



Synthesis and characterization of core–shell nanoparticles and their influence on the mechanical behavior of acrylic bone cements

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ABSTRACT

Core–shell nanoparticles consisting of polybutyl acrylate (PBA) rubbery core and a polymethyl methacrylate (PMMA) shell, with different core–shell ratios, were synthesized in order to enhance the fracture toughness of the acrylic bone cements prepared with them. It was observed by TEM and SEM that the core–shell nanoparticles exhibited a spherical morphology with ca. 120 nm in diameter and that both modulus and tensile strength decreased by increasing the PBA content; the desired structuring pattern in the synthesized particles was confirmed by DMA. Also, experimental bone cements were prepared with variable amounts (0, 5, 10 and 20 wt.%) of nanoparticles with a core–shell ratio of 30/70 in order to study the influence of these nanostructured particles on the physicochemical, mechanical and fracture properties of bone cements. It was found that the addition of nanostructured particles to bone cements caused a significant reduction in the peak temperature and setting time while the glass transition temperature (T_g) of cements increased with increasing particles content. On the other hand, modulus and strength of bone cements decreased when particles were incorporated but fracture toughness was increased.

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1. Introduction

Considerable efforts have been directed to improve the fracture toughness of acrylic bone cements, which exhibit generally a brittle behavior, as an inadequate fracture resistance can lead to cement breakup and subsequent implant loosening. A first approach to solve this problem is to incorporate a polymeric rubbery phase into bone cement formulations by using either elastomeric particles or beads of a polymer that has a low glass transition temperature. During the *in vivo* application, this polymeric rubbery phase will render bone cements with lower modulus of elasticity and higher ductility, compared to the current formulations that mainly use PMMA and are brittle [1]. A lower modulus will allow the cement to withstand large strains without fracture and high ductility would ensure that, if stressed locally in excess of the material's elastic limit, the cement layer would serve to distribute the load [1]. This is the rationale behind the development of experimental formulations including rubber-toughened acrylic particles [2–4], ABS particles [5] or beads of poly(butyl acrylate) [1] in the solid part of the formulation. A second approach consists on the modification of the liquid component by incorporating monomers such as *n*-butyl methacrylate [1,6], ethoxy triethylene glycol methacrylate [7], etc. that also conduct to cements with low modulus.

All these toughening techniques often require high concentrations of the modifier (10–60 wt.%) which implies considerable changes in the conventional formulations; also, the reduction in the elastic modulus of bone cements will not fulfill the requirements established in the ISO 5833 standard, in particular with the minimum flexural modulus that must be 1800 MPa.

An alternative approach to solve the problem abovementioned consists of using structured particles such as core–shell or multilayer [8,9] that improves the fracture resistance while leaving the stiffness practically unaffected or minimally affected, i.e., the addition of these nanoparticles can enhance the fracture toughness of cement without sacrifice its modulus. It has been demonstrated that this type of particles produces an enhanced toughness which has been attributed to a mechanism of plastic shear and cavitation rather than crazing [3]. The use of structured particles (particularly core–shell structures) in bone cements formulations has been scarcely reported in the literature being in these cases merely descriptive and not systematized; for example, Hill [4] studied the influence of core–shell microstructure on the fracture toughness of polybutadiene rubber-reinforced PMMA whereas Rusen et al. [10] synthesized core–shell structures with a core made of different barium salts of polymerizable unsaturated organic acid (methacryloyloxyethyl phosphate, 2-acrylamido-2-methylpropane sulfonic acid and methacrylic acid) and a shell that consisted of PMMA. These structured particles, however, were used in bone cement formulations taking advantage of its radioopacity but not due to its ability to increase the fracture toughness. Furthermore, Perek and Pilliar [2] and

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Murakami et al. [3] have reported the use of more complex structured particles (particularly three-stage shell structures) in bone cement formulations, but the study with this type of nanoparticles for us will be addressed in another work.

Taking into account the above considerations, the aim of the present study was to synthesize core-shell nanoparticles in order to enhance the fracture toughness of the acrylic bone cements prepared with them. Nanoparticles consisting of polybutyl acrylate (PBA) rubbery core and a polymethyl methacrylate (PMMA) shell, with different core-shell ratios, were synthesized and the influence of one of them on the physicochemical, mechanical and fracture properties of bone cements was studied.

2. Experimental

2.1. Materials

Butyl acrylate (99%) and methyl methacrylate (99%) used during the synthesis of nanoparticles were passed through a prepacked column for removing their inhibitors. Ethylene glycol dimethacrylate (98%), potassium persulfate (99%) and sodium dodecyl sulfate (99%) were used as received. All reagents were supplied by Aldrich Chemical Co.

2.2. Core-shell particles synthesis

Core-shell particles were prepared by emulsion polymerization in 2-liters four-necked glass reactor equipped with a mechanical stirrer, a reflux condenser and a thermometer. The reactor was immersed in a thermostatic water-bath for controlling the reaction temperature.

Polybutyl acrylate (PBA) seed was synthesized using ethylene glycol dimethacrylate (EGDMA) as crosslinking agent, sodium dodecyl sulfate (SDS) as surfactant and potassium persulfate (PPS) as initiator. First, distilled water (350 ml) and SDS (2 g) were added to the reactor and then purged with nitrogen gas through a gas inlet tube. When reactor temperature was stable at 80 °C, BA (175 g) and EGDMA (1.75 g) were charged to the reactor and after 10 min, aqueous PPS solution (1 wt.%) was added to the system. After 3 h the reaction was completed.

The PBA core was synthesized similarly by emulsion polymerization using the PBA seed. For this, a mixture of water (350 ml), SDS (1.5 g) and PBA seed was stirred and then an aqueous solution of initiator was added to the system. After 10 min, BA monomer was fed very slowly (0.5 ml/min). The reaction system was kept at 80 °C for another 2 h to obtain higher conversions.

Core-shell particles were obtained during a second stage of polymerization which employed the core formed in the previous stage. For this step, the PBA core and an aqueous solution of initiator (1 wt.%) were placed into the reactor and mixed for 10 min; then, methyl methacrylate (MMA) monomer was added dropwise (0.5 ml/min). After 2 h of polymerization at 80 ± 0.5 °C under nitrogen atmosphere, the reaction was completed.

Amounts of PBA seed, PBA and MMA were selected in order to obtain core-shell particles with different core/shell ratios (20/80, 30/70, 40/60 and 50/50).

2.3. Characterization of latex

2.3.1. Monomer conversion

The monomer conversion was calculated gravimetrically. Aliquots (5 ml) from reactor were withdrawn at each polymerization stage. These samples were set into preweighed petri dishes and dried at 60 °C in a preheated oven to constant weight. The fractional weight conversion is defined as the fraction of monomer that has been polymerized.

2.3.2. Average particle size

The average particle size of latexes was measured with a Malvern 4700 Quasielastic Light Scattering (QLS) analyzer at room temperature, using a fixed scattering angle of 90°. In order to minimize particle-particle interactions, latexes were diluted with deionized water up to 100 times before QLS measurements and then filtered through 0.2 mm Millipore filters to remove dust particles.

2.3.3. Electron microscopy

The latex particles were examined in a JEOL 1010 Transmission Electron Microscope (TEM) at an accelerating voltage of 100 kV to determine their shape and microstructure. In order to improve the contrast, samples were treated with a 1% ruthenium tetroxide (RuO₄) solution for 30 min, deposited over copper grids and allowed to dry at room temperature for 24 h before TEM examination.

Morphology of latex particles was also characterized by a JEOL 6360 LV Scanning Electron Microscope (SEM) at 20–25 kV. The original latex samples were diluted with water, deposited on graphite tape and coated with a thin layer of gold using an ion sputtering Delton vacuum (LLC model Desk II).

2.4. Characterization of powdered core-shell particles

2.4.1. FTIR analysis

Powdered core-shell particles obtained after a defrosted process of latexes were analyzed by FTIR. The analysis was performed using a Nicolet Protégé 460 Magna IR spectrometer with the KBr pellet technique. Spectra were recorded in the wavenumber range of 4000–650 cm⁻¹ with a resolution of 4 cm⁻¹ and averaging 100 scans.

2.4.2. Molecular weight

The weight average molecular weight (M_w) of powdered core-shell nanoparticles were determined by GPC using an Agilent HPSEC 1100 chromatographer with a refractive index detector. Measurements were carried out using THF as solvent and 1 ml/min flow rate using a ZORBAX PSM 1000S HPSEC column. The molecular weight was determined from the retention time using a calibration curve derived from monodisperse standard polystyrene (PS) obtained from Polymer Laboratories.

In order to characterize the dynamic mechanical behavior (DMA) and tensile properties of latex particles, films were obtained from them. For this, the precipitated core-shell particles obtained after a defrosted process of latexes were washed with abundant water to remove the excess surfactant, dried in a vacuum oven at 60 °C for 24 h and finally the resultant powder was hot-press laminated using an hydraulic Carver press.

2.4.3. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) of the resulting latex films was carried out using a Perkin-Elmer DMA-7 in tensile mode, from –100 to 150 °C, with an oscillatory frequency of 1 Hz and a heating rate of 3 °C/min. The samples were approximately 15 mm long, 5 mm width and 0.3 mm thick. Alpha transition (T_α), which is associated with glass transition temperature (T_g), for each phase was estimated from the maxima of tan δ versus temperature plot.

2.4.4. Mechanical properties

Tensile mechanical properties of the films were obtained according to the ASTM D-882 using a Minimat microtensometer with a crosshead speed of 2.5 mm/min. Specimens of 25 mm × 5 mm × 1 mm (length × width × thickness) were used and the average value of at least five replicates of each material was reported.

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