New Generation Nanogold and Nanosilver Polymer Composites and Their Applications

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ABSTRACT

A new generation of nanogold and nanosilver polymer composites with polyurethane and nylon respectively, have been produced and characterised accordingly. The composites exhibit the surface plasmon resonance absorption effects of nanogold and nanosilver, showing the presence of these entities in the polymer matrix. This was similarly confirmed by transmission and scanning electronmicroscopy which show the presence of nanoparticles within the polymer matrix. The nanoparticles are chemically bound to the N of the -NH_2 groups in the polymers. The nanogold and nanosilver particles are dispersed throughout the polymer matrix enabling the composites to be formed into a variety of shapes by conventional thermoplastic processing methods to produce uniform products. The nanosilver polymer composites show antimicrobial effectiveness against *S. aureus* and *E. coli* bacteria and the nanosilver and nanogold polymer composites exhibit good marine antifouling properties.

Keywords: nanogold, nanosilver, composite, polymers, polyurethane, nylon, antimicrobial, antifouling.

1 INTRODUCTION

An opportunity exists to functionalise commonly used polymers with nanoparticles to form new composite materials that exhibit the properties of both precursors in a synergistic way. Due to the increased surface area to volume ratio exhibited by metal nanoparticles as a result of their nanosize, they generally display interesting physical and chemical properties which are different to, or enhance those of their macroscale counterparts [1]. For example, nanogold and nanosilver exhibit interesting optical properties due to surface plasmon resonance effects and antimicrobial properties, particularly silver, due to its strong binding to the electron-donating groups in the bacterial cells [2].

Here we present such a development of a new generation of nanogold and nanosilver polymer composites with polyurethane and nylon respectively, and examples of their applications. Nanofunctionalised polyurethane latex suspensions used in paint formulations, have been developed similarly. This novel nanoscience and technology development and resulting product suite, provide the exciting opportunity to impart new functionality to the polymer substrates for industrial and consumer products. Respective applications include: non copyable security identification and labelling; catalytic surfaces; lightfast colorants; effective, long lasting and durable antimicrobial and antifouling surfaces for paints, textiles, healthcare equipment and water and air filters, and water purification devices.

The development innovatively uses the chemical affinity of gold and silver for N in the –NH_2 groups of the polymer chains, and the porous polymer matrix to form and bind the nanogold and nanosilver particles directly in the polymer matrix, and control their size. Polyurethane and nylon 6,6 beads were used initially to develop the science and technology which was then extended to sheet substrates and emulsions.

The work presented here utilises and builds on the proprietary knowhow of Johnston et al. who have developed new chemistry technology to bind gold and silver nanoparticles to natural and synthetic fibres and substrates, and generate new product suites [3,4]. The new composites, which exhibit surface plasmon resonance optical effects and antimicrobial properties, can be processed by any conventional thermoplastic extrusion and moulding techniques.

2 MATERIALS AND METHODS

All the chemicals were supplied by Sigma Aldrich. Nylon 6,6 and polyurethane beads were provided by Centre for Advanced Composite Materials and the Plastics Centre of Excellence at the University of Auckland, New Zealand.

The gold and silver analyses were carried out by Atomic Absorption spectroscopy using a GBC 9600 Atomic Absorption spectrometer. The UV–Visible spectra were obtained by using a Varian Cary 100 Scanning spectrometer over wavelengths of 200-800 nm. The Transmission electronmicroscopy (TEM) images of the nanocrystals were acquired on JEOL 2011 TEM operating at 200 kV. For TEM analyses, the polyurethane samples were dissolved in DMF subsequently placing a drop of the resulting solutions onto carbon-coated copper grids, air dried and further carbon coated. The extent of dispersion and elemental analysis of the nanoparticles into the polymeric matrix were studied by means of a JEOL 6500 F field-emission scanning electronmicroscope (SEM) and energy dispersive analysis (EDS) operating in a low-vacuum mode at 15 kV and a working distance of 9 mm. X-ray diffraction (XRD) was used to determine the crystalline phases of the polymer composites.

The antimicrobial activity of the polymer composites containing nanogold and nanosilver were tested against *Staphylococcus aureus* (ATCC 29213) and *Escherichia coli* (W3110) bacteria. Samples of the functionalised beads were placed on a Mueller Hinton agar plate and incubated at 35°C for 18hrs in aerob incubator and the zone of inhibition observed after incubation.

3 NANOGOLD AND NANOSILVER POLYMER COMPOSITES

Nanogold and nanosilver polymer composites with polyurethane and nylon beads were synthesised by a proprietary method. This involved the reduction of $AuCl_4^-$ and Ag^+ containing solutions to produce gold and silver nanoparticles respectively and taking advantage of the chemical affinity of Au and Ag for N in the $-NH_2$ groups of the polyurethane and nylon polymer chains to bind the nanoparticles to the polymer matrix. The methodology ensured the nanoparticles were reasonably well distributed throughout the polyurethane and nylon beads. The size and shape of the gold and silver nanoparticles and hence the colour of the polymer composites arising from the surface plasmon resonance absorption of the respective nanoparticles, are controlled in the synthesis process. Figure 1 shows nanogold-polyurethane and nanosilver-polyurethane beads that contain different amounts of the respective nanoparticles, exhibit an increased intensity of colour with increasing nanoparticle concentration. The same colours are seen in the "dog bone" test strips prepared from these beads respectively (Figure 2). Only very low levels of gold and silver are used.

Figure 1: Nanogold-polyurethane (top) and nanosilver-polyurethane (bottom) composite beads with increasing metal content from left (no metal) to right. The shade and intensity of the colour increase with increasing nanogold and nanosilver content respectively.

Figure 2: Nanogold-polyurethane moulded strips with increasing nanogold content. The colour within each strip and hence the distribution of nanoparticles is very uniform.

The Visible spectra for polyurethane, nanogold-polyurethane and nanosilver-polyurethane composites are presented in Figure 3. As expected, the spectrum for polyurethane shows no absorption peaks. The nanogold-polyurethane composite shows a broad absorption peak at 570 nm typical of the surface plasmon resonance absorption for gold nanoparticles of about 5-50 nm in size. Similarly the nanosilver-polyurethane composite shows an absorption peak at 420 nm which is typical of the surface plasmon resonance absorption for silver nanoparticles of a comparable size. The nanogold-nylon and nanosilver-nylon composites show similar surface plasmon resonance absorption peaks [1,5,6].

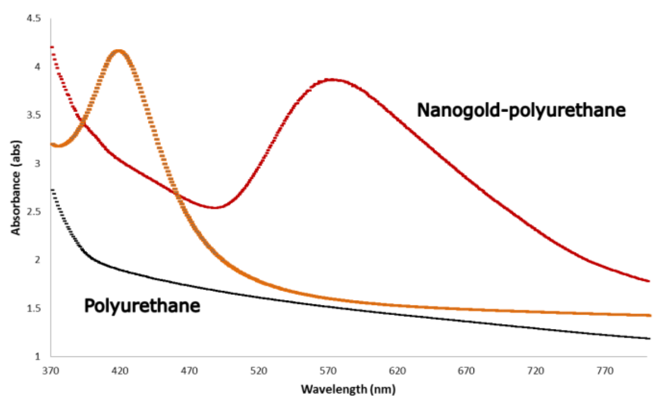

Figure 3: Visible absorption spectra of polyurethane (black), nanogold-polyurethane (red) and nanosilver-polyurethane (orange) composites.

X-ray powder diffraction confirmed the presence of these metallic gold and silver nanoparticles in the respective nanogold and nanosilver polyurethane and nylon polymer composites.

Transmission electronmicroscopy shows the size of the gold and silver nanoparticles to range between 5-50 nm

(Figure 4), consistent with the surface plasmon resonance colour. Scanning electronmicroscopy shows there is a greater concentration of nanoparticles nearer the surface of the polymer substrate than further into the bulk (Figure 5) due to the difficulty of diffusing gold and silver ions through the polymer matrix.

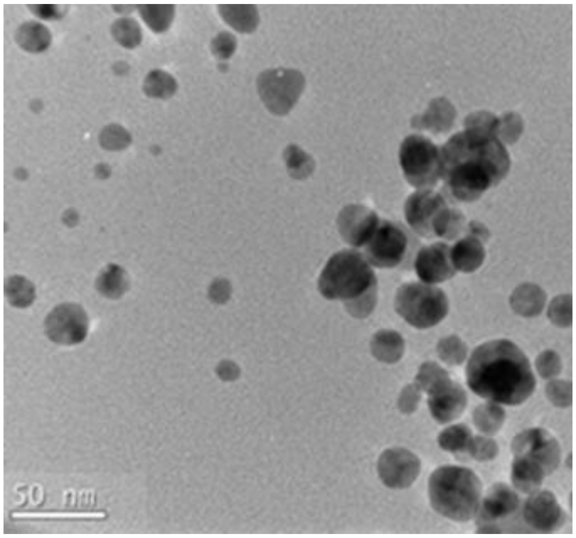

Figure 4: Transmission electron microscope images of a nanogold-polyurethane sample; marker bar = 5 nm.

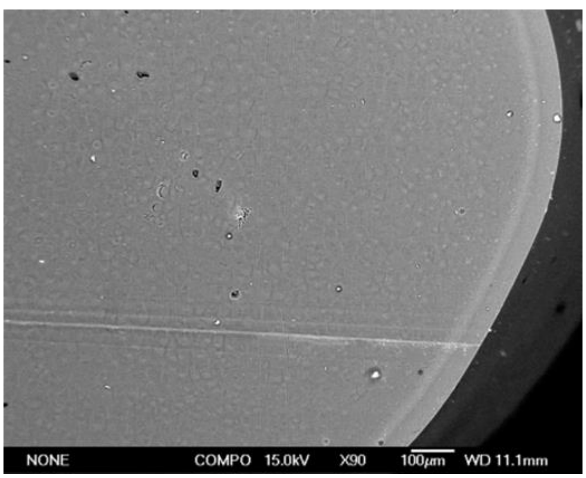

Figure 5: Scanning electron microscope image of a nanogold-polyurethane bead. The small light spots are the gold nanoparticles.

The respective nanogold and nanosilver polyurethane and nylon polymer composites were prepared as beads (Figure 1) and were formed into “dog bone” test strips in a subsequent thermoplastic mixing and extrusion process (Figure 2). In this process the gold and silver nanoparticles mixed evenly through the respective polymer matrix to form completely uniform nanometal polymer composites as shown by the colour (Figure 2). This shows that these nanometal polymer composites can be drawn into fibres, or moulded and shaped by any conventional thermoplastic process to produce a uniform product. XPS measurements confirmed the gold and silver nanoparticles are chemically bound to the respective polymer matrix through the N in the $-NH_2$ groups and as such they do not wash or wear off. This provides a robust product.

The nanometal polymer composites exhibit effective and durable antimicrobial activity against the gram-positive *Staphylococcus aureus* and gram negative *Escherichia coli* bacteria. Figure 6 shows an extensive zone of inhibition (clear area) on the *Staphylococcus aureus* inoculated agar plate where the nanosilver-polyurethane composite bead was originally positioned, confirming the antimicrobial effectiveness of this composite. A similar result was recorded for the nanosilver-nylon beads. Interestingly, the nanogold-polyurethane composites also showed some antimicrobial activity but the zone of inhibition was smaller than that for the nanosilver-polyurethane composite.

The antimicrobial effectiveness was also measured quantitatively by a colony counting method. This showed that the nanosilver polyurethane composite reduced the *Escherichia coli* count by 99.97 % and nanogold polyurethane composite by 52 % (Figure 7).

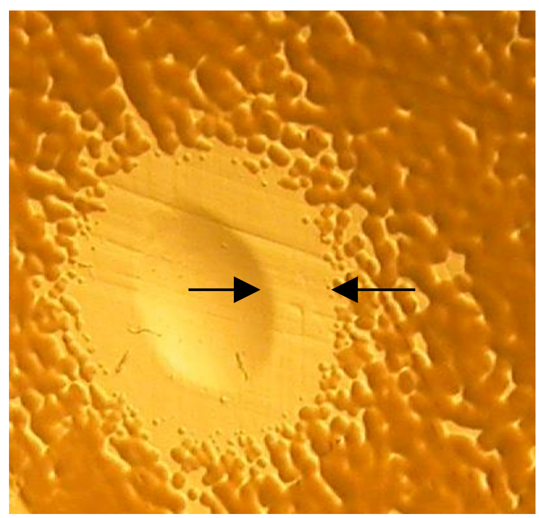

Figure 6: Zone of inhibition for *Staphylococcus aureus* bacteria (clear area) around a nanosilver-polyurethane bead (removed) that was positioned on the surface of an inoculated agar plate, as shown by the arrows.

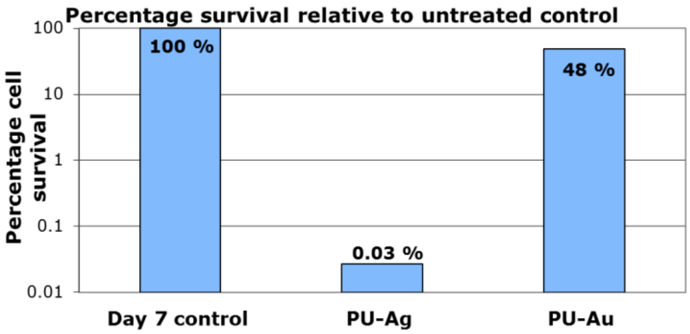

Figure 7: The antimicrobial effectiveness of the nanosilver-polyurethane and the nanogold-polyurethane composites against *Escherichia coli* bacteria measured quantitatively by the colony counting method.

Nanogold and nanosilver polyurethane paint formulations were prepared by similarly functionalising a polyurethane latex with nanogold and nanosilver respectively to produce a paint that exhibited comparable antimicrobial effectiveness. These were also tested for their effectiveness as a marine antifouling paint by painting blocks of wood and submersing them in the sea for six months in an area of prolific marine biota. Control samples were prepared using a polyurethane paint without the nanogold or nanosilver functionalisation. Figure 8 shows the control sample is heavily encrusted with marine biota, whereas then nanogold-polyurethane and nanosilver-polyurethane paints showed only very minor amounts of marine biota. This demonstrates the effective marine antifouling properties of these nanosilver-polyurethane and nanogold-polyurethane composites and offers an attractive alternative to the current environmentally questionable copper-based formulations.

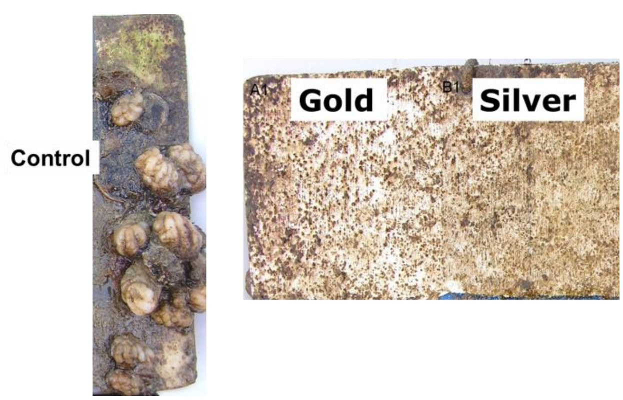

Figure 8: Marine antifouling effectiveness of nanogold and nanosilver polyurethane paint compared to a control sample.

4 CONCLUSIONS

A new generation of nanogold and nanosilver polymer composites with polyurethane and nylon respectively have been produced and characterised accordingly. The composites exhibit the surface plasmon resonance absorption effects of nanogold and nanosilver, showing the presence of these entities in the polymer matrix. This was confirmed by transmission and scanning electronmicroscopy. The nanoparticles are chemically bound to the N of the -NH_2 groups in the polymer chains. The nanogold and nanosilver particles are dispersed through the polymer matrix enabling the composites to be formed into a variety of shapes by conventional thermoplastic processing methods to produce uniform composite products.

The nanosilver composites with polyurethane and nylon display highly effective antimicrobial properties, and the nanogold composites to a lesser extent. Nanogold and nanosilver polyurethane paint formulations exhibit effective antifouling properties. As such, these nanogold and nanosilver polymer composites have considerable potential in commercial applications.

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