Palladium-Polyaniline and Palladium-Polyaniline Derivative Composite Materials
A BRIEF OVERVIEW OF THEIR PREPARATION AND POTENTIAL APPLICATIONS

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Palladium nanoparticles of different sizes and shapes combined with polyaniline and derivatives of polyaniline can give rise to a host polymer with interesting physical properties and important potential applications. The resulting composite can be produced in the form of nanofibres, nanorods, thin films, etc. Potential applications of this composite material for catalysis and sensor systems are discussed.

One key property distinguishing classical polymers from metals is their low electrical conductivity. A new class of organic polymers capable of conducting electricity has recently been developed (1, 2). These polymers become conductive upon partial oxidation or reduction, a process commonly referred to as ‘doping’. The electrical properties of conductive polymers can be changed reversibly over the full range of conductivity from insulators to metallic conductors. Their potential as novel materials in value-added industrial and consumer products is opening up wholly new avenues of application for polymeric materials.

Among conducting plastics, polyaniline has become a particular focus of interest because of its environmental stability (3), controllable electrical conductivity (4), and interesting redox properties associated with the chain nitrogen (5). The electrical properties of the aniline polymers can be improved substantially by secondary doping (6). Polyaniline compounds can be designed to achieve the particular conductivity required for a given application. The resulting blends can be as conductive as silicon and germanium or as insulating as glass. Additional advantages are that the compound can be mixed simply with conventional polymers, and it is easy to fabricate polyaniline products into specific shapes. The conductivity of polyaniline makes it an ideal shield against static electric discharges, and as a consequence polyaniline compounds have been used in the packaging of electronics products. Polyaniline compounds are being tested for use as protective materials against electromagnetic radiation. Further, scientists hope that one day printed circuit boards, electrochromic windows in houses and cars, and conductive fabrics will contain polyaniline compounds.

The presence of a number of intrinsic redox states (Figure 1) has substantially increased the number of potential applications of aniline polymers for use in practical devices. The aniline polymers have a general formula of the type \[ \left( -B-\text{NH}-B-\text{NH}- \right)_y, \left( -B-\text{N}=\text{Q}=\text{N} \right)_z \] \[ \text{x}, \] in which B and Q denote respectively the C₆H₄ rings in the benzenoid and the quinoid forms. In polyaniline, the neutral intrinsic redox states (Figure 1) can vary from that of the fully oxidised pernigraniline (PNA; \( \gamma = 0 \)), to that of the...
fully reduced leucoemeraldine (LM; \( y = 1 \)). The 50% intrinsically oxidised polymer has been named emeraldine (EM; \( y = 0.5 \)), and the 75% intrinsically oxidised polymer is named nigraniline (NA; \( y = 0.75 \)) (2). The synthesis and characterisation of polyaniline have been reviewed previously by Geniès et al. (7), Lux (8) and Gospodinova et al. (9). Polyaniline is a member of the semi-flexible rod polymer family. The synthesis and characterisation of electroactive polymers have become two of the most important areas of research into polymers, as well as in materials science over the past two decades.

Metal nanoparticles with different sizes and shapes can be combined with polyaniline to form hybrid materials. Hybrids represent a new class of materials that may combine desirable physical properties characteristic of both their organic and metallic components within a single composite. The metallic portion offers the potential for a wide range of electrical properties, substantial mechanical hardness and thermal stability, whereas the polymer part can provide high fluorescence efficiency, large polarisability, plastic mechanical properties, ease of processing and structural diversity.

The present article reviews both advances in methods of synthesis and application-related performance for various palladium-polyaniline and palladium-polyaniline derivative composite materials systems.

**Palladium-Polyaniline Composite Coating for LD Polyethylene**

Low-density polyethylene (LDPE) is a useful substrate for a wide range of laboratory experiments as well as many industrial applications (10–13). Although LDPE is a relatively inert substrate, it can be graft-copolymerised with acrylic acid to enhance the growth and adhesion of polyaniline coatings so as to achieve a thin conductive surface layer. In an earlier work, Neoh and coworkers (14) reported the formation of gold particles on the surface of a polyaniline film coated onto acrylic acid graft-copolymerised LDPE.

The thrust of this work was investigating how the electroactive polymer substrate was affected by the metal reduction process. The coating of LDPE films with a polyaniline-palladium composite layer was studied by Wang et al. (15). They used two methods for the synthesis of the polyaniline-palladium layer on the LDPE. Common to both was the initial step: the LDPE surface was first graft-copolymerised with acrylic acid to enhance the adhesion of the polyaniline-palladium layer. Subsequently, in the first method (Method 1 in Figures 2 and 3), polyaniline was deposited on the acrylic acid graft-copolymerised LDPE. This was followed by a reaction with palladium nitrate which resulted in a layer of palladium metal particles being deposited onto the polyaniline surface. In the
second method (Method 2 in Figures 2 and 3), polyaniline powder was first reacted with palladium nitrate. The powder was then treated with N-methylpyrrolidinone, after which it coated the acrylic acid graft-copolymerised LDPE. The latter method resulted in nanosized palladium metal particles being distributed in the polyaniline coating, rather than being confined to the surface of the polyaniline layer. In both methods, the palladium metal particles conferred surface conductivity on the LDPE substrate, even with the polyaniline in the undoped state. It was found that the polyaniline-palladium coating adhered excellently to the acrylic acid graft-copolymerised LDPE substrate at low palladium contents, but adhesion was weakened significantly at high palladium contents due to the palladium interfering with the interaction between the polyaniline and the acrylic acid graft-copolymerised chains. The polyaniline was synthesised in the reduced form, that is, leucoemeraldine (LM). The advantage of using LM is that it can very easily be oxidised, and palladium nitrate is reduced more rapidly.

X-ray photoelectron spectroscopy (XPS) analysis by Wang et al. (15) (Figure 2) of LM on acrylic acid graft-copolymerised LDPE after reaction with Pd(NO₃)₂ revealed two Pd 3d₅/₂ peaks at 335 and 338 eV, which are the characteristic peaks for the Pd(0) and Pd(II) species respectively. Initially, Pd(0) was the main oxidation state of palladium. For Method 1, the intensity of the Pd(II) peak increased with time, indicating that the Pd(II) species deposited on the surface of polyaniline without further reduction to Pd(0). By contrast, for the sample which was prepared using Method 2, XPS analyses confirmed that the Pd 3d₅/₂ peak at 335 eV was predominant throughout the reaction, while the peak at 338 eV did not show any significant incremental change as the reaction progressed. It was concluded that Pd(0) remained the predominant species on polyaniline for the sample which was prepared by Method 2. The disparity

Fig. 2 XPS Pd 3d spectra of LM on acrylic acid-graft copolymerised LDPE after reaction by Method 1 for: (a) 10 min; (b) 60 min; (c) 120 min; and (d) 180 min; and by Method 2 for: (e) 10 min; (f) 60 min; and (g) 180 min. Reproduced from (15) with permission from Elsevier
between the amounts of deposition of palladium species for the two samples results from the difference in the surface area and the availability of the reaction sites.

Figure 3 shows the scanning electron microscopy (SEM) images for the two methods corresponding to the palladium(0)-polyaniline composite on the acrylic acid graft-copolymerised LDPE film after different reaction times. In Figure 3 for Method 1, the average particle size of 100 nm or less as estimated from these images does not increase substantially during the early stages, ~10 to 60 min (Figures 3(b) and 3(c)), of the reaction. After a reaction time of 180 min or more, the surface of the LM film was covered with palladium (Figure 3(d)). In contrast, for Method 2, during the initial stages of the reaction (~10 min, Figure 3(f)), at a Pd(II):N molar ratio of 1:5, the average particle size was about 70 nm. After 180 min (Figure 3(h)), the average particle size had increased by some 300%. This increase in size was a direct result of the increase in size of the palladium clusters accumulated on the surface of the polyaniline powder as the reaction progressed and the subsequent dispersion of the particles in the polyaniline-N-methylpyrrolidinone solution.

Chemical Deposition of Palladium on Polyaniline

The reaction of polyaniline in its lowest oxidation state, LM, with palladium chloride and palladium nitrate has been investigated by Wang et al. (16). Polyaniline was synthesised via the oxidative polymerisation of aniline by ammonium persulphate, and converted to emeraldine (EM) or 50% oxidised base by treatment with excess 0.5 M sodium hydroxide. The fully
reduced form of the polyaniline, LM, was obtained by the reduction of the EM base with anhydrous 98% hydrazine for 3 h, followed by thorough washing with deionised water. The LM film obtained was then pumped dry under reduced pressure. Since the LM film is very easily oxidised, the palladium uptake experiments were conducted soon after the preparation of these films.

The LM film was used for the palladium uptake experiments using palladium chloride and palladium nitrate. The amounts of palladium deposited from the palladium precursors on the LM film are indicated in Figure 4. This figure shows that palladium nitrate reacts more effectively with LM than does palladium chloride, a finding that Wang et al. confirmed was reproducible. XPS measurements were performed to determine the state of the palladium deposited on the LM. Figure 5 shows the XPS Pd 3d spectra of the LM films after reaction in palladium chloride and palladium nitrate solutions for varying periods of time. For palladium nitrate, it is quite clear that Pd(0) is the principal state of the palladium deposited on the surface of the LM film. For palladium chloride, while Pd(II) was the predominant state on the LM surface at the beginning of the reaction, after 300 min, the Pd(0) state became the predominant species. Atomic force microscopy (AFM) images of the surface of the LM films after a 10 min immersion in palladium chloride and palladium nitrate solutions.
dium nitrate solutions are shown in Figures 6(a) and 6(b), respectively. A higher average roughness value, $R_a$, was achieved for the film when it was treated in palladium nitrate, as a direct consequence of the larger amount of palladium deposited on this film.

**Electrochemical Behaviour of Polyaniline-Palladium Composite Films**

The electrochemical behaviour of polyaniline films containing palladium nanoparticles was investigated by Park *et al.* (17) when the films were immersed in a propylene carbonate solution. To prepare the polyaniline-palladium nanoparticle composite film, a preformed poly(N-vinyl-2-pyrrolidone) stabilised palladium nanoparticle colloid was dispersed in a N-methyl-2-pyrrolidone (NMP) solution. Then, polyaniline (36% oxidised state) was added slowly to the solution which was then stirred for 24 h. The resultant solution was cast on glassy carbon and dried under vacuum for 4 h at room temperature. This assembly was used as the working electrode. A platinum coil and Ag/Ag$^+$ were used as the counter and reference electrodes, respectively.

Figure 7 shows the electrochemical behaviour of polyaniline and polyaniline containing 20 wt.% palladium nanoparticles. The cyclic voltammogram (CV) of the polyaniline film was characterised by the anodic peak near $-0.5$ V, which is associated with the transformation from the LM to the EM state. The second redox peak of polyaniline corresponds to the redox interconversion of polyaniline from EM to PNA. The anodic peak ($\sim -0.5$ V) and cathodic peak ($\sim -0.8$ V) current of the polyaniline film containing the palladium nanoparticles gradually decreased with successive cycles. In addition, the composite film showed new anodic and cathodic peaks at about $-0.1$ V and $-0.3$ V, respectively. The redox peak of the polyaniline-palladium nanoparticle composite film shifted to the positive potential.
region in comparison with the polyaniline film. This result implies the presence of strong electrochemical interactions between polyaniline and palladium nanoparticles. The complex formation process is readily evident in the CVs by the rapid growth of a pair of sharp redox waves at $E_{1/2} = -0.2 \, \text{V} \, \text{vs.} \, \text{Ag/Ag}^+$ in the presence of palladium nanoparticles.

The interaction between polyaniline and the palladium nanoparticles was studied by UV-visible spectroscopic measurements (Figure 8). Palladium nanoparticles, which were stabilised and well dispersed in NMP solutions, showed a characteristic plasmon absorption at 280 nm (Figure 8(a)). The absorption peaks observed for polyaniline at 340 nm and 640 nm (Figure 8(g)) indicate that the polyaniline was partially oxidised. Adding the polyaniline to a palladium-NMP solution caused a blue shift of the peak near 640 nm resulting from the charge transfer from the benzenoid to the quinoid (Figures 8(b)–8(f)). The peak near 320 nm, which is due to the $\pi-\pi^*$ transition of the phenyl ring, also blue shifted. These spectral changes indicate that the coordination of the palladium particles to the nitrogen atoms permitted the palladium nanoparticles to interact with each other through the $\pi$-conjugate chain. Such a blue shift of the band at $\sim 600 \, \text{nm}$ indicates the formation of a complex between the polyaniline and the palladium nanoparticles.

**Palladium and Polyaniline Derivative Composite Material**

The derivatives of polyaniline have attracted growing scientific attention since their chemical properties are similar to those of polyaniline. In comparison to the parent polymer, they exhibit better solubility in common organic solvents, which facilitates easier processing of these materials.

**Poly(3,5-dimethylaniline)-Palladium Nanofibre Composites**

For the preparation of polymer-palladium composite material an *in situ* synthesis approach is preferable. Since the polymer and the nanosized metal particles are produced simultaneously, this is expected to yield a highly intimate contact between the two components.

An *in situ* chemical synthesis route was used for the synthesis of a poly(3,5-dimethylaniline) nanofibre and palladium nanoparticle (polymer-metal) composite material in which the nanoparticles were highly dispersed in the polymer fibre matrix (18). Transmission electron microscopy (TEM) images (Figure 9) illustrate the composite material at different magnifications. Figure 9(a) shows an example of the large population of polymer fibres with different sizes, whereas Figure 9(b) images part of a single fibre, which is about 300 nm in diameter. The inset in Figure 9(b) shows the diffraction pattern from the fibre, revealing both diffuse scattering from the amorphous polymer and diffraction rings. Dark field imaging confirms that the rings originate from the palladium nanoparticles. Figures 9(c) and 9(d) show TEM images of the surface morphology and internal microstructure of the polymer. It is clear that the surface is not smooth. On both the rough surfaces and in the interior of the polymer, as shown by these and stereo pair images, there are highly distributed dark regions of diameter.
about 2 nm. Electron energy loss spectroscopy (EELS) mapping for the palladium distribution has confirmed that the dark spots are palladium. This is most clearly illustrated in Figure 10, which shows a fine strand of polymer composite, in which the particles were not overlapping. Figure 10(a) is a zero-loss image of the strand. This is an energy-filtered image; that is, it is derived only from electrons which have retained the energy of the beam when passing through the thin sample. The image therefore contains no analytical information. In contrast, Figure 10(b) is a palladium map from the same region. This palladium jump-ratio image was obtained by dividing the Pd-N₂,₃ post-edge loss image by the pre-edge loss image, thereby producing a signal derived from electrons that have lost energy by generating Pd-N shell X-rays.

Palladium Nanoparticles in Poly(ω-methoxyaniline)

Metal-polymer composites with a nano- or micro-structured morphology have potential applications in various fields such as sensors, organic light-emitting diodes (OLEDs), field-effect transistors and nonlinear optics. A microstructured 3D rod-like morphology of a palladium-poly(ω-methoxyaniline) composite material has recently been reported by our group (19). An in situ reaction between palladium acetate and ω-methoxyaniline was employed. Figure 11(a) is a SEM image showing the product, which consists of regular straight nanofibres. An image at higher magnification, Figure 11(b), reveals the 3D structure of the nanofibres, which were up to about 15 μm in length, 0.5 μm in width and 0.25 μm thick. All the fibres were uniform in morphology and very straight, suggesting a high degree of rigidity. Raman spectroscopy was employed to determine the structural orientation of the polymer. As seen in Figure 12, the benzene C–H bending deformation mode lies at 1140 to 1190 cm⁻¹ for the reduced semiquinone and quinoid ring structure. The band at 1260 cm⁻¹ can be assigned to the C–N stretching mode of the polaronic units. The band at 1337 cm⁻¹ corresponds to the C–N⁺ stretching modes of the delocalised polaronic charge carriers, while the C–C stretching of the benzenoid ring was observed at 1600 cm⁻¹. A small peak positioned at 1460 cm⁻¹ cor-
responds to the C=N stretching mode of the quinoid units. A band of moderate intensity at 1500 cm\(^{-1}\) corresponds to the bending deformation of the N\(^{•+}\)–H unit.

A wide variety of methods have been applied to the preparation of polyaniline or substituted polyaniline type compounds by oxidative polymerisation of the monomer (20). We have suggested (19) that the mechanism for the polymerisation process involves the formation of a radical cation accompanied by the release of an electron, this being the initiation process for the polymerisation reaction. During the addition of palladium acetate, the pH of the reaction mixture solution dropped to ~ 5. Spectroscopic analysis confirmed that the –OCH\(_3\) substituted aniline oxidation product had only a head-to-tail (–N–Ph–N–Ph–) like arrangement rather than a head-to-head (–Ph–N=N–Ph–) type. The N–N characteristics arise from the head-to-head coupling only under neutral or basic pH conditions. On the other hand, aniline or substituted aniline oxidation products obtained in acid media have a predominantly head-to-tail arrangement (2).

The presence of the electron-donating group (–OCH\(_3\)) in the \(o\)-methoxyaniline facilitates the relay of electrons through N\(^{•+}\)–H\(_2\), which forms a covalent bond with Pd(II) and attains a species like \([\text{OCH}_3\text{Ph}-\text{N}^{•+}\text{–H}_2]\). Under acidic conditions, the \([\text{OCH}_3\text{Ph}-\text{N}^{•+}\text{–H}_2]\) species undergo polymerisation (Figure 13), which is an oxidation process. Each step of polymerisation is associated with a release of an electron (21), leading to the reduction of Pd(II) to Pd(0). Subsequent coalescence of the atoms forms palladium clusters which are stabilised by the polymer. Figure 14(a) is a TEM image of this material revealing a uniform size distribution of palladium nanoparticles which are highly dispersed in the polymer matrix. A typical energy dispersive X-ray (EDX) spot analysis confirmed that dark regions in the polymer are palladium nanoparticles, Figure 14(b).

### Palladium Nanoparticles in Poly(\(o\)-aminophenol) Needles

Another example of an in situ chemical synthesis approach has been given by us (21) for the preparation of a palladium-poly(\(o\)-aminophenol) composite material. Figure 15(a) shows a SEM image of the needle-like morphology of the composite material. TEM micrographs, Figures 15(b) and 15(c), indicate that the palladium nanoparticles are of the order of 2 nm in diameter and are highly dispersed within the polymer matrix. An IR spectroscopic study was used to determine the chemical structure of the polymer. In the IR spectrum, Figure 16, the characteristic band at 1588 cm\(^{-1}\) can be assigned to the C=C stretching of the quinoid rings, while the two peaks at 1499 cm\(^{-1}\) and 1470 cm\(^{-1}\) are the characteristic bands of the C=C stretching vibration mode for benzenoid rings.

### Palladium-Polyaniline Composite as a Sensor

Athawale et al. (22) have shown that palladi-
um-polyaniline can be used as a methanol sensor. The nanocomposite material was synthesised by using a thermal reflux method followed by the oxidative polymerisation of aniline by ammonium persulfate, Figure 17. The synthesised nanocomposite was exposed to different aliphatic alcohol vapours such as methanol, ethanol and isopropanol. The results showed that the nanocomposite was highly selective and sensitive to methanol vapours. The sensor responded rapidly and reversibly in the presence of different concentrations of methanol vapour. The selectivity of the nanocomposite was further investigated by exposing it to mixtures of methanol–ethanol and methanol–isopropanol. Except for the response time, the nanocomposite was found to exhibit
an exactly identical response to that for pure methanol. The palladium-polyaniline nanocomposite was quite stable and showed no effects of ageing after exposure to different concentrations of methanol.

**Catalytic Activity for the Hydrogenation of Nitrobenzene**

The catalytic activities of palladium-containing electroactive polymer microparticles, typically 1.5 μm diameter, in the reduction of nitrobenzene to aniline have been studied by Huang and coworkers (23). Polyaniline was synthesised by adding ammonium persulfate to hydrochloric acid with vigorous stirring for 16 h. The resultant solid particles were then washed with excess hydrochloric acid and dried under reduced pressure. Polyaniline-SiO2 microparticles were also synthesised at ambient temperature by adding colloidal silica to a solution of ammonium persulfate in hydrochloric acid with constant stirring. Aniline was then added and the solution stirred vigorously for 16 h. The colloidal suspension was then centrifuged twice and stored in 1 M HCl until used. The oxidation state of the resultant polyaniline and polyaniline-SiO₂ was that of the emeraldine form (EM and EM-SiO₂, respectively). The fully reduced forms of polyaniline, LM, and polyaniline-SiO₂ (LM-SiO₂) were obtained after successive treatments with sodium hydroxide and hydrazine.

Palladium chloride was used as the precursor for incorporating palladium in EM, EM-SiO₂, LM and LM-SiO₂. Figure 18 shows the decrease in the concentration of palladium chloride as a function of reaction time. From Figure 18, it is apparent that LM and LM-SiO₂ are more effective in uptaking palladium from the solution than either EM or EM-SiO₂. It is also clear that SiO₂ plays no direct role in the reaction with palladium.

The catalytic activity of the palladium-containing LM-SiO₂ was tested for the hydrogenation of nitrobenzene and it was found that there was an almost complete conversion to aniline (Figure 19) after 2 h at 30°C, whereas the catalytic activity of the LM without palladium in the hydrogenation of nitrobenzene was shown to be negligible.

Huang et al. concluded that the reactions are rapid when these electroactive polymers are
reduced to their lowest oxidation states. The electroactive polymers synthesised with SiO₂ offer a larger specific surface area and a faster reaction rate for uptake reactions with palladium chloride than does the electroactive polymer without SiO₂. XPS analysis confirmed that the palladium accumulation was in the form of Pd(II) rather than elemental metallic palladium.

**Conclusion**

Palladium-polyaniline and the derivatives of polyaniline composite materials are a very important addition to the repertoire of novel materials. From the standpoint of synthesis techniques, the morphology of these composite materials can be in various forms such as thin films, nanorods and nanofibres. The *in situ* chemical synthesis route is one of the most versatile approaches for the preparation of metal-polymer composite materials. By exploiting this approach, our group first reported a palladium-based polymeric hybrid material in which palladium nanoparticles of size ~ 3 nm were uniformly dispersed and encapsulated in the matrices of various derivatives of polyaniline. The matrices had a range of morphologies. Considering the progress of research in this field, it can be concluded that, in the near future, palladium-polyaniline composites will produce further significant advances in the field of materials science.

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**References**


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