Effects of fiber length and volume fraction on the reinforcement of calcium phosphate cement

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A self-setting calcium phosphate cement (CPC) transforms into solid hydroxyapatite during setting at body temperature, and has been used in a number of medical and dental procedures. However, the inferior mechanical properties of CPC prohibits its use in unsupported defects, stress-bearing locations or reconstruction of thin bones. The aim of the present study was to strengthen CPC with fiber reinforcement, to examine the effect of fiber length and volume fraction, and to investigate the reinforcement mechanisms. Previous studies employed either short fibers for random distributions, or continuous fibers that were as long as the specimen size with preferred orientations such as unidirectional alignment. In the present study, a novel methodology was developed in which fibers several times longer than the specimen mold size were randomly mixed with the CPC paste to approximate the isotropy associated with short fibers, and at the same time achieve the high reinforcement efficacy associated with continuous fibers. Carbon fibers of 8 μm diameter were used with fiber lengths ranging from 3 mm to 200 mm, and fiber volume fraction from 1.9% to 9.5%. A three-point flexural test was used to fracture the specimens. Scanning electron microscopy was used to examine crack-fiber interactions and specimen fracture surfaces. The composite containing fibers of 75 mm in length at a volume fraction of 5.7% achieved a flexural strength about 4 times, and work-of-fracture 100 times, greater than the unreinforced CPC. It is concluded that randomly mixing the CPC paste with carbon fibers that were several times longer than the specimen mold size resulted in substantial improvements in strength and fracture resistance; the reinforcement mechanisms were crack bridging and fiber pullout; and fiber length and volume fraction were key microstructural parameters that determined the cement properties.

1. Introduction

Hydroxyapatite is one of the most often used restorative materials for repair of human hard tissues because of its chemical and crystallographic similarity to the carbonated apatite found in human teeth and bones [1–3]. Several formulations of calcium phosphate cements self-harden through a setting reaction to form hydroxyapatite [4–7]. A calcium phosphate cement, hereinafter referred to as CPC, forms hydroxyapatite at room or body temperature as the principal reaction product [5, 8] and has been studied extensively due to its excellent biocompatibility and bone-replacing properties [9–11]. CPC is comprised of a mixture of fine particles of tetracalcium phosphate [TTCP: $Ca_4(PO_4)_2O$] and dicalcium phosphate anhydrous (DCPA: $CaHPO_4$), which react in an aqueous environment to form hydroxyapatite [8, 9, 11–13]. The CPC powder can be mixed with water to form a thick paste that can be sculpted during surgery; within about 15 min this paste converts *in situ* to microporous solid hydroxyapatite crystallites [14].

Because CPC can be surgically shaped to conform to the defects in hard tissues and sets at the site of application to form solid hydroxyapatite, previous studies have suggested it to be useful in a number of medical and dental procedures, including the reconstruction of frontal sinus and augmentation of craniofacial skeletal defects [13, 15, 16], endodontics [17, 18], and the repair of periodontal bone defects and tooth defects [19, 20]. However, the brittleness and inferior mechanical strength of the cement have severely limited its use to only non load-bearing applications [9, 20, 21], and currently ''none of the indications include significant stress-bearing applications'' [22].

Fibers are widely used to reinforce matrix materials

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for engineering, structural, dental and medical applications [23–30]. Poly(methyl methacrylate) bone cement has been strengthened with carbon fibers, titanium fibers, and polymeric fibers [31–35]. Previous studies on fiber reinforcement can be generally categorized into two groups. Group 1 focused on short fiber reinforcement in which the fibers had lengths much shorter than the specimen size (e.g., a fiber length of 3 mm vs a specimen length of 25 mm) and were randomly distributed in the matrix, resulting in composites with relatively isotropic properties [24, 26, 32, 34]. Group 2 focused on continuous fiber reinforcement in which the fibers were nearly as long as the specimen size and were aligned in the matrix in certain directions (e.g., unidirectional) [23, 25, 27, 29, 30, 35]. The advantage of continuous fiber reinforcement is that the crack resistance is highly enhanced in the direction perpendicular to the fibers. The disadvantage, however, is that the fracture resistance of the composite is anisotropic, in that the crack can ''zip'' along the fibers in the direction parallel to the fibers.

Little efforts have been devoted to the study on fiber reinforcement of CPC. In one recent study, a flat fiber mesh was placed on the tensile surface of the CPC specimen [36], resulting in a significant increase in the work-of-fracture. The reinforcement in that study was anisotropic, in that the fibers were limited to the tensile side of the samples.

The present study, therefore, aimed at reinforcing the CPC with randomly-oriented fibers to improve the strength and fracture resistance. A methodology was developed, in which fibers with lengths several times longer than the specimen mold size were randomly mixed with the CPC paste. This resulted in fibers assuming tortuous nonlinear paths in the matrix, combining the advantage of relatively random distribution of short fibers together with the high reinforcement efficacy of continuous fibers. The mechanical properties of composites were investigated as a function of fiber length and fiber volume fraction. The reinforcement mechanisms were examined with scanning electron microscopy.

2. Materials and methods

2.1. Specimen fabrication

The tetracalcium phosphate (TTCP) powder was synthesized from a solid state reaction between equimolar amounts of commercial $CaHPO_4$ (dicalcium phosphate anhydrous, or DCPA) and $CaCO_3$ (Baker Analyzed Reagents, J. T. Baker Chemical Co., NJ), which were mixed and heated at 1500 °C for 24 h in a furnace (Model 51333, Lindberg, Watertown, WI). The heated mixture was quenched to room temperature in a desicator, ground and sieved to obtain TTCP powder of a mean size of approximately 12 μm. The commercial DCPA powder was ground and sieved to obtain a mean particle size of approximately 1 μm. The TTCP and DCPA powders were mixed in a micromill (Bel-Alert Products, Pequannock, NJ) in equimolar amounts to form the CPC powder [5].

Carbon fibers (AS4-12K, Hercules Inc., Wilmington, DE) that had a tensile strength of approximately 3.8 GPa, an elastic modulus of approximately 227 GPa, a diameter of 8 μm, and a specific density of 1.8 g/cm^3 were used. The fibers were cut with sharp surgical blades into discontinuous filaments of the lengths described below. The cut fibers were manually randomized by separating the fibers from each other and then mixing them together into tortuous random orientations. CPC powder and distilled water were mixed manually by spatulation into a paste having a CPC to water mass ratio of 3:1, and then manually blended with the random fibers. The fiber-paste mixture was placed into a 3 mm × 4 mm × 25 mm mold. The composite mixture in the mold was covered with a mechanically clamped glass slide. The assembly was incubated in a humidor with 100% humidity at 37 °C for 4 h, and then the hardened composite sample was demolded and immersed in distilled water at 37 °C for approximately 20 h prior to testing.

2.2. Fiber volume fraction and fiber length

Two groups of flexural specimens were made. The first group was for study of the effect of fiber volume fraction on the mechanical properties of the CPC composite. The fiber volume fraction was calculated as the volume of the fibers in each specimen divided by the total volume of the specimen. The volume of fibers in a specimen was equal to the measured weight of the fibers incorporated into the specimen divided by the fiber density. Five different fiber volume fractions were used: 1.9%, 3.8%, 5.7%, 7.6% and 9.5%. The CPC powder-to-water mass ratio was fixed at 3:1, and the fiber length was fixed at 75 mm. The CPC cement without fiber reinforcement was tested as a control. Six specimens were made for each condition providing a total of 36 specimens.

The second group of specimens was made to investigate the effect of fiber length on the mechanical properties of the CPC composite. Fibers were cut to five different lengths: 3 mm, 8 mm, 25 mm, 75 mm and 200 mm. The CPC-to-water mass ratio was kept at 3:1, and the fiber volume fraction was fixed at 5.7%. Six flexural specimens were made for each fiber length, following the procedures described above, yielding a total of 30 specimens.

2.3. Mechanical testing

A standard three-point flexural test [37] with a span of 20 mm was used to fracture the specimens at a crosshead speed of 0.5 mm per minute on a computer-controlled Universal Testing Machine (model 5500R, Instron Corp., MA). The 4 mm × 25 mm surface of the specimen was slightly polished by using silicon carbide papers with grits of 400, 600 and 1200 consecutively, and the specimen was fractured with the polished surface in tension. The following properties were evaluated: flexural strength, flexural modulus, and work-of-fracture (the energy required to fracture the specimen, obtained from the area under the load-displacement curve normalized by the specimen's cross-sectional area). After the matrices had cracked, most of the fiber-reinforced CPC specimens were still intact, due to fibers bridging the cracks and supporting the applied load. The test was stopped at a maximum crosshead displacement of 2 mm for a consistent calculation of the work-of-fracture values. After unloading, selected specimens were

manually fractured for the examination of fracture surfaces.

A scanning electron microscope (SEM, model JSM-5300, JEOL, Inc., Peabody, MA) was used to observe the specimens. The specimens were sputter coated with gold prior to SEM observations. The fiber orientations, fiber-crack interactions, and pullout of fibers were examined to obtain information regarding reinforcement mechanisms. One-way ANOVA was performed to detect significant ($\alpha = 0.05$) effects of fiber length and fiber volume fraction on mechanical properties. Tukey's multiple comparison test was used at a family confidence coefficient of 0.95 to group and rank the measured values.

3. Results

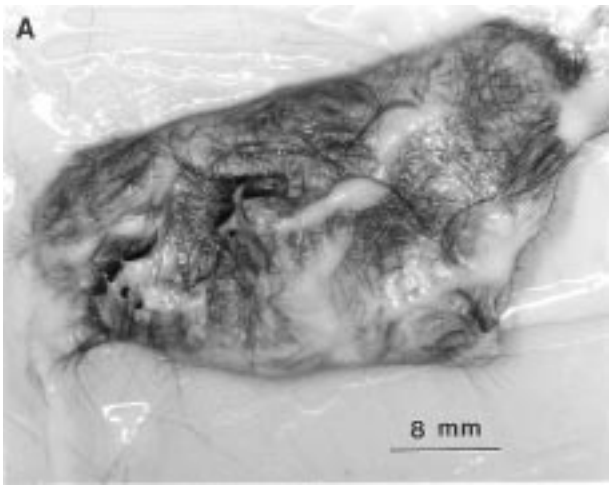
Fig. 1A is an optical photo of a typical batch of fibers 75 mm in length that were randomly mixed with a CPC paste. The CPC paste had a CPC:water mass ratio of 3:1. The fiber volume fraction was 5.7%. The randomness of the tortuous nonlinear fiber orientation is visible in Fig. 1A, and appears to have been maintained in the set specimens (Fig. 1B).

The effect of fiber volume fraction on composite mechanical properties is shown in Fig. 2. The flexural strength in MPa (mean $\pm$ SD; $n = 6$) at a fiber volume fraction of 5.7% was 59 ± 11, significantly higher than all other groups except that at 7.6% (Tukey's multiple comparison test; family confidence coefficient = 0.95). The strength of the CPC control (i.e. fiber volume fraction of 0%) was 13 ± 3, significantly lower than all other groups. The work-of-fracture in kJ/m^2 at a fiber volume fraction of 5.7% was 6.6 ± 1.2, significantly higher than all other groups; that of the CPC control was 0.04 ± 0.01, significantly lower than all other groups (Tukey's multiple comparison test; family confidence coefficient = 0.95). The flexural modulus in GPa was 3.6 ± 0.5 for the CPC control; it increased to 7.0 ± 0.9 at fiber volume fraction of 5.7%, then remained almost constant when the fiber volume fraction was further increased to 9.5%.

The effect of fiber length on the composite mechanical properties is shown in Fig. 3 at a fixed fiber volume fraction of 5.7%. Both the flexural strength and work-of-fracture increased rapidly when the fiber length was increased from 3 mm to 75 mm, then showed a slight decrease when the fiber length was further increased to 200 mm. The flexural modulus was generally unchanged with fiber length, except for a slight increase at a fiber length of 75 mm and a slight decrease at a fiber length of 200 mm. At a fiber length of 3 mm, the composite flexural strength and modulus were not significantly different from those of the CPC control ($p > 0.1$; Student's t-test), but the work-of-fracture was increased to approximately 35 times that of the CPC control.

Typical crack-fiber interactions and fracture surfaces are shown in the SEM micrographs of Fig. 4. Fig. 4A shows the polished surface of a specimen with a fiber volume fraction of 5.7% at a length of 75 mm; the surface shown was placed in tension during the flexural test. The bridging fibers kept the multiple-cracked specimen intact. The fracture surface in Fig. 4B shows long fiber pullout lengths with remnants of matrix CPC still adhered to the fibers, demonstrating that the fibers were relatively well dispersed in and wetted by the CPC. Fig. 4C shows a representative fracture surface of the CPC control specimens which was relatively flat, as is typical for brittle materials.

A higher magnification in Fig. 5A shows highly tortuous CPC fracture surfaces around a bridging fiber that appeared to be well embedded in the matrix. Fig. 5B shows that some areas of the surfaces of the pulled-out fibers had pieces of CPC matrix adhered while other areas of the fiber surfaces were smooth, demonstrating that fracture occurred both along the fiber-CPC interface as well as in the CPC matrix away from the interface. Hydroxyapatite crystallites are shown in a representative SEM micrograph in Fig. 5C. The similarity of crystallites observed in the CPC control, in the CPC matrix of the fiber composite, and in the CPC pieces bonded on the



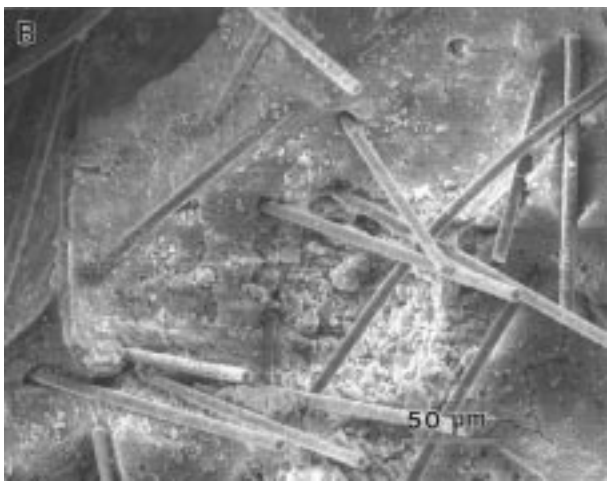


Figure 1 (A) Optical photo of fibers 75 mm in length that were randomly mixed with a CPC paste. The randomness of the tortuous nonlinear fiber orientation was visible in the paste. (B) SEM micrograph shows that the relatively random fiber orientation was maintained in the set cement.

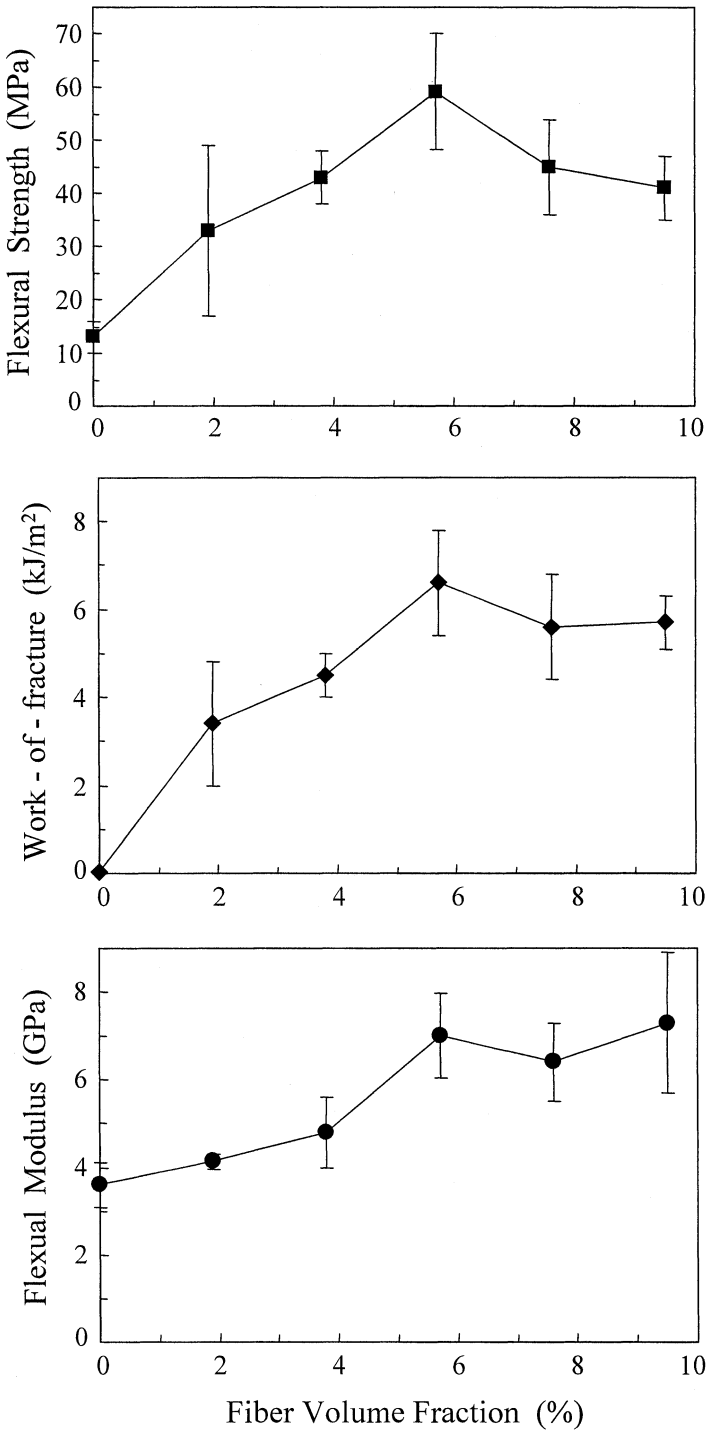


Figure 2 Effect of fiber volume fraction on mechanical properties (mean = SD; $n = 6$). Values of CPC are plotted on the left axes at 0% fiber volume fraction. The fiber length was 75 mm.

fibers showed that the incorporation of carbon fibers into the CPC had not affected the crystal formation process during the setting of CPC.

4. Discussion

In the present study, self-setting calcium phosphate cement was substantially strengthened and toughened by fiber reinforcement. Previous investigations on fiber reinforcement of medical and dental materials [24–27, 38, 39] either used short fibers randomly distributed in the matrix, or continuous fibers that were nearly as long as the specimen but aligned in the matrix in certain directions, e.g., unidirectional. Examples of short fibers with random distribution were chopped polymer fibers in poly(methyl methacrylate) matrix [32], glass fibers in dental resin composites [24, 38], titanium fibers in bone cements [34], and ceramic whiskers in dental resin composites [39, 40]. Examples of continuous fibers were glass, polymer and carbon fibers aligned usually unidirectionally, with each fiber extending continuously through the entire specimen or a large part of the specimen [23, 25–27, 29, 30, 35]. Compared with short and randomly distributed fibers, aligned continuous fibers can result in superior reinforcement, but only in the direction perpendicular to the fibers [23, 25–27, 29, 30, 35].

The present study proposed to combine the advantages

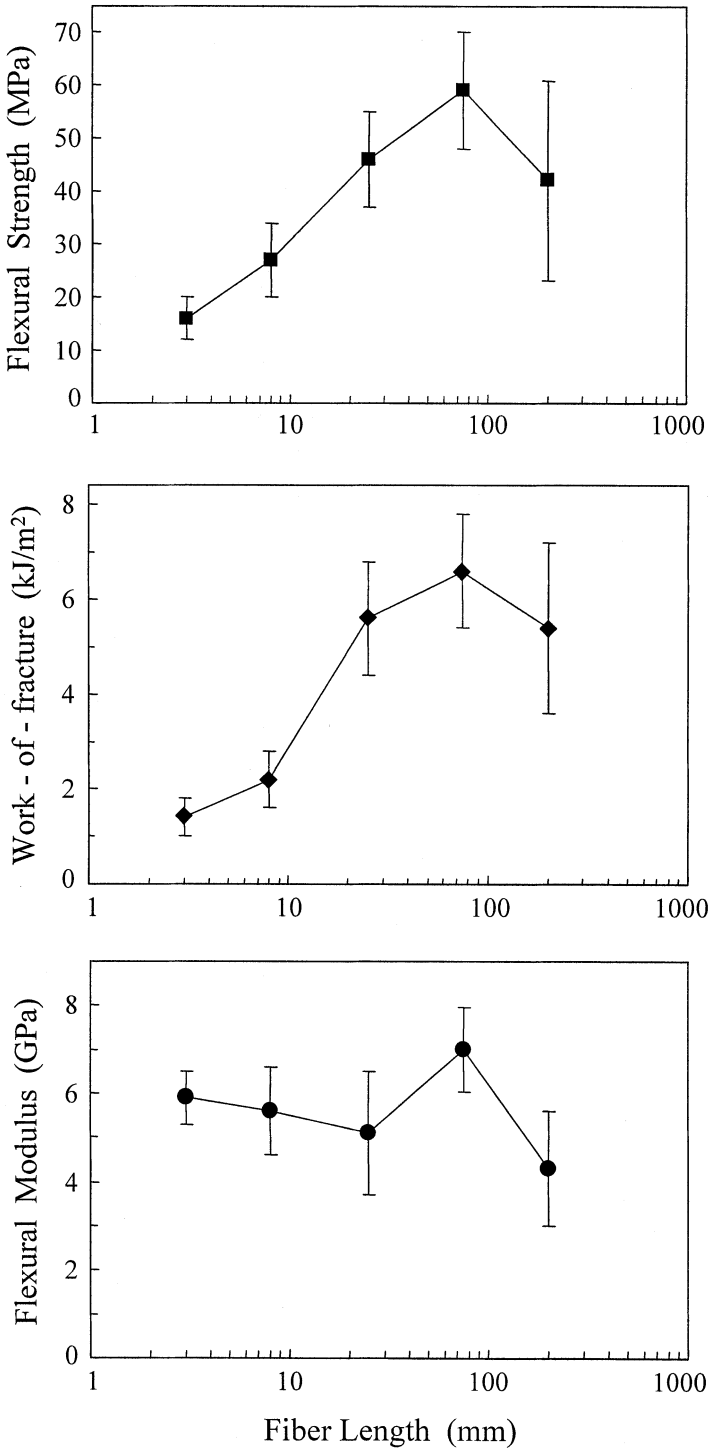


Figure 3 Effect of fiber length on composite mechanical properties (mean ± SD; $n = 6$). The fiber volume fraction was fixed at 5.7%.

of the property isotropy associated with short random fibers together with the high reinforcement efficacy associated with continuous fibers. The flexibility of the small diameter carbon fibers and the relatively easy mixing with a water-based CPC paste have allowed the bending and random orientation of the long fibers. The methodology of randomly mixing the CPC paste with fibers that were several times longer than the specimen size yielded substantially improved CPC composites. The reinforced cement possessed flexural strength as high as 4 times, and work-of-fracture 100 times, greater than the unreinforced CPC. The mechanisms of reinforcement in the present study appeared to be: (1) fibers bridging the crack to resist its further opening and propagation; (2) multiple cracking of the matrix consuming the applied work in creating new surfaces; and (3) frictional sliding of the fibers during pullout. Enamel rods in tooth enamel behave in a way similar to fibers by deflecting and resisting crack propagation [41]. CPC is an oxide ceramic, and fiber bridging and pullout have also been observed to be the toughening mechanisms in other ceramic composites [28, 42].

Both the fiber length and fiber volume fraction played key roles in determining the mechanical properties of the

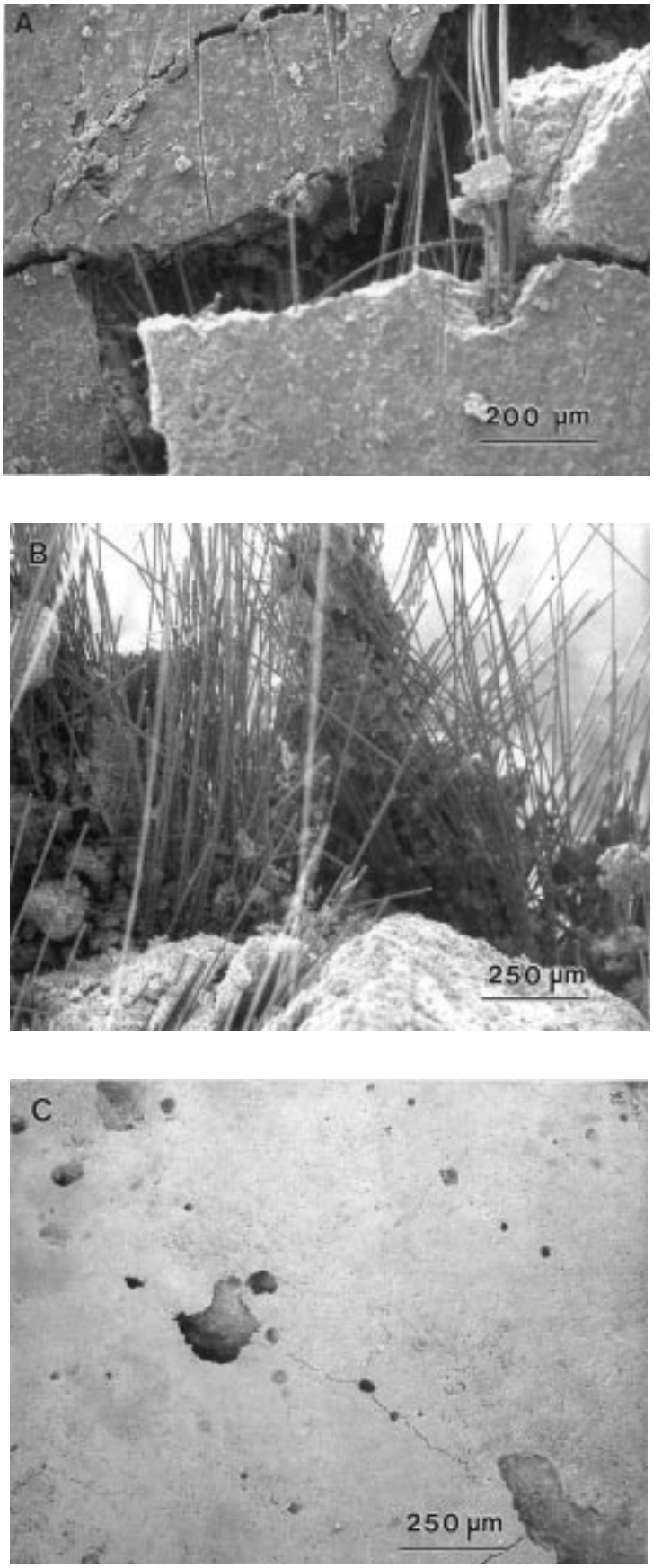


Figure 4 (A) Cracking during flexural test in a specimen with fiber volume fraction of 5.7% at a length of 75 mm. The bridging fibers and multiple matrix cracks suggest energy consumption and high resistance to further crack opening and propagation. (B) Fracture surface with pulled-out fibers and adhered CPC, indicating that the fibers were well dispersed in and wetted by the CPC paste during mixing. (C) Relatively flat fractured surface of a CPC control sample, typical for brittle materials.

CPC composites. The rapid increase in flexural strength and work-of-fracture of the CPC composite when the fiber length was increased from 3 mm to 75 mm was likely a result of more effective fiber bridging and higher resistance to fiber pullout associated with longer fibers. The slight decrease in composite mechanical properties

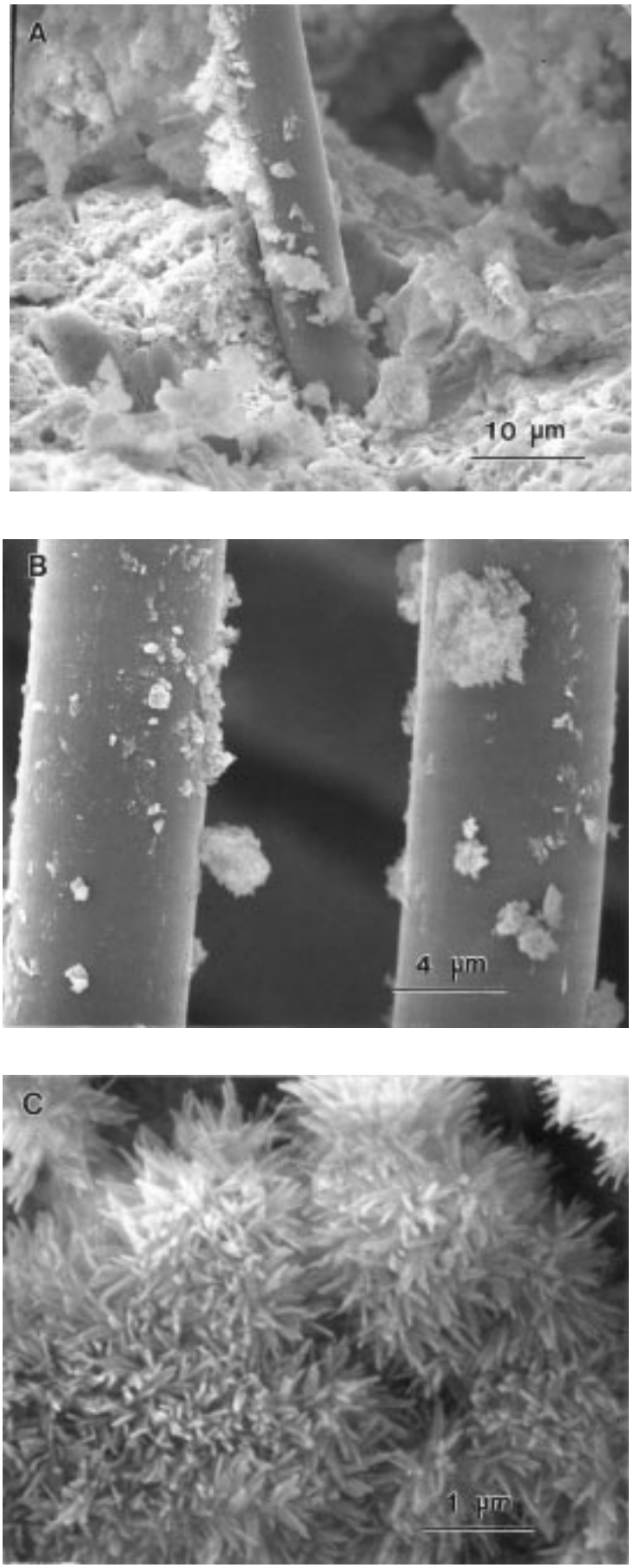


Figure 5 (A) SEM shows tortuous CPC fracture surfaces around a bridging fiber that was well embedded in the matrix. (B) Some areas of the surface of the pulled-out fibers had adherent matrix pieces while other areas of the fiber surface were smooth, indicating that fracture had occurred both along the fiber-CPC interface and in the CPC away from the interface. (C) Hydroxyapatite crystallites in the CPC control, in the CPC matrix of the fiber composite, and in the CPC that adhered to the fibers, had similar sizes and shapes.

when the fiber length was further increased was probably related to an observed less uniform distribution of the fibers in the matrix. With the fiber volume fraction being fixed, as the fiber length was increased the number of fibers in the paste decreased, and achieving a uniform distribution of the fibers was not as easy as with short fibers. Therefore, two competing factors were suggested to be operative: the increased reinforcement efficacy associated with longer fibers, but the decreased degree of uniform distribution of longer fibers in the CPC composite.

Similarly, two competing factors appeared to be operative regarding the effect of fiber volume fraction: the increased reinforcement efficacy when the fiber volume fraction was increased, but the greater difficulty in mixing and wetting the fibers with the CPC paste when the fiber volume fraction was increased. At a fiber volume fraction of 9.5%, SEM examinations of the set composite showed fiber agglomerates that were not wetted and completely surrounded by CPC. This may explain why the composite strength and work-of-fracture first increased rapidly with fiber volume fraction up to 5.7%, then decreased when the fiber mass fraction was further increased to 9.5%.

Carbon fibers have been used extensively because of their mechanical properties [43] and biocompactibility [44–46]. Carbon fiber-reinforced polymeric composites have been proposed for use in denture bases [47], fixation of implants in orthopaedic surgery [48], and crown and fixed partial denture applications [49, 50]. However, further studies should also investigate the reinforcement of calcium phosphate cement with bioactive and resorbable fibers [2, 3]. Nevertheless, the methodology of randomly mixing a paste with fibers that are longer than the specimen size for property isotropy and superior strength, together with the reinforcement mechanisms and the effects of fiber length and volume fraction, established in the present study, are expected to be applicable to other cement-fiber systems. The four times increase in flexural strength and nearly two orders of magnitude increase in work-of-fracture (toughness) of the fiber-reinforced calcium phosphate cement may help extend the medical and dental applications into the repair of larger defects, use in stress-bearing locations, and reconstructive treatments for thin bones.

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Disclaimer

Certain commercial materials and equipment are identified in this paper to specify experimental procedures. In no instance does such identification imply recommendation by NIST or the ADA Health Foundation or that the material identified is necessarily the best available for the purpose.

References

1. J. F. OSBORN and H. NEWESELY, *Biomaterials* **1** (1980) 108.
2. L. L. HENCH, *J. Am. Ceram. Soc.* **81** (1998) 1705.
3. W. SUCHANEK and M. YOSHIMURA, *J. Mater. Res.* **13** (1998) 94.
4. H. MONMA, M. GOTO and T. KONMURA, *Gypsum and Lime* **188** (1984) 11.
5. W. E. BROWN and L. C. CHOW, in Cements Research Progress, edited by P. W. Brown (American Ceramic Society, Westerville, OH, 1986) p. 352.
6. B. R. CONSTANZ, B. BARR and K. MCVICKER, US Patent 5,053,212 (October 1, (1991)).
7. M. P. GINEBRA, E. FERNANDEZ, E. A. P. DE MAEYER, R. M. H. VERBEECK, M. G. BOLTONG, J. GINEBRA, F. C. M. DRIESSENS and J. A. PLANELL, *J. Dent. Res.* **76** (1997) 905.
8. L. C. CHOW, S. TAKAGI, P. D. CONSTANTINO and C. D. FRIEDMAN CD, in Mater. Res. Soc. Symp. Proc., edited by B. E. Scheetz, A. G. Landers, and L. Odler (Materials Research Society, Pittsburgh, PA, 1991) p. 3.
9. Y. FUKASE, E. D. EANES, S. TAKAGI, L. C. CHOW and W. E. BROWN, *J. Dent. Res.* **69** (1990) 1852.
10. K. ISHIKAWA, S. TAKAGI, L. C. CHOW and Y. ISHIKAWA, *J. Mater. Sci.: Mater. Med.* **6** (1995) 528.
11. Y. MIYAMOTO, K. ISHIKAWA, K. FUKAO, M. AWADA, M. NAGAYAMA, M. KON and K. ASAOKA, *Biomaterials* **16** (1995) 855.
12. P. D. CONSTANTINO, C. D. FRIEDMAN, K. JONES and L. C. CHOW, *Arch. Otolaryngol. Head Neck Surg.* **117** (1991) 379.
13. C. D. FRIEDMAN, P. D. CONSTANTINO, K. JONES and L. C. CHOW, *ibid.* **117** (1991) 385.
14. P. D. CONSTANTINO and C. D. FRIEDMAN, *Otolaryngol. Clin. North Am.* **27** (1994) 1037.
15. M. L. SHINDO, P. D. CONSTANTINO, C. D. FRIEDMAN and L. C. CHOW, *Arch. Otolaryngol. Head Neck Surg.* **119** (1993) 185.
16. Y. MIYAMOTO, K. ISHIKAWA, M. TAKECHI, T. TOH, Y. YOSHIDA, M. NAGAYAMA, M. KON and K. ASAOKA, *J. Biomed. Mater. Res.* **37** (1997) 457.
17. A. A. CHOHAYEB, L. C. CHOW and P. TSAKNIS, *J. Endodont.* **13** (1987) 384.
18. A. SUGAWARA, M. NISHIYAMA, K. KUSAMA, I. MORO, S. NISHIMURA, I. KUDO, L. C. CHOW and S. TAKAGI, *Dent. Mater. J.* **11** (1992) 11.
19. S. H. DICKENS-VENZ, S. TAKAGI, L. C. CHOW, R. L. BOWEN, A. D. JOHNSTON and B. DICKENS, *Dent. Mater.* **10** (1994) 100.
20. Y. MATSUYA, J. M. ANTONUCCI, S. MATSUYA, S. TAKAGI and L. C. CHOW, *ibid.* **12** (1996) 2.
21. K. MIYAZAKI, T. HORIBE, J. M. ANTONUCCI, S. TAKAGI and L. C. CHOW, *Dent. Mater.* **9** (1993) 41.
22. C. D. FRIEDMAN, P. D. CONSTANTINO, S. TAKAGI and L. C. CHOW, *J. Biomed. Mater. Res. (Appl. Biomater.)* **43** (1998) 428.
23. K. EKSTRAND, I. E. RUYTER and H. WELLENDORF, *J. Biomed. Mater. Res.* **21** (1987) 1065.
24. W. R. KRAUSE, S. H. PARK and R. A. STRAUP, *J. Biomed. Mater. Res.* **23** (1989) 1195.
25. A. J. GOLDBERG and C. J. BURSTONE, *Dent. Mater.* **8** (1992) 197.
26. N. H. LADIZESKY, Y. Y. CHENG, T. W. CHOW and I. M. WARD, *ibid.* **9** (1993) 128.
27. A. J. GOLDBERG, C. J. BURSTONE, I. HADJINIKOLAOU and J. JANCAR, *J. Biomed. Mater. Res.* **28** (1994) 167.
28. B. R. LAWN, Fracture Of Brittle Solids (Cambridge University Press, London, 1993) Chapter 7.
29. H. H. K. XU, C. P. OSTERTAG, L. M. BRAUN and I. K. LLOYD, *J. Am. Ceram. Soc.* **77** (1994) 1889.
30. P. K. VALLITTU, V. P. LASSILA and R. LAPPALAINEN, *Dent. Mater.* **10** (1994) 116.
31. S. SAHA and S. PAL, *J. Biomech.* **17** (1984) 467.

32. B. POURDEYHIMI, H. H. ROBINSON, P. SCHWARTZ and H. D. WAGNER, *Ann. Biomed. Eng.* **14** (1986) 277.
33. L. D. T. TOPOLESKI, P. DUCHEYNE and J. M. CUCKLER, *J. Biomed. Mater. Res.* **26** (1992) 1599.
34. L. D. T. TOPOLESKI, P. DUCHEYNE and J. M. CUCKLER, *ibid.* **29** (1995) 299.
35. J. KETTENEN, A. MAKELA, H. MIETTINEN, T. NEVALAINEN, M. HEIKKILA, P. TORMALA and P. ROKKANEN, *J. Biomed. Mater. Res.* **42** (1998) 407.
36. A. S. VON GONTEN, J. R. KELLY and J. M. ANTONUCCI, *J. Mater. Sci.: Mater. Med.* **11** (2000) 95.
37. American Society for Testing and Materials, ASTM F417-78. ''standard Test Method For Flexural Strength Of Electrical Grade Ceramics'' (ASTM, Philadelphia, PA, 1984).
38. G. WILLEMS, P. LAMBRECHTS, M. BRAEM, J. P. CELISP and G. VANHERLE, *Dent. Mater.* **8** (1992) 310.
39. H. H. K. XU, T. A. MARTIN, J. M. ANTONUCCI and F. C. EICHMILLER, *J. Dent. Res.* **78** (1999) 706.
40. H. H. K. XU, *ibid.* **78** (1999) 1304.
41. H. H. K. XU, D. T. SMITH, S. JAHANMIR, E. ROMBERG, J. R. KELLY, V. P. THOMPSON and E. D. REKOW, *J. Dent. Res.* **77** (1998) 472.
42. H. H. K. XU, C. P. OSTERTAG, L. M. BRAUN and I. K. LLOYD, *J. Am. Ceram. Soc.* **77** (1994) 1897.
43. J. DELMONTE, Technology Of Carbon And Graphite Fiber Composites (Reinhold Co., New York, 1981).
44. J. C. BOKROS, *Carbon* **15** (1977) 355.
45. R. NEUGEBAUER, G. HELBING, O. WOLTER, W. MOHR and G. GISTINGER, *Biomaterials* **2** (1981) 182.
46. K. TAYTON, G. PHILLIPS and Z. RALIS, *J. Bone Joint Surg.* **64** (1982) 110.
47. C. K. SCHREIBER, *Br. Dent. J.* **137** (1974) 21.
48. S. PAL and S. SAHA, *Biomaterials* **3** (1982) 93.
49. I. E. RUYTER, K. EKSTRAND and N. BJORK, *Dent. Mater.* **2** (1986) 6.
50. G. MALQUARTI, R. G. BERRUET and D. BOIS, *J. Prosthet. Dent.* **63** (1990) 251.

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