

Chemical Surface Treatment of Ultrahigh Molecular Weight Polyethylene for Improved Adhesion to Methacrylate Resins

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Received 11 March 2004; accepted 12 October 2004

DOI 10.1002/app.21598

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ultrahigh molecular weight polyethylene (UHMWPE) has high yield strength and modulus, but is nonpolar and chemically inert. For it to be used as an effective reinforcing agent for composites, methods to make the UHMWPE wettable or capable of reaction with the matrix are critical. In the current work, Spectra 900™ (UHMWPE) fibers were surface modified by swelling in *p*-xylene with: (1) methylmethacrylate (MMA) monomer; (2) PMMA; (3) camphorquinone (CQ); (4) 3-methacryloxypropyltrichlorosilane (Cl-MPS); (5) trimethoxysilyl modified polyethylene, *N*-(triethoxysilylpropyl)-dansylamide (fluorescent silane), or octadecyltrimethoxy silane (OMS), followed by hydrolysis and reaction with Cl-MPS; and (6) by coating with SiO₂ films followed by reaction with MPS. These modifiers were used to improve wettability and provide sites for

chemical interactions with the resin matrix. Beads of resin [60/40 BisGMA-TEGMA (bis-phenol A bis-(2-hydroxypropyl) methacrylate and tri(ethylene glycol) dimethacrylate)] were light-cured around the treated fibers and the improvement in adhesion was tested by microbond shear strength (τ) tests. The improvements were comparable to those reported by acid etching and plasma treatments. The OMS, fluorescent silane, and SiO₂/Cl-MPS treatments yielded the best results, that is fourfold increases in τ compared with untreated fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1564–1572, 2005

Key words: dental polymers; composites; interfaces; polyethylene (PE); plasma-enhanced chemical vapor deposition (PECVD)

INTRODUCTION

The characteristics of the interfacial region between the reinforcing material and the matrix play a crucial role in determining the properties of the composite. If the mechanical properties of the filler are to be effectively imparted to the composite, there should be good stress transfer at the interface, which requires good adhesion between the fiber and the matrix. Ultrahigh molecular weight polyethylene (UHMWPE) fibers are excellent candidates as reinforcing materials for low-temperature, high-performance composites because of their low density (0.97 g/cm³), high specific modulus and strength, as well as excellent chemical resistance. As with other polyolefins, however, the inherent chemical inertness, low surface energy, and

smooth surface of these fibers result in poor fiber/matrix adhesion, leading to poor mechanical performance of the composites.^{1,2} It has been suggested³ that physicochemical interactions, mechanical interlocking, and chemical interactions or bonding affect adhesive strength. Both chemical^{4,5} and plasma-etching treatments^{6,7} have been used to improve UHMWPE/resin matrix interfacial adhesion.⁸ The degree of adhesion enhancement is determined by the power of and the particular surface changes introduced by the etchant. The etching mechanism consists of replacing hydrogen atoms from the polymer backbone by polar groups, which may improve resin wetting. The surface roughening introduced by the etchant may also lead to improved mechanical interlocking, yielding improved adhesion. Gamma radiation has also been used to graft short monomers onto UHMWPE fibers⁹ or beads,¹⁰ to attach units that can polymerize with the resin.

Recently, improved adhesion, as measured by lap shear testing, and improved mechanical properties were obtained for acrylic bone cement bonded to UHMWPE by precoating the surface of the latter with polymethylmethacrylate (PMMA).¹¹ This was achieved by diffusing

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Contract grant sponsor: National Institute for Dental and Craniofacial Research; contract grant number: R01 DE-09530.

Contract grant sponsor: National Science Foundation; contract grant number: NSF-0137664.

MMA monomer into the UHMWPE with xylene as the cotransporting agent. The initiator in the bone cement polymerized the MMA into PMMA, forming chemical and/or mechanical bonds between PMMA and UHMWPE. Swelling of peroxide initiator into low-density polyethylene (PE) has also been reported for the case of PE/acrylamide, where it was suggested that grafting occurred by abstraction of hydrogen from the PE, resulting in the formation of radicals on the PE surface that initiated polymerization of acrylamide; evidence for the grafting was the inability to solvent extract all of the homopolymer acrylamide (as evidenced by FTIR spectra).¹² Similarly, swelling UHMWPE fibers in a free-radical initiator solution (for acrylate monomers) yielded improved mechanical properties for the composite, which were also suggested to arise through a grafting mechanism.¹³

Improved adhesion can also be achieved by forming an interfacial layer of SiO₂ on the UHMWPE fiber, followed by silanization with a reactive methacrylate. The SiO₂ layer can bond a silane, and thus improve wettability or reactivity with a polar monomer that will be polymerized.¹⁴ Recently, it was demonstrated that high-quality SiO₂ films can be deposited onto Si substrates by plasma-enhanced chemical vapor deposition (PECVD) from alkoxysilane/O₂ plasmas using precursors such as tetraethoxysilane (TEOS), triethoxysilane (TriEOS), tetramethoxysilane (TMOS), trimethoxysilane (TrimOS),¹⁵ tetramethylcyclotetrasiloxane (TMCTS), dimethyldimethoxysilane (DMDMOS), and trimethylsilane (TMS).¹⁶ PECVD of SiO₂ on polymers has also been reported.^{17,18} We also previously reported the conformal coating of nonwoven polyester fibers with PECVD of SiO₂, using hexamethyldisiloxane (HMDSO)/O₂ plasmas.¹⁹

The focus of the current investigation is a comparison of surface-modification methods for UHMWPE fibers, which may facilitate wetting, grafting, and/or mixing of the UHMWPE chains with the methacrylate matrix during cure. Surface modification was achieved by (1) diffusion of reactive molecules (adhesion promoters) near the surface of UHMWPE after swelling of UHMWPE; (2) deposition of a PE-silane; or (3) deposition of SiO₂ from alkoxysilane/O₂ plasmas, followed by silanization with a reactive methacrylate. The adhesion promoters included MMA, PMMA, camphorquinone (CQ), and functional silanes; the first three molecules were previously used.¹¹⁻¹³ The effect of the surface treatments on the interfacial shear strength was measured using a microbond shear strength test.

EXPERIMENTAL

Chemicals

Spectra 900™ fibers (1200 denier, kindly provided by Honeywell Inc., Boca Raton, FL) were washed by

refluxing with acetone at 56°C for 2 h followed by overnight evacuation at room temperature (RT), to remove the sizing. Bis-phenol A bis-(2-hydroxypropyl) methacrylate (BisGMA), tri(ethylene glycol) dimethacrylate (TEGDMA), hydroquinone monomethylether (HMME), tertiary amine dimethylaminoethyl methacrylate (DMAEMA), polymethylmethacrylate (PMMA), and camphorquinone (CQ) were obtained from EssTech (Essington, PA), stored under refrigeration and used as received. Methylmethacrylate (MMA, 99%) monomer, from Aldrich (Milwaukee, WI), was first passed through an inhibitor removal column and then stored at low temperature. UHMWPE powder, *p*-xylene, triethylamine (TEA), acetone, decahydronaphthalene (decalin) (procured from Aldrich), 3-methacryloxypropyltrimethoxysilane (MPS) and 3-methacryloxypropyltrichlorosilane (Cl-MPS), *N*-(triethoxysilylpropyl)-dansylamide (a fluorescent silane), trimethoxysilyl modified polyethylene (PE-silane), and octadecyltrimethoxy silane (OMS) (from Gelest, Inc., Tullytown, PA) were used without further purification. For deposition of SiO₂, SiH₄ (Voltaix, 99.999%) or tetramethylcyclotetrasiloxane (TMCTS, >95%; Gelest) were used as the deposition precursors and O₂ (99.993%; General Air, Inc., Lodi, NJ) as the oxidant.

Preparation of the resin (used for bead)

BisGMA (0.06 kg) was weighed into a Teflon beaker and mixed with 0.04 kg of TEGDMA (in the dark). This mixture was stirred manually with a glass rod until a uniform consistency was achieved, and then it was allowed to rest for a day. After addition of 0.0005 kg photosensitizer (CQ), 0.0005 kg reducing agent (DMAEMA), and 0.000085 kg HQ, it was stirred overnight in the dark using a magnetic stirrer. The homogeneous mixture was then bottled and stored for future use.

Modification of UHMWPE fibers

The UHMWPE Spectra 900™ fibers were treated with various adhesion promoters to modify their surface using the following procedures: (a) refluxing in 50 : 50 mixture of MMA and *p*-xylene for 1 h; (b) refluxing with 20% (w/w) solution of PMMA in *p*-xylene overnight; (c) soaking in 5% solution (w/w) CQ in *p*-xylene for 2 days at RT; (d) soaking in 5% solution (w/w) CQ in *p*-xylene for 5 h at 60°C; (e) soaking in 5% solution (w/w) CQ in *p*-xylene for 2 days at 60°C; (f) swelling 10% (w/w) 3-methacryloxypropyltrichlorosilane (Cl-MPS) into the fibers at 60°C in *p*-xylene for 5 h with and (g) without TEA catalyst; (h) swelling with a 5% solution of trimethoxysilyl modified polyethylene (PE-silane) composed of a 0.5–1.2 mol % vinyltrimethoxysilane–ethylene copolymer, in decahydro-

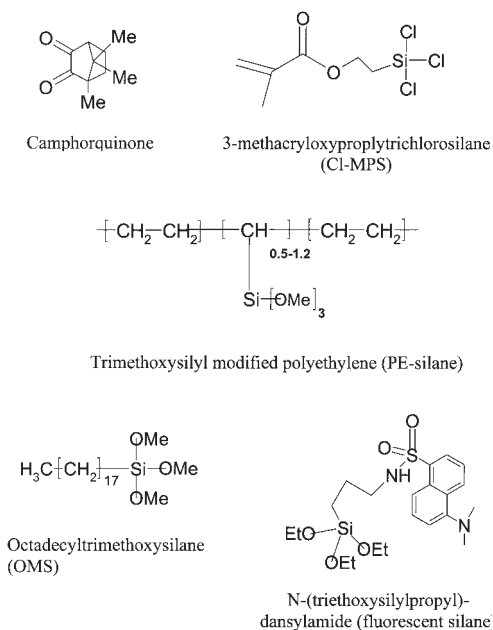


Figure 1 Structure of adhesion promoters for UHMWPE fibers.

naphthalene (decalin) at 110°C for 15, 30, 60, and 120 min, followed by hydrolysis and reaction with Cl-MPS; (i) swelling with 5% octadecyltrimethoxy silane (OMS) solution in *p*-xylene at 110°C for 15, 30, 60, and 120 min followed by hydrolysis and reaction with Cl-MPS; (j) swelling with 1% *N*-(triethoxysilylpropyl)-dansylamide (fluorescent silane) in *p*-xylene at 110°C for 15, 30, 60, and 120 min, and a 5% solution for 15 min, followed by hydrolysis and reaction with Cl-MPS; (k) coating with SiO₂, followed by reaction with 3-methacryloxypropyltrichlorosilane (MPS). The structures of the adhesion promoters are shown in Figure 1 and Table I.

All the CQ reactions were carried out in the dark. The stability of CQ [used in methods (c), (d), and (e)] at elevated temperatures (60°C) for 2 days was confirmed by UV-visible spectroscopy, which showed no change in the characteristic absorbance (440–480 nm) of CQ under these conditions. The use of CQ was intended to initiate polymerization of MMA on or close to the surface of the UHMWPE fibers so that a grafted layer of PMMA or an entangled layer of PMMA and UHMWPE would form. A PMMA layer on the fiber surface [methods (a) and (b)] was used to ensure improved wetting of the UHMWPE and resin.

UHMWPE powder, which had much higher surface area than that of the fibers, was also treated with MMA and CQ, using methods (a) and (c), to investigate, by thermogravimetric analysis, whether there was trapped and/or attached material. After refluxing for 1 h in MMA, or stirring for 2 days in 5% CQ, the UHMWPE powder was centrifuged and then washed twice with acetone, followed by overnight evacuation at RT. The MMA did not polymerize under these conditions.

For method (f), Cl-MPS has both trichlorosilane and methacrylate end groups; the former were used to form a crosslinked silane layer on or below the fiber surface and the latter to react with the methacrylate resin. Cl-MPS attachment was attempted both in the presence and absence of TEA, which serves as a catalyst for enhanced silane attachments on silica surfaces,^{20,21} and thus might facilitate crosslinking of the chlorosilane groups.

In the case of the fluorescent silane treatment (i), a fluorescent silane was used to confirm spectroscopically that the silane was incorporated into the fiber. A 0.1% (w/w) solution of *N*-(triethoxysilylpropyl)-dansylamide (fluorescent silane) in *p*-xylene was heated with the fibers at 110°C for 2 h, and quenched in ice to

TABLE I
List of Adhesion Promoters and Their Functionalities

Name	Functionality
Methylmethacrylate (MMA)	Methacrylate groups react with methacrylate resin
Polymethylmethacrylate (PMMA)	Improve wetting with methacrylate resin
Camphorquinone (CQ)	Free-radical generator for methacrylate resin cure
3-Methacryloxypropyl-trichlorosilane (Cl-MPS)	Si-(Cl) ₃ forms crosslinked network at fiber surface
PE-silane/Cl-MPS	Methacrylate groups react with methacrylate resin Hydrophobic PE incorporated at UHMWPE surface Trimethoxy groups hydrolyzed to attach Cl-MPS
<i>N</i> -(Triethoxysilylpropyl)-dansylamide/Cl-MPS (fluorescent silane)	Methacrylate groups react with methacrylate resin Fluorescent imaging to confirm incorporation into UHMWPE Triethoxy groups hydrolyzed to attach Cl-MPS
Octadecyltrimethoxysilane (OMS)/Cl-MPS	Methacrylate groups react with methacrylate resin Hydrophobic C ₁₈ incorporated at UHMWPE surface Trimethoxy groups hydrolyzed to attach Cl-MPS
SiO ₂ /MPS	Methacrylate groups react with methacrylate resin Surface silanols react with MPS Methacrylate groups react with methacrylate resin

entrap the silane molecules into the swollen fibers. After overnight evacuation at RT, the fibers were washed with isopropanol (7×) to remove loosely bound silane and evacuated again. Fluorescence spectroscopy was used to confirm that the fluorescence yield of the silane was not affected by the heat treatment, that further rinsing did not remove more silane, and that the fibers were fluorescent after washing.^{22,23}

SiO₂ coating on UHMWPE fibers and powders was accomplished by PECVD methods. The plasma reactor used in this experiment is a capacitively coupled parallel-plate reactor. RF power (13.56 MHz) was applied through two aluminum plates (7.5 cm in diameter). The distance between the two plates was 2 cm. The flow of TMCTS into the reactor was controlled ($\pm 2\%$) with a Nupro bellows-sealed metering valve (Chromatography Research Supplies, Louisville, KY), whereas SiH₄ and O₂ were introduced into the reactor through MKS mass flow controllers (MKS Instruments, Inc., Wilmington, MA). The pressure in the reactor was monitored with an MKS Baratron capacitance manometer, which is insensitive to differing gas compositions. The total pressure in the reactor was maintained at 50 mTorr ($\pm 2\%$). The ratio of precursor to O₂ was calculated from partial pressures and was maintained at 1 : 10 for both TMCTS/O₂ and SiH₄/O₂. UHMWPE fibers/powders along with a piece of Si wafer (scribed to about 20 × 15 mm) were placed on the lower plate, which was allowed to self-bias during the deposition. The applied rf power was 50 W and the deposition time was 6 min for TMCTS/O₂ and 10 min for SiH₄/O₂.

The methoxy/ethoxy groups that were on or near the surface for methods (h), (i), and (j) were then hydrolyzed in 0.1M HCl for 30 min at 50°C, followed by washing (3×) with isopropanol and overnight evacuation at RT. Finally, the -Si(OH)₃ groups of the silanes were reacted with Cl-MPS and the silanol groups of the SiO₂ were reacted with MPS, as described previously,¹⁴ to attach methacrylate double bonds that could be incorporated into the resin. The Cl-MPS reaction was carried out in anhydrous pentane, in the presence of TEA (catalyst) for 5 h at RT in an argon-purged glove box. The Cl-MPS and MPS-treated fibers were sonicated in pentane and methanol to remove the unattached free Cl-MPS (or MPS) and TEA, respectively. The self-polymerized but unattached Cl-MPS floated or remained dissolved in both solvents (whereas the Cl-MPS attached to the UHMWPE fibers sank) and could be removed.

All fiber treatments were followed by acetone wash and overnight evacuation at RT and were carried out under an argon purge.

Characterization

TGA and spectroscopic measurements

A Hi-Res 2950 thermogravimetric analyzer (TA Instruments, New Castle, DE), heated from 25 to 800°C at a ramp rate of 10°C/min, was used for thermogravimetric analysis (TGA) of the samples. An FP-750 fluorimeter (Jasco, Tokyo, Japan) was used for the solution spectra and UV-vis spectra were obtained on an HP 8453 single-pass UV-vis spectrometer (Hewlett-Packard, Palo Alto, CA). The SiO₂ coating on UHMWPE fibers/powders was examined with FTIR and SEM. Microscopic FTIR analyses were obtained with a Magna 760 FTIR spectrometer (resolution of 4 cm⁻¹ and averaging 500 scans; Nicolet Instrument Technologies, Madison, WI). Coating morphology and conformality were determined with a JSM-6500F scanning electron microscope (JEOL, Tokyo, Japan), with an accelerating voltage of 1 kV. SiO₂ film thickness was measured with a variable angle spectroscopic ellipsometer (VASE; model HS 190, J. A. Woollam Co., Lincoln, NE) on the Si wafers that were placed in the reactor along with the UHMWPE fibers/powders.

Preparation and testing of microbond shear strength samples

The method followed to make the shear strength samples was similar for all the fibers. Fine resin beads, of about 0.1 to 0.4 mm embedded length, were placed on the fibers by holding the dry fiber at one end and pulling it through the resin droplet. The beads formed spontaneously and care was taken to ensure a spacing distance between them such that several specimens could be prepared along one fiber length. The fibers were cured in a light-curing oven (model TCU-II, 115 V, 600 W; Dentsply, York, PA) for 4 min, and then placed in petri dishes overnight. One end of the fiber was fixed onto a piece of cardboard using (5 min) epoxy, and allowed to completely cure overnight. The cardboard end of the sample was inserted in the top grip of a Model 1122 tensile tester (Instron, Canton, MA). The fixed bottom grip consisted of a specially made device²⁴ that had two glass slides that could be moved horizontally. The upper grip was used to position the bead just below the slides, which were closed until they just touched the outer surface of the fiber. The load was measured at a crosshead speed of 1 mm/min and testing was complete when the bead had been pulled from the fiber or the fiber failed.

The peak load from the load versus displacement curve was recorded and used to calculate the interfacial shear strength (τ) from the following equation:

$$\tau = (F / \pi dl)$$

where τ is the interfacial shear stress at failure, F is the peak debonding load, d is the fiber diameter, and l is

TABLE II
Effect of Surface Treatment on the Interfacial Shear Strength (τ) of UHMWPE Fibers

Fiber treatment	Interfacial strength (MPa)
No treatment	1.06 (± 0.18)
(a) Refluxing with 50 : 50 MMA, xylene for 1 h	2.44 (± 0.43)
(b) Stirring with PMMA solution at 60°C for 12 h	2.61 (± 0.49)
(c) Swelling with CQ at RT for 2 days	2.26 (± 0.42)
(d) Swelling with CQ at 60°C for 5 h	1.77 (± 0.28)
(e) Swelling with CQ at 60°C for 2 days	2.24 (± 0.58)
(f) Swelling with Cl-MPS at 60°C for 5 h	2.12 (± 0.28)
(g) Swelling with Cl-MPS in the presence of TEA at 60°C for 5 h	2.54 (± 0.94)
(h) Swelling with PE-silane at 110°C for 2 h followed by hydrolysis and Cl-MPS + TEA treatment	2.98 (± 0.41)
(i) Swelling with fluorescent silane at 110°C for 2 h, followed by hydrolysis and Cl-MPS + TEA treatment	4.09 (± 0.75)
(j) Swelling with OMS at 110°C for 2 h followed by hydrolysis and Cl-MPS + TEA treatment	4.22 (± 0.28)
(k) Plasma coating with SiO ₂ followed by MPS treatment for 5 h at RT	4.01 (± 0.52)

the embedded length of the resin bead. Sample sizes for the microbond shear strength specimens ranged from 10 to 14.

RESULTS AND DISCUSSION

The effects of various surface treatments on the interfacial shear strengths (τ) of UHMWPE Spectra 900™ fibers are presented in Table II, and Table III presents the dependence of the fiber treatment times on the values of τ for the OMS, PE-, and fluorescent silane treatments. Figure 2(A) and (B) show TGA curves of UHMWPE powder samples treated with MMA and CQ, respectively, and show the presence of both species in the powder. UHMWPE always shows an increase at about 240°C, the melting temperature of the crystalline regions, which is not of interest in the current investigation. Pure PMMA degrades at a lower

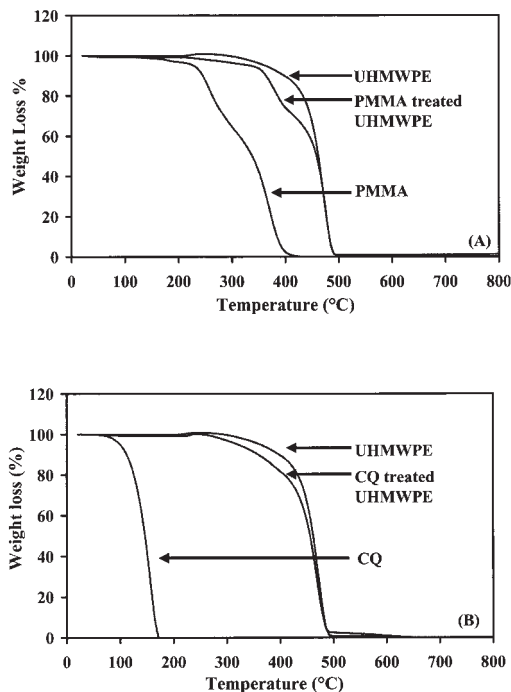


Figure 2 TGA curves of UHMWPE and UHMWPE modified with (A) MMA and (B) CQ.

temperature than that of UHMWPE, as shown in Figure 2(A). The MMA-treated fibers show the presence of MMA indirectly, by a TGA curve that is affected by the presence of PMMA. This occurs because the MMA left in the fibers polymerizes in the TGA as the temperature is increased, resulting in a decreased initial weight loss temperature for the PMMA/UHMWPE sample. Similarly, Figure 2(B) shows a low-temperature weight loss indicative of the adsorbed CQ.

FTIR results for the SiO₂-coated UHMWPE fibers/powders show strong Si—O—Si stretching absorption bands at around 1100 cm⁻¹, as well as a broad silanol/water absorption around 3500 cm⁻¹ (Fig. 3). In addition, strong methylene stretching vibrations (3000–3200 cm⁻¹) are observed in all the spectra. The SEM images in Figure 4 also demonstrate the presence of SiO₂ films with good morphology and conformal coverage of the fibers. The amount of SiO₂ vapor deposited onto the UHMWPE fibers was 13.5 wt % for SiH₄

TABLE III
Interfacial Shear Strength (MPa) as a Function of UHMWPE Fiber Treatment Time

UHMWPE fiber treatment	Fiber treatment time			
	15 min @ 110°C	30 min @ 110°C	60 min @ 110°C	120 min @ 110°C
PE-silane	2.13 (± 0.22)	2.64 (± 0.34)	2.78 (± 0.30)	2.98 (± 0.41)
OMS	1.36 (± 0.07)	2.01 (± 0.29)	3.37 (± 0.34)	4.22 (± 0.28)
Fluorescent silane				
0.1%	2.48 (± 0.12)	3.00 (± 0.40)	3.28 (± 0.33)	4.09 (± 0.52)
5%	2.55 (± 0.10)			

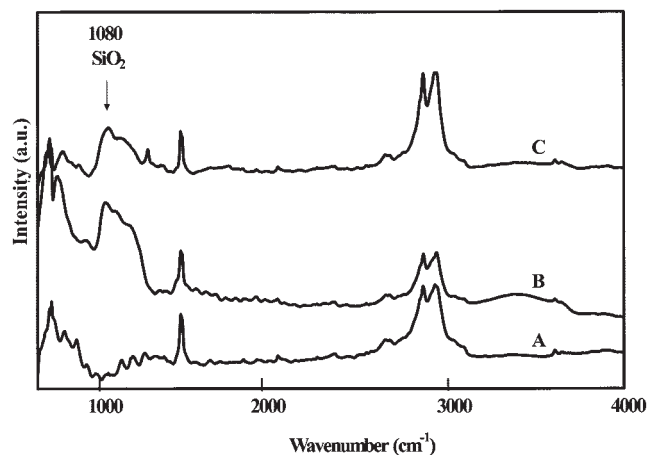


Figure 3 Micro-FTIR spectra of (A) untreated Spectra 900™ fibers, and the same fibers treated with (B) SiH_4/O_2 and (C) TMCTS/O_2 .

and 5 wt % for TMCTS by TGA weight loss. Using the measured fiber diameter of 38 μm , fiber length of 100 mm, and a density of 0.97 g/mL for UHMWPE, and assuming a density of 2.2 g/mL for the SiO_2 , the SiO_2 thickness was estimated to be 580 nm when using SiH_4/O_2 and 200 nm when using TMCTS/O_2 . Ellipsometry results for film thicknesses on Si wafers that were put into the reactors at the same time as the fibers were 670 nm for the SiH_4/O_2 and 890 nm for the TMCTS/O_2 treatments. Deposition of SiO_2 onto silicon wafers thus overestimates the amount actually deposited on the fibers.

All the treatments lead to improved interfacial shear strengths compared with that of the untreated UHMWPE fiber. The CQ, MMA, PMMA, and Cl-MPS treatments increased τ by about 2–2.5 and PE-silane increased τ by about 3, compared with the untreated samples. The OMS, fluorescent silane, and SiO_2 treatments showed the greatest improvement, increasing τ by a factor of 4. Time rather than temperature improved τ for the CQ treatment; the same value of τ was obtained for the RT or 60°C 2-day treatment. The length of time for the PE-silane, OMS, and fluorescent silane treatments increased τ at fixed temperature; the increase was more pronounced for the OMS and fluorescent silane treatments, where diffusion of the silane into the interfacial region was expected to be time dependent. Increase in the concentration of the fluorescent silane, at least for short times, had no effect on τ . Addition of MMA or PMMA had almost the same effect on τ .

Untreated Spectra 900™ fibers displayed the poorest interfacial adhesion with the methacrylate resin matrix as a result of the poor wetting characteristic of UHMWPE. Thermally aided diffusion of MMA monomer into UHMWPE swollen with *p*-xylene or physical adsorption of PMMA onto UHMWPE swollen with

p-xylene [methods (a) and (b)] lead to a precoated layer of PMMA, as confirmed by TGA data for the UHMWPE powder, which improved the resin wettability and increased values of τ . In the latter case, some diffusion of PMMA may have occurred and been trapped in the UHMWPE. In the former case, polymerization of MMA occurred during cure of the Bis GMA/TEGMA resin, when initiator was introduced into the system; the MMA might have polymerized as the homopolymer and/or have been incorporated into the crosslinked resin. Our results are consistent with those reported for improved interfacial tensile strengths for PMMA precoated with UHMWPE.¹¹ However, no significant improvement was observed for PMMA-treated compared with untreated Tekmilon™ fibers in PMMA resins based on tensile strength measurements.¹³

The presence of CQ at the UHMWPE fiber surface may result in chemical grafting between the fiber and matrix or simple entrapment of entangled BisGMA-TEGMA chains in the UHMWPE. During the light cure step, grafting can occur either when free radicals are generated in CQ or when the coinitiator, DMAEMA, diffuses to the CQ, generating more free radicals. The TGA data confirm the presence of the initiator diffusion into the UHMWPE, although our results cannot distinguish between initiation of resin polymerization near the surface of the UHMWPE, followed by entrapment, or hydrogen abstraction from UHMWPE followed by polymerization. The smaller τ compared with that provided by the PMMA treatments (a) and (b), suggests that if there is grafting, it was not significant, and did not offer any advantage over chain entanglement as provided by treatments (a) and (b) (PMMA coating). The similar interfacial strengths of RT and higher-temperature (60°C) CQ-treated samples indicate similar degrees of CQ incorporation despite increases in temperature. CQ incorporation was found to be time dependent, as is shown by the properties after treatments (d) and (e).

Our results are consistent with earlier studies in which initiator swelling into polyethylene fibers was shown to improve mechanical properties.¹³ The tensile strength of composites of Tekmilon™ polyethylene fibers and bone cement (PMMA powder/liquid MMA) increased by about 1.4 when the fibers were treated with benzoyl peroxide (BP). For composites of epoxy and Spectra 900™ UHMWPE, grafting of acrylic acid (AA) and acrylamide (AM) monomers was initiated by UV irradiation after presoaking with monomers and initiator, and confirmed by ESCA and IR-ATR.²⁵ Although bulk tensile properties (tensile strength, elongation at break, Young's modulus) did not improve compared with those of untreated fibers, adhesion, measured by fiber pullout tests, showed increases of three- to fivefold for the AA and AM treatments, respectively; the greater improvement in

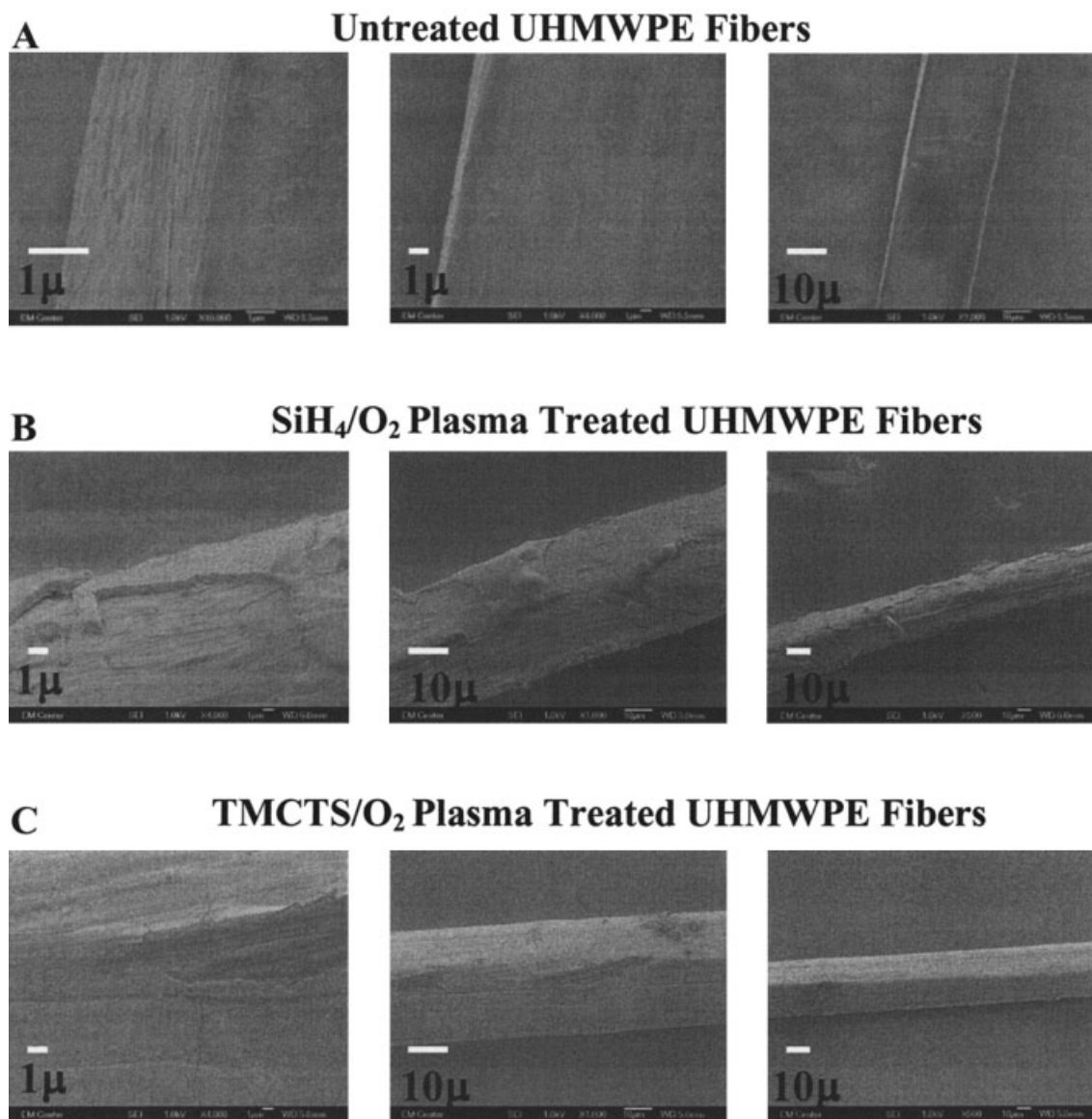


Figure 4 SEM images of (A) untreated and (B) SiH₄/O₂ and (C) TMCTS/O₂ treated Spectra 900™ fibers.

the latter case was attributed to covalent bonds formed between the epoxy and amine groups, compared with the hydrogen bonding and polar interactions for the AA monomer.

CI-MPS is a bifunctional molecule that can form a three-dimensional structure at or below the surface of the UHMWPE and also covalently attach to the resin. The higher value of τ for CI-MPS treatment with TEA (g) compared to the same treatment without it (f), suggests that the catalyst promotes a slightly greater reaction between the chlorosilane moieties. The interfacial shear strength is then comparable to that of the PMMA (a and b) and CQ (c) treatments.

The OMS (j), fluorescent silane (i), and SiO₂ coating (k) treatments provided the greatest improvements in interfacial shear strength. This may be attributable to the greater possibility of attaching methacrylate

groups at the surface of the fiber. For silanes at the surface (j, i), the three ethoxy groups can react with three CI-MPS molecules, increasing the number of methyl-methacrylate groups at the surface, which in turn can participate in the cure with the resin. A schematic of the proposed surface is shown in Figure 5. For the SiO₂ coating, the surface SiOH groups react with the OMS. Results from investigations of film adhesion of plasma deposited SiO₂ onto polycarbonate, using microscratch tests, suggest that the adhesive failure in the present case occurs at the SiO₂/OMS to resin interface, not at the UHMWPE/SiO₂ interface.²⁶ The decreased interfacial shear strengths for the other treatments considered in this investigation may be the result of less attachment of the reactive species to the UHMWPE surface and the lack of accessibility of the attached species to facilitate reaction with the resin groups.

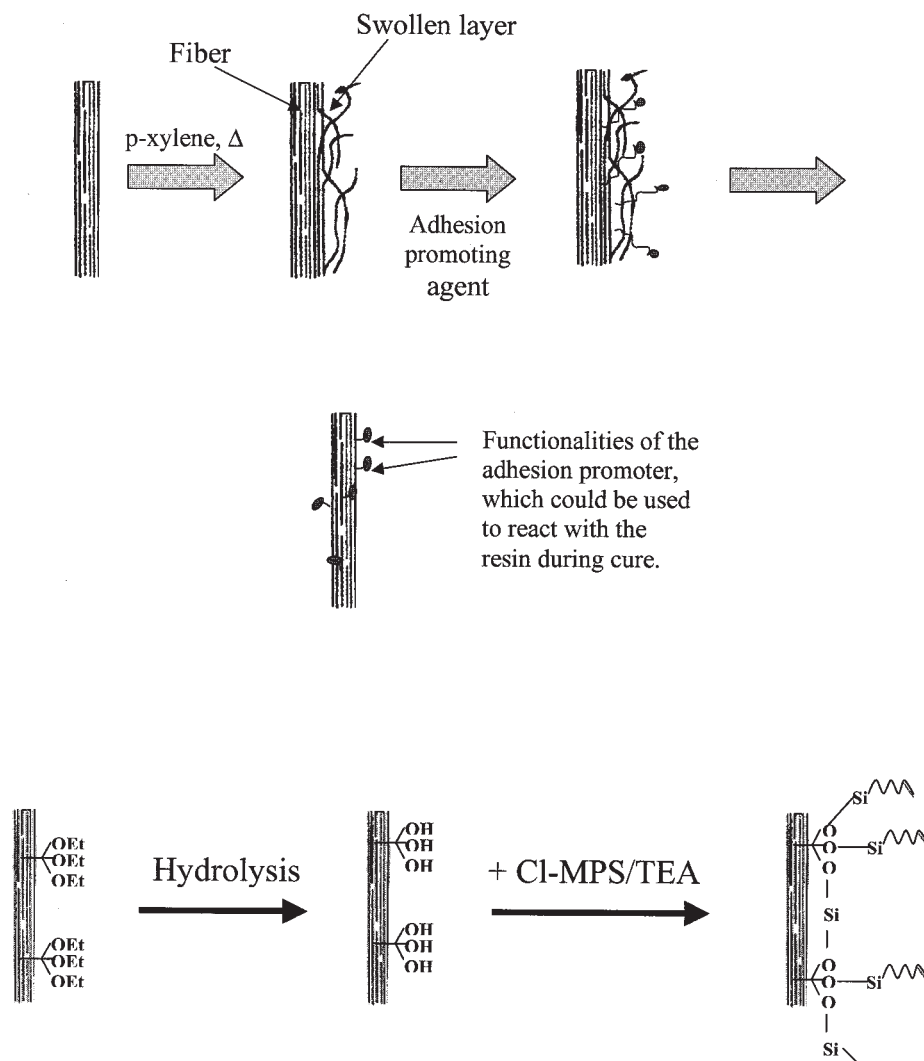


Figure 5 Schematic of incorporation of adhesion promoters into swollen UHMWPE (top) and the subsequent hydrolysis of the fluorescent silane or OMS and reaction with Cl-MPS (bottom).

The fourfold improvement in τ for the OMS, fluorescent silane, and SiO_2 treatments can be compared with previous microbond shear strength tests using high-modulus UHMWPE fibers and epoxy resin beads. In the case of chemically etched (using aqua regia) Spectra 900TM fibers, τ increased 1.4 fold without significant decreases in the fiber strength.⁵ For chemically (chromic acid) or plasma-etched UHMWPE fibers of different draw ratios, τ increased three- to fourfold for the chromic acid etchant and four- to tenfold for the plasma treatment.⁶ However, plasma etching degraded the tensile strength of the plasma-etched fibers. Values of τ may depend on details of both the fibers and resin. For the epoxy/UHMWPE systems, τ for the untreated fibers was 1.81 MPa (Spectra 900TM, 0.038 mm, Ciba-Geigy XD927 epoxy) and 0.6 MPa (for 1.4 mm diameter initially drawn filaments, Epon 815 epoxy). In the current investigation, τ for the untreated fibers (Spectra 900TM, 0.038 mm, 60/40 BisGMA/TEGMA) was 1.06 MPa.

CONCLUSIONS

Microbond shear strength tests for Spectra 900TM UHMWPE, treated with MMA, PMMA, CQ, and Cl-MPS, showed improvements of about 2–2.5 compared with those of untreated fibers. A fourfold improvement was obtained using treatments that consisted of swelling the fibers with a *p*-xylene/OMS or fluorescent silane solution, or coating the fibers with SiO_2 . The accessible $-\text{Si}-(\text{OCH}_3)_3$ groups on the surface of the fiber (for OMS or the fluorescent silane) were hydrolyzed and subsequently reacted (anhydrously) with Cl-MPS in the presence of TEA, forming a network of polymerizable methacrylates. The silanol groups on the surface of the SiO_2 were reacted with OMS, also forming a network of polymerizable methacrylates. The SiO_2 treatment is promising because it may be possible to optimize the amount of OMS attached to the surface. By varying diffusion times and the compatibility of the silane with the UHMWPE, it may also be possible

to increase the number of surface silanols and the amount of attached CI-MPS. In both cases, increased covalent bonding with the resin may occur.

This investigation was supported by Research Grant R01 DE-09530 from the National Institute for Dental and Craniofacial Research, Bethesda, MD. The contribution of resin materials by EssTech (Essington, PA) is also gratefully acknowledged. E.R.F. and J.Z. gratefully acknowledge financial support from the National Science Foundation (NSF-0137664).

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