New Generation Hybrid Plastics Functionalised by Nanogold and Nanosilver

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ABSTRACT

This paper reports the innovative development of a new generation of hybrid plastics comprising polyurethane and nylon functionalised with gold or silver nanoparticles respectively. The synthesis of these new nano-functionalised plastics has been successfully carried out by utilising the chemical affinity of gold and silver for nitrogen in order to bind nanogold and nanosilver entities to the nitrogen groups in polyurethane and nylon. The size of the metal nanoparticles can be controlled by the synthesis conditions. Electron microscopy, XRD and UV-Visible spectroscopic measurements have been used to characterize these new hybrid plastics. The antimicrobial properties of the nanogold and nanosilver hybrid plastics have been successfully tested against gram positive *Staphylococcus aureus* and gram-negative *Escherichia. coli* bacteria.

Keywords: gold, silver, nanoparticles, antimicrobial, polymers, polyurethane, nylon.

1 INTRODUCTION

The demand for new materials with improved properties and are smaller, lighter and stronger has become an ongoing challenge for scientists and engineers. An example is the development of new hybrid plastics with modified surfaces and novel properties for applications in various areas such as food packaging, wound dressings, antimicrobial surface coatings in hospitals and factories, multi-functional textiles, water supply systems, air filters, etc. [1], which open up new business opportunities.

Due to the increased surface area to volume ratio of metal nanoparticles compared with their bulk counterparts, they display interesting physical and chemical properties relative to materials with the same chemical composition synthesized on the macroscale size. For example, they can exhibit intense colours due to surface plasmon resonance light scattering effects and also antimicrobial properties, particularly the nanosilver plastics, due to the strong binding of silver ions to the electron-donating groups in the bacterial cells [2]. As such, there are opportunities to incorporate metal nanoparticles into commodity materials, such as plastics, thus imparting the unique properties of the nanoparticles to the plastics, producing modified surfaces and imparting antimicrobial, catalytic and optical properties to them.

The work presented here utilises and builds on the proprietary knowhow of Johnston et al. who have developed new chemistry technology to form and bind gold and silver nanoparticles to natural and synthetic fibres and substrates, and generate new product suites [3]. The chemical affinity of gold and silver for nitrogen has been used to bind nanogold and nanosilver entities to the nitrogen groups in polyurethane and nylon to produce new hybrid plastics functionalised by nanogold and nanosilver entities. These hybrid plastics, which exhibit surface plasmon resonance colourant effects and antimicrobial properties can be processed by any conventional plastics extrusion and moulding techniques.

2 MATERIALS AND METHODS

2.1 Materials and reagents

All the chemicals were supplied by Sigma Aldrich. Nylon 66 and polyurethane (TPU) beads were provided by the Centre for Advanced Composite Materials and the Plastics Centre of Excellence at the University of Auckland, New Zealand.

2.2 Analysis Methods

The absorption or the extent of uptake of gold and silver by the plastic substrates was analysed 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 Electron Microscopy (TEM) images of the nanocrystals were acquired on JEOL 2010 TEM operating at 200 kV. For TEM analyses, the composite TPU bead samples were prepared by dissolving the nanohybrid plastics in DMF and placing a drop of the resulting solutions onto carbon-coated copper grids, air dried and further carbon coated. The morphology of the nanogold and nanosilver nylon and polyurethane hybrid plastics was studied using a JEOL 6500 F field-emission scanning electronmicroscope (SEM) with energy dispersive X-ray analysis (EDS) operating in a low-vacuum mode at 15 kV and a working distance of 9 mm. EDS elemental analysis was used to confirm the

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presence of nanogold and nanosilver in the polymer matrices and to characterise the dispersion and distribution of the nanoparticles in these matrices. Synchrotron X-ray diffraction measurements were used to characterise the crystalline phases of the nanohybrid plastics using the beamline BM-10 at the Australian Synchrotron in Melbourne. Data were collected in transmission mode, with a beam size of 5 mm in horizontal length and 2 mm in vertical height. A wavelength of 0.6196 Å and beam energy of 20 keV were used. The XRD patterns were obtained using the Mythen detector over an angular range of 80 ^{o}. Sample preparation included pressing the solid hybrid plastic beads into 1 mm thick disks and sandwiching them between two sample holder plates with a hole in the centre (15 mm in diameter). The average crystallite size was calculated from the peak line broadening using the Topas software.

The antimicrobial activity of the hybrid plastics containing nanogold and nanosilver were tested against gram positive ATCC 29213 *Staphylococcus aureus* and gram-negative *E. coli* (W3110) bacteria. For this, samples of the functionalised beads were placed on a Mueller Hinton agar plate and incubated at 35 °C for 18 hours in an Aerob incubator and the bacterial colonies counted.

2.3 Synthesis of nanogold and nanosilver hybrid plastics

The initial uptakes of dissolved gold and silver by the TPU polyurethane and nylon substrates were determined by soaking samples of the plastics in different concentrations of gold or silver solutions for different times and temperatures, and subsequently analysing the resulting solution for any residual dissolved gold or silver respectively. The studies have shown that at low concentrations of about 100 mg kg^{-1} all the dissolved gold and much of the dissolved silver were absorbed by the nylon and polyurethane substrates respectively. The formation of nanogold and nanosilver on the surface and within the plastics was then achieved by the reduction of the absorbed gold and silver ions respectively under controlled conditions. The polyurethane or nylon act as the substrate to bind the nanogold and nanosilver entities through the nitrogen functionality and also to control the distribution within the hybrid materials [3]. The size and shape of the metal nanoparticles (and hence the colour of the hybrid plastics) can be controlled by the polymer matrix, metal ion concentrations and the reduction process. The resulting nanogold-polyurethane and nanogold-nylon hybrids are a pink-purple colour with the purple colour intensifying with increasing nanogold concentrations. The nanosilver-polyurethane and nanosilver-nylon hybrids are a light yellow in colour at low nanosilver concentrations and colour intensifies to yellow-brown with increasing nanosilver concentrations (Fig. 1). These colours are consistent with those arising from the surface plasmon resonance absorption of light by gold and silver nanoparticles respectively. Also, the colours are more intense on the outside of the plastics where the concentrations of the nano entities are higher.

Figure 1: (a) nanogold-polyurethane and (b) nanosilver-polyurethane hybrids; the shade and intensity of the colour increase with increasing nanogold and nanosilver content respectively.

3 RESULTS AND DISCUSSION

The UV-Visible spectrum of the nanosilver-nylon hybrid material shows the typical 420 nm surface plasmon resonance absorption peak of nanosilver, which confirms the presence of silver nanoparticles in the hybrid plastic [4]. For nylon samples containing gold nanoparticles the UV-Visible spectrum shows a peak with the maximum absorption at about 550 nm (Fig. 2) consistent with the surface plasmon resonance band for gold nanoparticles. As previous reported, UV-Vis spectra for nanogold-polyurethane and nanosilver-polyurethane hybrid plastics similarly indicate the presence of gold and silver nanoparticles in the polyurethane hybrid plastics [5].

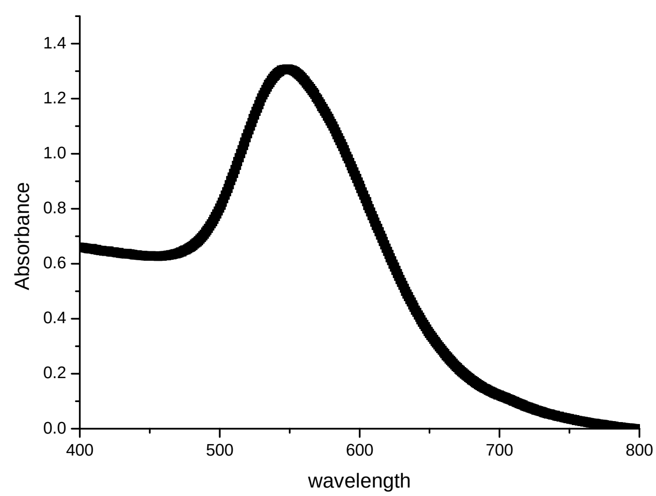

Figure 2: UV-Visible spectrum of a nanogold-nylon 66 hybrid plastic, showing the 550 nm surface plasmon resonance absorption peak of gold nanoparticles.

The morphology of the nanogold particles in a nanogold-polyurethane hybrid plastic observed by TEM is presented in Fig 3. This shows the characteristic spherical gold nanoparticles within the polyurethane matrix. The SEM and EDS analyses also confirm the presence of nanogold and nanosilver on the polymer surface and within the bulk of these new hybrid polyurethane and nylon plastics.

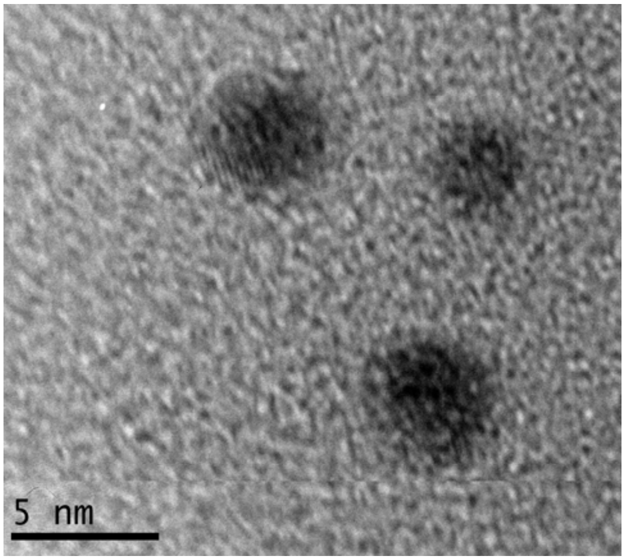

Figure 3: Transmission electronmicroscope image of a nanogold-polyurethane sample showing the gold nanoparticles; marker bar = 5 nm.

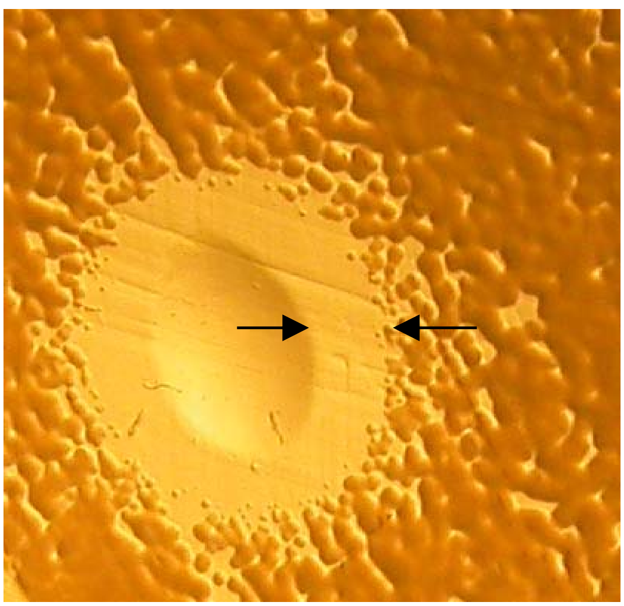

Figure 4: Zone of inhibition for *Staphylococcus aureus* around a nanosilver –polyurethane bead as shown by the arrows.

The nanogold and nanosilver hybrid plastics exhibit effective antimicrobial activity against the gram-positive bacteria *Staphylococcus aureus* (ATCC 29213) as well as the gram-negative bacteria *Escherichia. coli* (W3110). This is shown by the extensive zone of inhibition (clear area) around a nanosilver-polyurethane hybrid bead (Figure 4). Nanogold hybrid plastics are similarly effective, but to a lesser extent.

Synchrotron X-ray powder diffraction analyses have confirmed the silver and gold entities are in their respective metallic forms. For example, the XRD pattern shown in Fig. 5 contains only peaks which can be assigned to crystalline face centred metallic gold. By using XRD line broadening and TEM images it has been shown that the size of the nanoparticles bound to the polyurethane or nylon plastic substrates range between 2 - 50 nm in diameter for nanogold and between about 2 - 26 nm in diameter for nanosilver. The size is controlled during the preparation method and is determined by the reaction conditions, pH and metal ion concentrations.

The incorporation of gold and silver nanoparticles onto and within the polymeric matrix of polyurethane or nylon does not adversely affect the physical properties of the polyurethane or nylon. Hence the hybrid plastics can be drawn into fine fibres, or moulded and shaped by any conventional process. The nanogold and nanosilver particles remain dispersed throughout the plastic substrate. This makes them useful for fashioning into a number of consumer items where the desired functionality is provided by the nanogold or nanosilver.

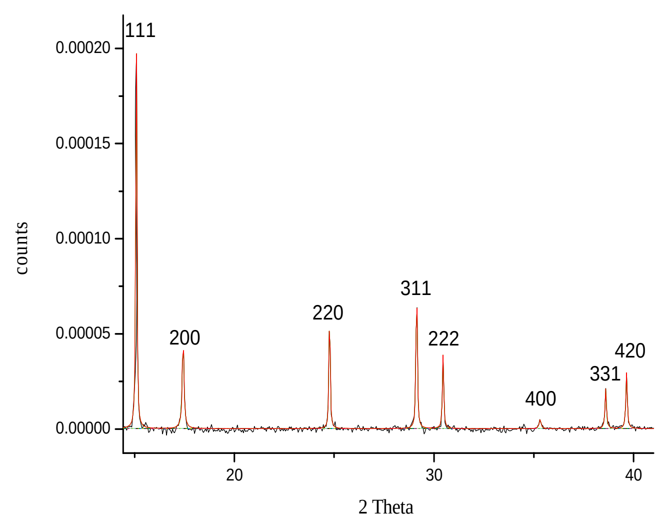

Figure 5: Synchrotron XRD pattern of a nanogold - polyurethane hybrid plastic.

4 CONCLUSIONS

New hybrid plastics of polyurethane and nylon 66 functionalised by nanogold and nanosilver have been successfully synthesised and characterised. The novel methodology is based on the absorption and reduction of gold and silver ions together with the simultaneous stabilisation of the formed metal nanoparticles by the polymer matrix. The size and shape of the respective metal nanoparticles can be controlled by the reaction conditions and the polymer matrix. These new hybrid plastic materials exhibit different colours due to the surface plasmon resonance absorption effects of the nanogold and nanosilver. They exhibit highly effective antimicrobial properties, particularly the nanosilver plastics. As such, these nanosilver plastics have considerable potential in commercial applications which require antimicrobial properties, such as surface coatings in medical and health areas, water and air filters, protective clothing and gloves.

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