Novel Organic–Inorganic Chemical Hybrid Fillers for Dental Composite Materials

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Received 13 October 1997; accepted 18 March 1998

ABSTRACT: A series of new polymethacrylate—silica chemical hybrid dental fillers has been prepared by the sol–gel reactions of poly[methyl methacrylate-*co*-3-(trimethoxysilyl) propyl methacrylate] or poly[3-(trimethoxysilyl)propyl methacrylate] with tetraethyl orthosilicate at various compositions. In these hybrid fillers, the polymethacrylate chains are uniformly distributed in and covalently bonded to the silica networks at molecular level without macroscopic organic—inorganic phase separation. The contact angle and surface tension parameters indicate that the hybrid fillers have better wetting properties with the 2,2-bis(*p*-2-hydroxy-3-methacryloxypropoxyphenyl)propane/triethyleneglycol dimethacrylate resin and stronger interfacial bonding with the polymer matrix than pure silica fillers. The compressive testing results demonstrate that the dental composites prepared with the silane-treated fused silica and the pure sol-gel silica fillers at the same silica content. Scanning electron micrographic study reveals that upon compressive tests the dental composites with the hybrid fillers have fewer failures at the filler-matrix interface than those with pure silica fillers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1689–1699, 1998

Key words: organic–inorganic hybrid materials; dental composites; fillers; polymethacrylates; sol–gel processing

INTRODUCTION

Introduced to dental clinical practices a few decades ago, dental composites are usually made up of organic polymer matrix, pure inorganic fillers, and interfacial coupling agents.¹ One of the widely used polymer matrices in the dental composites is derived from 2,2-bis(*p*-2-hydroxy-3-methacryloxypropoxyphenyl)propane (Bis-GMA).² The viscous Bis-GMA resin is often diluted with low-viscosity monomers, such as triethylene glycol dimethacrylate (TEGDMA), methyl methacrylate (MMA), and/or ethylene glycol dimethacrylate.^{3–5} To compensate for the volume shrinkage of polymerization of the methacrylates, a number of spiro monomers have been developed and introduced to the dental resin formulations.⁶ The fillers are used to improve the mechanical properties of the composites and also to reduce the volume shrinkage. The mechanical properties, such as elastic modulus, hardness, compressive yield strength, etc., were found to depend on the nature, volume fraction, and particle size and distribution of the fillers employed.⁷

Silicon dioxide (SiO_2) is one of the most common fillers in the dental composites. A variety of SiO_2 have been developed, including fused silica⁸⁻¹¹ and quartz^{12,13} in either powder or short fiber¹⁴ form. Recently, amorphous silicas prepared by sol-gel processing have also been used as the fillers.¹⁵⁻¹⁸ Because of the thermodynamic incompatibility between the organic polymer matrices and the inorganic fillers, the filler particles are usually subjected to some surface treatment

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Contract grant sponsor: National Institutes of Health; contract grant number: RO1-DE09848.

Journal of Applied Polymer Science, Vol. 70, 1689-1699 (1998)

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with the coupling agents prior to mixing with the resins. The coupling agents, such as γ -methacryl oxypropyltrimethoxysilane, are typically difunctional molecules having both the vinyl group to react with the resins and the alkoxysilyl groups to interact with the filler surfaces. The treatment with these agents could form covalent bonding and, hence, improve the adhesion between the otherwise incompatible inorganic fillers and organic polymers.

Generally, the mechanical properties tend to improve when the volume of filler is increased.¹⁹ Based on size, the filler particles are traditionally classified into three broad categories: macrofillers $(\sim 5-50 \ \mu m)$, microfillers ($\sim 0.01-0.1 \ \mu m$), and physical hybrids (i.e., a physical mixture of macrofillers and microfillers).⁷ The decrease in filler size appears to reduce the stress concentration, maintain a smooth sample surface, and extend the durability of the composites. However, the smaller the particles, the more difficult it is to volume-load a resin because of the increase in the surface area, which limits wetting of the small particles by the resin. Stress concentration will occur around the unwetted interfacial defects and the aggregates of filler particles, resulting in the failure of the composite materials $^{20-22}$

We have been interested in the synthesis of a new family of organic-inorganic chemical hybrid materials in which the vinyl polymer chains are uniformly distributed in and covalently bonded to the inorganic networks at the molecular level via the sol-gel process.²³⁻³³ The composition of the hybrid materials can be varied to afford desired combination of properties of both the polymer [such as poly(methyl methacrylate) (PMMA)] and the inorganic component (such as silica).^{23,25,26} We reasoned that the polymethacrylate-silica chemical hybrid materials as fillers should have better thermodynamic compatibility with the methacrylate resins and polymers than the simple silica fillers have because the polymethacrylate chains are already present on the surface of the hybrid fillers. The improvement in the compatibility should enhance the wetting and lower the surface energy at the interface between the fillers and the polymer matrix in the composites, which in turn should lead to better filler-matrix adhesion and mechanical properties. Furthermore, the surface characteristics could be tailored by varying the organic-inorganic composition of the hybrid fillers. The strengthened filler-matrix adhesion might also reduce the need for conventional surface treatment with silane coupling agents.

In this article we present a new class of organic-inorganic chemical hybrid fillers for dental composites. These fillers are derived from the acid-catalyzed sol-gel reactions³⁴⁻³⁶ of inorganic precursor [i.e., tetraethyl orthosilicate (TEOS)], with various amounts of polymer precursor (i.e., polymethacrylate containing reactive trialkoxysilyl functional groups). The mechanical properties of the dental composites prepared with the new hybrid fillers and the Bis-GMA/TEGDMA resin system have been investigated in comparison with those prepared with conventional silica fillers with or without the silane treatment.

EXPERIMENTAL

Materials and General Instrumentation

MMA (Aldrich) was purified by the standard treatment with aqueous NaOH followed by distillation; 3-(trimethoxysilyl)propyl methacrylate (MSMA; Aldrich) was purified by distillation prior to use. Benzovl peroxide (BPO; Fisher) was purified by recrystallization. Benzene was dried over sodium metal. TEOS (Aldrich), tetrahydrofuran (THF, HPLC grade; Aldrich), and hydrochloric acid (Fisher) were used as received. Bis-GMA and TEGDMA were supplied by EssTech Co., Essington, PA. Fused silica fillers with average particle size of 8 to 17 μ m with and without the surface treatment with γ -methacryl oxypropyltrimethoxvsilane were provided by Microcrystalline Arkansas Novaculite (product codes S174 and S325, respectively). Proton nuclear magnetic resonance (¹H-NMR) spectra of the polymer precursors were measured on an IBM Bruker AW250 FT-NMR spectrometer with CDCl₃ as solvent. Infrared spectra of KBr powder-pressed pellets were recorded on a Perkin-Elmer 1610 FTIR spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters GPC-IIA with THF as eluant and monodispersed polystyrenes as calibration standards. Scanning electron micrographs (SEM) of the fracture surfaces of the composite materials were taken on an Amray 1830D4 scanning electron microscope.

Preparation of Polymer Precursors

Trimethoxysilyl-functionalized polymethacrylate precursors were prepared by free radical polymer-

ization of MSMA or copolymerization of MSMA with MMA using BPO as initiator in benzene at 60 to 80°C under nitrogen for 3 h following the previously reported procedures.²⁶ The products were purified twice by dissolution in dry benzene, followed by precipitation in *n*-hexane. The polymers were dried under vacuum for 24 h at ambient temperature. The content of MSMA unit in the polymer precursors varied from 20 to 100% by mole (mol %). The number-average molecular weight of the polymer precursors was estimated to be about 10^4 , based on GPC measurements with the standard polystyrene calibration. The chemical structures and compositions of the precursors were characterized by ¹H-NMR and Fourier transform infrared (FTIR) spectroscopy.

Preparation of Polymethacrylate-Silica Hybrid Fillers

The polymer precursors were hydrolyzed and cocondensed with TEOS in the presence of HCl as catalyst to yield hybrid sol-gel materials.^{25,26} As a typical procedure for the preparation of polymethacrylate-silica hybrid filler (Sample FF5), 0.78 ml (1.56 mmol) of 2.0 M HCl (aq.) was added to a mixture of 32.56 g (156 mmol) of TEOS, 33.81 g of THF, and 11.26 g (626 mmol) of distilled water. After stirring at room temperature for 30 min, the solution was combined with a solution of 0.76 g (4.36 mmol, based on the repeating unit) of the polymer precursor containing 50 mol % of MSMA in 3.04 g of THF. The resultant solution was stirred at room temperature for ~ 30 min until it became homogeneous. The solution was allowed to gel in 50-mL beakers open to ambience. The gelation times varied from a few minutes to 2 days, depending on the polymer content. Usually, the higher polymer content, the shorter the gelation time. The clear gel was dried at room temperature (~ $20-25^{\circ}$ C) for 1 mo to give homogeneous and transparent material. Upon further drying at 60°C for 12 h, the product was broken into small pieces in a molar and was subjected to multistage thermal treatment under nitrogen at 100°C for 2 h, 120°C for 1 h, 150°C for 1 h, 180°C for 1 h, and 200°C for 3 h. Such a slow and stepwise thermal aging could ensure the removal of volatile compounds, minimize coloration, and increase the density and hardness of the materials.²⁶ After the thermal treatment, the light yellow, transparent particles were ground into fine powders in a ball-milling machine (U.S. Stoneware Corp. Model 755 RMV). After passing

through a 500-mesh (25- μ m opening) sieve, the pulverized powder was further dried under vacuum at 100°C for 24 h. The resultant powder, with average size of ~ 10 to 18 μ m, was ready as filler for the preparation of dental composites. The materials were characterized by FTIR spectroscopy and thermogravimetric analysis (TGA).

Preparation of Dental Composites

The Bis-GMA/TEGDMA resin system was prepared by mixing equal weights of Bis-GMA and TEGDMA following the literature procedures.¹⁴ To one-half (resin A) of the Bis-GMA/TEGDMA mixture, 0.4% by weight (wt %) of BPO and 0.01 wt % of butylated hydroxytoluene were added. To the other half (resin B), 0.4 wt % N,N-dimethyl*p*-toluidine was dissolved. To increase the homogeneity of the components, resins A and B were both stirred magnetically at a high speed for 24 h at room temperature in a dark hood at a relative humidity of \sim 50 to 60%. To both resins were added 40 wt % of the hybrid fillers or the commercial silica fillers under vigorous stirring. The paste containing resin A was then combined with an equal amount of the paste containing resin B. After mixing thoroughly, the mixture was filled into the molds of appropriate dimensions required for specific test specimens and was allowed to polymerize at room temperature for 10 to 20 min. To facilitate specimen removal, a very small amount of a mold release agent, silicone oil, was applied to the molds. After polymerization, the hardened specimens were obtained and characterized with FTIR spectroscopy.

Compression Tests

Compressive strength and elongation were measured at ambient condition using an Instron Model 1127 equipped with a 1,000-kg cell, following standard ASTM F451-86 procedures.¹⁴ The crosshead speed was 20 mm/min. Usually about 10 specimens were tested per sample. The specimens were cylinders of 12 mm in height and 6 mm in diameter. Both the top and bottom surfaces of the specimens were flat and parallel to each other at right angles to the long axis of the cylinder. To prepare the specimens for compression tests, the resin mixture was filled into stainless-steel molds, which sat on a flat, smooth stainless-steel plate. The molds were slightly overfilled. A second stainless-steel plate was placed on the top of the molds. The molds and plates were firmly clamped together. After 15 min polymerization, the specimens were removed from the molds, washed thoroughly in a mild detergent solution, and immersed in distilled water at $37 \pm 1^{\circ}$ C for 24 h. Before the tests, the specimens were polished using 240-grit silicon carbide abrasive papers on a LECO VP-160 polishing machine to the exact height and diameter per specifications.

TGA

TGA measurements were performed on a TA 2000 thermal analysis system equipped with 951 TGA module at a heating rate of 10°C/min in a temperature range of 30 to 800°C under air or nitrogen atmosphere. The samples for TGA measurements were fine powders with particle size less than 25 μ m and were preheated at 100°C for 24 h under vacuum. Before recording each TGA curve, the sample was held isothermally at 120°C for 10 min to ensure the complete removal of any volatile compounds.

Hardness Tests

Hardness tests were run on a LECO M400 DPH Vicker's microhardness tester with a loading of 100 or 200 g for the samples with high or low hardness, respectively, and an indentation time of 10 s at 25°C. The hardness measurements were performed on the hybrid samples before they were broken or ground.

Contact Angle Measurements

Contact angles were measured on Tantac contact angle meter at 23.0 °C using triple-distilled water, diiodomethane, and the Bis-GMA/TEGDMA resin mixture (1 : 1 by weight). The liquid drop size was 10 μ l. At least five parallel measurements were made per sample. The contact angle measurements were performed on films of the hybrid materials, which were spin-coated on micrograph glass slides before the gelation of the sol-gel reaction systems.

RESULTS AND DISCUSSION

As illustrated in Scheme 1, the new polymethacrylate-silica chemical hybrid fillers were synthesized from the sol-gel reactions, i.e., hydrolysis and cocondensation, of the inorganic precursor TEOS with the polymer precursors at room temperature with



Scheme 1 Synthesis of the precursor polymers and their sol-gel reactions with inorganic precursor TEOS.

aqueous HCl as catalyst in THF and water mixture. The polymer precursors, i.e., poly[3-(trimethoxysilyl)propyl methacrylate] (PMSMA) and poly[methyl methacrylate-co-3-(trimethoxysilyl)propyl methacrylate] [P(MMA-MSMA)] were prepared by free radical polymerization of MSMA and copolymerization of MSMA with MMA, respectively.²⁶ The number of sol-gel reactive trialkoxysilyl groups in the polymer precursors was controlled by the amount of MSMA relative to MMA employed. Four precursors were synthesized to contain 100 (PMSMA, y = 1), 80 (TE, y = 0.8), 50 (FF, y = 0.5), and 20 mol % $(ET, \gamma = 0.2)$ of MSMA units in the polymer backbones (Scheme 1). Higher MSMA content in the precursor should lead to greater extent of covalent crosslinking between the polymer chains and the silica networks in the hybrid materials.

The organic-inorganic composition (as represented by the silica content) in the polymethacrylate-silica hybrid materials was designed to range from \sim 9 to 95 wt % by varying the amount of TEOS introduced to the sol-gel reactions (Table I). For comparison, pure sol-gel silica (SGS) was also prepared from TEOS alone under the identical conditions. The compositions were further determined experimentally by TGA measurements under air. Figure 1 shows a typical set of TGA curves. Thermal decomposition of the polymethacrylate component occurred at ~ 300 to 400 °C. At 750 °C the organic component decomposed completely and only the inorganic silica remained. As listed in Table I, the values of SiO₂ weight percent determined at 750°C are in reasonable agreement with those calculated from the reactant stoichiometry. As general trends, both the decomposi-

		${\mathop{\rm TEOS^b}}\ ({ m g})$	Polymer ^b (g)	${\rm SiO}_2 \ ({\rm wt} \ \%)^{\rm c}$			
Sample Code	MSMA ^a (mol %)			Calc.	TGA	$\overset{T_d}{(^{\circ}\mathrm{C})^{\mathrm{d}}}$	Hardness (kg/mm ²)
$\mathrm{SGS}^{\mathrm{e}}$		34.7	0.0	100	97	_	156
PMT5	100	32.3	1.0	95	89	360	_
PMT10	100	29.8	2.0	90	85	354	124
PMT20	100	24.9	3.9	80	77	349	101
PMT40	100	15.1	7.8	60	60	345	_
$\rm PMSMA^{f}$	100	0.0	19.6	29	35	314	_
TE5	80	32.4	0.8	95	88	359	151
TE10	80	30.0	1.8	90	84	351	109
TE20	80	25.4	3.6	80	74	338	_
TE40	80	32.1	7.2	60	59	324	_
$\mathrm{PTE}^{\mathrm{f}}$	80	0.0	18.0	26	30	319	_
FF5	50	32.6	0.8	95	90	365	150
FF10	50	30.4	1.5	90	84	346	125
FF20	50	26.1	3.1	80	76	333	83
FF40	50	17.6	6.1	60	58	330	_
$\mathrm{PFF}^{\mathrm{f}}$	50	0.0	15.4	19	22	316	21
ET5	20	32.8	0.6	95	89	347	137
ET10	20	30.9	1.2	90	83	336	129
ET20	20	27.0	2.5	80	76	332	103
ET40	20	19.4	4.9	60	59	327	82
$\operatorname{PET}^{\mathrm{f}}$	20	0.0	12.3	10	11	305	25

Table ICompositions, Thermal Analysis, and Vicker's Hardness Data of the Hybrid Sol–Gel FillersDerived from P(MMA-MSMA), PMSMA, and TEOS

^a MSMA contents in the precursor polymers.

^b Amounts of TEOS and the precursor polymer employed in the sol-gel reactions, which were chosen for each composition so that 10.0 g of the final product would be obtained, assuming 100% conversion in the sol-gel reactions and complete removal of volatile compounds.

^c Silica contents calculated from the reactant stoichiometry (Calc.) and determined by TGA experiments at 750°C.

^d Onset decomposition temperature.

^e SGS derived from TEOS alone.

^f Materials derived from the precursor polymers alone without addition of TEOS.

tion temperature (T_d) and the Vicker's hardness of the hybrid materials increased as the silica content increased. It should be noted that prior to ball-milling, all the hybrid materials obtained were transparent to visible light, indicating that the polymer chains were uniformly distributed in the silica matrix and that the organic-inorganic phase separation, if any, should be in the scale of smaller than 400 nm.

In general, the thermodynamic incompatibility of pure inorganic fillers (such as silica) with organic matrices can be attributed to their significant differences in molecular polarity, which are reflected by the surface contact-angle values. We measured the contact angles of water, diiodomethane, and the liquid resin used for dental composites (i.e., Bis-GMA/TEGDMA (1 : 1) mixture) on the surfaces of the hybrid materials with various silica contents (Table II). As anticipated,



Figure 1 Representative TGA curves of (a) pure SGS and polymethacrylate (20 mol % MSMA)–silica hybrid materials with silica contents of (b) 11, (c) 17, (d) 24, (e) 41, and (f) 89 wt %.

Sample Code		Contact Angl	Surface Tension (mJ/m ²)			
	Organic (wt %) ^a	Water	${ m Dental} { m Resin}^{ m b}$	γ^p	γ	γ^p/γ
SGS	3	16.5 ± 1.2	35.3 ± 0.6	42	72	0.58
FF5	10	43.5 ± 2.1	19.8 ± 2.6	29	60	0.49
FF10	16	48.8 ± 1.0	20.3 ± 1.5	27	57	0.47
FF20	24	54.0 ± 1.0	22.0 ± 2.0	24	54	0.43
FF25	27	59.3 ± 1.2	24.0 ± 1.7	21	51	0.40
FF40	42	66.0 ± 2.0	26.7 ± 1.5	17	48	0.36
PFF	78	66.7 ± 2.3	15.0 ± 1.0	15	51	0.29
PMMA ^c	100	80.0 ± 0.6	10.3 ± 0.6	10	41	0.25
$Matrix^{d}$	100	61.3 ± 3.1	10.0 ± 2.0	18	54	0.33

Table II Conta	ct Angles and Surface	e Tension Para	meters of PMMA,	SGS, and
Polymethacryla	te–Silica Hybrid Mate	erials Derived f	from the Sol–Gel l	Reactions
of TEOS with P	(MMA-MSMA) Contai	ning 50 mol % N	MSMA Units	

^a Organic content as determined by TGA experiments.

^b Bis-GMA/TEGDMA (1 : 1 w/w) resin.

^c Commercial PMMA (PlexiglasTM) plate.³⁷

 $^{\rm d}$ Pure polymer derived from Bis-GMA/TEGDMA (1 : 1 w/w) resin.

the pure PMMA exhibits the highest contact angle with water, whereas the pure SGS showed the lowest. As exemplified in Figure 2, the water contact angle generally increases with the increase in the organic content in the hybrid materials. On



Organic Content (wt%)

Figure 2 Contact angles of (a) water and (b) the dental resin (Bis-GMA/TEGDMA 1 : 1 wt/wt) on the surface of polymethacrylate (50 mol % MSMA)-silica hybrid materials at various organic contents.

the other hand, the contact angle with the organic resin appears to have an overall tendency of decreasing with the organic content. Thus, the incorporation of polymethacrylate into the silica network at the molecular level does indeed change the surface characteristics of the filler materials significantly and does improve the compatibility of the fillers with the dental resin.

From the contact-angle analysis, thermodynamic parameters such as surface tension could be obtained as a function of the organic–inorganic composition of the hybrid materials. According to the theory of fractional polarity, various molecular forces are linearly additive and therefore the surface tension (γ) can be separated into two components: the dispersion (γ^d) and polar (γ^p)^{37,38}:

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

The values of γ^d and γ^p of a given surface can then be calculated from the contact angles of two liquids of known surface tensions, such as water and methylene iodide, using the well-established method.³⁷ The calculated surface tensions and their polar components of the hybrid fillers are listed in Table II. Since the dispersion component in this system varies relatively little ($\gamma^d = 31.1$ ± 2.2 mJ/m²), the magnitude of interfacial tension is determined primarily by the difference in

the polarities of the two phases (i.e., the filler and the resin).³⁷ Smaller polarity difference usually results in lower interfacial tension and hence better wetting properties. As illustrated in Figure 3, there is a clear trend that the polarity (γ^p/γ) decreases as the organic content in the fillers is increased. Thus, the polarity of fillers can be adjusted to match that of the resin to effect a better wetting of the hybrid fillers by the resin, which would minimize interfacial voids and the undesired aggregation of filler particles.^{20–22} Furthermore, the polarities of the hybrid materials are much closer to those of the polymer matrix than to the pure silica fillers, resulting in a stronger interfacial bonding. Both the better wetting and the stronger bonding should improve the mechanical properties of the composite materials.

To study the mechanical properties, we prepared a series of dental composites using the hybrid materials as fillers and the Bis-GMA/ TEGDMA polymer as matrix. The polymerization of Bis-GMA/TEGDMA was initiated by a redox system (i.e., BPO and N,N-dimethyl-p-toluidine) at room temperature.¹⁴ For comparison, the composites with pure SGS and commercial fused silicas, with or without the silane treatment, as fillers at similar particle sizes were prepared under the same conditions. The content of the fillers



Figure 3 Relationship between the surface polarity and the organic content in the polymethacrylate (50 mol % MSMA)-silica hybrid material.



Figure 4 Representative stress-strain curves of the dental composites containing 40 wt % of S174, PMT5, and PMSMA fillers and of pure matrix polymer.

was identical (40.0 wt %) in all the composite specimens for compressive tests. Figure 4 shows a representative compressive behavior of the dental composites, from which the Young's modulus, stress and strain at yield and maximum points, and their standard deviations were obtained. Usually the stress at yield point is quite close to the maximum stress and the yield strain remains relatively unchanged at 5.9 \pm 0.5%. As summarized in Table III, the composite with fused silica fillers without the silane treatment (S325) has, as anticipated, a significantly lower Young's modulus than that with the silane-treated fused silica (S174) fillers. However, the composite with the pure SGS fillers without the silane treatment exhibits a modulus similar to that with the silanetreated fused silica filler. This can be understood based on the fact that the unsintered SGSs are microporous and therefore the interface can be strengthened by physical interlock of the polymer chains with the filler surfaces. The microporous nature of the SGS is further revealed by its lower bulk density (1.85 g/cm^3) in comparison with the fused silica (2.19 g/cm^3) .

Figure 5 shows a plot of the measured Young's modulus against the organic content in the hybrid fillers. It appears that the increase in the organic content leads to a decrease in the modulus. However, the hybrid fillers contain various amounts of organic components that are expected to contribute little to the enforcement of the dental composites. As the organic contents become higher, the fillers have lesser amounts of the inorganic silica that plays a dominant role in enforcing the com-

		Young's Modulus		Maximum Stress and Strain			Yield Stress ^c	
Filler Code	Org. ^a (wt %)	(MPa)	Norm. ^b	Stress (MPa)	Norm. ^b	Strain (%)	(MPa)	Norm. ^b
S325	0	2501 ± 162	2501	148 ± 5	148	18.8 ± 0.7	109 ± 1	109
S174	0	3892 ± 240	3892	182 ± 8	182	17.7 ± 1.1	$142\pm~2$	142
SGS	3	3896 ± 138	4016	144 ± 6	148	8.1 ± 3.6	142 ± 5	146
$Matrix^{d}$	100	1898 ± 151		118 ± 15		22.1 ± 3.1	$102\pm~8$	_
PMT5	11	3770 ± 113	4236	162 ± 3	182	14.4 ± 0.6	148 ± 2	166
PMT10	15	3599 ± 185	4234	154 ± 3	181	10.1 ± 1.6	148 + 1	174
PMT20	23	3508 ± 105	4556	146 ± 8	190	9.4 ± 2.4	141 ± 10	183
PMT40	40	2960 ± 72	4933	102 ± 15	170	6.2 ± 1.5	93 ± 17	155
PMSMA	65	2158 ± 219	6166	103 ± 19	294	7.4 ± 2.2	94 ± 24	269
TE5	12	3480 ± 230	3955	$143\pm~6$	162	6.2 ± 0.7	$142\pm~6$	161
TE10	16	3440 ± 97	4095	$131\pm~8$	156	5.1 ± 0.8	125 ± 12	149
TE20	26	3175 ± 160	4291	112 ± 21	151	4.9 ± 1.3	106 ± 23	143
TE40	41	2690 ± 119	4559	111 ± 12	188	5.5 ± 0.4	103 ± 13	175
PTE	70	1907 ± 114	6357	113 ± 10	377	11.9 ± 2.7	100 ± 3	333
FF5	10	3577 ± 179	3974	149 ± 6	166	9.2 ± 2.6	144 ± 4	160
FF10	16	3365 ± 114	4006	127 ± 14	151	6.4 ± 1.8	121 ± 16	144
FF20	24	2940 ± 224	3868	122 ± 10	161	5.4 ± 0.5	114 ± 15	150
FF40	42	2520 ± 210	4345	117 ± 19	202	5.9 ± 1.3	109 ± 19	188
PFF	78	1630 ± 170	7409	125 ± 18	568	12.1 ± 4.7	$113\pm~9$	514
ET5	11	3194 ± 170	3589	110 ± 14	124	4.8 ± 1	102 ± 20	115
ET10	17	3661 ± 134	4411	145 ± 8	175	6.8 ± 1	143 ± 10	172
ET20	24	3450 ± 180	4539	129 ± 20	170	6.2 ± 2.3	120 ± 23	158
ET40	41	3020 ± 210	5119	124 ± 20	210	6.6 ± 2.1	117 ± 24	198
PET	89	2610 ± 140		133 ± 17	—	14.7 ± 9.1	119 ± 3	—

Table III Compressive Testing Results for the Dental Composites Prepared from the Bis-GMA/TEGDMA (1:1 w/w) Resin and 40.0 wt % of Various Silica and Polymethacrylate-Silica Chemical Hybrid Fillers

^a Organic content in the hybrid filler as determined experimentally by TGA.

^b Normalized to 40 wt % silica in all composites by dividing the measured value by the experimental weight percent silica content in the fillers.

^c Values taken with +0.2% strain offset.

 $^{\rm d}$ Pure polymer derived from Bis-GMA/TEGDMA (1 : 1 w/w) resin without filler.

posite materials. Furthermore, it is known that the elastic modulus increases linearly with the amount of inorganic fillers in conventional dental composites.¹⁴ Therefore, to make a fair comparison with pure silica fillers, the silica content in the hybrid fillers should be normalized to 40 wt % for all the composite samples. The data after normalization, i.e., dividing the measured values by the actual silica content (SiO₂ wt %) in the hybrid filler, are listed in Table III. In Figure 6, the normalized Young's modulus is plotted against the organic content in the hybrid fillers. There is a clear trend that higher organic contents result in greater modulus values. The net enhancement could be attributed to the improvement of wetting between the hybrid fillers and the resin, and of the thermodynamic compatibility at the fillermatrix interfaces as evidenced by the contactangle analysis.

The increase in the filler-matrix compatibility and, hence, the interfacial bonding strength is further supported by SEM studies of the fracture surfaces of the composite materials after the compressive tests. As typical examples, Figures 7 and 8 show micrographs of the fracture surfaces of the specimens with the pure SGS filler and the hybrid filler (FF5), respectively, at magnifications of $\times 200$ and $\times 2,000$. The SGS composite appears to break down at the filler-matrix interfaces, as indicated by the large number of filler particles observed (Fig. 7, top) and clear edges of the particles (Fig. 7, bottom). In comparison, the fracture surface of the FF5 composite (Fig. 8) exhibits fewer discernible filler particles with clear edges, suggesting that the material failure was caused, to a greater extent, by the breakdown in the polymer matrix rather than that at the interfaces.

Other mechanical properties such as maximum and yield stresses (Table III), although the data are more scattered, seem to follow the same trends as the Young's modulus. It is interesting to note that the number of covalent bondings between the polymethacrylate and silica components in the hybrid fillers, as governed by the MSMA mol % in the polymer precursors, does not significantly affect the mechanical properties of the composite materials. This observation suggests that even a small number of covalent bonds generated by MSMA (e.g., at 20 mol %) might be sufficient to incorporate the polymethacrylate chains uniformly into the silica networks to afford the hybrid dental fillers of reasonably good performance. On the other hand, when pure PMMA without any MSMA unit was used as the polymer



Figure 5 A plot of Young's modulus of the dental composites containing 40 wt % fillers versus the organic content (wt %) in the fillers. The hybrid fillers were made with the polymer precursors containing 100 (\bullet), 80 (\bigcirc), 50 (\diamond), and 20 (\bigtriangledown) mol % of PMSMA. The control group (\Box) includes conventional silica fillers (~ 0% organic), SGS fillers (~ 3% organic), and pure matrix polymer (100% organic).



Organic Content

Figure 6 A plot of normalized Young's modulus of the dental composites containing 40 wt % fillers versus the organic content (wt %) in the fillers. The hybrid fillers were made with the polymer precursors containing 100 (\bullet), 80 (\bigcirc), 50 (\diamond), and 20 (\bigtriangledown) mol % of PMSMA. The control group (\Box) includes conventional silica fillers (~ 0% organic), SGS fillers (~ 3% organic), and matrix polymer (100% organic).

precursor, the sol-gel materials obtained were translucent to visible light, indicating severe organic-inorganic phase separation at large scales (i.e., ≥ 400 nm).

SUMMARY AND CONCLUSIONS

In sum, we have successfully synthesized a new family of polymethacrylate-silica chemical hybrid fillers, potentially useful in dental composites, through the HCl-catalyzed sol-gel reactions of TEOS with polymethacrylates containing reactive MSMA units at various compositions. In these hybrid fillers, the polymethacrylate chains are uniformly distributed in and covalently bonded to the silica networks at molecular level without macroscopic organic-inorganic phase separation. The contact angle and surface tension parameters indicate that the hybrid fillers have



Figure 7 SEM of the fracture surface of the dental composite with the pure SGS filler at magnifications of $(top) \times 200$ and $(bottom) \times 2,000$.

better wetting properties with the dental resin (Bis-GMA/TEGDMA) and stronger interfacial bonding with the polymer matrix than pure silica fillers, because the surface of the hybrid fillers inherently contains the polymer components that are structurally similar to the dental resins and polymer matrix. The compressive testing results demonstrate that the dental composites prepared with the Bis-GMA/TEGDMA resin and hybrid fillers tend to have enhanced Young's moduli as well as yield and maximum strengths comparable to the composites with the silane-treated fused silica and the pure SGS fillers at the same silica content. The improvement of the interface strength with the hybrid fillers is further evidenced by the electron micrographic observations that upon compressive tests the composites with pure silica fillers show more fractures at the filler-matrix

interface than those with the hybrid fillers. Currently, we are studying other physicochemical and biological properties of these new composite materials related to dental applications. Investigation is also in progress to prepare new hybrid fillers containing other inorganic (e.g., zirconia, titania, alumina) and organic (e.g., polystyrene and epoxy polymer) components following the same methodology presented in this work.

The authors are grateful to Drs. G. Baran and M. A. Bassiouny of the School of Dentistry, Temple University, and G. Cowperthwaite of EssTech Company for many valuable discussions and suggestions. The authors thank Mr. C. M. Sherly of Drexel University, Dr. J. Tian of Princeton University, and Dr. G. Min of the University of Pennsylvania for their assistance in me-



Figure 8 SEM of the fracture surface of the dental composite with the hybrid filler of 10 wt % organic content (FF5) at magnifications of (top) \times 200 and (bottom) \times 2,000.

chanical tests and contact angle and SEM measurements, respectively.

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