped polypyrrole.²⁰ Elemental microanalyses indicated a S/N doping level (assuming 5-SSA to be the major dopant anion) of around 30% but were unusually low (C = 32.41%; H = 3.27%; N = 7.22%; S = 4.92%), indicating the presence of other elements. Given the high oxidant-monomer mole ratio used in our Sussex synthesis recipe, the obvious additional elements present in the polypyrrole precipitate are likely to be Fe and Cl. Indeed, both our thermogravimetric analyses and atomic absorption spectroscopy assays indicate the presence of substantial levels of Fe (at least 10.6%). This suggests that at least one of the dopant anions for the cationic polypyrrole chains is actually a 1 : 1 complex of Fe^{3+} (or possibly Fe^{2+}) with 5-SSA (we calculate an approximate Fe/S ratio of 1.25 : 1). Our scanning electron microscopy studies of this solution-polymerized polypyrrole bulk powder reveal a fused, globular morphology (not shown). This morphology is very similar to the material deposited on top of the (initially) compact thin polypyrrole films after multiple coating treatments (see Fig. 5). On the basis of the above morphological observations we tentatively suggest that the initial *surface* polymerization of pyrrole directly onto the PCB surface

is eventually superceded by the deposition of solution-polymerized polypyrrole.

CONCLUSIONS

Our new Sussex recipe for the chemical deposition of polypyrrole onto PCB substrates offers the following advantages over the Los Alamos recipe previously reported:

1. A reduced immersion time of 20 min per PCB sample.
2. At least 15 PCB samples can be treated using a *single* polymerization bath without significant loss in polypyrrole quality (sheet resistances remain below $10^4 \Omega$ per square).
3. Much more efficient use of the (expensive) pyrrole monomer. Approximately five times less pyrrole is required to treat a given size of PCB sample since a higher proportion of the pyrrole is polymerized on the PCB surface rather than in the solution.

Furthermore we have shown that a simple methanol-rinse pretreatment of the PCB substrate to remove surface contaminants prior to immersion in the polymerization bath results in a *significant* increase in the mass of polypyrrole deposited onto the PCB (from 1.5 up to 4.0 mg g^{-1}).

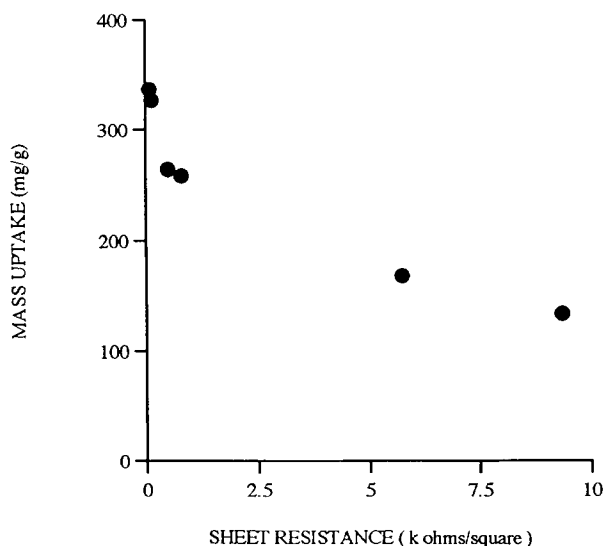


Figure 10 Effect of sheet resistance on the mass of copper deposited onto a polypyrrole-coated PCB sample during electroplating process (immersion time = 30 mins; current density = 2.0 A dm^{-3}).

We note that the Sussex recipe offers no particular advantage over the Los Alamos recipe in terms of morphological control of the deposited polypyrrole coatings. In both processes the polypyrrole is initially formed as a dense thin film on the PCB surface but subsequent deposition eventually leads to a more globular morphology. Finally, the relatively high initial oxidant–monomer mole ratio utilized in the Sussex recipe leads to the incorporation of iron-based complexes as dopant anions for the cationic polypyrrole chains. The conductivity of polypyrrole bulk powder synthesized using the Sussex recipe is approximately $1 \Omega^{-1} \text{ cm}^{-1}$, despite the relatively high initial oxidant–monomer mole ratio.

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