Surface Treatment of Phosphate Glass Fibers Using 2-Hydroxyethyl Methacrylate: Fabrication of Poly(caprolactone)-Based Composites

Ruhul A. Khan,* A. J. Parsons, I. A. Jones, G. S. Walker, C. D. Rudd

Composites Group, School of Mechanical, Materials and Manufacturing Engineering, The University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

ABSTRACT: 2-Hydroxyethyl methacrylate (HEMA) solution (1–10 wt %) was prepared in methanol and phosphate glass fibers were immersed in that solution for 5 min before being cured (irradiation time: 30 min) under UV radiation. Maximum polymer loading (HEMA content) was found for the 5 wt % HEMA solution. Degradation tests of the fibers in aqueous medium at 37°C suggested that the degradation of the HEMA-treated fibers was lower than that of the untreated fibers. X-ray photoelectron spectroscopy revealed that HEMA was present on the surface of the fibers. Using 5 wt % HEMA-treated fibers, poly(caprolactone) matrix unidirectional composites were fabricated by *in situ* polymerization and compression molding. For *in situ* polymerization, it was found that 5 wt % HEMA-treated fiber-based composites had higher bending strength (13.8% greater) and modulus (14.0% greater) than those of the control composites. For compression molded composites, the bending strength and modulus values for the HEMA-treated samples were found to be 27.0 and 31.5% higher, respectively, than the control samples. The tensile strength, tensile modulus, and impact strength of the HEMA composites found significant improvement than that of the untreated composites. The composites were investigated by scanning electron microscopy after 6 weeks of degradation in water at 37°C. It was found that HEMA-treated fibers inside the composite retained much of their original integrity while the control samples degraded significantly. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 246–254, 2009

Key words: 2-hydroxyethyl methacrylate; compression molding; phosphate glass fibers, poly(caprolactone); *in situ* polymerization

INTRODUCTION

Phosphate-based glass fibers have many unique properties, the most interesting of which is its ability to dissolve completely in aqueous media.[1] In phosphate glass fibers (PGF), the primary network former is phosphorous pentaoxide (P_2O_5). These fibers can be synthesized to include ions routinely found in the body. Thus phosphate-based glass materials have potential for use as biomaterials, because their chemical composition can be made similar to that of natural bone. In the last two decades, PGF have been considered as potential biomaterials for the repair and reconstruction of bone.[2,3]

Poly(caprolactone) (PCL) belongs to the aliphatic polyester family and is synthesized via the ring opening polymerization of ε-caprolactone and is shown in Scheme 1.[4] PCL is a thermoplastic bioresorbable polymer with a low melting point (59–64°C). PCL is degraded by water via hydrolysis. The main commercial application of PCL is in the manufacture of biodegradable bottles and films, synthetic wound dressings, encapsulants for drug release systems, contraceptive implants, etc.[5,6] Other synthetic bone replacement materials reported in the literature include Bioglass® with polyethylene and polysulfone matrices,[7] poly(ortho-ester) reinforced with calcium-sodium-metaphosphate fibers,[8] and PCL reinforced with calcium phosphate glass fibers.[9]

Poly(2-Hydroxyethyl methacrylate) (PHEMA) hydrogels are used in contact lenses, biocompatibilization, and drug delivery systems.[10,11] PHEMA hydrogels are well known because of their hydrophilicity, softness, high water content, and permeability.[12] It is reported that PHEMA has adequate biocompatibility and has many potential applications in medical sciences.[13,14] Some researchers have successfully implanted PHEMA-collagen (fibrillar) composite implants into bone (to the popliteal region of rats and to dog femurs).[15,16] 2-Hydroxyethyl methacrylate (HEMA), a vinyl monomer, is used as a coupling agent for natural fibers like jute, cotton, silk,

*Present address: Polymer Composite Laboratory, Bangladesh Atomic Energy Commission, G.P.O. Box: 3787, Dhaka 1000, Bangladesh

Correspondence to: R. A. Khan (dr.ruhul_khan@yahoo.com).
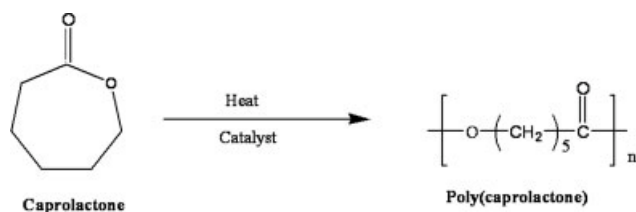
Scheme 1 Synthesis of poly(caprolactone).

etc.[17–19] Fujiki et al.[20] used vinyl monomers as coupling agent for E-glass fibers and found that graft copolymerization occurred from the surface of the fiber. The purpose of this study is to investigate the use of HEMA as coupling agent for PGF and to measure the mechanical properties of the HEMA-treated fiber reinforced PCL matrix unidirectional composites.

EXPERIMENTAL

Production of PGF

Sodium dihydrogen phosphate (NaH_2PO_4), magnesium phosphate trihydrate ($MgHPO_4 \cdot 3H_2O$) and calcium phosphate ($CaHPO_4$) (Aldrich, UK) were used as received. Appropriate ratios of the salts were combined using a Turbula powder mixer. Phosphate salts (100 g) were then placed into a platinum crucible (5%Au/95%Pt) and heated at 350°C for 1 h to dehydrate the salts. The crucible was then placed in a Carbolite furnace at 1200°C for 2 h. During heating, the phosphate salts become molten and reacted together to form liquid glass. The melt was poured directly onto a steel plate ($25 \times 25 \times 1$ cm^3) at room temperature and allowed to cool. The composition (mol %) of the phosphate glass was as follows: $20Na_2O\text{-}24MgO\text{-}16CaO\text{-}40P_2O_5$. Pieces of glass were introduced to the top of the in-house fiber drawing rig and heated. Once the glass was molten, fibers were drawn at a pulling speed of 2000 m/min using a 100 cm circumference drum. The fibers were then stripped from the drum and stored in a desiccator prior to further tests and composites fabrication.

Surface treatment of the glass fibers using HEMA

Phosphate glass fibers were immersed in 1–10 wt % solution of HEMA [$CH_2{=}C(CH_3)COOCH_2CH_2OH$] (Sigma-Aldrich) and 0.1 wt % photoinitiator, Irgacure 184 ($HOC_6H_{10}COC_6H_5$) (Ciba-Geigy, Switzerland) in methanol for 5 min. Fibers were cured for 30 min via a UV source. The UV lamp (350 nm, Philips, UK) had 8 W intensity. After irradiation, the fibers were washed with acetone by submerging the fiber samples in the solvent for 5 min, to remove

any weakly bound or unreacted HEMA. The fibers were then dried at 105°C for 24 h. HEMA-treated fibers were stored in a desiccator prior to use. The HEMA content (polymer loading) at the surface of the PGF was determined on the basis of weight gained by the fibers after the treatment processes.

Degradation tests of the fibers

A small batch of fibers (around 400 mg) $\sim$ 30-mm long was placed into a glass bottle and accurately weighed. The bottle was then filled with deionized water and placed into an oven at 37°C. After a predetermined period, the water was removed and the flask dried overnight at 120°C and then reweighed.

Preparation of the composites by *in situ* polymerization

ε-caprolactone (Sigma-Aldrich) was distilled under reduced pressure over fresh calcium hydride (CaH_2) just before use. The purpose of distillation was to remove inhibitors from the monomer. The catalyst, tin (II) 2-ethylhexanoate, $Sn(Oct)_2$, and boron trifluoride dimethyl etherate, $BF_3 \cdot O(CH_3)_2$ (Sigma-Aldrich) were used as received. A reaction mixture was prepared in which the molar ratio of catalysts (both) to ε-caprolactone was 1/1000. As an example, for 100 mL of monomer, 295 μL of tin (II) 2-ethylhexanoate and 11 μL of boron trifluoride dimethyl etherate were used. After thoroughly mixing in a nitrogen atmosphere, the reaction mixture was injected at ambient pressure into a dried mold containing a predetermined amount of unidirectional phosphate glass fibers. The internal dimensions of the mold was 84 mm × 30 mm × 2 mm, and the fiber content was calculated to be $\sim$ 25% by volume. The mold was sealed and then put into an oven at 120°C to initiate the polymerization. After 24 h, the mold was taken out of the oven and cooled down using ice. The composite sample was then taken out of the mold and stored in a desiccator prior to mechanical testing.

Preparation of the composites by compression molding

The PCL matrix unidirectional composites were made by compression molding. The granulated PCL was purchased from Sigma-Aldrich, UK, with a quoted average $M_n \sim 42,500$ and average $M_w \sim 65,000$. For making PCL sheets, granulated PCL (15 g) was placed into a steel mold and heated at 100°C for 5 min to melt the polymer, after which a 5 bar consolidation pressure was then applied for 30 s. The mold was then cooled for 1 min in a separate press under 5 bar pressure at room temperature.
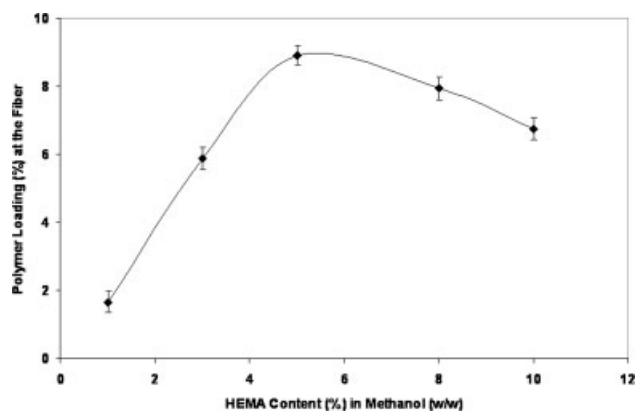
Figure 1 Polymer loading of HEMA in phosphate glass fibers at different weight percent of HEMA in methanol solution.

The resulting PCL sheets were cut into rectangles (80 mm × 50 mm × 0.4 mm) for composite production.

Composite laminates were prepared by sandwiching fibers (5 wt % HEMA treated or untreated fibers) between seven sheets of PCL. Fibers were placed unidirectionally between the sheets of PCL and the resulting sandwich construction was fixed tightly (so as to prevent movement during hot pressing) using adhesive tape. This was then placed in a steel mold and heated at 180°C for 10 min to soften the polymer prior to pressing at 100°C and 1 bar for 2 min. The thickness of the composites was controlled using 2-mm steel shims. The fiber volume fraction of the composites was calculated to be ~ 10%. Samples were sealed in a polyethylene bag prior to mechanical tests.

Mechanical properties of the composites

The bending and tensile properties of the composites (10 samples) were evaluated using Hounsfield series S testing machine (UK) with a crosshead speed of 1 mm/s at a span distance of 25 mm. The dimensions of the test specimen were (ISO 14125): 60 × 15 × 2 mm^3. Composite samples were cut to the required dimension using a band saw. Impact strength (Charpy) of the composites was measured using Impact tester (MT-3016, Pendulum type, Germany). Hardness was determined by HPE Shore-A Hardness Tester (model 60578, Germany).

Degradation tests of the composites

Degradation tests of the composites were performed in water at 37°C. Up to 6 weeks degradation tests were carried out. The degradation specimens (60 × 15 × 2 mm^3) were placed into flasks containing 25 mL of deionized water (10 samples were placed in 10 separate flasks). The flasks were then placed in
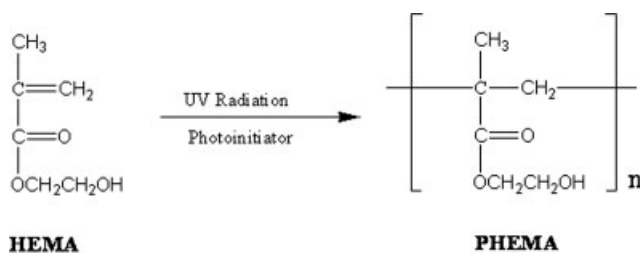
Scheme 2 Formation of PHEMA.

an oven at 37°C. At set time points, samples were taken out and dried overnight at 40°C before being subjected to flexural testing.

Scanning electron microscope

Untreated and HEMA-treated fibers were examined using a JEOL 6400 SEM at an accelerating voltage of 10 kV. Scanning electron microscope (SEM) specimens were sputter-coated with gold. Fracture sides of the composites (after flexural tests) were also observed using SEM.

X-ray photoelectron spectroscopy

Data was collected on a VG ESCALab Mk2 electron spectrometer with an aluminum X-ray source of sample excitation. The X-ray photoelectron spectroscopy (XPS) survey spectra were recorded by accumulating two scans with pass energy of 50 eV. For high-resolution spectra for individual elements, 20 scans were taken using pass energy of 20 eV. Data processing and curve fitting were performed using CasaXPS® developed by Casa Software Ltd.
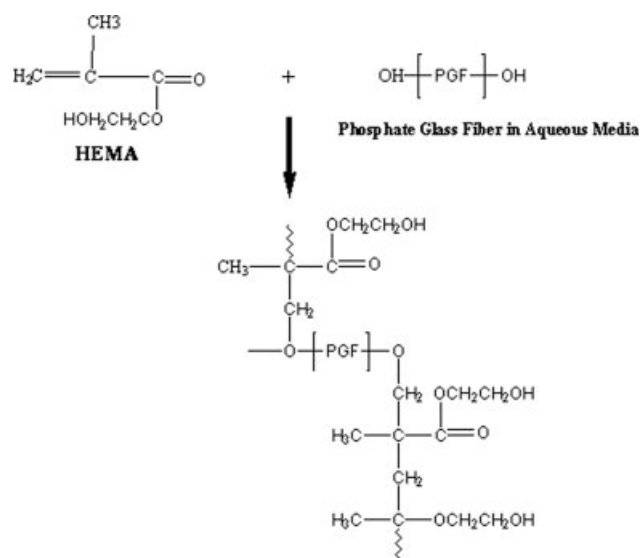
Scheme 3 Reaction mechanism between HEMA and phosphate glass fibers in aqueous media.
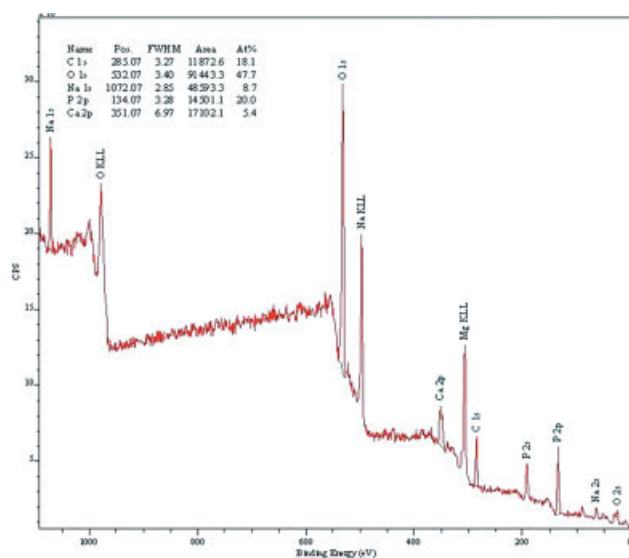
Figure 2 XPS spectrum of untreated phosphate glass fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Measurement of polymer loading (HEMA content) at the fiber surface

The polymer loading at the surface of the phosphate glass fibers was determined from the mass gain of the fibers after treatment. The results are shown in Figure 1, where the polymer loading (wt
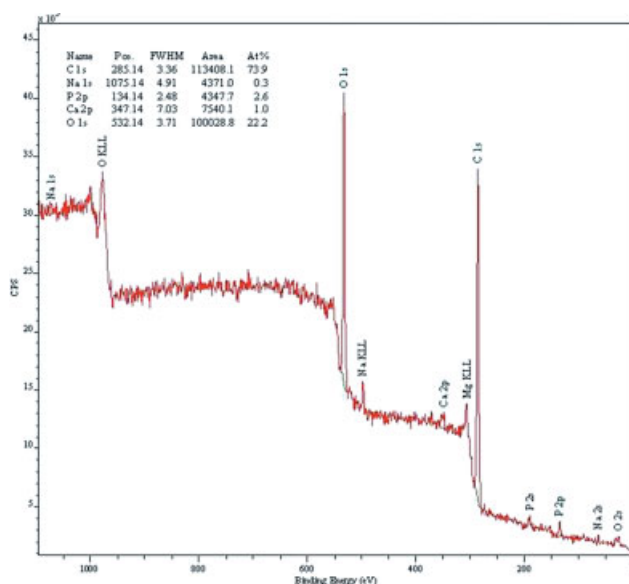
TABLE I
Atomic Composition (wt %), as Detected by XPS, at the Surface of the Untreated and 5 wt % HEMA-Treated Phosphate Glass Fibers

Fiber type	Na	Ca	P	O	C
Untreated fiber	8.7	5.4	20.0	47.7	18.1
5 wt % HEMA-treated fiber	0.3	1.0	2.6	22.2	73.9

%) is plotted against the HEMA content (wt %) in methanol. It was found that with the increase of HEMA content in the solution, the polymer loading (mass gain) at the fiber surface increased and reached the highest at 5 wt % HEMA content and thereafter decreased. The maximum polymer loading of the fiber was found to be 8.9 wt %. At the glass fiber surface two types of reaction might occur. First, a coating of PHEMA may form around the fibers and secondly HEMA might react with the glass fibers surface. The inefficacy of higher HEMA content in the solution may be associated with homopolymerization of HEMA that is not involved in coating the fiber. The reaction mechanism for the formation of PHEMA is shown in the Scheme 2. At higher HEMA content in the solution, the greater availability of monomer yields more homopolymer (PHEMA).[17] The highly reactive acrylate moiety of HEMA may react with hydroxyl group of the glass fiber through graft-copolymerization (Scheme 3).[18]

Figure 3 XPS spectrum of 5 wt % HEMA treated phosphate glass fibers. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
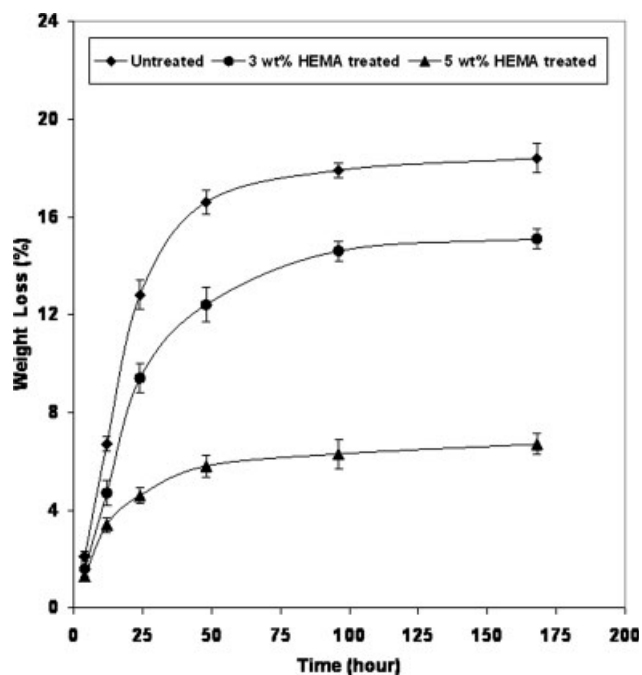

Figure 4 Weight loss (%) versus time graph of untreated and HEMA-treated phosphate glass fibers.
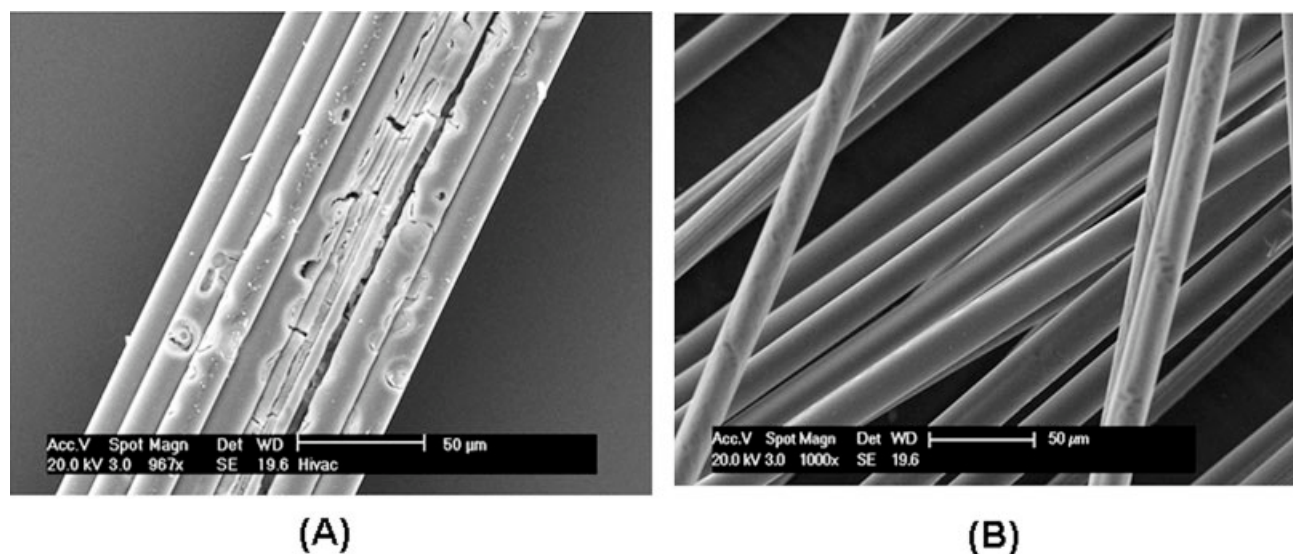
Figure 5 SEM images of 7 days degraded in water at 37°C untreated (A) and 5 wt % HEMA-treated (B) phosphate glass fibers.

Surface characterization of HEMA-treated phosphate glass fibers by XPS

To study the chemical environment of the HEMA-treated phosphate glass fiber surfaces, XPS analysis was used. The XPS spectra of untreated and HEMA-treated fibers are given in Figures 2 and 3. For untreated spectra (Fig. 2), major peaks (Na, Ca, Mg, P, and O) are clearly exhibited, but for HEMA-treated spectra, the intensity of the peaks reduced. But a large peak at 287 eV indicated the presence of HEMA at the surface of the fibers. Atomic composition (wt %) at the surface of untreated and 5 wt % HEMA-treated phosphate glass fiber is given in Table I. It was found that the atomic composition of sodium (Na), calcium (Ca), phosphorus (P), and oxygen (O) of 5 wt % HEMA-treated phosphate glass fibers decreased significantly, but carbon (C) composition increased in the fiber surface compared to the composition of untreated fiber surface. This indicates that HEMA covered the glass fiber surface either by

forming PHEMA (Scheme 2) or by reacting with the glass fiber (Scheme 3).

Degradation tests of untreated and HEMA-treated phosphate glass fibers

Degradation tests (up to 7 days) of the untreated and HEMA-treated phosphate glass fibers were carried out at 37°C in de-ionized water. The results are presented in Figure 4. Both treated (3 and 5 wt % HEMA) and untreated fibers showed similar degradation kinetics, i.e., initial rapid loss and then almost static in rate with time. After 4 h of degradation, the weight loss found for untreated, 3 and 5 wt % HEMA-treated fibers was 2.1, 1.6, and 1.3%, respectively. After 4 days (96 h), the weight loss reached a plateau. After 7 days, the weight loss was found to be 18.4, 15.1, and 6.7% for untreated, 3 and 5 wt % HEMA-treated fibers, respectively. Fibers treated with a 5 wt % solution of HEMA saw a significant

TABLE II
Bending Properties of the Untreated and the 5 wt % HEMA-Treated Phosphate Glass Fiber/PCL Composites Made by *In Situ* Polymerization and by Compression Molding

	Bending properties			
	In situ polymerization (25% fiber by volume)		Compression molding (10% fiber by volume)	
Composite system	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Untreated phosphate glass fiber/PCL	101 ± 12	5.7 ± 0.4	52 ± 8	1.9 ± 0.3
5 wt % HEMA-treated phosphate glass fiber/PCL	115 ± 10	6.5 ± 0.2	66 ± 10	2.5 ± 0.3

Values are the average of 10 samples.
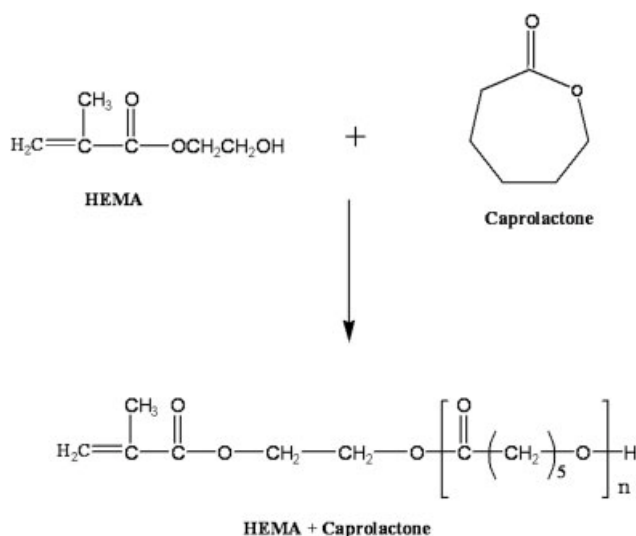
Scheme 4 Reaction between HEMA and caprolactone.

reduction in degradation in comparison to untreated fibers. This effect may be attributed to HEMA reacting with the glass fiber or a coating of PHEMA may form at the fiber surface which reduces dissolution rate. SEM studies were carried out to observe the mode of dissolution of untreated and HEMA-treated fibers (Fig. 5). The SEM images of untreated and 5 wt % HEMA-treated PGFs degraded in water at 37°C for 7 days are shown in Figure 5(A,B), respectively. For the degradation specimens, HEMA-treated fibers are attacked by the aqueous medium to a far lesser extent than their untreated counterparts. For untreated fibers, some pits and holes are evident and these depict degradation phenomena quite similar to those in metallic pitting corrosion.[21,22] In PGF, pitting type degradation occurred which may arise from sodium and or calcium ions leaching out from the glass fibers. Prabhakar et al.[23] and Knowles et al.[24] reported that phosphate glasses release higher amount of sodium or calcium in aqueous media. Thus metallic ion release (sodium, calcium, or magnesium) may be responsible for the rapid onset of pitting at the surface of the glass fibers for untreated fibers. But for HEMA-treated

fiber, a PHEMA coating may protect the fiber surface from rapid dissolution in the aqueous media.

Effect of HEMA on the mechanical properties of the composites

For composite fabrication, 5 wt % HEMA-treated glass fibers were used because this formulation showed the highest polymer loading (HEMA content) at the fiber surface and lower dissolution (weight loss) compared to other formulations mentioned above. The bending strength and moduli of the untreated and 5 wt % HEMA-treated glass fiber reinforced PCL matrix unidirectional composites are given in Table II. For *in situ* polymerization (25% fiber content), it was found that 5 wt % HEMA-treated fiber-based composites had 13.8% higher flexural strength and 14% higher flexural modulus than those of the untreated fiber-based composites. The increased properties may be attributed to the fact that HEMA reacted with both the glass fiber and the monomer caprolactone, shown in Scheme 4. On the other hand, for compression molded composite (10% fiber content), the flexural strength and modulus of the 5 wt % HEMA composites were 27 and 31.5%, respectively, higher than those of the untreated composites.

The tensile strength and moduli of the untreated and 5 wt % HEMA-treated phosphate glass fiber reinforced PCL-based composites are given in Table III. It was found that for both the processes, the strength and moduli increased for HEMA-treated composites. The composite produced using 5 wt % HEMA-treated fibers by *in situ* polymerization shows some promising results. The tensile strength (80–150 MPa) and modulus (17–26 GPa) of cortical bone[25] is close to that found for the HEMA composites. The impact strength and hardness of the untreated and 5 wt % HEMA-treated fiber reinforced PCL-based composites are given in Table IV. The impact strength of HEMA composite increased about 37% in comparison to the untreated composite. But the hardness of the HEMA-treated and untreated composites did not

TABLE III
Tensile Properties of the Untreated and the 5 wt % HEMA-Treated Phosphate Glass Fiber/PCL Composites Made by *In Situ* Polymerization and by Compression Molding

	Tensile properties			
	In situ polymerization (25% fiber by volume)		Compression molding (10% fiber by volume)	
Composite system	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
Untreated phosphate glass fiber/PCL	82 ± 6	6.6 ± 0.6	43 ± 5	1.4 ± 0.6
5 wt % HEMA-treated phosphate glass fiber/PCL	96 ± 10	8.4 ± 0.4	54 ± 7	2.5 ± 0.4

Values are the average of 10 samples.

TABLE IV
Impact Strength and Hardness of the Untreated and the 5 wt % HEMA-Treated Phosphate Glass Fiber/PCL
Composites Made by *In Situ* Polymerization and by Compression Molding

|	Impact strength and hardness			
	In situ polymerization (25% fiber by volume)		Compression molding (10% fiber by volume)	
Composite system	Impact strength (kJ/m^2)	Hardness (Shore A)	Impact strength (kJ/m^2)	Hardness (Shore A)
Untreated phosphate glass fiber/PCL	24 ± 4	93 ± 0.6	12 ± 5	90.5 ± 0.4
5 wt % HEMA-treated phosphate glass fiber/PCL	33 ± 2	93 ± 0.5	16 ± 10	91.0 ± 0.5

Values are the average of 10 samples.

show any significant difference. For *in situ* polymerization, the composite performed better hardness than that of the compression molded composite.

SEM studies of the fracture sides of the composites

Fracture surface of the composites prepared by compression molding was investigated by SEM and is given in Figures 6 and 7. A clear difference is observed for untreated fibers [Fig. 6(A)] and 5 wt % HEMA-treated fibers [Fig. 6(B)] inside the composites. The HEMA-treated samples show a much shorter pull-out length, indicating better adhesion between the fiber and the matrix. After 6 weeks of aqueous degradation at 37°C, the fracture surfaces of the untreated and 5 wt % HEMA-treated composites gave remarkable changes and is shown in Figure 7(A,B). The untreated control specimen shows [Fig. 7(A)] clear evidence that a fraction inside the fiber has dissolved during the degradation test and there are also signs that the interface has opened up significantly. The HEMA composites [Fig. 7(B)] how-

ever retained much of their original integrity and again have a short pull-out length. The HEMA-treated fibers are relatively intact with no significant evidence of the "tunneling" effects visible, although there are signs of an opening of the interface which may help to account for some of the property losses. After 6 weeks of aqueous immersion of the composites at 37°C, HEMA-based composites showed much lower weight loss compared to the control composite and the results are given in Figure 8. This result may be attributed to HEMA reacting with the glass fiber and or a coating of PHEMA may form at the surface of the fiber. The composites produced in the study show some promises as bone implant materials. The bending strength (100–200 MPa) and modulus (6–30 GPa) of cortical bone[26–28] is comparable to that found for the PGF-based composites produced using *in situ* polymerization (bending strength and modulus found: 101 MPa and 5.7 GPa). The flexural properties and degradation rate were improved by using HEMA as coupling agent in the composite. HEMA is biocompatible and widely used
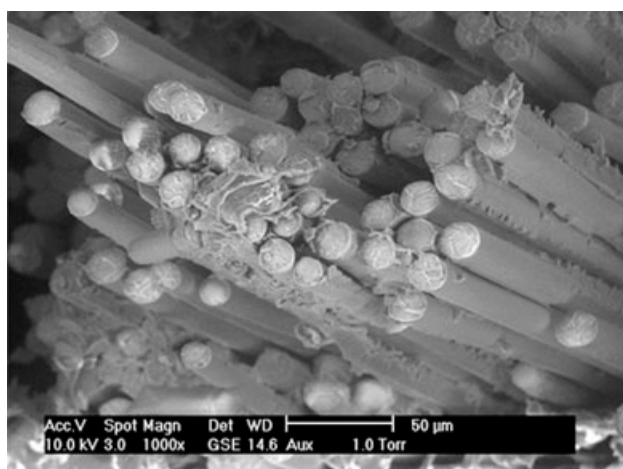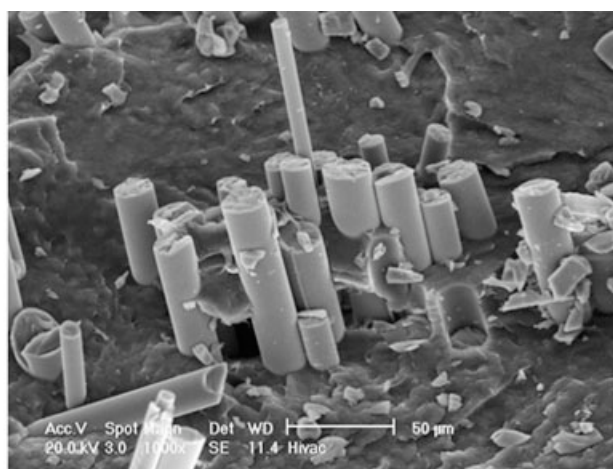
Figure 6 SEM images of the fracture surface of the untreated (A) and the 5 wt % HEMA-treated (B) phosphate glass fiber/PCL composites.
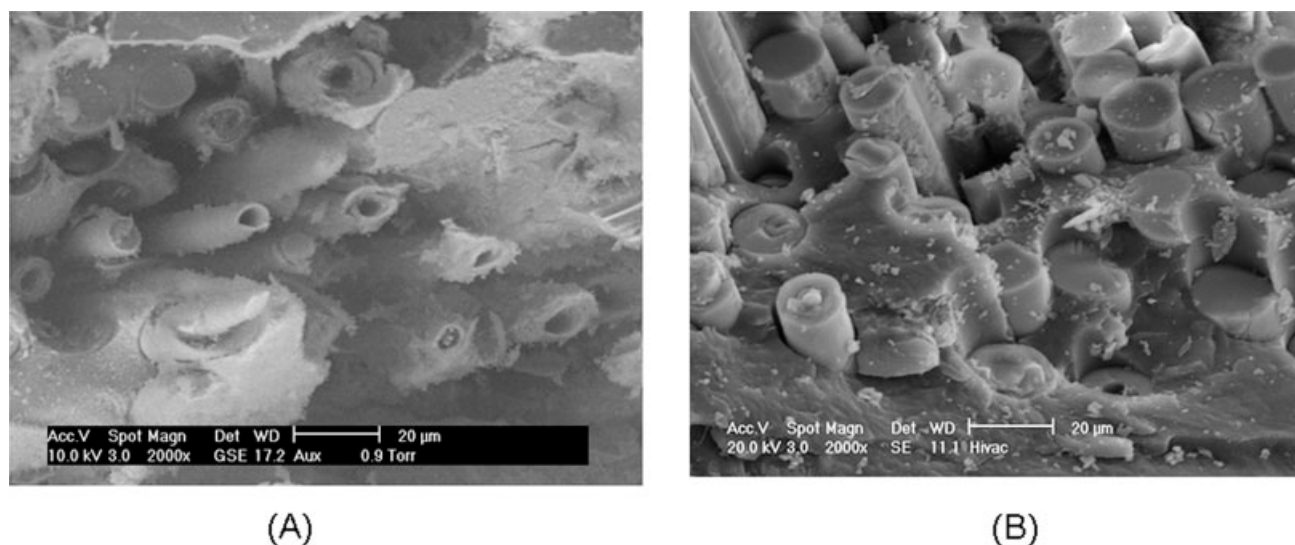
(A)

(B)

Figure 7 SEM images of the fracture surface of the 6 weeks degraded (in water at 37°C) untreated (A) and the 5 wt % HEMA-treated (B) phosphate glass fiber/PCL composites.

in pharmaceutical industries but has not previously been used as coupling agent for PGF. From this investigation it was found that the dissolution rate of the PGF can be reduced by more than 50% when the PGF is treated with a 5 wt % solution of HEMA. The flexural properties of the 5 wt % HEMA composites were 14–32% higher than those of untreated samples. Fiber content in the composite is an important factor in controlling its mechanical properties. Here *in situ* polymerization and compression molding were used for the fabrication of the composites. For compression molded composite, only 10% fiber

(by volume) was used. It was difficult to use higher volume of fibers due to control of the unidirectional alignment. For *in situ* polymerization it is also possible to use higher fiber content. Further investigation using *in situ* polymerization to produce higher volume fraction composites will be very helpful to move the composite properties further into the required property range necessary to support cortical bone.

CONCLUSIONS

It can be concluded that phosphate glass fibers treated with HEMA in methanol solution followed by UV radiation exhibited a lower degradation than untreated fibers. XPS studies indicated that HEMA was present on the surface of the fibers. Maximum HEMA loading on the surface of the fibers was found using 5 wt % HEMA solution. HEMA-treated fiber/PCL composites prepared by both *in situ* polymerization and compression molding provided superior mechanical properties in comparison to untreated fiber-based composites. After 6 weeks of degradation in water, SEM studies found that HEMA-treated fibers inside the composite kept much of the original integrity compared to untreated fibers.
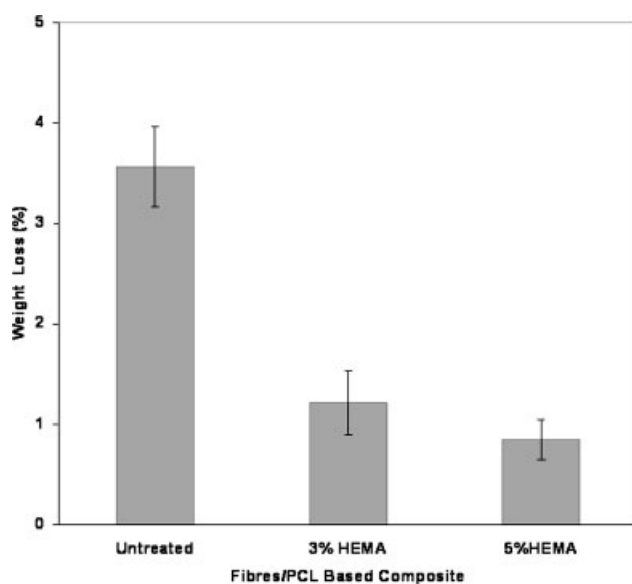

Figure 8 Percentage weight loss (after 6 weeks) of the PCL matrix composites reinforced with untreated and HEMA-treated phosphate glass fibers.

References

1. Parsons, A. J.; Evans, M.; Rudd, C. D.; Scotchford, C. A. J Biomed Mater Res 2004, 71, 283.
2. Brow, R. K. J Non-Cryst Solids 2000, 263, 1.
3. Ahmed, I.; Lewis, M.; Olsen. I.; Knowles, J. C. Biomaterials 2004, 25, 491.
4. Middleton, J. C.; Tipton, A. J. Biomaterials 2000, 21, 2335.

5. Hutmacher, D. W.; Schantz, T.; Zein, I.; Tan, K. C. J Biomed Mater Res 2001, 55, 203.
6. Hou, Q. P.; Grijpma, D. W.; Jan, F. J Macromol Rapid Commun 2002, 23, 247.
7. Hench, L. L.; Thomson, I. In Medical Applications of Composites, Comprehensive Composite Materials; Kelly, A.; Zweben, C., Eds.; Elsevier: The Netherlands, 2000; Vol. 6, p 727.
8. Andriano, K. P.; Daniels, A. U. J Appl Biomater 1992, 3, 197.
9. Charvet, J. L.; Cordes, J. A.; Alexander, H. J Mater Sci Mater Med 2000, 11, 101.
10. Mirzadeh, H.; Katbab, A. A.; Gorgin, E.; Golestani, A. Biomaterials 1995, 16, 641.
11. Guice, K. B.; Loo, Y. L. Macromolecules 2006, 39, 2474.
12. Khorasani, M. T.; Mirzadeh, H.; Sammes, P. G. Radiat Phys Chem 1999, 55, 685.
13. Hoffman, A. S.; Cohn, D.; Hanson, S. R.; Ratenar, B. D.; Reynolds, L. O. Radiat Phys Chem 1985, 22, 267.
14. Kejlova, K.; Labsky, J.; Jirova, D.; Bendova, H. Toxicol In Vitro 2005, 19, 957.
15. Cifkova, I.; Stolt, M.; Holuza, R.; Adam, M. Biomaterials 1987, 8, 3034.
16. Smetana, K.; Stol, M.; Novak, M.; Adam, M. Biomaterials 1992, 13, 639.
17. Ali, K. M. I.; Khan, M. A.; Ali, M. A.; Akhunzada, K. S. J Appl Polym Sci 1999, 71, 841.
18. Khan, M. A.; Hassan, M. M.; Drazel, L. T. Compos A 2005, 36, 71.
19. Shukla, S. R.; Athalye, A. R. J Appl Polym Sci 1992, 44, 435.
20. Fujiki, K.; Sakamoto, M.; Yoshida, A.; Maruyama, H. J Polym Sci Part A: Polym Chem 1999, 37, 2121.
21. Fontana, M. G.; Greene, N. D. Corrosion Engineering; McGraw-Hill: New York, 1967; p 1.
22. Chatterjee, U. K.; Bose, S. K.; Roy, S. K. Environmental Degradation of Metals; Marcel Dekker: New York, 2001; p 5.
23. Prabhakar, R. L.; Brocchini, S.; Knowles, J. C. Biomaterials 2005, 26, 2209.
24. Knowles, J. C.; Franks, K.; Abraham, I. Biomaterials 2001, 22, 3091.
25. Converse, G. L.; Roeder, R. K. Mater Res Soc Symp Proc, Vol. 898E, Warrendale, PA, 2006.
26. Jiang, G.; Walker, G. S.; Jones, I. A.; Rudd, C. D. Appl Surf Sci 2005, 252, 1854.
27. Christian, P.; Jones, I. A.; Rudd, C. D.; Campbell, R. I.; Corden, T. J. Compos A 2001, 32, 969.
28. Davis, J. Handbook of Materials for Medical Devices, ASM International: Materials Park, OH, 2003; p 1.