

A USAXS Study of Dispersion of Barium Sulfate Particles in Polymethylmethacrylate Bone Cement

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Introduction

Polymethylmethacrylate (PMMA) bone cement is widely used for fixation of total joint replacement prostheses. The cement is prepared by mixing PMMA liquid monomer into a powder component. Several factors are important for clinical application, such as setting times of the cement, volumetric shrinkage, and fatigue life. Among these factors, the fatigue life of cement has received the most attention, since cement fracture in patients can lead to implant loosening, resulting in early revision surgery. Fractographic studies have shown that cracks, which can ultimately lead to cement fracture, are associated with defects such as voids and large agglomerates of radiopacifier particles [1-4] within the cement. Most cements contain approximately 10 wt% radiopacifier particles, usually barium sulfate or zirconium oxide, so that orthopaedic surgeons can monitor fracture in implanted cements by using x-ray radiographs. Improved dispersion of these hard radiopacifier particles would prevent the formation of agglomerates and thereby improve the fracture toughness of bone cement. In this study, ultrasmall-angle x-ray scattering (USAXS) was used to characterize the surface-area-to-volume ratio (specific surface area) of dispersed radiopacifier particles as well as voids within the PMMA matrix. A reduction in the specific surface area of radiopacifiers detected by USAXS would imply particle agglomeration. Thus USAXS can be used for quantitative comparison of well-dispersed and poorly dispersed filler particles in the polymer matrix. USAXS is advantageous in comparison to imaging methods in that the experiment estimates the average specific surface area over a relatively large sampling volume of approximately 1 mm³.

Commercial cements are "microcomposites" typically composed of 10 wt% of approximately 1- to 3- μ m barium sulfate or zirconium oxide radiopacifier particles dispersed within the PMMA matrix. In this study, micrometer-size barium sulfate particles were replaced with 100-nm barium sulfate particles in a commercial cement. Previous studies have demonstrated that the nano-size fillers provide a higher resistance to crack propagation in bone cement [5]. USAXS was used to quantify the dispersion of radiopacifier particles in the resulting microcomposite and nanocomposite PMMA cements. In addition, low-voltage scanning electron microscopy (LVSEM) was used as a supplementary

technique to compare the dispersion of radiopacifiers within the cements.

Methods and Materials

All tests were performed by using CMW1 bone cement (Johnson & Johnson/Depuy, Warsaw, IN), since the powder component does not contain premixed barium sulfate. The 1- μ m barium sulfate powder included separately in CMW1 packages and the 100-nm (nano-size) powder (Sachtleben, Duisburg, Germany) were mixed into separate batches of CMW1 in the standard quantity of 10 wt%. A standard vacuum hand-mixing method followed by setting for 3 d at 37°C resulted in "microcomposite" cement (conventional CMW1 cement) and "nanocomposite" cement. The nano-size barium sulfate powder contained 2 wt% sodium citrate as a coating to prevent particle agglomeration. Radiolucent CMW1 cement in which no radiopacifiers were added served as a control to study the effect of the presence of barium sulfate, particle size, and dispersion. USAXS was performed on 0.5-mm-thick cement specimens at the UNICAT beamline [6] of the APS at Argonne National Laboratory by using 10-keV x-rays and a beam cross-sectional area of 2 \times 0.6 mm. In addition, a JEOL 6320FV LVSEM operating at 1 kV and a working distance of 4 mm were used to examine the fracture surfaces of both microcomposite and nanocomposite cements.

Results

SEM of freeze fracture surfaces of the CMW1 nanocomposite (Fig. 1 left) and CMW1 microcomposite (Fig. 1 right) showed that in both cases, barium sulfate particles were finely dispersed within the cement, with no large agglomerates present. As expected, particles in the microcomposite were approximately 0.5 to 2 μ m in diameter, whereas the nanocomposite contained particles that were much smaller than 1 μ m. USAXS scattering curves were obtained by plotting the scattered intensity I vs. q , where $q = (4\pi/\lambda)\sin\theta$ such that θ = one-half of the scattering angle and λ = the wavelength of x-rays (2.38 Å). USAXS revealed a substantial scattering intensity due to the presence of both voids (radiolucent cement) and barium sulfate particles (Fig. 2). The region of the scattering curve at $q > 0.008$ (Å⁻¹) was curve-fitted

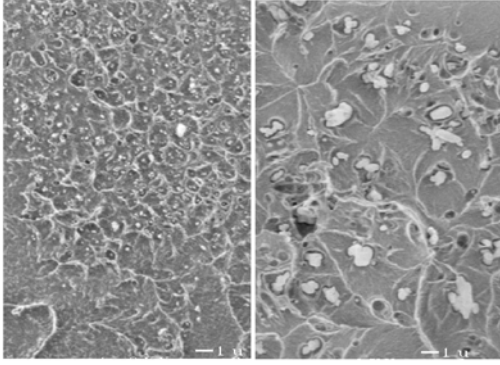


FIG. 1. Low-voltage scanning electron micrographs of nanocomposite (left) and microcomposite (right) fracture surfaces. (Scale bar = 1 μm .)

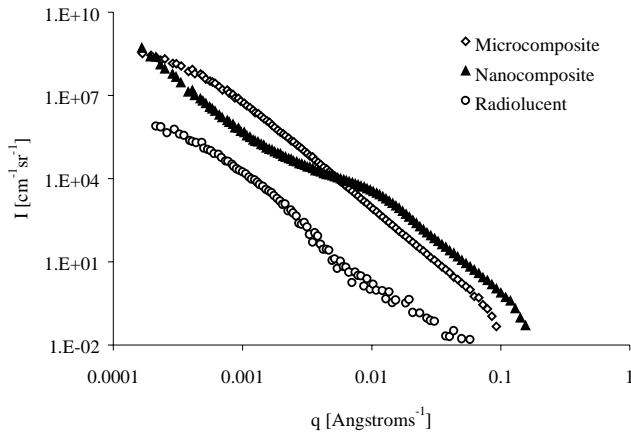


FIG. 2. USAXS scattering curves for microcomposite, nanocomposite, and radiolucent cements.

to a Power law function, which is $I(q) = Kq^{-4}$, where $K = 2\pi\Delta\rho^2S$ such that $\Delta\rho$ = the electron density difference between barium sulfate (or voids, in the case of radiolucent cement) and PMMA and S = the surface area of the scattering entity (radiopacifier or voids). The scattering invariant Q defined by the following equation was calculated for all cement samples by using the area under the scattering curve, $q^2I(q)$, vs. q :

$$Q = \int_0^{\infty} q^2 I(q) dq .$$

The invariant for an angular range of 0 - q_{min} was calculated by fitting the low q region of the scattering curve by using Guinier's law [7] and for $q_{max} - \infty$ by using

Porod's law. The specific surface area can then be defined as $S/V = \pi(K/Q)$. The ratio of the specific surface area (Table 1) for the nanocomposite and microcomposite cements was 9.16.

Table 1. USAXS specific surface areas for all cements.

Sample	Specific surface area (S) (cm^{-1})
Radiolucent	6.16147×10^5
Microcomposite	2.39404×10^5
Nanocomposite	2.19348×10^6

Discussion

This study showed that USAXS is effective in quantitatively measuring the specific surface area of barium sulfate radiopacifiers dispersed within PMMA bone cement. It is expected that for the same volume (or weight) fraction, the nanometer-size particles must have a total specific surface area that is 10 times larger than the micrometer-size particles in bone cement, since there would be 1000 times more particles of one-tenth of the diameter. The value of 9.16 is in excellent agreement with this calculation, considering that the inherent particle size distributions that result from the manufacturing process can alter the ratio of specific surface area. Agglomeration of particles would result in a reduction in specific surface area. USAXS therefore showed that both microcomposite and nanocomposite cement had relatively well-dispersed radiopacifier particles. In addition, USAXS was able to provide the specific surface area of voids. SEM confirmed the quantitative analysis provided by USAXS measurements by revealing fracture surfaces where particles were uniformly dispersed throughout the PMMA matrix. In the future, new bone cement mixing methods could be evaluated by using USAXS in order to reduce the amount of voids and to improve dispersion of radiopacifiers within the PMMA matrix, both of which are factors known to improve the mechanical performance of PMMA bone cements.

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