A USAXS study of filler dispersion in orthopaedic cement

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Introduction

Polymethylmethacrylate (PMMA) bone cement is widely used for fixation of orthopaedic implants. These cements contain micrometer-size filler particles of either barium sulfate or ceramic particles such as zirconium oxide. The purpose of adding fillers is to radiopacify the cement, thereby enabling the orthopedic surgeon to monitor the cement using x-ray radiographs. A problem associated with the use of 1–10 μm diameter radiopacifier particles is that incomplete dispersion of the particles during mixing of the monomer and powder components results in the formation of particle agglomerates of 50–200 μm diameter. These large defects are sites of high stress concentration that reduce the fracture toughness of PMMA cements, leading to early fracture of the cement [1, 2, 3] and loosening of the implant, ultimately necessitating early revision surgery to replace the implant.

In this study, the micrometer-size radiopacifier particles in PMMA bone cements were replaced by commercially available nanophase aluminum oxide particles. The nanocomposite PMMA bone cements were characterized using ultrasmall-angle x-ray scattering (USAXS) at the UNI-CAT beamline of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). Low-voltage scanning electron microscopy (LVSEM) was performed on the fracture surfaces of tensile specimens and on both micro- and nanosized filler particles. The nanocomposite and control PMMA bone cements were also subjected to ASTM standard tensile tests to determine their mechanical properties.

Methods and Materials

Commercially available PMMA bone cement used in orthopaedic surgery is usually provided as a two-component system: first, a powder component consisting of prepolymerized PMMA, radiopacifying particles (barium sulfate or zirconium oxide at 10 weight %), and benzoyl peroxide (or BPO at 2 weight %) as initiator; and a second liquid component of methylmethacrylate (MMA) monomer, hydroquinone (25 ppm) as a stabilizer, and N,N-dimethyl-p-toluidine (DMPT at 2 weight %) as a promoter. Both components are mixed under a vacuum to reduce the formation of voids and bubbles during setting. Average setting time of such cements is 10–15 minutes. In this study, Osteobond™ (Zimmer Inc., Warsaw, IN) bone cement containing $BaSO_4$ radiopacifying particles of 1–3 μm diameter was purchased as a control. A separate PMMA powder component without radiopacifiers (Zimmer Inc., Warsaw, IN) was used for the nanocomposites. Acrylic-coated aluminum oxide particles dispersed in ethanol with an average diameter of 60 nm were purchased (Nanophase Technologies Inc., Burr Ridge, IL). The particles were dried, redispersed in MMA, and mixed with PMMA for a final volume fraction of filler particles identical to that of radiopaque cements.

Specimens for USAXS were molded into sheets of 0.5 mm thickness, while tensile testing utilized Type V dumbbell shaped samples as specified in ASTM D638-97 [4].

A JEOL 6320FV low-voltage scanning electron microscope (LVHRSEM) operating at 1 kV with a working distance of 3 mm was used to examine each type of radiopacifier particle and freeze-fractured samples of the cured cements. The samples were also subjected to USAXS at the UNI-CAT beamline of the APS, ANL. The Bonse-Hart [5] type of camera is capable of measurement of structures over a large size range of a few micrometers to one nanometer.

An Instron 4201 tensile tester was used to perform ASTM D638-97 standard tensile tests on all cement samples to determine their ultimate stress, ultimate strain, and work-of-fracture (WOF) (defined by the area under the stress-strain curve). Testing was performed at a crosshead speed of 1 mm/s using a 5 kN load cell. A minimum of four specimens were tested for each cement composition as required by ASTM standards.

Results

Investigation of freeze-fractured samples containing micro-sized fillers revealed agglomerates of 30–70 μm (Figure 1), while nanocomposite-containing samples showed no comparable defects (Figure 2).

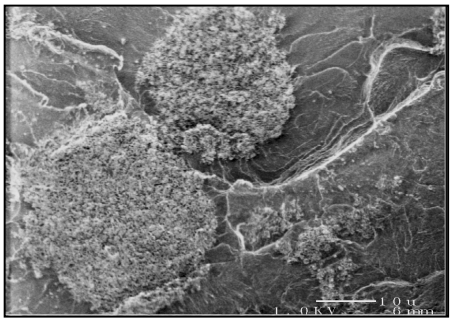

Figure 1: Freeze-fracture cross section of $BaSO_4$-containing PMMA bone cement. (scale bar = 10 micrometer)

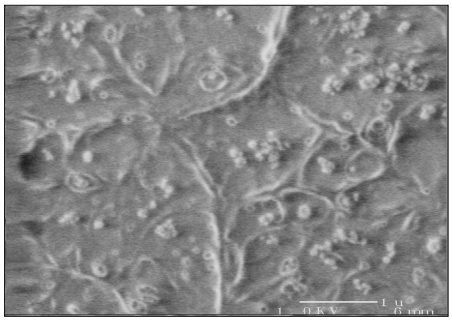

Figure 2: Freeze-fracture cross section of nanoparticle-containing PMMA bone cement (scale bar = 1 micrometer).

USAXS experiments performed on cements filled with barium sulfate showed substantially higher scattering intensity at ultralow angles compared to that of the alumina filled cements (Figure 3). The interagglomerate distance was calculated using Bragg's law (Equations 1 and 2):

$$q = (4\pi/\lambda)\sin\theta \quad (1)$$

$$d = 2\pi/q \quad (2)$$

where θ = one half the scattering angle, λ = wavelength of x-rays, and d = interagglomerate distance. Porod's law was used to compare the specific surface areas as a function of volume fraction of filler (Equation 3):

$$q^3 I = 2\pi\Delta\rho^2(S/V) \quad (3)$$

where I = smeared intensity, (S/V) = specific surface area, and $\Delta\rho$ = electron density difference between PMMA and the particle. The interagglomerate distance was larger than 5 μm for barium sulfate agglomerates while the inter-agglomerate distance was approximately 0.2–0.1 μm for alumina agglomerates (Figure 3).

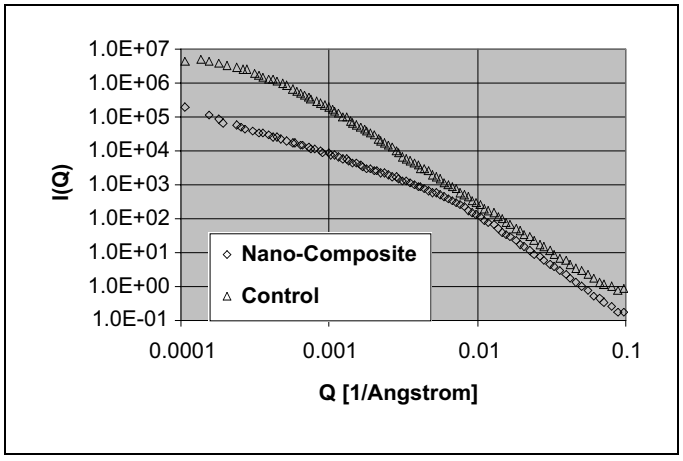

Figure 3: Plot of scattering intensity versus "q" for cements.

The Porod plot shows that upon doubling the volume fraction of alumina particles in the cement, the specific surface area is also nearly doubled (Figure 4). This indicated that the larger amount of alumina particles did not increase agglomeration.

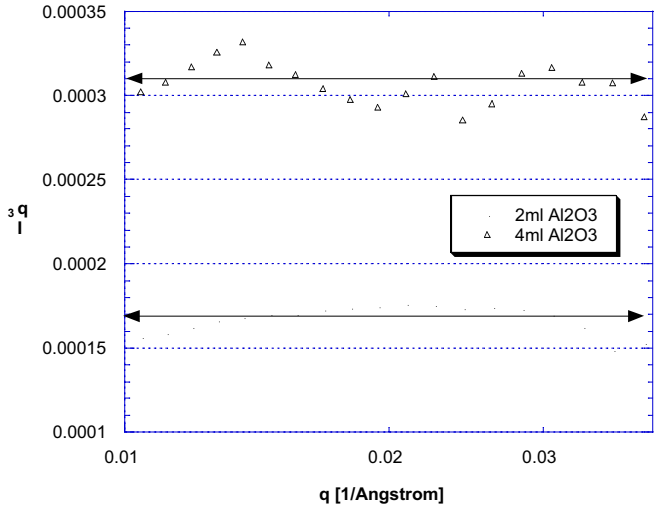

Figure 4: Porod plot of Iq versus q for cements to which 2 ml and 4 ml of alumina particle suspension were added.

Statistical analysis revealed significant increases in WOF, elongation-to-break (ETB), and ultimate-tensile-stress (UTS) ($p < 0.05$ each) when nanocomposite samples were compared to the control (Figure 5). The reduction of particle size increased the mean of WOF by 74%, ETB by 35%, and UTS by 25%.

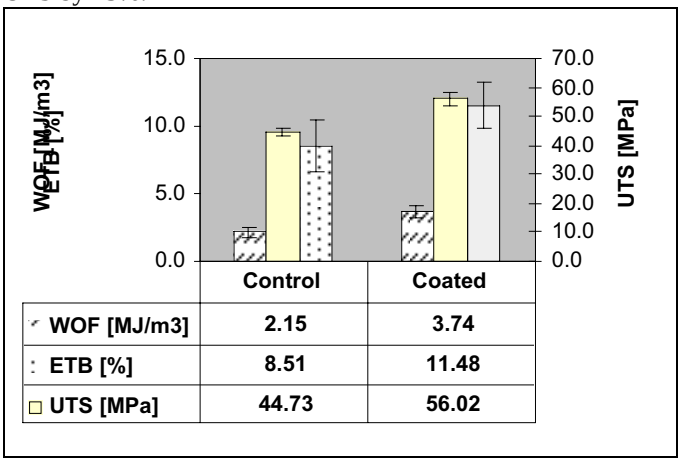

Figure 5: Results of tensile testing of control vs. nanophase cement.

Discussion

USAXS and LVSEM showed that there was negligible agglomeration of particles in cements when they were precoated. USAXS was especially useful in providing

quantitative morphological characterization over a large range of length scales, from approximately 4 μm down to 2 nm. Since the source of scattering was agglomerated particles against the PMMA matrix, higher scattering intensity at ultralow angles indicated that the inter-agglomerate distance was larger for barium sulfate cements. A larger interagglomerate distance implies a larger agglomerate size since both control and alumina-containing cements contained the same volume fraction of fillers. When the volume of alumina was doubled, the total specific surface area nearly doubled, indicating that precoating of the filler prevents the formation of large agglomerates. Mechanical tests revealed that tensile properties increased for precoated-alumina-containing cements.

These results are in agreement with a previous study [4], suggesting that uniform dispersion of micrometer-size radiopacifier particles in current acrylic bone cements can improve the mechanical performance of PMMA cements.

Acknowledgments

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