J Mater Sci: Mater Med (2006) 17:743–748
DOI 10.1007/s10856-006-9685-9

Improved mechanical properties of acrylic bone cement with short titanium fiber reinforcement

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Received: 14 July 2004 / Accepted: 24 October 2005

Abstract Acrylic bone cements are widely used in total joint arthroplasties to grout the prosthesis to bone. The changes in the tensile properties and fracture toughness of polymethylmethacrylate (PMMA) bone cements obtained by the addition of control and heat treated short titanium fibers are studied. Heat treatment of titanium fibers is conducted to precipitate titania particles on the fiber surface, which may improve the biocompatibility of the metal. Control (non-heat treated) and heat treated short titanium fibers (250 μm long and 20μm diameter) were used as reinforcements at 3 volume %. X-ray diffraction indicated the presence of a rutile form of titania due to the heat treatments. Results indicate that the tensile and fracture properties of unfilled bone cement were improved by the addition of control and heat-treated fibers. The fracture properties of bone cements reinforced with control titanium fibers were at least 10% higher than those reinforced with heat treated titanium fibers. Therefore, we recommend further studies on the use of non-heat treated titanium fibers to reinforce acrylic bone cement.

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Introduction

A thin poly(methyl methacrylate) (PMMA) mantle has been used as a grouting and stress transfer agent in cemented total joint arthroplasties. The failure of implants by asceptic loosening has been ascribed to the failure of the bone cement mantle surrounding the implant [1, 2]. This may be prevented by increasing its fracture toughness. The fracture toughness of a polymer (PMMA) can be increased by increasing the molecular weight [3, 4] of the polymer. Increasing the molecular weight of the polymer results in an increase in the viscosity of the cement and may prevent penetration into the cancellous bone structure. This may inhibit the mechanical interlocking between the cancellous bone and the injected cement and decrease the effectiveness of the cement mantle surrounding the implant. Therefore, fiber reinforcements may be a practical route to enhance the fracture toughness of the bone cements.

Commercial bone cements generally consist of a solid component and a liquid part that are mixed together in the operating room just before implant insertion [5]. Benzoyl peroxide (BPO) is present in the solid and acts as an initiator. The solid also contains 10%–15% by weight of radiopacifiers (generally Barium sulphate or Zirconia). The liquid component is made of monomers of methylmethacrylate (MMA), with some n,n-dimethyl-para-touluidine (n,n-DMPT, between 1%–2.5% by volume) and 50–100 ppm of hydroquinone. The amine, DMPT, acts as an accelerator while hydroquinone acts as an inhibitor (to scavenge free radicals in the liquid so that storage life is increased). On mixing the two components, the DMPT cleaves the BPO forming free radicals. These free radicals are used in the addition polymerization of the MMA monomers to form PMMA within 10–15 minutes.

Different reinforcements have been added to the polymerizing matrix in order to improve the fatigue properties and fracture toughness of the PMMA [26]. These include fibers made of Kevlar [6], polyethylene [7, 8], carbon [9, 10], hydroxyapatite [11], bone mineral [12], high-strength PMMA fibers [13] and titanium [14, 15] as well as particles of glass [16], alumina [17] and acrylonitrile-butadine-styrene (ABS – 18). The addition of 5 vol% titanium fibers with lengths of 1.5 mm in the polymerizing matrix has been shown to increase the fracture toughness of the reinforced bone cement without significantly affecting the viscosity [14, 15]. Studies using stainless steel fibers with lengths greater than 1 mm had indicated that long fibers were oriented depending on the rheology and boundary conditions [19] and might not penetrate the interstices within trabecular bone [15]. In order to obtain a more randomly oriented distribution of fibers for uniform reinforcement of the bone cement, we investigate the addition of fibers with lengths of ∼250 μm and 20 μm in diameter.

The presence of titania on implanted titanium is believed to enhance the biocompatibility of the metal [20, 21]. We investigate a heat treatment process to form titania on the titanium fibers. We assess the changes to the tensile properties and fracture toughness of bone cements by the addition of control and heat treated titanium fibers. The phase of the titania coating is characterized using X-ray diffraction (XRD) and the fiber surface is characterized using scanning electron microscopy (SEM).

Materials and methods

The acrylic beads used in this study were poly(methyl methacrylate)–co–stryrene with ∼0.8 wt% residual BPO (kindly supplied by Zimmer Inc., Warsaw, IN). The average diameter of these spherical beads is 34 μm with diameters ranging between 10 μm–150 μm. The beads had an average molecular weight of 420,000 with a polydispersity of 3.23 and a residual monomer content of 3 wt%. The fibers used in this study are:

Fiber 1) Control–21.9 μm diameter, 0.25 mm long SS (packing density of 19%)
Fiber 2) The above fiber heated at 550°C for 4 hrs
Fiber 3) Fiber 1 heated at 550°C for 1 hour followed by heating at 800°C for 30 minutes

The packing density is defined as the ratio of the mass of fibers, as received, poured into a given volume to the mass of a block of solid occupying the same volume. Though the packing density of the fibers is higher than the steel fibers tested in our earlier studies, we could not incorporate a larger content of these fibers into the polymerizing matrix. Titanium fibers were obtained from Micron Metal Fibers Inc. (Gahanna, OH) and heat treated in an oven.

Scanning electron microscopy of heat-treated titanium fibers was performed on a Hitachi SEM 4500. XRD was performed on a Scintag diffractometer with a copper source at an operating voltage of 40 kV and a current of 45 mA with a solid state fixed slit detector. Scanning was performed between 10° – 90° 2θ with a step width of 0.02° and scanning time of 0.04 sec/step. Only the region between 34°–90° 2θ is shown here.

The MMA monomer used in this study contained 10–100 ppm of the monomethylether of hydroquinone (Aldrich Chemicals, Milwaukee, WI). Barium sulphate (kindly provided by Zimmer Inc., Warsaw, IN) and n,n-DMPT (Aldrich Chemicals, Milwaukee, WI) were used without further purification. In order to make the samples, 10% by weight barium sulphate was blended with the polymer beads in a commercial mixer. The liquid was mixed into the polymer beads and blended for less than a minute. Fiber reinforced cements were made by adding the fibers (14% by weight) to the polymerizing matrix (which contained barium sulphate). The same weight of control and heat-treated fibers were added to the cement. The amount of activator, DMPT, was kept constant at 1.25% in all cases. After blending the fibers, the cement was filled in a cement cartridge and injected using a commercial cement gun (Power Flo cement injection gun, Zimmer Inc., Warsaw, IN) into suitable molds through a tube that was 9.5 mm in diameter and 228 mm long. The viscosity of the cement increased slightly with the addition of titanium fibers, but it could be easily ejected out of the cement gun without visible fiber agglomeration.

Samples for tensile tests were made by injecting the polymerizing cement into polysulphone molds while samples for fracture toughness measurements [22] were made by injecting into polyacetal molds. The cement in the molds was cured in an oven at 37°C for 1 hour. After the samples were removed from the mold, excess material was machined off. A groove was subsequently machined into the fracture toughness samples and sharpened with a razor blade [22]. Fracture toughness and tensile tests were conducted on an ATS screw driven universal testing machine (Series 910) at a crosshead speed of 0.3 mm/min. All the mechanical tests were conducted within 3 days of manufacture of the samples.

Results and discussion

Scanning electron micrograph (SEM) of fiber 1 (titanium fiber as obtained) shows the uniform length of the fibers as well as the surface texture obtained during drawing the fibers (Fig. 1a). Notice that the fiber surface is very smooth (Fig. 1b). On heating these fibers at 550°C for 4 hours (fiber 2), small changes were observed on the surfaces of the fibers

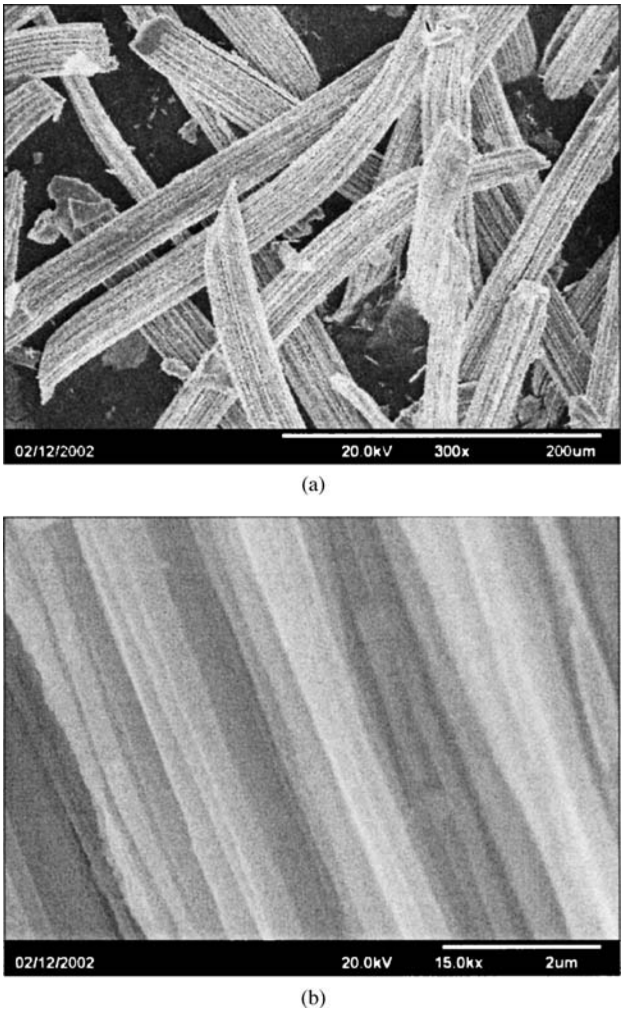


Fig. 1 Figure 1a) Low magnification and Figure 1b) High magnification image of the titanium fibers as obtained.

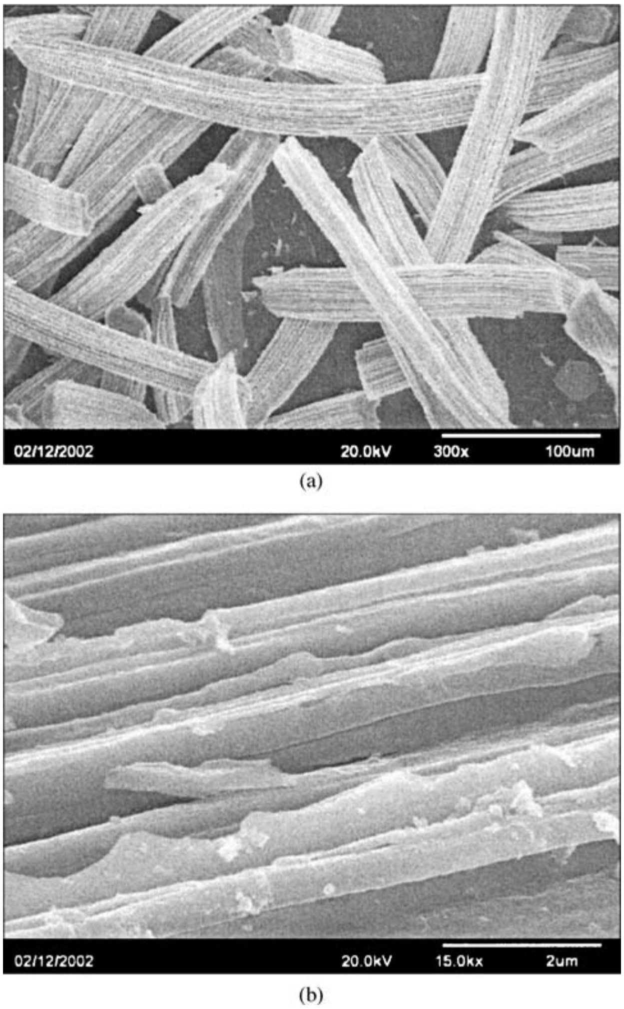
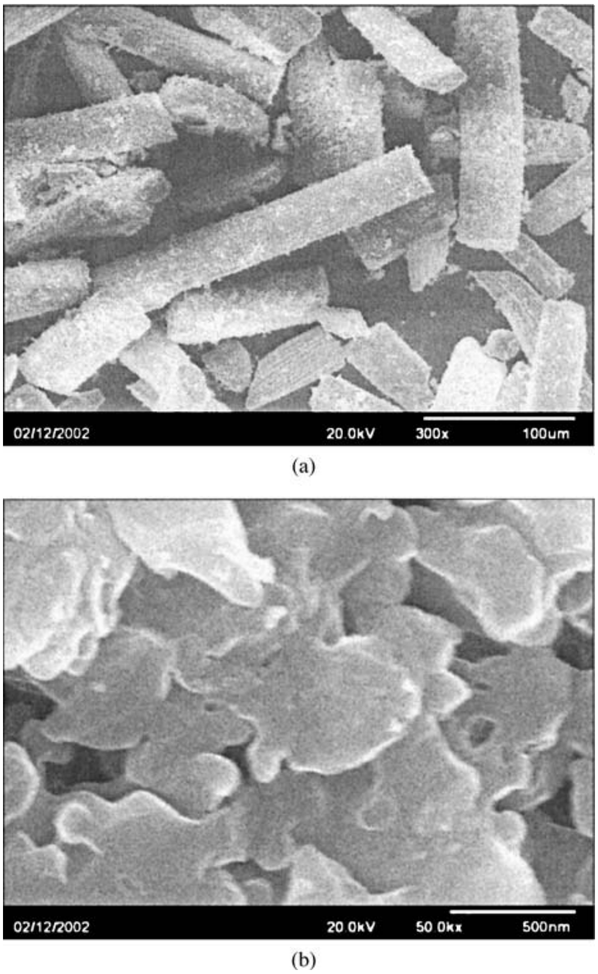


Fig. 2 Figure 2a) Low magnification and Figure 2b) High magnification image of the titanium fibers heat-treated to 550°C. Notice the beginning of distortion of the smooth surface of the fiber surfaces.

—where there may be a scale of titania over a titanium core (Fig. 2a and Fig. 2b). It is not possible to distinguish the phase of the titania coating on these fibers using X-Ray diffraction (Fig. 4). This indicates that the volume of titania coating on the fibers is very small, consistent with the SEM images (Fig. 2a and Fig. 2b). When the titanium fibers (Fiber 1) were heated at 550°C for an hour followed by heating at 800°C for half an hour to obtain Fiber 3, clusters of fibers were sintered together. These fibers (Fiber 3) broke during the procedure for mechanical separation and appear to have shorter lengths (due to handling and processing—Fig. 3a). All the titanium metal is converted to titania nano-particulates that are sintered together in a porous construct with a pore size of 1 μm–5 μm (Fig. 3b). XRD indicates that the precipitated nano-particles are the rutile form of titania (Fig. 4). The appearance of the fibers changes from gray to dark blue to light green for fibers 1, 2 and 3 respectively.

Heat treatments have been used to induce porous titania formation on titanium plates or large rods [24, 25]. As the manufacturing process (drawing) used in the formation of the short fibers used in this study causes a orientation of the titanium grains as well as affects the surface energy, heat treatments may produce different results on the short fibers used in this study.

When the fibers are mixed into the cements, the color of the polymerized cement samples appears to be black, black and light green for cements reinforced with fibers 1, 2 and 3 respectively. The fracture toughness of the bone cement increases by ∼19%–30% over controls by the addition of the fibers (Fig. 5). The fracture toughness of non-heat treated titanium fiber reinforced cement is at least 10% higher than that of bone cement reinforced with heat treated fibers (Fig. 5). There is a trend towards a decrease in the fracture toughness with heat-treatments conducted at higher temperatures. This may be due to a decrease in the energy absorption capacity of the metal on being converted to brittle and porous ceramic fibers. The increases in fracture toughness of the reinforced



(a)

(b)

Fig. 3 Figure 3a) Low magnification and Figure 3b) High magnification image of the titanium fibers heat-treated to 800°C. Notice that the titania particles are sintered together to form a porous structure.

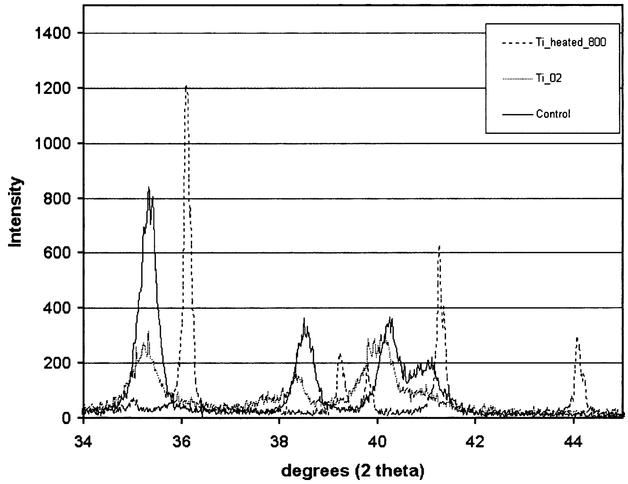


Fig. 4 X-ray diffraction (XRD) profile of the three fibers. XRD indicates that a rutile phase of titania is formed during heat-treatment at 800°C for half an hour from the titanium fibers.

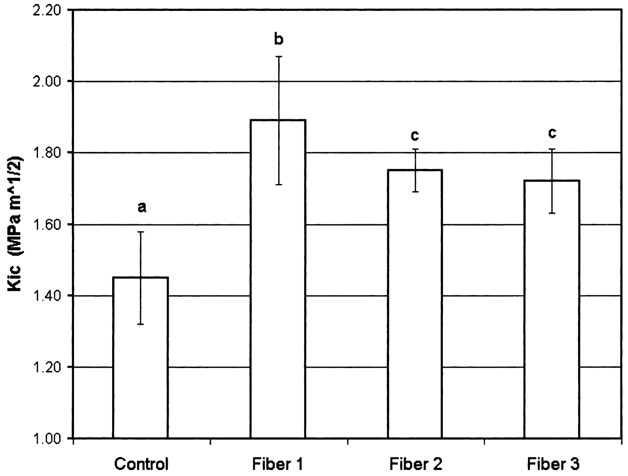


Fig. 5 Fracture toughness of the reinforced cements. The fracture toughness of all fiber reinforced cements is higher than that of controls.

cements in the present study are smaller in comparison to longer metal fiber reinforced cements [14, 23] but similar to particulate reinforced cements [16].

Tensile tests show that the modulus increases between 20%–50% by the addition of fibers (Fig. 6). The increase in elastic modulus is the largest for fiber 2 while it is the least when fiber 3 is added to the polymerizing matrix (Fig. 6). The formation of a thin ceramic titania layer on the surfaces of fiber 2 may increase their elastic modulus and therefore, the modulus of the cements. The increased porosity within fiber 3 (Fig. 3b) lowers it's mechanical properties (elastic modulus and strength). Combined with the smaller lengths of fiber 3 (Fig. 3a), the increase in elastic modulus is the least for cements reinforced with these fibers. There are small increases in ultimate strengths and no significant changes in the ultimate strains of the fiber reinforced cements (Fig. 7 and Fig. 8 respectively). Thus, the addition of fibers to the bone

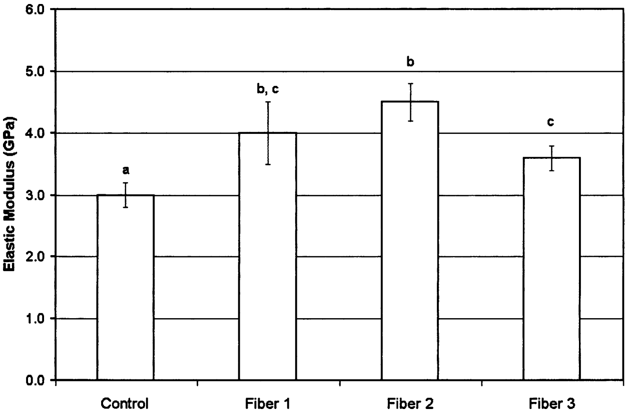


Fig. 6 Elastic modulus of control and fiber reinforced bone cements. 1– control, 2– titanium fibers as obtained, 3– titanium fibers heat-treated at 550°C for four hours and 4– titanium fibers heat-treated at 800°C for half an hour.

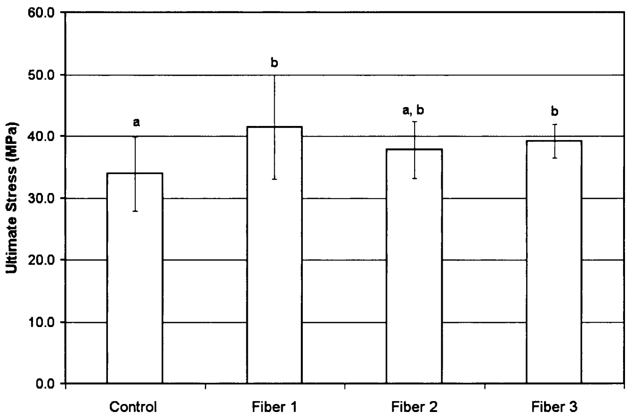


Fig. 7 Ultimate strengths of control and fiber reinforced bone cements. 1–control, 2–titanium fibers as obtained, 3–titanium fibers heat-treated at 550°C for four hours and 4–titanium fibers heat-treated at 800°C for half an hour.

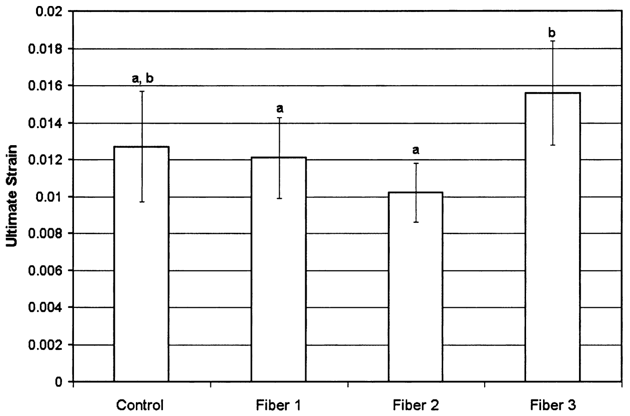


Fig. 8 Ultimate strains of control and fiber reinforced bone cements. 1–control, 2–titanium fibers as obtained, 3–titanium fibers heat-treated at 550°C for four hours and 4–titanium fibers heat-treated at 800°C for half an hour.

cements increases the fracture toughness, without a decrease in the ultimate strengths and strains of the bone cement. As reinforcement of bone cement with non-heat treated titanium fibers results in improved fracture toughness as compared to reinforcement with heat treated titanium fibers, we do not recommend further studies on the use of heat treated titanium fibers in acrylic bone cements.

The use of longer metal fibers (∼1 mm or greater) increases the elastic modulus to a larger extent than those observed in this study [19]. This is accompanied by higher ultimate strengths and lower ultimate strains in the longer metal fiber reinforced composites [19]. In this study, the increased ultimate strengths are obtained without affecting the ultimate strains of the cements. Thus, the reinforcements used in this study may provide a better overall reinforcement of acrylic bone cements.

In conclusion, significant increases in fracture toughness values were observed with the titanium fiber reinforcements. All the formulations in this study could be easily injected out of a cement gun. Therefore, they can easily replace existing cements and we recommend further studies on the use of non-heat treated titanium fiber reinforcements.

Acknowledgements This research is supported by the 21^{st} century research fund from the State of Indiana, USA. The authors would like to thank Mr. Anthony Lozier, Mr. Michael Hawkins, Mr. Don Yakimicki and Ms. Sarah Thalen from Zimmer Inc. for their support.

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