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Functionalised Hybrid Materials of Conducting Polymers with Individual Fibres of Cellulose

Fern M. Kelly,*[a] James H. Johnston,[a] Thomas Borrmann,[a] and Michael J. Richardson[a]

Keywords: Polypyrrole / Polyaniline / Cellulose / Fibres / Conductivity / Antimicrobial activity

Polypyrrole and polyaniline conducting polymer composites with individual fibres of cellulose have been successfully prepared and characterised. For this, individual Kraft paper pulp fibres have been fully encapsulated with polypyrrole and polyaniline by direct polymerisation of the respective monomers using ferric chloride and ammonium persulfate as the oxidants. These novel conducting polymer/cellulose fibre composite materials exhibit the inherent properties of both components. They include the electrical and chemical properties of polypyrrole and polyaniline and the strength, flexibility and available surface areas of the cellulose fibre. This allows for interesting opportunities for the development of new added-value products in the paper and packaging industries. Additionally, by utilising the redox active surface of the fibre's polymer coating, silver ions have been reduced to silver metal, thereby producing cellulose/conducting polymer/silver composites. Silver and its compounds have long been identified for their bactericidal effects and thus antimicrobial properties are imparted to the hybrid materials. This gives rise to applications requiring the inhibition of microbial growth. The chemical and physical characterisation of such products has been carried out using scanning electron microscopy (SEM), cyclic voltammetry, X-ray photoelectron spectroscopy (XPS) energy dispersive spectroscopy (EDS) and electrical conductivity measurements, and additionally the testing of their antimicrobial activity.
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1. Introduction

Inherently conducting polymers have been widely investigated since their introduction in the 1970's due to their excellent electrical and optical properties.[1] Electrical conductivity arises from the conjugation of π electrons formed by the overlapping of carbon *p* orbitals along the polymer-chain backbone which allows for the efficient transfer of electrons along the polymer backbone.[2] High electrical conductivity can be achieved by doping the conductive polymer with an appropriate agent, which can be either electron-rich (*n*-dopant) or -poor (*p*-dopant) in comparison to the polymer.

Two of the most commonly studied conductive polymers are polypyrrole (PPy) and polyaniline (PAn). This is due to their high electrical conductivity, good environmental stability, chemical properties (oxidation/reduction) and relative ease of synthesis. However, due to their poor mechanical properties and processability industrial application has been cautious. Improvement of the properties of conducting polymers is achievable by creating hybrid materials, in which textile fibres are coated with conducting polymers. In doing so, the hybrids possess the tensile strength, flexibility and relatively high surface area associated with the fibre whilst retaining the desired chemical and electrical properties of the polymer.[3]

Previous studies have shown that individual synthetic organic polymer fibres, such as Nylon and Lycra, may be successfully coated with conducting polymers.[4–6] These materials have applications as chemical and bio-mechanical sensors. This paper conversely presents individual natural fibres of cellulose (Kraft paper pulp) that have been successfully coated by PPy and PAn, using ferric chloride or ammonium persulfate to facilitate polymerisation. As the surface morphology of nylon and other synthetic polymer fibres is much smoother and more uniform than cellulose, the surface of a conducting polymer/nylon fibre, which similarly encapsulates the fibre substrate, is also smoother than that of the PPy/cellulose and PAn/cellulose composite fibres. The chemical and physical properties of the conducting polymer coating and the bonding between the conducting polymer coating and cellulose fibre substrate have been characterised accordingly. The resultant cellulose fibre/conducting polymer hybrids have applications on their own (e.g. antistatic and chemical sensing papers), or can also be incorporated into other host materials (conventional polymer sheeting and extrusions) thereby adding new functionality due to the polymer coated fibres.

Additionally, by utilising the redox active surface of the fibre's polymer coating, silver metal nanoparticles may be incorporated into the composite. Electrochemical deposition of metals on electrodes by conducting polymers such

[a] School of Chemical and Physical Sciences, Victoria University of Wellington,
P. O. Box 600, Wellington, New Zealand
Fax: +64-4-463-5237
E-mail: Fern.Kelly@vuw.ac.nz

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as PPy and PAn has been well studied.[7–13] Electroless deposition for the recovery of metals has also been reported in which polymer films are oxidised by metal ions of relatively high oxidation potential, effectively reducing the metal to its neutral form. Silver,[14–16] gold[17] and palladium[18–19] have proved successful in this procedure.

This paper outlines an electroless deposition method of metal recovery, whereby silver from solution is reduced, from Ag^+ to Ag^0, by an oxidised form of the polymer coating. The removal of silver ions from aqueous media indicates the potential application of conducting polymer composites for the recovery of noble metals or in wastewater treatment. Furthermore, through the incorporation of silver, the fibre/polymer composites possess an inhibitory action against bacterial growth. Thus, future applications of such materials may include antimicrobial papers. To the best of our knowledge, this is the first report of the preparation and characterisation of cellulose/conducting polymer/silver hybrid materials.

2.Results and Discussion

2.1 Conducting Polymer/Cellulose Hybrid Materials

Neat Kraft paper fibres are white, approximately 2.5 to 3.0 mm in length and with a fibre diameter of approximately 30 to 40 μm. The fibres have a relatively smooth surface (Figure 1), but at higher magnifications individual micro-fibrils (indicated by arrows) unwinding from the parent fibre can be observed. Composites based on PPy yielded black fibres of Kraft paper, with each fibre being individually coated with the PPy polymer. The surface morphology of a cellulose fibre/PPy composite is shown in Figure 2. With increasing magnification, it is seen that the PPy coating comprises small uniform spheres about 100 to 150 nm in diameter which are fused together to fully encapsulate the fibre. The polymer coating closely follows the original morphology of the fibres such that even individual fibrils of the parent paper fibre are entirely encapsulated, but remain discernible.

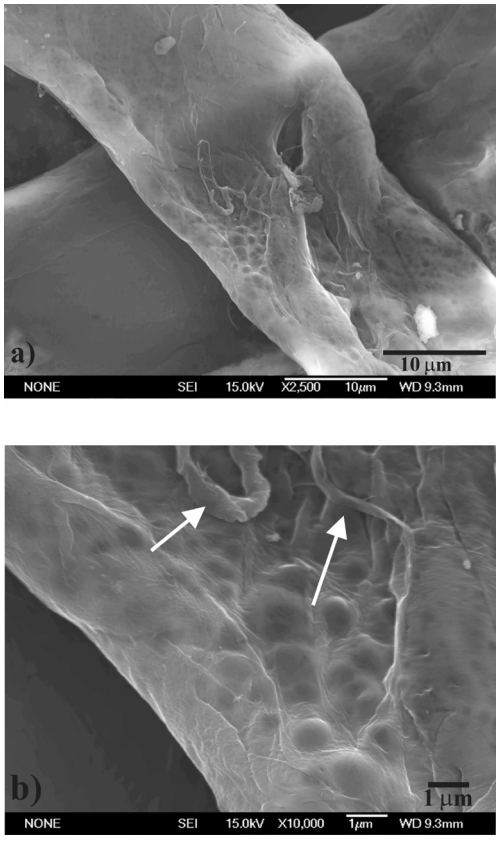

Figure 1. a) Neat cellulose fibres, 2500 times magnification; b) indicating unwinding micro-fibrils, 10000 times magnification.

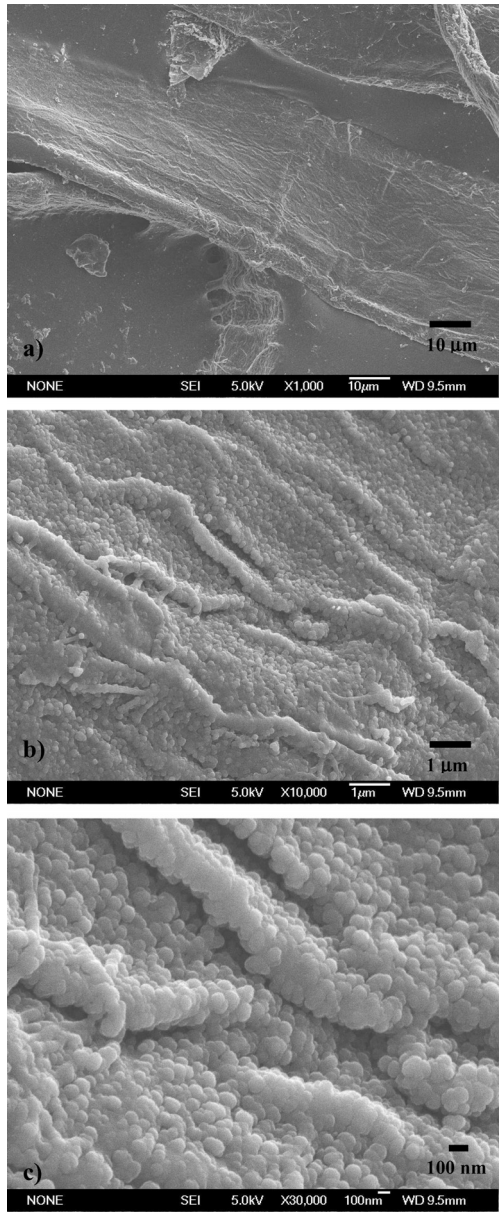

Figure 2. a)–c) Electron microscope images showing increasing magnifications of a paper fibre/polypyrrole composite ($FeCl_3$ as oxidant).

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When ferric chloride was employed as the oxidising agent in the preparation of fibre/PAn composites, the polymer coating resulted in the emeraldine salt form. Conversely, when the oxidant utilised was ammonium persulfate the resulting PAn coating was in the emeraldine base form. These results were implied by the respective green and blue colours observed and confirmed by UV/Vis spectroscopy. Composites of PAn similarly exhibit a polymer coating wherein the fibres are fully encapsulated yet the underlying morphology and micro-fibrils remain similarly clearly distinguishable. The average size of the polymer spheres of PAn is observed to be smaller than those of PPy, approximately 50 to 100 nm in diameter (Figure 3).

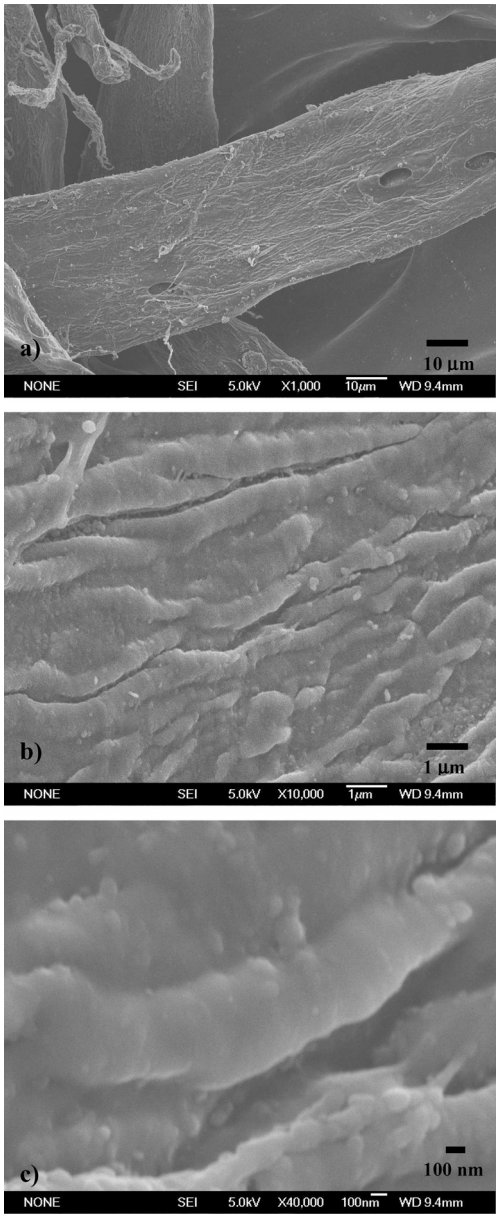

Figure 3. a)–c) Electron microscope images showing increasing magnifications of a paper fibre/polyaniline composite ($FeCl_3$ as oxidant).

2.2 Cyclic Voltammetry

Cyclic voltammetry was used to determine the electrochemical transitions of the fibre composites and to ascertain their thermodynamic stability. The cyclic voltammograms for the cellulose/polymer composites, despite being dissimilar from their corresponding electrochemically synthesised free polymers, still showed transitions from reduced to oxidised forms. This demonstrates that the important redox feature of conducting polymers was retained in the preparation of the composites.

When the scan rate of the cyclic voltammograms for the free polymer was altered, from 10 to 50 $mV s^{-1}$, the positions of the peaks representing the electrochemical transitions remain unchanged. This implies that the polymers themselves are thermodynamically stable and the kinetics of the redox transitions are faster than the scan speeds used in the measurements. It also indicates that there is only one method of electron transport in the free polymer.

When repeating these measurements for the fibre/polymer composites, the position of the redox peaks relating to the respective electrochemical transitions change as the scan speed is altered (Figure 4). Additionally, the transition peaks from emeraldine to pernigraniline and the reverse are not observed. This may indicate two things.[20–21] Firstly, the specific transition that yields the redox peak in the particular voltammogram is either not thermodynamically stable or the kinetics of the redox transition are slower than the scan rates. Secondly, contact between the fibres and the electrode may not be ideal. However, the first explanation is preferred as the expected colours and changes in the UV/Vis spectra for the transition from emeraldine (blue) to pernigraniline (purple) are indeed observed.

As both the substrate and the polymer are themselves thermodynamically stable, the change in peak position relating to these electrochemical transitions with changing scan speeds also implies that there is chemical bonding between the polymer and the underlying fibre with a complex electron interaction. The interaction between the substrate and the coating presumably gives rise to alternative and slower pathways for the electron transfer in the redox processes taking place in the fibre/polymer composite.

2.3 X-ray Photoelectron Spectrometry

The nature of the chemical bond between the cellulose-fibre substrate and polymer coating, inferred by cyclic voltammetry is further elucidated by XPS. Previous studies have suggested that the bond between polymer and cellulose substrates exists in the form of hydrogen bonding.[22,23] For cellulose composites with PAn and PPy, this implies that there is an interaction between nitrogen-bound hydrogen atoms (NH) on the polymer chain backbone and the lone pairs of electrons of the surface hydroxy (OH) groups of cellulose. This bonding may be in conjunction with, or may be substituted by, bonding between the hydrogen (H) of the surface OH groups of cellulose and the free electron pair of nitrogen (N) atoms in the polymer backbone.

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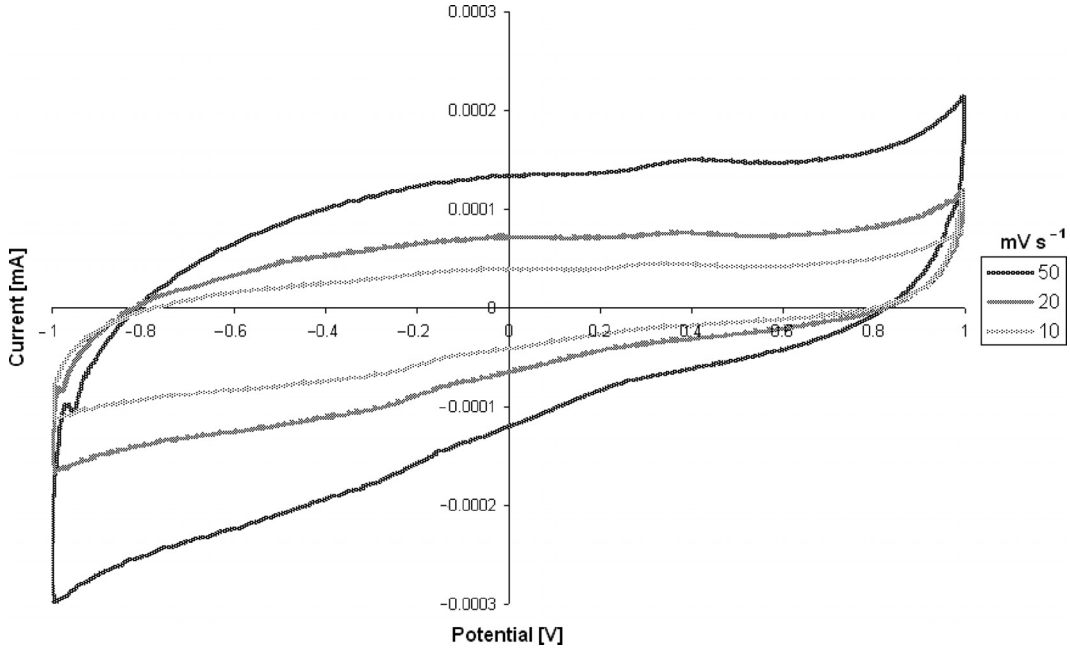

Figure 4. Cyclic voltammograms of paper/polyaniline composite ($FeCl_3$ as the oxidant) at different scan speeds.

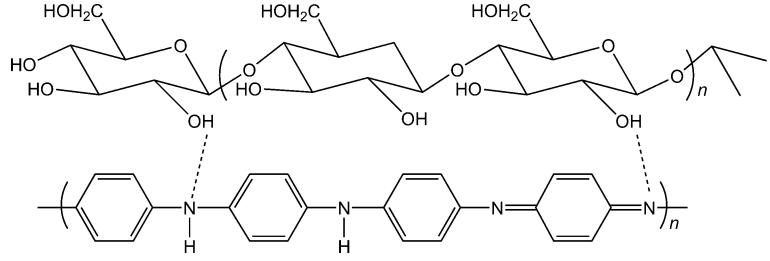

Figure 5. Possible bonding of cellulose to polyaniline.

XPS analyses carried out reinforce the suggestion that the chemical bonding is, in fact, hydrogen bonding between the nitrogen lone pairs of the polymer coating with the OH groups of the underlying cellulose substrate (Figure 5). This is shown by the oxygen XPS spectrum for the cellulose/PAn composite (Figure 6, b), in which there are distinct changes when compared to the same spectra for free cellulose fibres (Figure 6, a).

Of specific importance, is the appearance of a shoulder associated directly with C–OH bonding to N in the O 1s spectrum for the cellulose/PAn composite (Figure 6, b). The shift in the primary O 1s peak relating to C–OH bonds, from 533.3 to 530.6 eV for cellulose and the PAn-coated analogue, respectively, further indicates the presence of a chemical interaction between OH and N. The binding of the hydroxyl groups of cellulose to nitrogen lone pairs of PAn would result in lowering the binding energy of the oxygen from which the attached hydrogen atoms are being delocalised. This is supported by studies on oxygen binding for cellulose published by Wagner et al.[24]

The XPS spectrum for nitrogen for the cellulose/PAn composite was poorly resolved. However, the position and line width of the peak is comparable to that provided by Rodrigues et al.[25] for the N 1s spectrum of PAn bound to

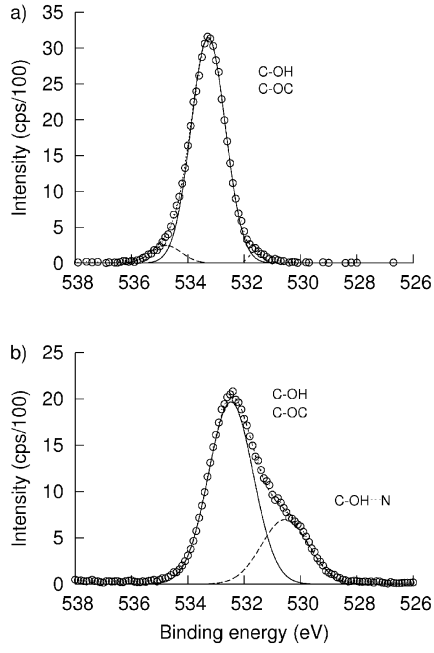

Figure 6. XPS spectra for (a) O 1s for cellulose; (b) O 1s for cellulose/polyaniline composite.

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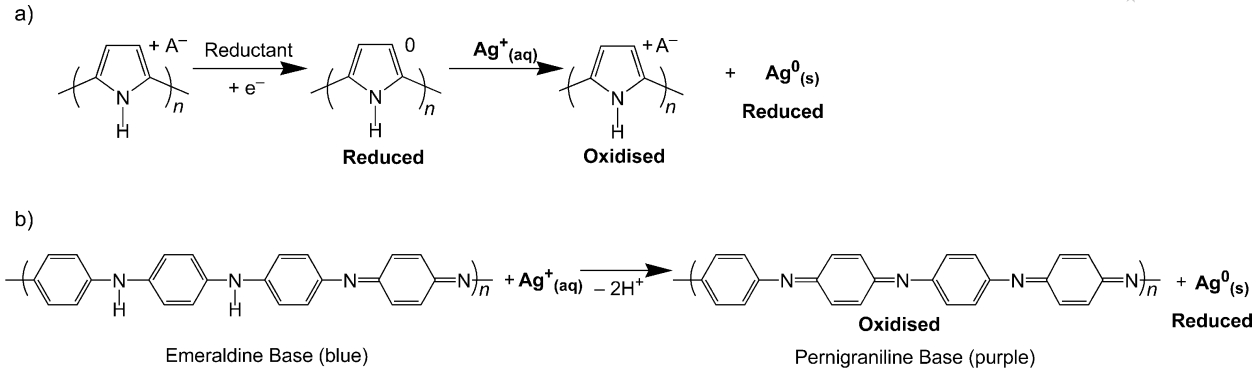

Figure 7. Chemical reduction of Ag^+ to Ag^0 by polypyrrole (a) and polyaniline (b).

lignin. On this basis it can be assumed that both imine and amine groups are present on the composite surface and that the mode of bonding is similar, whereby PAn binds from the nitrogen lone pairs through to the OH groups of cellulose rather than OH groups of lignin.

2.4 Fibre/Conducting Polymer/Silver Composites

A scheme of the reduction processes of silver ions by PPy and PAn, respectively, is shown in Figure 7. Under ambient conditions, PPy exists in an oxidised form due to atmospheric oxygen. Thus, PPy composites were first reduced by treatment with the reducing agent sodium borohydride. Upon addition of silver nitrate PPy is re-oxidised, therefore chemically reducing ionic silver to silver metal, which is deposited on the surface of the polymer.

Under ambient conditions PAn exists in its half-oxidised, emeraldine, form. Thus, by placing emeraldine base PAn/fibre composites directly into a silver nitrate solution, the polymer surface is oxidised to pernigraniline base, effectively reducing silver ions on the polymer surface to metallic silver. The redox reaction was noted by a colour change of the fibres from blue (emeraldine base) to purple (pernigraniline base).

Energy dispersive spectroscopy (EDS) was employed to determine the chemical composition of the surface of the fibre/polymer/silver composites. Figure 8 presents a secondary electron SEM image together with EDS representative of silver (lower levels of silver denoted with black, high levels of silver denoted with grey) for fibre/PAn/silver composites. As indicated by these images, a uniform coating of silver exists across the surface of the fibre polymer composites. The same is observed for the fibre/PPy composites.

SEM imaging of silver composites at higher magnifications shows the silver is present as individual nanoparticles (Figure 9). The greater spatial resolution of the SEM images shows that, although silver metal is distributed evenly across the polymer surface, the coating is not complete as implied by the lesser resolution of the EDS elemental maps.

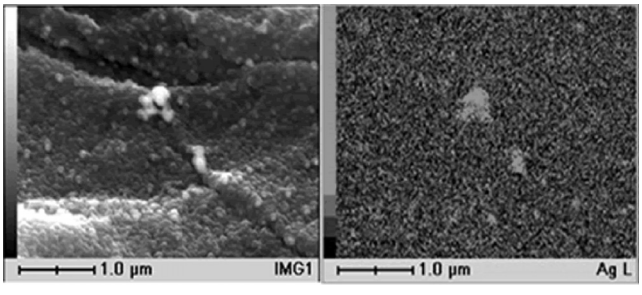

Figure 8. EDS overlay of C and Ag for cellulose fibre/polypyrrole/silver composite.

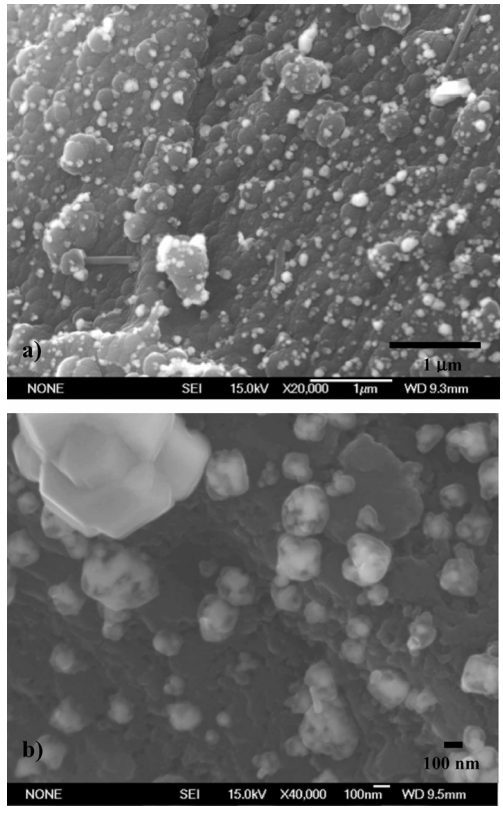

Figure 9. a)–b) Individual particulates of silver on the surface of a cellulose fibre/polypyrrole/silver composite at increasing magnification.

2.5 Electrical Conductivity

The Van der Pauw method was used to measure the electrical conductivities of the cellulose fibre/polymer hybrids

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produced. The calculated conductivities ranged from 5.6×10^{-4} S cm^{-1} to 6.0×10^{-4} S cm^{-1} for PAn composites and 2.1×10^{-3} S cm^{-1} to 2.6×10^{-1} S cm^{-1} for PPy composites. The conductivity of single cellulose fibres has been measured as 0.1×10^{-6} S cm^{-1} at 50% relative room humidity.[26] Thus, this considerable increase in electrical conductivity from insulating to weak semiconductivity is indeed significant. Therefore, substantial opportunities exist for the development and application of conducting papers and packaging products from these materials. By incorporation into plastic materials the electrical conductivity (antistatic), redox properties (chemical sensing) and tensile strength can be imparted to the host plastic.

Interestingly, an increase in conductivity was not observed for the silver-coated composites. This may be attributed to silver being deposited on the surface in the form of individual nanoparticles (Figure 9) with poor electrical contact between particles. Conductivities were in fact seen to be lower for silver-coated composites compared to their polymer counterparts (Table 1). Contributing to the apparent decrease in conductivity may be the removal of the Cl^- dopant and/or the lesser conductivity of the oxidised form of the underlying polymer due to a reduction in the electron transfer along the polymer backbone due to the chemical reduction of silver onto its surface.

Table 1. Electrical conductivities of merino cellulose fibre/polymer composites.

Description	Conductivity [S cm^{-1}]	Potential oxidation state of polymer
PPy/Cellulose	2.6×10^{-1}	reduced
PPy/Cellulose/Ag	3.8×10^{-4}	oxidised
PAn/Cellulose	6.0×10^{-4}	emeraldine
PAn/Cellulose/Ag	3.6×10^{-9}	pernigraniline

2.6 Antimicrobial Testing

For all samples, the silver-coated composites actively inhibited the growth of *Staphylococcus aureus* microbes and hence tested positive for their antimicrobial activity. White, hazy areas indicate bacterial growth, whereas the more transparent circles surrounding the fibre/polymer/silver composites, in the agar, indicate bacterial-free regions, i.e. zones of inhibition (Figure 10).

Silver is thought to migrate from the surface of the fibre composite inhibiting the growth of microbes in its path. The extent of silver-induced antimicrobial activity is directly proportional to ionic silver concentration.[27] Hence, the greater the silver ion concentration, the greater the antimicrobial efficacy will be. The release rate of unbound, free silver ions may therefore be correlated with the antimicrobial activity of the composite materials. As the zone of inhibition is similar for the fibre/PAn/silver and fibre/PPy/silver composites it can be assumed that the concentrations of silver across the surface of the composites are relatively similar. The release mechanism, which is deemed to be the same for all composites investigated, will theoretically be the limiting factor. This will also determine the effective lifetime of the antimicrobial activity. As the silver is strongly tethered to the polymer/fibre surface, this activity period will be desirably long.

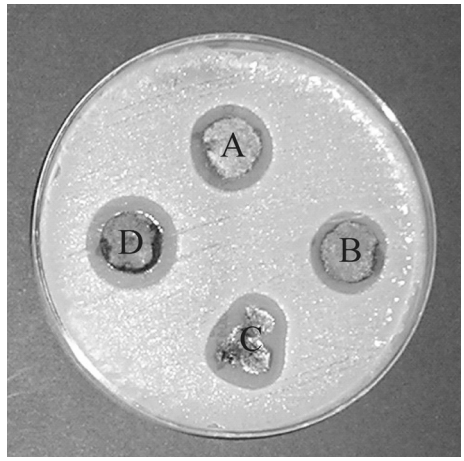

Figure 10. Zones of inhibition of *Staphlococcus aureus* microbial growth; cellulose fibre/polypyrrole/silver composites (A and B), cellulose fibre/polyaniline/silver composites (C and D).

3. Conclusions

New hybrid materials of cellulose fibres with conducting polymers have been successfully produced, in which individual Kraft fibres have been fully encapsulated by PPy and PAn spheres fused together in a continuous sheet to coat the fibres in their entirety. The bond between the fibre substrate and polymer coating is believed to be hydrogen bonding between the respective polymer (NH, N) and the OH groups of the cellulose on the fibre surface. The electrical conductivity of the prepared hybrid materials increased substantially from that of Kraft paper pulp, with conductivities as high as 2.6×10^{-1} S cm^{-1}. Fibre/conducting polymer/silver composites were also successfully produced by utilising the redox capability of the polymer surface. The conductivities for the silver analogues decreased compared with the fibre/polymer hybrids. This is likely due to poor electrical contact between adjacent silver nanoparticles, as indicated by findings from scanning electron microscopy, and the lesser conductivity of the underlying oxidised polymer. Silver composites tested positive in their antimicrobial activity against *Staphylococcus aureus*. The conducting polymer/cellulose fibre composite products and their silver analogues can be used in plastics and packaging materials, whereby the unique properties of the composites, such as redox, electrical conductivity and antimicrobial properties, can be imparted to these materials thereby adding important functionality to them.

4. Experimental Section

4.1. Reagents and Equipment

Kraft paper pulp, produced from bleached *P. radiata*, was obtained from Carter Holt Harvey NZ. All chemicals employed were of ana-

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lytical grade and used as received unless otherwise stated. Pyrrole (Pyr, 97%) and aniline (Ani, 99%) monomer were purchased from Aldrich Chemicals, as were *p*-dodecyl benzyl sulfonate and ferric chloride. Aniline and pyrrole were distilled twice prior to use. Ammonium persulfate was obtained from Koch-Light Laboratories Ltd.

The morphology of the fibre/polymer/silver hybrids were characterised utilising a JEOL 6500 F field-emission gun scanning electron microscope. The redox properties of the conducting polymer/fibre composites were measured by cyclic voltammetry, comprising an Amel 7050 potentiostat and Junior Assist software. Fibre composites were attached to the electrode using Parafilm®. After soaking in the degassed conductive potassium perchlorate/perchloric acid (pH = 2) solution for 30 min the connection was tightened, ensuring ample contact between the sample and the electrode, and measurements were carried out. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos Axis Ultra system with an aluminium filament operating at 10 mA and 15 kV using the K_α line. The pass energy for the survey scans was 160 eV and 10 eV for the narrow scans, and the sample area 300 × 700 μm. The binding energies were calibrated using the C–C 1s photoelectron peak at 285.0 eV. Conducting polymer-coated cellulose fibres were pressed into discs, using IR pellet-making apparatus, and their direct current (DC) electrical conductivity analysed by the Van der Pauw method for determining the conductivity for pressed discs and irregularly shaped samples.

4.2 Preparation of Conducting Polymer/Cellulose Fibre Hybrid Materials

Conducting polymer/cellulose fibre hybrids, using individual fibres of Kraft pulp, were prepared by the following method: Kraft pulp (0.5 g of 1 cm^2 pieces) was mixed with distilled water (100 cm^3) in a blender to give a fully dispersed suspension of individual pulp fibres. The resultant suspension was filtered by Büchner filtration and the fibres re-dispersed, with stirring, in a solution of pyrrole or aniline monomer (0.5 M) and *p*-dodecylbenzyl sulfonate (0.05 M) in water (200 cm^3). Stirring for approximately 1 h allowed for the monomer to be absorbed onto the surface of individual cellulose fibres. Then the fibres were filtered and washed with further monomer solution (0.5 M, 100 cm^3) and added to the oxidant, ferric chloride or ammonium persulfate (0.5 M, 100 cm^3). Polymerisation ensued, noted by a change in colour from orange to dark green to black, over a time period of approximately 5 min. However, the solution was left for a further 3 h to ensure complete polymerisation.

The resultant conducting polymer-coated cellulose fibres were filtered and washed on a 100 μm sieves with water and then subjected to repeated sonication with ethanol. This procedure was repeated several times in order to remove any excess and unbound polymer. Then the hybrid fibres were washed with hydrochloric acid (1.0 M) to effect doping with Cl^- ions, followed by further washing with water. The resulting fibres were air-dried to give individual conducting polymer-coated cellulose fibres, which were black in colour.

4.3. Preparation of Fibre/Conducting Polymer/Silver Composites

A silver coating was deposited on the surface of the polymer-coated fibres by chemical reduction of Ag^+ to Ag^0. In the case of PPy/fibre composites, the polymer coating was first reduced in the presence of excess reducing agent ($NaBH_4$, 2.0 M in triethylene glycol dimethyl ether), and the resulting fibres filtered and washed quickly with water to remove residual reductant. Then the reduced polymer fibres were suspended in $AgNO_3$ (0.1 M, 100 cm^3), allowed to react with the Ag^+ ions and then washed, filtered and sonicated in ethanol to remove excess Ag^+ and Ag^0.

A reducing agent was unnecessary for the reduction of silver on the surface of PAn/fibre composites. PAn composites in the form of emeraldine base were added directly to $AgNO_3$ (0.1 M, 100 cm^3). The redox reaction ensued in which emeraldine base was oxidised to pernigraniline, thus simultaneously reducing Ag^+ to Ag^0 at the surface of the coated fibre (see part b of Figure 7, section 2.4). The oxidation reaction was noted by a colour change from blue (emeraldine base) to purple (pernigraniline base). The resultant fibres were similarly washed with distilled water, filtered and then sonicated in ethanol to remove excess silver.

Acknowledgments

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