A USAXS and Tensile Properties Study of Polymethyl Methacrylate Orthopedic Cement Containing Radiopacifier Particles

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Introduction

Polymethyl methacrylate (PMMA) based bone cements are commonly used for fixation of the metallic stems of total joint replacement prostheses to the peri-prosthetic bone tissue. They contain approximately 10 wt % of 1 μm size $BaSO_4$ or ZrO_2 particles, which are radiopaque, enabling orthopedic surgeons to monitor fatigue fracture in the implanted cement using x-ray radiographs. During *in vivo* use, bone cements are subjected to cyclic loading, which can cause fatigue fracture and implant loosening, thereby requiring revision surgery to replace the implant. It is well known that agglomerated radiopacifier particles can contribute to early fatigue fracture since they act as sites of high stress concentration [1, 2]. In this study, we tested the mechanical properties of a new cement that contains pre-polymerized beads of MMA-styrene co-polymer and nanometer-sized $BaSO_4$. The morphology of each cement was characterized using ultra-small-angle x-ray scattering (USAXS). The cements were subjected to tensile tests to measure tensile properties and to determine potential for improved fatigue properties.

Methods and Materials

A commercial orthopedic bone cement (Endurance™, Depuy Orthopedics Inc., A Johnson & Johnson Co.) was obtained from the manufacturer in the form of a two-component monomer and powder system. These components were mixed in a commercial vacuum mixing device (Cemvac™, Depuy Orthopedics Inc., A Johnson & Johnson Co.). For this study, three cement groups were studied: unfilled Endurance cement (no $BaSO_4$), Endurance with 10 wt % 1000 nm $BaSO_4$ particles, and Endurance with 10 wt % 100 nm $BaSO_4$ (Sachtleben, Duisberg, Germany). The cements were molded into ASTM D638-97 standard Type V tensile specimens. Tensile tests were performed using an Instron 4201 tensile tester at a crosshead-speed of 1 mm/s. The work-of-fracture (WOF) was calculated from the area under the stress-strain curves. The USAXS was performed at the UNI-CAT beamline of the Advanced Photon Source, Argonne National Laboratory, using a Bonse-Hart ultra-small-angle scattering instrument. The 10 keV x-ray beam with a rectangular cross section of 2.0 mm × 0.6 mm was scanned over an angular scattering range "q" of 0.001 nm^{-1} - 1.0 nm^{-1} where $q = (4\pi/\lambda)\sin\theta$ such that θ equaled one half of the scattering angle, and λ was the wavelength of x-rays. The thickness of all specimens was 0.5 mm. $BaSO_4$ or pore particle size distributions were determined from the scattering curves using a regularization method similar to the maximum entropy method for converting USAXS scattering curves [3].

Results

Tensile tests revealed that the WOF of unfilled cement was the highest of the three groups tested (Fig. 1). There was a 47% decrease in WOF upon addition of 1000 nm $BaSO_4$ particles. The WOF of the cement containing 100 nm $BaSO_4$ particles had a 45% higher WOF than the cement containing the 1000 nm $BaSO_4$. Statistical analyses using Fishers protected least significant difference (PLSD) showed that these results were statistically significant ($p<0.05$, ANOVA).

The USAXS revealed pores at both the micrometer and nanometer length scales, and showed a broad distribution of pore sizes with a peak at 600 nm. A broader particle size distribution was observed for the 1000 nm size (specified by manufacturer) $BaSO_4$ particles. The 100 nm size $BaSO_4$ particle size distribution had peaks at 35 nm and 160 nm.

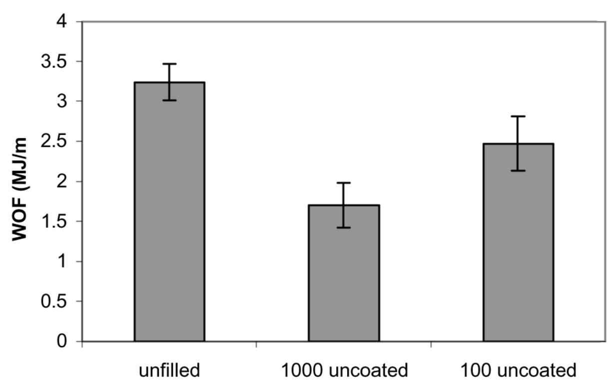

FIG. 1. Plot of work of fracture of unfilled cement, cement containing 1000 nm $BaSO_4$ particles and cement containing 100 nm $BaSO_4$ particles.

Discussion

The results showing improved tensile WOF of the nanoparticle containing cements compared to cements containing microparticles were consistent with our previous work [4] on a different cement, CMW1 (Depuy Orthopedics Inc., A Johnson & Johnson Co.), which showed a 70% increase in the tensile WOF. A higher WOF of the 100 nm $BaSO_4$ containing cement compared to the 1000 nm $BaSO_4$ containing cement is generally desirable since it implies that a larger amount of energy must be expended for the material to fracture.

The USAXS was particularly useful in measurement of the size distributions of $BaSO_4$ particles or particle aggregates in the filled cements, as well as the size distributions of pores in the unfilled cement (Fig. 2). It is well known that there is porosity present in cement due to air entrapment in the powder component of cements and also due to incomplete fusion of the polymerizing monomer and the pre-polymerized beads [2]. This has previously been revealed using scanning electron microscopic examination, which is limited to micrometer size pores. In contrast, USAXS was able to measure pore sizes down to the nanometer length scale. It is well known that porosity can decrease the fatigue life of bone cement leading to early failure of joint replacement prostheses. In the future, new processing techniques associated with reduced porosity in bone cements can be developed using studies that combine processing, USAXS and fatigue tests.

The USAXS also showed that the commercial barium sulfate particles used in this study had a wide distribution of particle sizes. This must have an effect on the WOF of the cement, since this study showed that smaller particles of barium sulfate lead to higher WOF of cements. Future studies to develop quantitative structure-property relationships between particle size and macroscopic mechanical properties such as WOF would require the use of monodisperse barium sulfate particle sizes along with mechanical testing and characterization using a technique such as USAXS.

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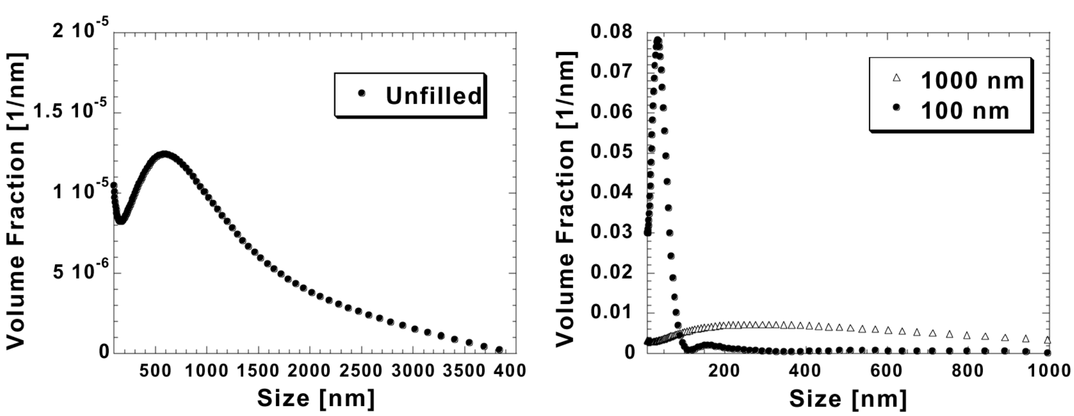

FIG. 2. The USAXS size distribution of pores in unfilled cement (left) and size distribution of $BaSO_4$ particles in cement containing 1000 nm and 100 nm $BaSO_4$ particles (right).