Nanogold and Nanosilver Hybrid Plastics

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ABSTRACT

This paper presents an innovative development of proprietary new hybrid plastic materials functionalised by nanogold and nanosilver entities which exhibit optical and anti-microbial effects. The syntheses of these new nano-functionalised plastics have been successfully performed 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 other N-containing polymers such as nylon. The electron microscopy has shown that nanogold and nanosilver particles have been formed on the surface and within the bulk of the plastic substrates.

Keywords: gold, silver, nanoparticles, anti-microbial, polymers, polyurethane, nylon.

1 INTRODUCTION

Major developments in the properties of thermoplastic polyurethanes (TPUs) were carried out in the 1950s in the research laboratories of BF Goodrich by Schollenberger et al. [1]. Today TPUs are one of the most versatile plastic materials in the world because of their unique properties such as the high elasticity of rubber combined with toughness and durability of metal, flexibility and resistance to many environmental factors. TPU elastomers can be also moulded into any shape which makes the processing easier. TPU is utilized in many applications such as in footwear production, industrial machinery, coatings and paints, production of elastic fibres, water heaters, insulation for buildings, refrigeration, medical devices etc. [2]

The incorporation of metallic nanoparticles into polymers arouses a great deal of interest amongst researchers because of their unusual physical and chemical properties. This paper presents an innovative proprietary development of new plastic materials functionalised by nanogold and nanosilver entities which exhibit surface plasmon resonance optical effects and anti-microbial properties for applications such as air and water filters, membranes, protective textiles, wound dressings and coatings on medical implants [3], which open up new business opportunities. Nanogold and nanosilver entities have increased chemical activity resulting from their large surface to volume ratios and crystallographic surface structures compared with their bulk forms. They exhibit interesting optical properties due to surface plasmon resonance effects and anti-microbial properties, particularly silver, due to their strong binding to the electron-donating groups in the bacterial cells [4]. There is an increasing demand for new hybrid plastics with modified surface, chemical and anti-microbial properties. Nanogold plastics offer low temperature catalyst applications. The work presented here utilises and builds on the proprietary knowhow of Johnston et al. who have developed new chemistry technology to bind nanogold and nanosilver to natural and synthetic fibres and substrates, and generate new product suites. [5]. The chemical affinity of gold and silver for nitrogen has been used to bind nanogold and nanosilver entities to the nitrogen groups in polyurethane to produce new functionalised plastics that can be moulded and shaped by conventional processes. In a comparable manner, nanogold and nanosilver have been chemically bound to other N-containing polymers such as nylon 66.

2 MATERIALS AND METHODS

2.1 Materials and reagents

All the chemicals were supplied by Sigma Aldrich. Polyurethane beads and nylon 66 beads were provided by Centre for Advanced Composite Materials and the Plastics Centre of Excellence at the University of Auckland, New Zealand.

2.2 Analysis Methods

The extent of uptake or absorption of gold and silver by the plastic substrates was determined by Atomic Absorption using a GBC 9600 Atomic Absorbance Spectrometer. The Transmission Electron Microscopy (TEM) images of the nanocrystals were acquired on JEOL 2011 TEM operating at 200 kV. For TEM analyses, the TPU samples were dissolved in DMF and a drop of the resulting solution was placed 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 investigated by means of a JEOL 6500 F field-emission scanning electron microscope (SEM) and energy dispersive analysis (EDS) operating in a low-vacuum mode at 15 kV and a working distance of 9 mm. The UV–Vis spectra were recorded using a Varian Cary 100 Scanning spectrometer over wavelengths of 200-900 nm.

The antimicrobial activity of nanogold and nanosilver functionalised plastics were tested against ATCC 29213 *Staphylococcus aureus*. Samples of the functionalised beads were placed on a Mueller Hinton agar plate and incubated at 35°C for 18hrs in aerob incubator.

2.3 Synthesis of Nanogold and nanosilver plastics

The uptake of dissolved gold and silver by TPU and nylon was studied by soaking samples of the plastics in different concentrations of gold or silver solutions for different times and temperatures, and analyzing the resulting solution for residual dissolved gold or silver respectively. This showed that at low concentrations all the gold and much of the silver were absorbed respectively.

The nanosilver-TPU hybrid material was then synthesized by the reduction of the absorbed Ag^+ on and within the TPU under controlled conditions. Here the TPU acted as the substrate and simultaneously as the reducing agent due to its amine functionality [5]. A similar procedure was used for synthesis of gold nanoparticles by reduction of an Au^{3+} ($AuCl_4^-$) containing solution in the presence of TPU. By varying the metal ion concentration, temperature and time, the nanoparticle size can be controlled and therefore the color can be tuned. The formation of nanogold on and within the plastics is evident by the appearance of a pink-purple colour resulting from the surface plasmon resonance scattering of light by gold nanoparticles about 20 nm in size. The shade and intensity of the colour increase with increasing nanogold content (Figure 1). For nanosilver, the surface plasmon resonance colour is yellow which similarly increases in shade and depth with increasing nanosilver content (Figure 2). An example of polyurethane containing paint shows that with increasing reaction time the colour develops from light pink to purple (Figure 3).

Figure 1: Polyurethane with increasing nanogold content.

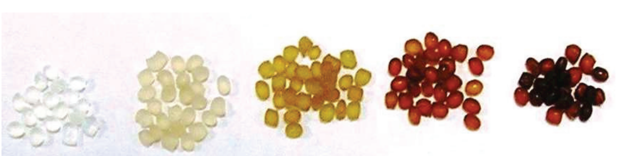

Figure 2: Polyurethane with increasing nanosilver content.

Figure 3: Polyurethane paint with increasing reaction time.

3 RESULTS AND DISCUSSION

The morphologies of the nano-sized silver and gold particles observed by TEM are shown in Fig 4. Higher magnification reveals the characteristic spherical and polyhedral structure of silver nanoparticles in TPU. The diameter of the particles was measured at 6–20 nm (Fig. 4 a). A TEM image of typical gold nanoparticles in TPU is shown in Fig. 4 b. These are about 2-50 nm in size. The SEM and EDS analysis have confirmed the formation of nanogold and nanosilver on the polymer surface and within the bulk of these new hybrid TPU and nylon 66 plastic materials.

The UV-Vis spectrum of the nanosilver TPU sample shows a peak at 420 nm, which clearly indicates the presence of silver nanoparticles (Fig. 5a) [6]. For TPU samples containing gold nanoparticles the UV-Vis spectrum shows a broader peak with the maximum absorption at about 590 nm (Fig. 5b) consistent with the surface plasmon resonance band for gold.

The nanogold and nanosilver hybrid plastics also exhibit effective anti-microbial activity against Gram-positive bacteria *Staphylococcus aureus* (ATCC 29213) as shown by the extensive zone of inhibition (clear area) around a nanosilver TPU bead (Figure 6). Nanogold is similarly effective.

A comparable suite of nanosilver nylon and nanogold nylon materials have been prepared which exhibit the same characteristics and properties as the nanosilver and nanogold TPU hybrid plastic materials.

Examples of the nanosilver and nanogold TPU beads which have been moulded into conventional “dog bone” test strips are shown in Fig. 7. These are very uniform in colour and show that the nanogold and nanosilver entities are distributed evenly through the moulded plastic, confirming that these entities do not affect the thermoplastic forming properties of the polymer substrates.

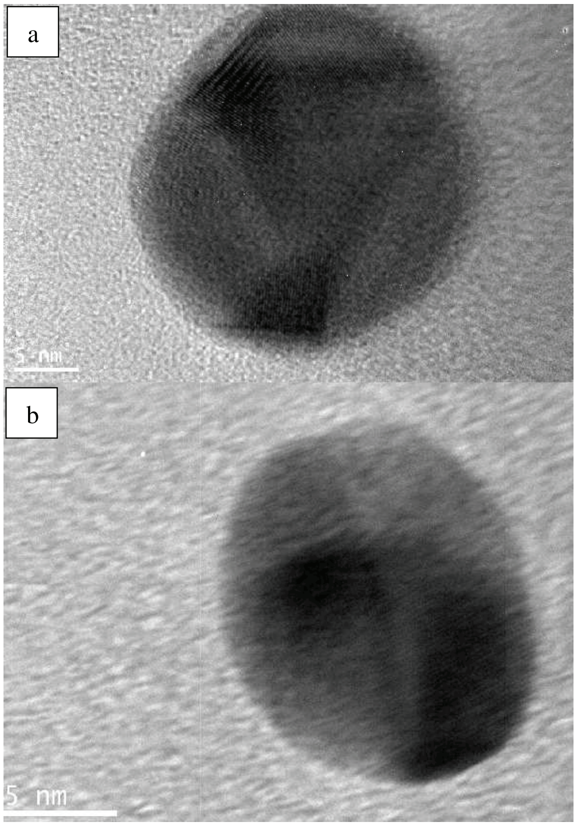

Figure 4: Transmission electron microscope images of a silver nanoparticle (a) and gold nanoparticle (b). Marker bar = 5 nm.

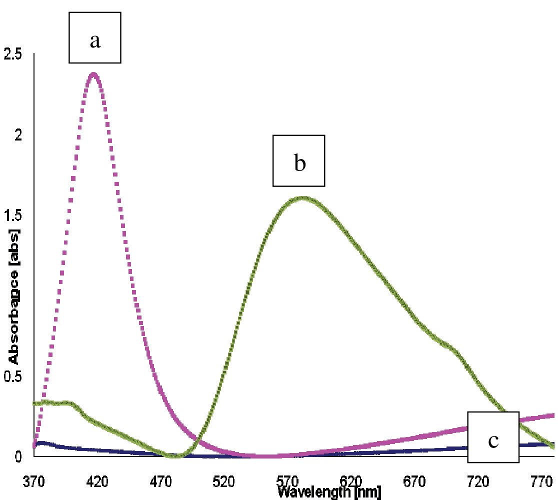

Figure 5: UV-Visible spectra of treated TPU with silver solution (a); treated TPU with gold solution (b); and untreated TPU (c).

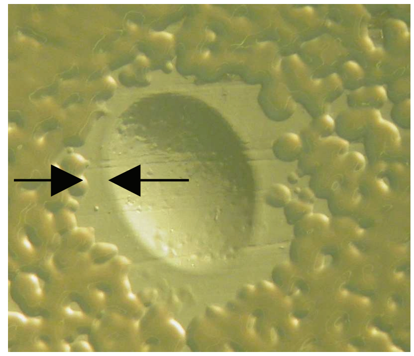

Figure 6: Zone of inhibition for *Staphylococcus Aureus* around a nanosilver TPU bead as shown by the arrows.

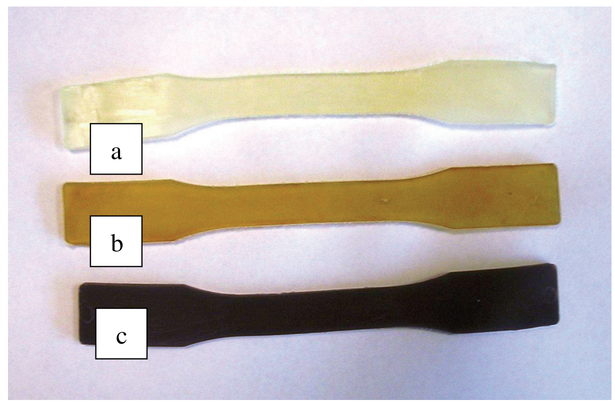

Figure 7: Molded polyurethane "dog bones"; untreated TPU (a); TPU with nanosilver (b); and nanogold (c)

4 CONCLUSIONS

New TPU and nylon hybrid plastic materials functionalised by nanogold and nanosilver entities have been successfully prepared and characterised. These can be moulded into different shapes. by conventional thermoplastic processes. They exhibit different colours due to the surface plasmon resonance effects of the nanogold and nanosilver and have highly effective anti-microbial properties, particularly the nanosilver plastics. As such these nanosilver plastics have considerable potential in commercial applications.

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