Application of Polypyrrole to Flexible Substrates

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ABSTRACT: Conducting polymers such as polypyrrole may be useful in smart packaging products, provided application methods can be developed that circumvent the insolubility and infusibility of these materials. Experiments were conducted in five research areas relevant to the application of polypyrrole to nonrigid substrates. The studies reveal that application of polypyrrole from the liquid phase, either by deposition from depleted bulk solution or inkjet printing dispersions, is unlikely to give films as regular as those produced by vapor phase polymerization. Using the latter approach, two potential methods of applying patterned polypyrrole films to nonrigid substrates were developed. The first used hypochlorite to pattern a continuous film of polypyrrole, previously applied by vapor phase polymeriza-
tion. The second used inkjet printing to apply an oxidant solution, whose pH had been raised with a volatile base, to nonrigid substrates. The higher pH reduced corrosion of the print head, increasing the lifetime of printers exposed to oxidative compounds. The base was subsequently evaporated by heating, and the dried oxidant used as a template for vapor phase polymerization of polypyrrole. This method gave smooth, shiny and adherent polypyrrole films on papers and polyester transparency, with high resolution. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3938–3947, 2007

Key words: conducting polymers; polypyrroles; thin films; nanotechnology; dispersions

INTRODUCTION

Conducting polymers are promising building blocks for Smart Packaging. The potential exists for replacement of more expensive metals and silicon-based semiconductors in a broad range of applications, and in packaging, cost is the principal driver. Producing formulations based on lower cost materials is one way of keeping unit costs down, but it will also be important to develop application methods that run at speeds comparable with that of reel-to-reel printing processes. Clever device design is a third necessary research objective that interacts with both formulations and application methods.

In previous work conducted within our group,[1] polypyrrole (PPy) and poly(3,4-ethylene dioxythiophene (PEDOT) were identified as conductive polymers suitable for use in packaging products, with a preference for PPy for specific end uses due to both technical and cost considerations, despite difficulties related to its processability (PPy is insoluble in most solvents and does not melt when heated). In this arti-
cle, we summarize our progress in five research areas, which included the development of a new method for applying polypyrrole to nonrigid substrates.

Deposition of polypyrrole from depleted bulk solution

Since packaging was the context for our project, application of PPy to paper substrates was one of the options considered. Huang et al.[2] reported a method for producing a uniform PPy nanocoating on cellulosic substrates by deposition from a depleted solution of monomer and oxidant. The method was confirmed in our laboratory and then extended to other substrates to determine whether the procedure could be applied more generally.

Inkjet printing of polypyrrole dispersions

The low solubility of many conductive polymers in common solvents is often addressed by preparing dispersions rather than solutions[3–5] and it is now possible to obtain commercial PEDOT dispersions from companies such as Agfa Gevaert, and PPy dispersions from Sigma Aldrich (Australia).[6]

Conducting polymer dispersions have been applied using a variety of printing techniques including inkjet printing.[7] Inkjet printing imposes stringent restrictions

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on the properties of inks. Not only must the particles be small enough to pass through the nozzles of the print head, but also the dispersion must not be too acidic, so that metal parts of the print head do not corrode. PEDOT dispersions have been used for production of transistor circuits[8] and PPy for semiconductors,[9] where conductivity requirements are not extreme. A patent by Ferraris et al.[10] gave details of a device made by inkjet printing conductive polymer dispersions. The latter was produced by ultrasonicating polymers synthesized in the presence of large molecules such as polyvinyl methyl ether (PVME) or polyvinyl acetate (PVAc). The incorporation of these large molecules in the polymer matrix reduces polymer chain interaction and therefore enhances solubility.

In our work we attempted to synthesize dispersions directly by chemically polymerizing pyrrole in the presence of surfactants (polyvinyl alcohol and sodium dodecylsulphate) designed to sterically stabilize the polymer particles as they formed, preventing agglomeration of the PPy chains into larger particles.

Vapor phase polymerization

The literature has many references to the use of vapor phase deposition of PPy, going back some twenty years[11] and including several patents.[12–14] The process has several major advantages over other methods for depositing PPy. Being a chemical method of deposition, the polymer can be deposited on nonconductive substrates, whereas electrochemical deposition methods can generally only be applied to materials suitable for use as the electrodes of an electrochemical cell. Since the pyrrole monomer is applied as a vapor rather than as a solution, there is no liquid phase present to act as a transport medium for particle agglomeration and there is generally no need for dispersants or stabilizers. Accordingly, even coatings can be prepared, in theory at least. However, there are some disadvantages to vapor phase deposition. Application of PPy is slow compared to conventional printing operations as the reaction between monomer and oxidant may be limited by the rate of vapor diffusion. Secondly, the evenness of the final polymer film is highly dependent on the evenness of the oxidant layer on which the polymer is deposited, which in turn depends on the chemical and physical interaction between the oxidant and the substrate.

Recent work has focused on the use of ferric tosylate in vapor phase polymerization, in place of more common oxidants such as ferric chloride. On drying, the latter exhibits precipitation of hydroxides and other salts that leads to uneven PPy films.[15,16] In this part of the project, the objective was to optimize conditions for the application of PPy to polyester film, as a preliminary step in the subsequent development of methods for preparing patterned PPy films.

Patterning of polypyrrole film by inkjet printing hypochlorite solution

Yoshioka et al.[17] suggested that sodium hypochlorite solution can be used to pattern PEDOT conductive polymer films by inkjet printing. The hypochlorite denatures the PEDOT surface, increasing resistivity. In our laboratory, this approach was confirmed and extended to the patterning of PPy films that had been previously applied to polyester film by vapor phase deposition.

Inkjet printing of oxidant solution followed by vapor phase polymerization of polypyrrole

Most oxidants used for chemical polymerization of PPy (e.g., ferric chloride, ammonium persulfate and ferric tosylate) are acidic and corrosive. This makes inkjet printing of oxidant solutions a significant challenge, as normal desktop inkjet printers are not resistant to these chemicals. Even industrial inkjet printers, which may have print heads constructed principally of stainless steel, can suffer catastrophic corrosion in the presence of oxidative solutions at pH 1–2.

Flexographic printing has been used to apply oxidant solutions such as ferric chloride or ferric ethylbenzenesulfonate, and then the printed surface exposed to the monomer vapor.[14] Similarly, silver nitrate solution has been inkjet-printed onto a substrate previously soaked in an aqueous solution of conducting polymer monomer.[18] UV light was used to initiate *in situ* polymerization and develop the printed characters on the substrate surface.

In our project, pyridine was used to raise the pH of the oxidant solution. The oxidant was inkjet printed and the pyridine driven off by heating, allowing the printed pattern to be used as a template for vapor phase polymerization of PPy.

EXPERIMENTAL

Reagents, solutions, and procedures

Deposition of polypyrrole from depleted bulk solution

The method described by Huang et al.[2] was employed. Briefly, 2.5 mL $CuCl_2.2H_2O$ solution (10 mg/mL in 2-propanol) was added dropwise into a 50.0 mL pyrrole solution (5 vol % in 2-propanol) with stirring. The polymerization was allowed to proceed for 30 min, and then the reaction mixture was filtered to remove the bulk PPy. The clear filtrate, a very dilute polymerization solution, was used to coat filter paper (Whatman No.540, Australia), ITO glass (Delta Technologies part no. CG-50IN-S207) and polyester overhead transparency film (3M part no. PP2410), by immersion for up to 3 h. To provide a sample of

Figure 1 Spectra Nova print head (left) and passing a substrate under the running print head (right).

electrochemically prepared PPy for comparison, PPy was applied to ITO glass in an electrochemical cell.

Inkjet printing of polypyrrole dispersions

PPy dispersions were synthesized directly by chemically polymerizing pyrrole in the presence of surfactants (polyvinyl alcohol and sodium dodecylsulphate). By neutralizing the acidity of the dispersion with triethanolamine, a stable nano-dispersion with pH 7.1 and 3% solids content was prepared.

Vapor phase deposition of polypyrrole

The oxidant was a 40% solution of Fe(III)tosylate in butanol, marketed as Baytron C-B 40 PE FL by H.C. Starck. This solution was used either as received or after 1 : 1 dilution with absolute ethanol. Polypropylene glycol (MW_t = 2000, PPG) was added in some trials to further inhibit precipitation during drying. The PPG was added either neat or as a 5% solution in ethanol, the amount normally used being 4% of the mass of the undiluted Baytron solution, corresponding to 0.2 g of surfactant to 5 g of Baytron C. Other proprietary surfactant formulations, Teric BL8 (C12 ethoxylated fatty acid alcohol, Huntsman, Australia) and Glysolv (1-methoxy-2-propanol, Huntsman, Australia), were tried at similar application rates to the PPG.

The prepared oxidant solution was applied to polyester overhead transparency film (3M part no. PP2410), either manually with a pipette or using a bar coater. Several different bars of varying diameter and ribbing amplitude were tried in an attempt to optimize the smoothness and uniformity of the oxidant film. The coated substrates were dried, either in an oven at 50°C for 10 min or by placing them directly on a hot plate on a low heat setting for 1 or 2 min. The substrates were exposed to pyrrole vapor in equilibrium with pyrrole liquid inside a flask at room temperature for a few minutes; normally until there was no further visible darkening of the film. After treatment with pyrrole, the substrates were removed from the treatment flask and exposed to an air flow for 5–10 min to allow any remaining pyrrole to evaporate. The substrates were then immersed in ethanol for 20 min to remove unreacted oxidant and reaction products, and then allowed to dry in air. The PPy films were examined to assess uniformity and adhesion to the substrate.

Patterning of polypyrrole film by inkjet printing hypochlorite solution

A 2% (w/w) solution of sodium hypochlorite (pH 12) with 0.12% Teric BL8 surfactant was prepared and injected into a thermal inkjet printer cartridge (HP c6615 d) that had been previously emptied of ink and purged with water. The cartridge was replaced in the printer and a test pattern printed on conductive PEDOT film (Agfa Orgacon EL-350) or polyester overhead transparency film (3M part no. PP2410) previously coated with polypyrrole by vapor phase polymerization. The printed film was dried at 55°C in an oven for 1 h prior to rinsing with distilled water, and then air dried before images were acquired with SEM.

Inkjet printing of oxidant solution followed by vapor phase polymerization of polypyrrole

Ferric tosylate (3.25 mL of 40% solution marketed commercially as Baytron C by H. C. Starck) was modified by the addition of pyridine (1 mL), ethanol (1 mL), PPG (0.25 mL of 5% 2000 MW in ethanol) and 0.1 mL Teric BL8 (Triton X-100 was also successfully employed). The modified oxidant solution (pH 4–5) was injected into a thermal inkjet printer cartridge (HP c6615 d) that had been previously emptied
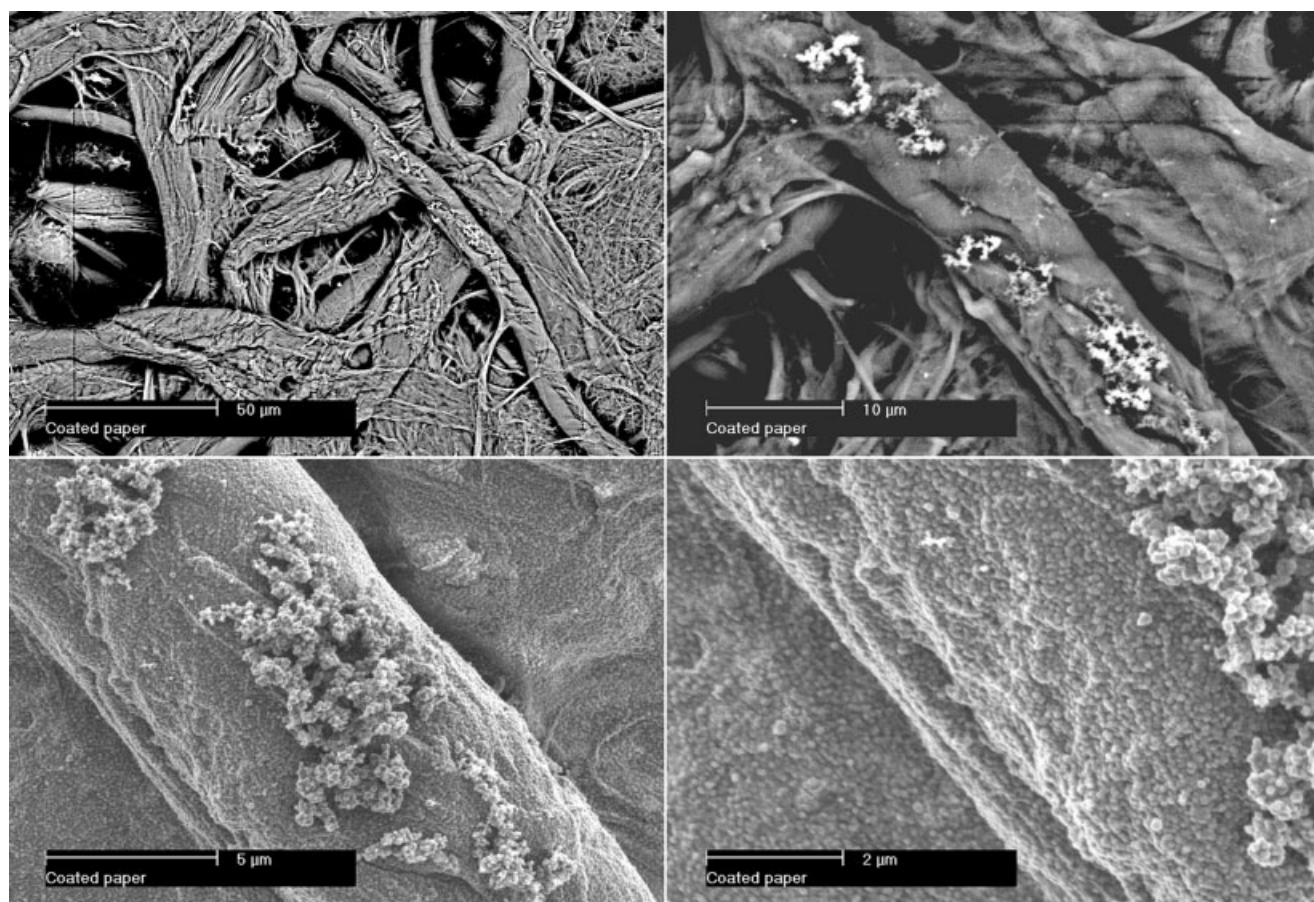
Figure 2 SEM images at increasing magnification of filter paper, upon which PPy had been deposited from depleted solution. At low magnification only a few small clumps of PPy were evident on the fiber surface. At higher magnification it was clear that the surface of each fiber had an exceptionally uniform coating of PPy.

and purged with ethanol. Test patterns were printed on a range of substrates, including copy paper (Reflex 80gsm), filter paper (Whatman No. 540), photo paper (Epson part no. S041285), polyester overhead transparency film (3M part no. PP2410), inkjet transparency film (Epson part no. S041063) and polyvinyl chloride film (GBC Australia part no. 01415/100). The printed patterns were heated on a hotplate set to a low temperature to remove the pyridine and then the substrates were placed in a treatment chamber containing pyrrole vapor and allowed to react. After treatment with pyrrole, the substrates were removed from the treatment flask and exposed to an air flow for 5–10 min to allow any remaining pyrrole to evaporate. They were then immersed in an ethanol/isopropanol solution for 20 min to remove unreacted oxidant and reaction products, and then allowed to dry in air.

Instrumentation

The PPy dispersion printing trials used a Spectra Apollo inkjet printer with a Nova JA 256-80AAA print head (Fig. 1), located at Digital Ink Technologies (a division of Ensign Laboratories) in Hallam, Victoria. The print head was first primed with solvent, then a quantity of the dispersion was loaded into the reservoir and the print head turned on. Substrates were manually passed beneath the running print head. The printing trial was repeated after the addition of a proprietary surfactant (BYK 346[TM], polyether modified polydimethylsiloxane) and/or 10% ethanol to the dispersion.

The printed substrates were examined under an optical microscope to assess the uniformity of the coating. An Olympus BX61 optical microscope was used fitted with a ColorView Softimaging System digital camera connected to a PC. The images were collected and interpreted with analySIS Ver. 8.31 software. The morphology of the PPy films formed on each substrate was examined using a Philips XL 30 Field Emission Scanning Electron Microscope. On polyester substrates, PPy film thickness was determined using a Dektak 6M stylus profiler, taking the mean of four replicate measurements. The profiler could not be used for paper substrates because the surfaces were too rough. Surface resistances of the PPy films were measured with a four-point probe.
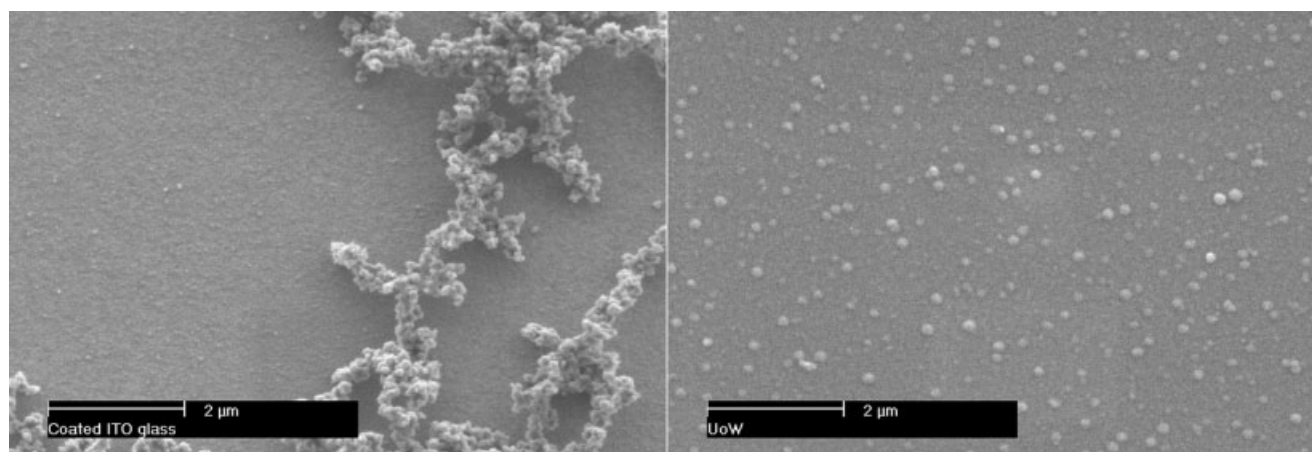
Figure 3 SEM images of ITO-glass surfaces with PPy deposited from depleted bulk solution (left) compared with electrochemically deposited PPy (right).

RESULTS AND DISCUSSION

### Deposition of polypyrrole from depleted bulk solution

SEM images of paper with PPy deposited from depleted solution are presented in Figure 2. These results were comparable with those obtained by Huang et al.[2] and implied that the deposition method might provide a pathway towards PPy coatings with exceptional uniformity. However, on the macroscale these coatings had surface resistances beyond the range of the available 4-point probe, probably reflecting the discontinuous electrical path across a rough paper surface. Moreover, application of PPy to other substrates by the same method gave much worse morphology. The PPy was deposited not as an even coating but as isolated clumps on an otherwise bare surface. This was quite unlike the uniform coating of PPy applied electrochemically (SEM of PPy on ITO glass is shown in Fig. 3). The results for other substrates were similar, whether they were smooth or roughened by chemical etching.

When deposited chemically, PPy can have low adhesion to smooth substrates such as polyester film or glass,[19] perhaps contributing to the unevenness of the PPy coating observed here. Clearly, in a liquid medium the opportunity exists for agglomeration and this is more likely to occur when the PPy is not strongly bound to the substrate surface. Hence the even coating on paper fibers may be related to the natural, nanoscale roughness of cellulosic fibers, and is therefore unlikely to be replicated on smooth, man-made substrates, even when chemically etched. Nevertheless, these results gave some hope for the application of even coatings of polypyrrole to paper substrates, perhaps by printing.
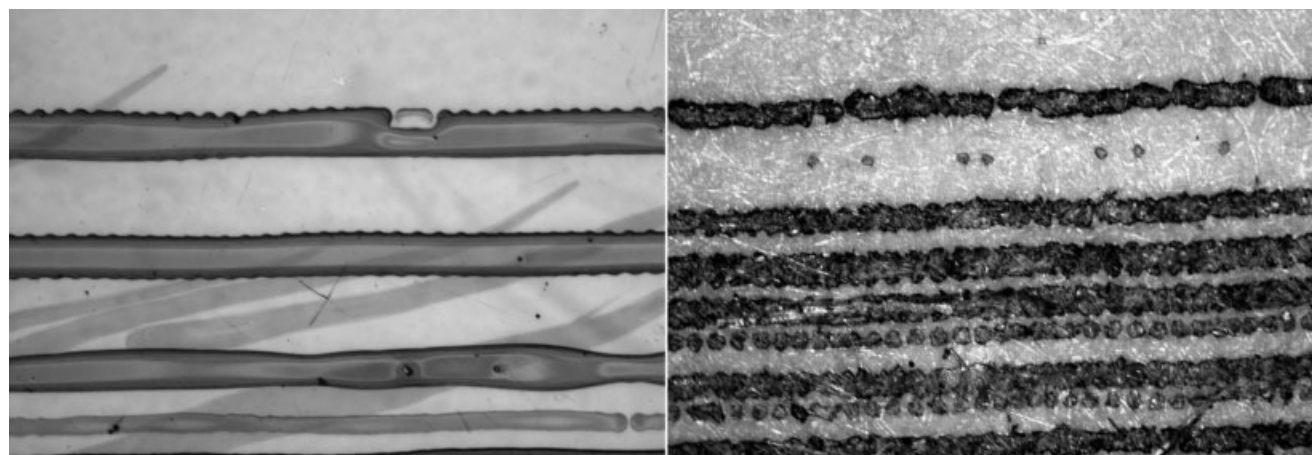
Figure 4 Images of the PPy dispersion inkjet printed on polyester film (left) and copy paper (right), collected with an optical microscope at ×5 magnification. Only some of the nozzles in the inkjet head operated due to priming difficulties, so gaps appeared in the printed pattern.
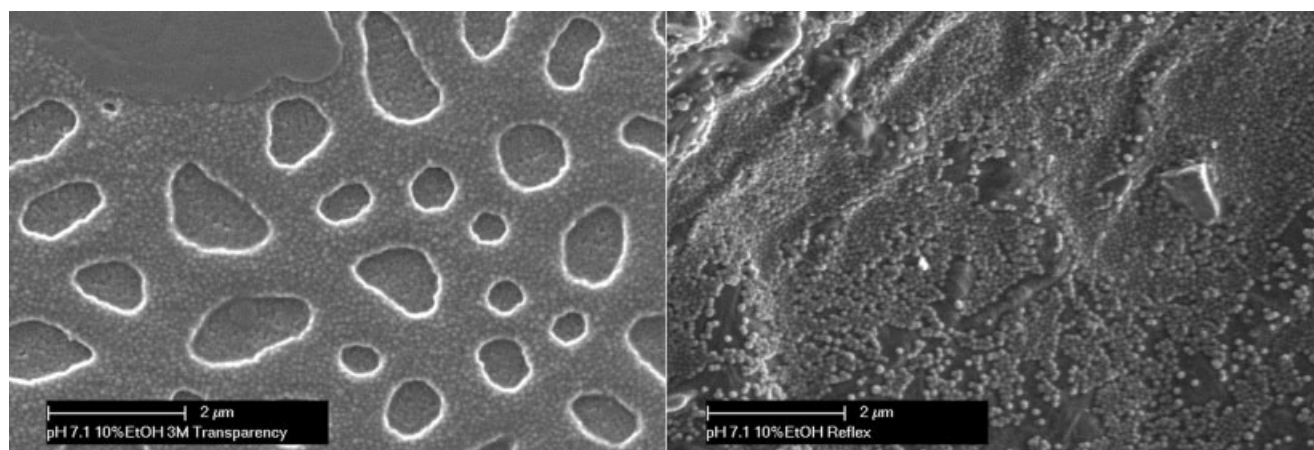
Figure 5 PPy dispersion inkjet printed on polyester film (left) and copy paper (right) under SEM. On polyester film the droplets tended to shrink on drying, whereas on paper the coating was more even.

### Inkjet printing of polypyrrole dispersions

Microscopic images of the inkjet-printed PPy dispersion at pH 7.1 are shown in Figures 4 and 5. There was no visible difference in the results obtained after the addition of a surfactant (BYK 346[TM]) and/or 10% ethanol to the dispersion. On nonabsorbent substrates the droplets sometimes coalesced into a continuous film, depending on the particular printing conditions (for example, how quickly the substrate was moved under the print head and how near to the print head the substrate was held). On absorbent substrates like paper, there was less coalescence and more isolated droplets.

The printed samples, even those on nonabsorbent polyester film, had surface resistances beyond the range of the available 4-point probe. This disappointing result may reflect the high pH, the high concentration of stabilizers (PVA and SDS) required to prevent PPy agglomeration, or the drying behavior of the dispersion. As each droplet of the dispersion dried out,

the perimeter tended to shrink, changing the dispersion composition by concentrating the dispersants in the middle of the droplet. Warren et al.[14] suggested that a mixed solvent might overcome this kind of behavior. Initial evaporation of a volatile component causes a rapid increase in the viscosity of the remaining less-volatile components, immobilizing the droplet and preventing shrinkage. Further work would be required to determine whether this approach would improve the printing results.

Vapor phase deposition of polypyrrole

Smooth, shiny, adherent films of PPy could be prepared on polyester film by vapor phase polymerization using Baytron C as the oxidant. PPy films produced in this way (Fig. 6) seemed to be more porous than electrochemically deposited PPy films (Fig. 3). SEM measurements on a representative sample sug-
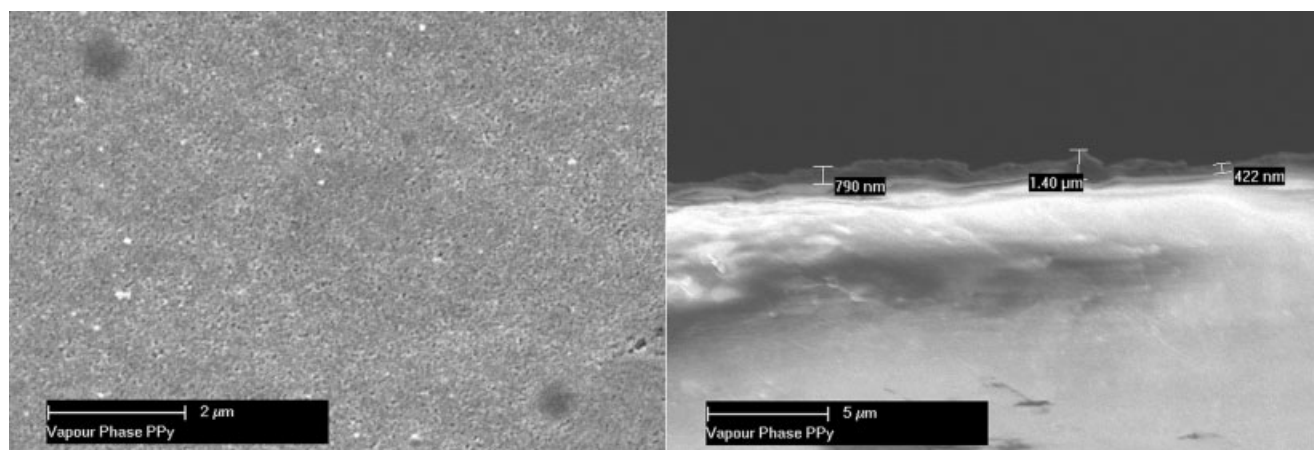
Figure 6 Surface of PPy applied by vapor phase polymerization (left) and cross section showing measurements of film thickness (right). The PPy film was smooth, porous and averaged about a micron in thickness.
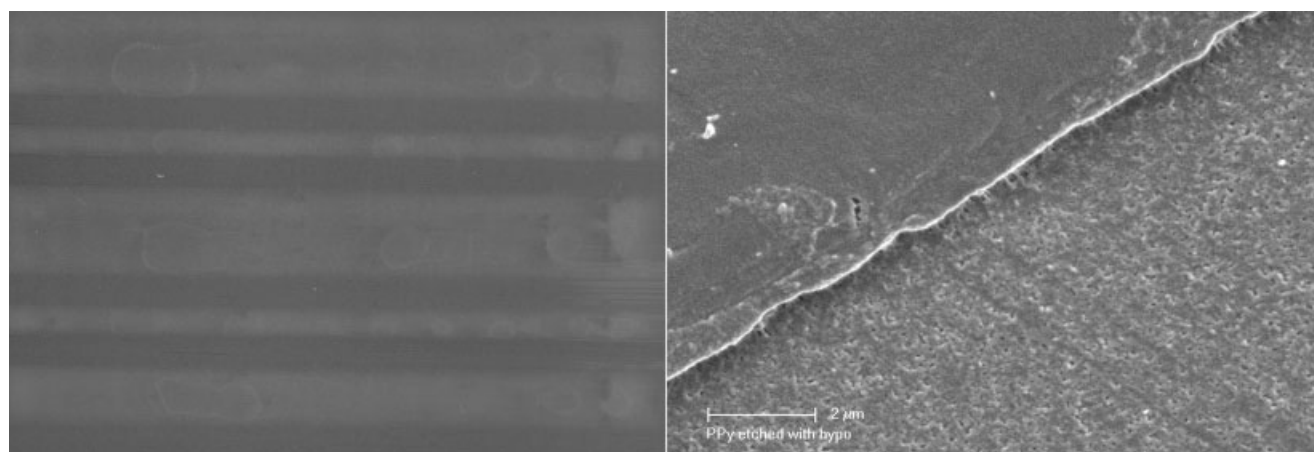
Figure 7 Photograph of PPy applied by vapor phase deposition to polyester film and patterned by etching with hypochlorite solution (left). Where the polymer had been removed the surface regained the nonconductive properties of the underlying substrate. The boundary between nonconductive polyester film and the porous conductive PPy was quite distinct under SEM (right).

gested that PPy thickness was variable but averaged about 1 μ.

The PPy films were found to be conductive (surface resistance about 0.3 kΩ/square). The thickness of the final PPy film was highly dependent on the thickness and uniformity of the preceding oxidant film: thin oxidant films resulted in thin PPy films. Uniform oxidant films could be applied either manually or with the bar coater, the latter giving good results with a no. 2 bar with only very fine ridges. Bars with deeper ridges gave less uniform results because more of the oxidant was applied per unit area, causing more rapid depletion of the oxidant reservoir ahead of the moving bar and consequently progressive starvation of oxidant solution on those parts of the substrate coated later in any given coating pass. The only effect of diluting the Baytron C with ethanol was a thinner film; no improvement in coating uniformity was evident.

Drying conditions were important to avoid oxidant crystallization. Good results were obtained by drying on the hotplate or by placing the coated substrate on a glass plate heated in an oven to 50°C. The resulting rapid and uniform heat transfer prevented crystallization without risk of damage to the substrate. However, if a film was dried for longer than a few minutes, polymerization was slower and did not appear to proceed to the same extent.

Patterning of polypyrrole film by inkjet printing hypochlorite solution

Images of PPy films produced by vapor phase polymerization and patterned by ink-jetted hypochlorite solution are presented in Figure 7. Application of hypochlorite destroyed the PPy, allowing its removal from the nonconductive underlying substrate by rinsing. The boundary between PPy and the underlying film was quite distinct.

This demonstrates that the application of hypochlorite by inkjet printing was effective in patterning the
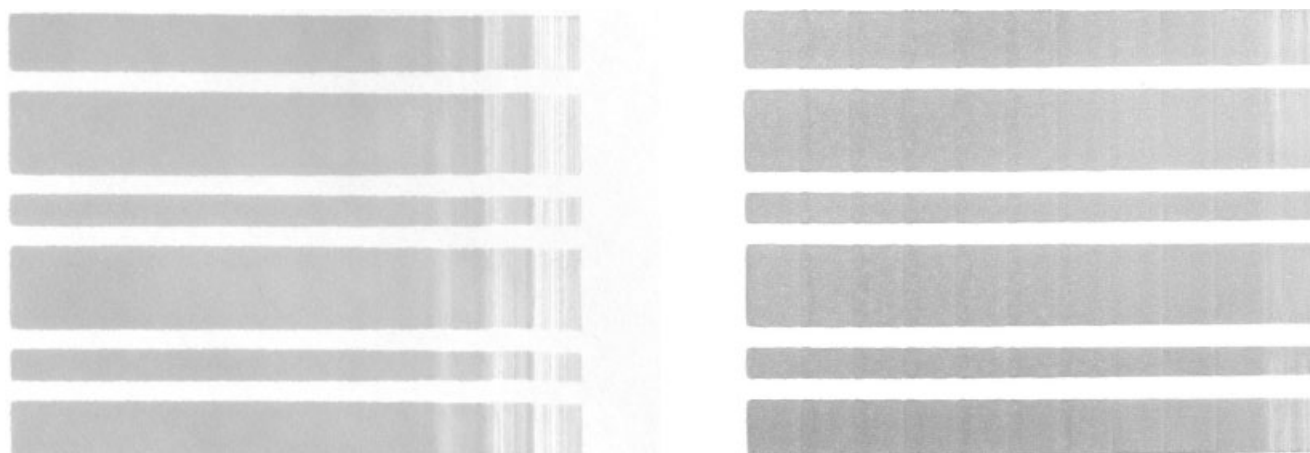
Figure 8 PPy applied to filter paper (left) and photo quality paper (right).
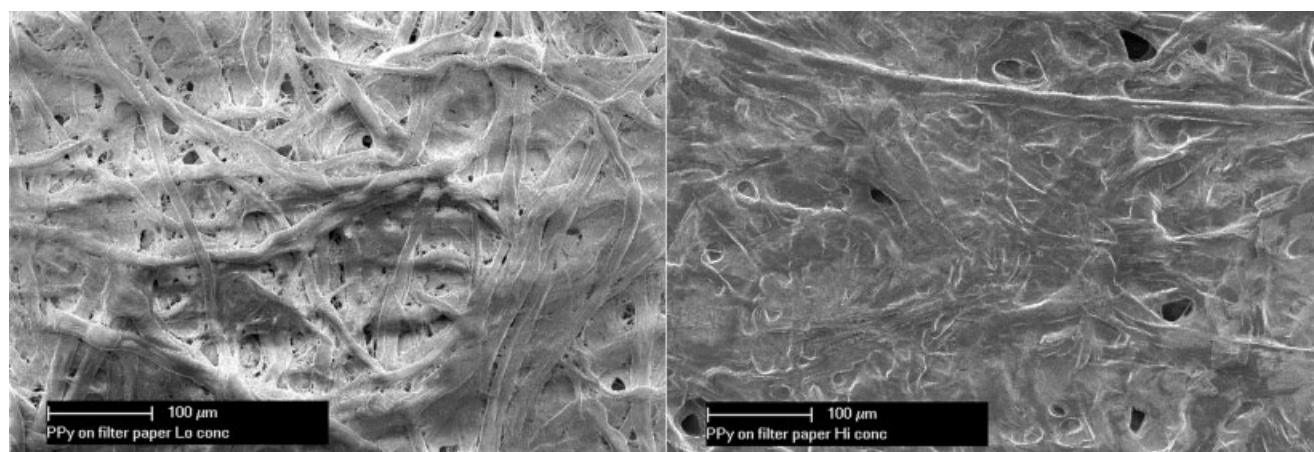
Figure 9 Nonconductive paper (left) prepared by printing an oxidant solution prior to vapor phase polymerization of PPy, compared with conductive paper (right) saturated with oxidant solution prior to polymerization. The surface of the nonconductive paper had many voids, whereas the surface of the conductive paper was almost entirely filled with PPy.

surface of conductive polymer films. The advantage of the process is that the conductive polymer coating can be applied separately to the patterning step, allowing print-on-demand applications. However, extended testing indicated the use of 2% hypochlorite solution caused significant corrosion to metal components of the desktop inkjet printer used in the experiments. Industrial application would require the use of a stainless steel inkjet head, such as those currently available from companies such as FujiFilm Dimatix Inc. Further, the cost associated with producing a large area of PPy film for patterning by this method would be higher than applying PPy only to those areas requiring a con-

ductive layer, assuming a method for the latter could be devised (see following heading).

Inkjet printing of oxidant solution followed by vapor phase polymerization of polypyrrole

The pyridine-modified Baytron oxidant solution could be printed on copy paper and polyester film. It could not be printed properly on polyvinyl chloride film, as the solution shrank inwards as it dried as a result of dramatic surface tension effects. It was also not possible to obtain good results on Epson inkjet transparency film, as the solution spread outward at the edges
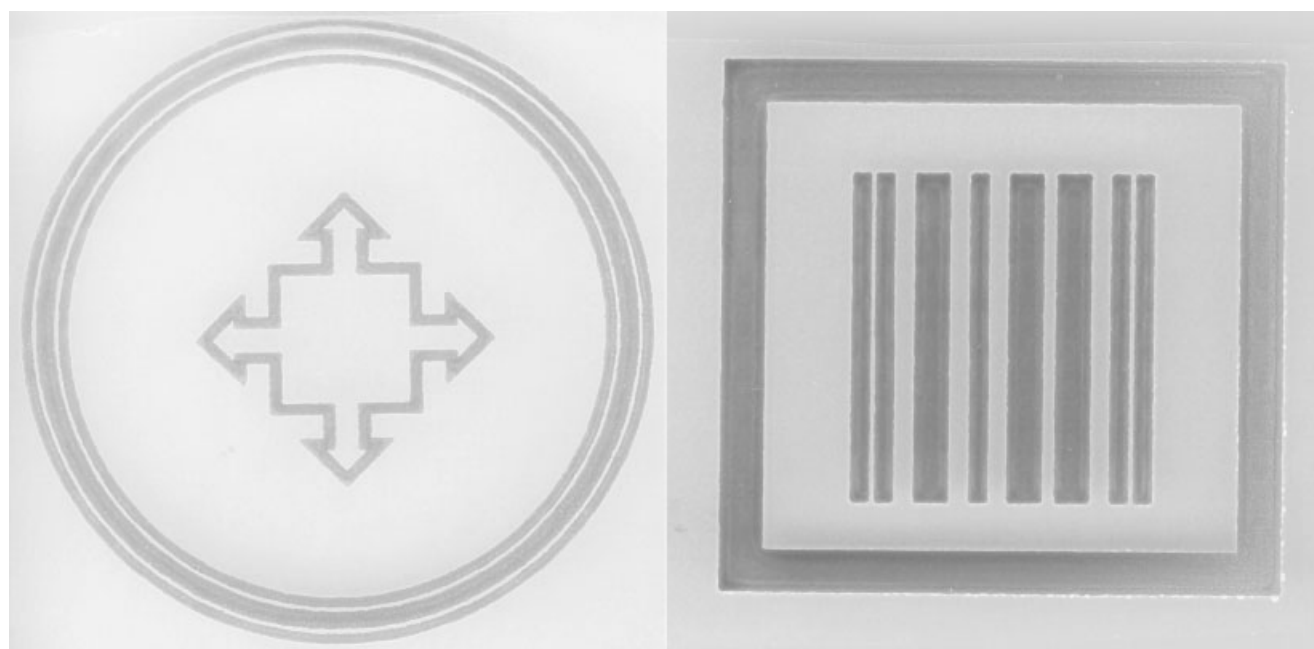
Figure 10 Patterned PPy applied to polyester film by inkjet printing an oxidant followed by vapor phase polymerization.

TABLE I
Surface Resistance and Mean Film Thickness of PPy Applied to Polyester Transparency Film by Pipette or Inkjet Application of Fe(III)tosylate Oxidant Solution, Followed by Vapour Phase Polymerisation

| Sample	Application method	Surface resistance (kΩ/square)	Film thickness (nm)
1	Pipette	0.3	450
2	Pipette	0.2	570
3	Inkjet	1.5	580
4	Inkjet	2.2	820
5	Inkjet	5.6	510
6	Inkjet	14	340

of the print, blurring lines and markedly affecting pattern resolution. On exposure to pyrrole vapor, PPy formed wherever the oxidant had been printed. Resolution was good on absorbent paper substrates (Fig. 8).

Unfortunately, PPy applied to paper using this method showed a surface resistance above the range of the available four-point probe. The high resistance was probably the result of morphology, as the absorbent nature of the paper meant that the PPy was distributed in three dimensions. When the oxidant solution completely saturated the sheet (by applying a larger volume of oxidant solution by pipette) the PPy subsequently formed completely filled the sheet voids, and the paper was conductive (surface resistance 0.058 kΩ/square, Fig. 9). These results suggest that the poor conductivities of papers to which PPy had been applied, either from depleted solution or by ink-jetting dispersions, may well have been related to the absorbent substrate, in part at least.

Application of PPy to polyester overhead transparency film gave slightly poorer resolution (Fig. 10), probably because the volume of oxidant solution applied was not appropriate for nonporous film. Unfortunately, the desktop printer available for these tests did not have the facility to change the droplet volume dispensed without causing undesirable side effects.

The PPy applied to polyester overhead transparency film was smooth and adherent, and electrically conductive when surface resistance was measured with a 4-point probe (Table I). The surface resistances obtained were comparable with the range reported by other workers using the vapor phase polymerization method.[20,21] Film thickness, as measured with a contact profilometer, was variable but of the same order as films produced by applying the oxidant solution with a pipette. Although the thinnest film (sample 6) had the highest resistance, overall there was little correlation between film thickness and surface resistance. This may be a consequence of the variability associated with film thickness measurement on nonrigid substrates, as demonstrated by the sloping surface profile of the substrate (Fig. 11). Clearly, estimates of film thickness are difficult if the substrate is not flat, as step heights cannot be accurately determined.

It was observed that washing the polyester film in ethanol/isopropanol solution resulted in a change in the appearance of the film, causing it to turn slightly opaque, even where no PPy had been deposited. Water was tried as a substitute washing medium and the effects of the two washing solvents on the morphology of the polypyrrole film were examined by SEM (Fig. 12). The ethanol-washed film was notably rougher in appearance than the water-washed film,
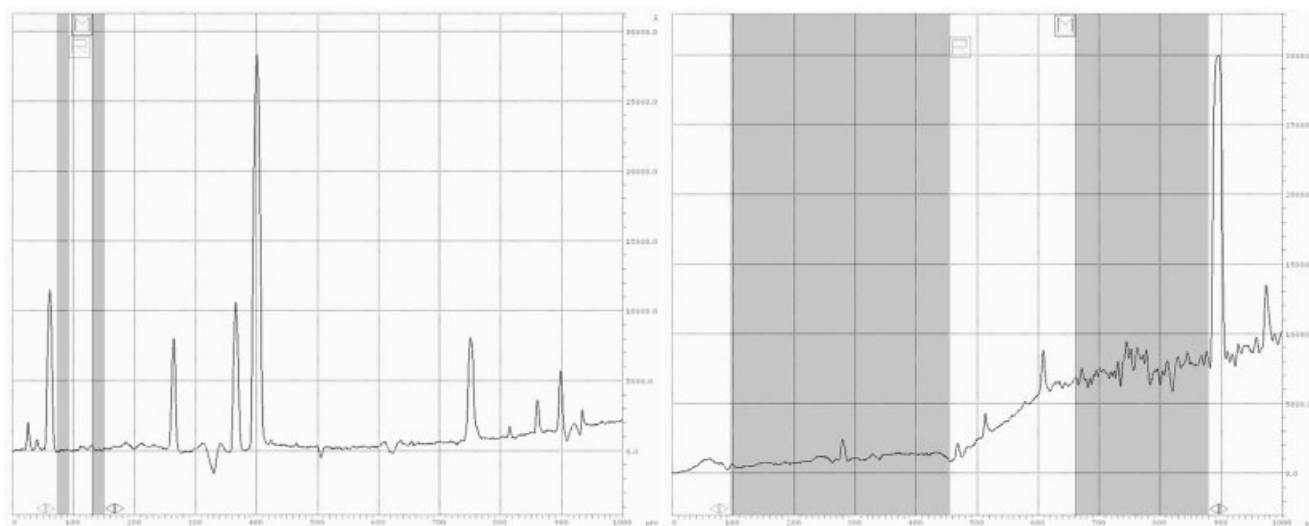
Figure 11 Contact profilometer trace of substrate (left) and substrate with PPy (right). Note the upward drift in the left-hand substrate profile. The step in the right-hand profile represents PPy film thickness. The sharp peaks probably indicate the presence of dust or other contaminants on the surface of the sample.
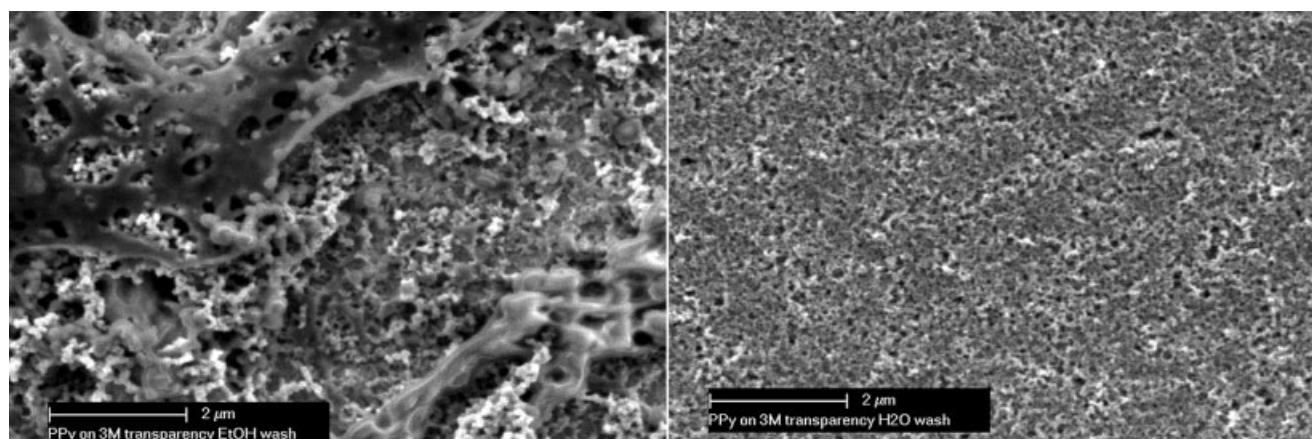
Figure 12 PPy applied to transparency film and washed in ethanol/isopropanol (left) and water (right).

suggesting the polyester substrate beneath the PPy had one or more surface layers soluble to some extent in alcohols.

CONCLUSIONS

Application of PPy to papers from depleted bulk solution gave coatings that were very uniform on the microscale, whereas PPy applied by the same method to nonporous substrates formed clumps on an otherwise bare surface, probably as a result of particle agglomeration in the liquid phase. Inkjet printing a PPy dispersion at pH 7.1 gave films of low conductivity on both paper and polyester film, either as a result of the high pH, the high concentration of PVA/SDS dispersants required to stabilize the dispersion, or shrinkage of the dispersion droplets on drying. In contrast, vapor phase polymerization of PPy gave smooth, shiny and adherent films on a range of substrates. These films could be patterned by inkjet printing hypochlorite solution. It also proved feasible to inkjet print a Baytron C oxidant solution whose acidity had been lowered by addition of pyridine. The pyridine could be subsequently removed by heating and the dried oxidant used as a template for vapor phase polymerization. On papers and polyester substrates this method gave even PPy films, which in some cases were highly conductive.

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