Acta Biomaterialia 8 (2012) 1201-1212

Contents lists available at SciVerse ScienceDirect

# Acta Biomaterialia



journal homepage: www.elsevier.com/locate/actabiomat

# Fatigue and biocompatibility properties of a poly(methyl methacrylate) bone cement with multi-walled carbon nanotubes

Ross Ormsby<sup>a</sup>, Tony McNally<sup>a</sup>, Peter O'Hare<sup>b</sup>, George Burke<sup>b</sup>, Christina Mitchell<sup>c</sup>, Nicholas Dunne<sup>a,\*</sup>

<sup>a</sup> School of Mechanical and Aerospace Engineering, Queen's University of Belfast, Ashby Building, Stranmillis Road, Belfast BT9 5AH, UK
<sup>b</sup> School of Engineering, University of Ulster, Jordanstown Campus, Shore Road, Newtownabbey BT37 0QB, UK
<sup>c</sup> School of Medicine, Dentistry and Biomedical Science, Queen's University of Belfast, Grosvenor Road, Belfast BT12 6BP, UK

#### ARTICLE INFO

Article history: Received 27 July 2011 Received in revised form 5 October 2011 Accepted 6 October 2011 Available online 13 October 2011

Keywords: PMMA bone cement Multi-walled carbon nanotubes Chemical functionality Fatigue properties Biocompatibility

### ABSTRACT

Composites of multi-walled carbon nanotubes (MWCNT) of varied functionality (unfunctionalised and carboxyl and amine functionalised) with polymethyl methacrylate (PMMA) were prepared for use as a bone cement. The MWCNT loadings ranged from 0.1 to 1.0 wt.%. The fatigue properties of these MWCNT-PMMA bone cements were characterised at MWCNT loading levels of 0.1 and 0.25 wt.% with the type and wt.% loading of MWCNT used having a strong influence on the number of cycles to failure. The morphology and degree of dispersion of the MWCNT in the PMMA matrix at different length scales were examined using field emission scanning electron microscopy. Improvements in the fatigue properties were attributed to the MWCNT arresting/retarding crack propagation through the cement through a bridging effect and hindering crack propagation. MWCNT agglomerates were evident within the cement microstructure and the degree of agglomeration was dependent on the level of loading and functionality of the MWCNT. The biocompatibility of the MWCNT-PMMA cements at MWCNT loading levels upto 1.0 wt.% was determined by means of established biological cell culture assays using MG-63 cells. Cell attachment after 4 h was determined using the crystal violet staining assay. Cell viability was determined over 7 days in vitro using the standard colorimetric MTT assay. Confocal scanning laser microscopy and SEM analysis was also used to assess cell morphology on the various substrates.

© 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Poly(methyl methacrylate) (PMMA) bone cement has been primarily used as a grouting agent in total joint replacement (TJR) surgery for more than 50 years. The PMMA bone cement fills the free space between the implant and the bone and constitutes a crucial interface, therefore, successful transfer of the forces generated at the bone–implant and implant–bone interfaces during everyday activities is an important determinant of the long-term survival of a cemented TJR [1].

Bone cement is subjected to a repetitive loading pattern in vivo [2]. It has long been recognised that PMMA bone cement is susceptible to fracture as a result of tensile stresses and fatigue damage accumulation. Topoleski et al. [3] compared the fracture surfaces of retrieved cement mantles with in vitro fatigued specimens. Both sets of surfaces demonstrated similar fracture characteristics, thereby supporting the hypothesis that the PMMA bone cement mantle fails from fatigue in vivo. An investigation of cement mantles retrieved post-mortem showed that fatigue cracking is present even in hip replacements that are relatively "pain free" [4], and it

was suggested that fatigue failure would have occurred eventually had the patients survived. Culleton et al. [5] examined the fracture surfaces of a retrieved cement mantle and found striations indicating fatigue crack growth.

Many research groups have investigated mechanisms to improve the fatigue performance of bone cement. These methods have included the effect of vacuum mixing [6] and incorporating additives such as carbon [7–11], polyethylene [12,13], titanium [14,15], hydroxyapatite [16], glass beads [17], glass flakes [18], glass fibres [13], and steel [19]. A recent study by Marrs et al. [20] has shown that the addition of multi-walled carbon nanotubes (MWCNT) to PMMA bone cement may significantly improve the static and fatigue properties, with an optimal loading of 2 wt.% MWCNT. Marrs et al. achieved a high level of homogeneous dispersion by high speed shear mixing and vacuum hot pressing. However, these methods are of limited use in clinical applications. It has since been demonstrated that inclusion of MWCNT in PMMA bone cement using a clinically acceptable mixing technique can significantly augment the static mechanical properties [21]. It was noted that ultrasonically dispersing low loadings (≤0.25 wt.%) of MWCNT in the liquid monomer phase prior to cement mixing provided the optimum static mechanical properties [21]. Ormsby et al. [22] have also demonstrated that the incorporation of MWCNT into PMMA bone cement



<sup>\*</sup> Corresponding author. Tel.: +44 2890 974122; fax: +44 2890 661729. *E-mail address:* n.dunne@qub.ac.uk (N. Dunne).