Microstructural characterisation of silver/polymer nanocomposites prepared using supercritical carbon dioxide

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Abstract. A feasibility study into the use of supercritical carbon dioxide for the preparation of silver nanoparticles embedded within Teflon® AF and poly(methyl methacrylate) polymer hosts is presented, being of interest for their optical properties. TEM investigation of the dispersion and size distribution of the nanoparticles as a function of depth demonstrated the relative ease of infusion of species into Teflon® AF as compared with PMMA.

1. Introduction
Metal nanoparticles are gaining increasing interest because of their unique functional properties [1]. The embedding of nanoscopic metal structures into polymeric matrices represents a very simple way to stabilise a controlled dispersion of protected nanoparticles whilst taking advantage of their physical characteristics [2]. Silver nanoparticles have attracted particular interest due to their favourable optical properties, displaying surface plasmon resonance[3], non-linear optical limitation [4], and the ability to modify the refractive index of host materials [5]. Here, the use of supercritical carbon dioxide [6, 7] (scCO2) to produce silver nanoparticles in Teflon® AF and poly(methyl methacrylate) (PMMA) optically transparent polymer matrices is described. This method allows fine scale dispersions of particles to be produced in situ within a prefabricated polymer component, without leaving by-products or residue. Structural characterisation of these nanocomposites has been performed using conventional transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis. The statistical distributions of the nanoparticle dispersions as a function of depth allowed the diffusion of silver within such polymer matrices to be profiled. The use of scCO2, as well as being a green alternative to conventional solvent based techniques, represents an interesting new approach to the fabrication of these materials.

2. Experimental
The reaction process used to prepare the nanoparticulate composites comprised impregnation, decomposition and purge steps (Fig. 1a). During impregnation, the polymer host and the
precursor complex (Fig. 1b) were placed in an autoclave which was then filled with CO₂. The combined temperature and pressure were increased above the CO₂ critical point, inducing a supercritical fluid state. The scCO₂ was then able to act as a solvent for the precursor complex whilst infusing into the polymer taking the precursor with it. The scCO₂ was then vented, leaving the precursor dispersed within the polymer. During decomposition, hydrogen was used to reduce the precursor complex, resulting in the formation of a dispersion of silver nanoparticles and dissociated ligands. Finally, during purging, scCO₂ was allowed to slowly flow through the autoclave, extracting the dissociated ligands whilst leaving the silver nanoparticles distributed within the polymer host. Detailed conditions for sample processing are summarised in Table 1.

Samples were sectioned to a thickness of ~200nm for TEM observation using a Reichet Ultra microtome and supported on holey carbon films on a copper grid. Conventional bright field
images were acquired using a Jeol 2000FX operating at 200 kV under low dose conditions to minimize sample degradation under the imaging electron beam.

Figure 3 (a,b) Bright field TEM images showing the silver nanoparticle dispersions within PMMA, recorded at the surface and at a depth of ~30 µm respectively; and (c,d) associated particle distributions. The arrows denote the boundary of furthest silver impregnation. (e,f) EDX spectra acquired from either side of the boundary denoted in (b) confirm the presence and absence of silver.

3. Results and Discussion
Figures 2a and 2b illustrate the dispersion and size distribution of silver nanoparticles within Teflon® AF. In this instance nanoparticles were found to be present throughout the entire host, with sizes in the range appropriate for plasmonic applications. Processing of digitised images was performed using ImageJ software allowing a statistical size distribution to be calculated, giving a mean particle size of ~7.5nm, in this instance (Fig. 2b).

Comparison was made with the dispersion of silver nanoparticles within PMMA processed under similar conditions. TEM investigation revealed a dispersion of smaller silver nanoparticles than those produced in Teflon® AF being confined within a near surface band of the polymer host to a depth of ~30 µm (Fig. 3). The mean particle size at the original surface of the sample was 3.1 nm (Figs. 3a,c) falling to a mean value of 1.9 nm at a depth of ~30 µm into the
sample, beyond which no more silver was detected, as confirmed by EDX measurements (Figs. 3e,f).
The differences in dispersion, size distribution and impregnation depth result from the differing
natures of the polymeric hosts and the processing conditions used. The fluorinated structure, as
well as the high gas permeability, of Teflon® AF is a possible cause for the deeper infusion of the
precursor complex during scCO₂ processing. scCO₂ has been shown to have a greater affinity for,
and plasticizing effect upon, fluorinated polymers [8], thereby increasing the ease of infusion of
the dissolved species. As the precursor complex itself is also fluorinated, improved partitioning of
the precursor into the polymer host is envisioned for Teflon® AF as compared with PMMA. The
larger mean nanoparticle size within Teflon® AF is attributed to a greater mobility of species
within the polymer during decomposition combined with a higher concentration of precursor
within the polymer prior to decomposition.

4. Conclusions
The technique of scCO₂ processing can be adapted for the production of nanocomposites of
interest for their optical properties. The size distribution and dispersion of silver nanoparticles is
found to be dependent on the nature of the polymer host and processing conditions used. TEM
may be used to provide information on the size distribution and dispersion of the nanoparticles as
a function of depth within the polymer host, providing information for the refinement of the
conditions used for the controlled production of these nanocomposite structures.

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References
[1] Heilmann A 2003 Polymer Films with Embedded Metal Nanoparticles 1 Berlin
Heidelberg New York (Springer)
[2] Carotenuto G and Nicolais L 2004 Compos. Part B-Eng. 35 385
[3] Kelly KL, Coronado E, Zhao LL and Schatz GC 2003 J. Phys. Chem. B 107 668
[4] Sun YP, Riggs JE, Rollins HW and Guduru R 1999 J. Phys. Chem. B 103 77
[5] Zimmermann L, Weibel M, Caseri W and Suter UW 1993 J. Mater. Res. 8 1742
[6] Woods HM, Silva M, Nouvel C, Shakesheff KM and Howdle SM 2004 J. Mater.
Chem. 14 1663
[7] Furno F, Morley KS, Wong B, Sharp BL, Arnold PL, Howdle SM, Bayston R,
Brown PD, Winship PD, and Reid HJ 2004 J. Antimicrob. Chemoth. 54 1019
[8] Tomasko DL, Li HB, Liu DH, Han XM, Wingert MJ, Lee LJ and Koelling KW
2003 42 6431