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Research Paper

Multiscale characterization of acrylic bone cement modified with functionalized mesoporous silica nanoparticles

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ABSTRACT

Acrylic bone cement is widely used to anchor orthopedic implants to bone and mechanical failure of the cement mantle surrounding an implant can contribute to aseptic loosening. In an effort to enhance the mechanical properties of bone cement, a variety of nanoparticles and fibers can be incorporated into the cement matrix. Mesoporous silica nanoparticles (MSNs) are a class of particles that display high potential for use as reinforcement within bone cement. Therefore, the purpose of this study was to quantify the impact of modifying an acrylic cement with various low-loadings of mesoporous silica. Three types of MSNs (one plain variety and two modified with functional groups) at two loading ratios (0.1 and 0.2 wt/wt) were incorporated into a commercially available bone cement. The mechanical properties were characterized using four-point bending, microindentation and nanoindentation (static, stress relaxation, and creep) while material properties were assessed through dynamic mechanical analysis, differential scanning calorimetry, thermogravimetric analysis, FTIR spectroscopy, and scanning electron microscopy. Four-point flexural testing and nanoindentation revealed minimal impact on the properties of the cements, except for several changes in the nano-level static mechanical properties. Conversely, microindentation testing demonstrated that the addition of MSNs significantly increased the microhardness. The stress relaxation and creep properties of the cements measured with nanoindentation displayed no effect resulting from the addition of MSNs. The measured material properties were consistent among all cements. Analysis of scanning electron micrographs images revealed that surface functionalization enhanced

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particle dispersion within the cement matrix and resulted in fewer particle agglomerates. These results suggest that the loading ratios of mesoporous silica used in this study were not an effective reinforcement material. Future work should be conducted to determine the impact of higher MSN loading ratios and alternative functional groups.

1. Introduction

Proper implant fixation is vital to ensure the long-term success of an orthopedic implant. Two primary methods are used to achieve fixation: press-fit/biological fixation where bone growth onto the implant's surface provides anchorage or with acrylic bone cement that acts as a grouting material between the implant and bone (Jayasuriya et al., 2013; Khanuja et al., 2011). With respect to data obtained from long-term joint registry databases, the use of bone cement is considered the 'gold standard' of implant fixation (Hailer et al., 2010). Despite this, aseptic loosening remains the primary cause of revision arthroplasty regardless of the chosen fixation technique (Adelani et al., 2013; Sonntag et al., 2012). One of the leading factors contributing to the development of aseptic loosening is mechanical failure of the cement mantle (Jeffers et al., 2007), which can occur at one or more of the three 'weak zones': the cement-implant interface, within the cement mantle itself or the cement-bone interface (Lewis, 2003).

In an effort to enhance the static and dynamic mechanical properties of bone cement, reinforcement materials can be incorporated within the powder or monomer component prior to mixing. A wide variety of materials have been investigated such as carbon nanotubes (Marrs et al., 2006; Ormsby et al., 2010b, 2012), titanium oxide fibers (Khaled et al., 2011), zirconia fibers (Kane et al., 2010), and polyethylene terephthalate fibers (Kumar and Cooke, 2006), along with others. Issues regarding interfacial adhesion, high stiffness and poor handling characteristics have generally prevented these composite cements from transitioning from the bench top to clinical practice, despite several encouraging in vitro results (Lennon, 2008).

Mesoporous silica nanoparticles (MSNs) show high potential for use as a polymer reinforcement due to their small particle size, large surface area, high pore volume and homogeneous structure (Izquierdo-Barba et al., 2008; Zhang et al., 2010). The high surface area of MSNs indicates that small loading ratios can be used to provide significant mechanical reinforcement, similar to that observed with carbon nanotubes (Ormsby et al., 2010a). Additionally, the spherical nature of MSNs offers an advantage over other reinforcement materials such as carbon nanotubes, which are often difficult to disperse due to strong Van der Waals forces and physical entanglements (Pegel et al., 2008), which can severely limit their usefulness (Ania et al., 2006). Silica/polymer nanocomposites have been shown to possess superior mechanical properties relative to neat polymers (Ji et al., 2003; Lach et al., 2006), however, the weight percentage ratios typically employed are high (10–20% wt/wt). While this is acceptable for industrial applications that can utilize specialized homogenization and mixing techniques, high particle-loading ratios are difficult to disperse within bone cement since the cement must be prepared immediately at the time of surgery. It is important therefore that the addition of particles does not alter the mixing and handling characteristics of cement, otherwise the clinical usefulness may be compromised.

A wide variety of testing methods spanning multiple length scales can be used to characterize particle-reinforced polymers. Indentation techniques, such as micro and nanoindentation, can provide details on reinforcement mechanisms since they operate at small force/displacement scales allowing for individual components to be analyzed which may thus otherwise be difficult to quantity with traditional bulk testing methods (Beake et al., 2002; Dhakal et al., 2006). With respect to acrylic cements, microindentation has been used to examine the change in mechanical properties resulting from the addition of antibiotics (Musib et al., 2012), particulate-fillers (Chung et al., 2005), and silica-fused whiskers (Xu et al., 2002) and changes induced following implantation in patients (Chaplin et al., 2006). Similarly, nanoindentation has been used to characterize the fracture properties (Ayatollahi and Karimzadeh, 2012), elastic modulus, and hardness (Karimzadeh and Ayatollahi, 2012) of acrylic bone cement. Additionally, Arun et al. used nanoindentation to evaluate the mechanical properties of bone cement modified with functionalized single-walled carbon nanotubes and determined the optimal loading ratio for peak modulus and hardness to be 0.15% wt/wt (Arun et al., 2014).

Previously, we reported on the static and fatigue properties of acrylic bone cement modified with various loadings of MSNs (0.5, 2 and 5% wt/wt) and found a general decrease in several mechanical properties with increasing MSN content (Slane et al., 2014). These results were attributed to inadequate dispersion and poor interfacial adhesion between the particle and polymer matrix, compounded by the relatively high loading ratios used. A potential method to overcome these shortcomings is to use surface modified nanoparticles, where various functional groups are linked to the particle surface. Surface functionalization can act to stabilize nanoparticles while enhancing their dispersion and compatibility with the polymer matrix (Guo et al., 2006; Kordás et al., 2013). Therefore, the aim of the current study was to investigate the influence of low-loadings of surface-modified mesoporous silica on the mechanical and material properties of acrylic bone cement. A commercially available acrylic bone cement was modified with several different loading ratios of unmodified MSNs (as a control) and two types of surface functionalized MSNs. A multiscale approach was used to characterize the cement's mechanical properties and the macro,